*Technology Development, Evaluation,
and Application (TDEA)*

FY 1999 Progress Report

Environment, Safety, and Health (ESH) Division

Los Alamos
NATIONAL LABORATORY

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Abstract

This progress report presents the results of 10 projects funded (\$500K) in FY99 by the Technology Development, Evaluation, and Application (TDEA) Committee of the Environment, Safety, and Health Division. Five are new projects for this year; seven projects have been completed in their third and final TDEA-funded year. As a result of their TDEA-funded projects, investigators have published thirty-four papers in professional journals, proceedings, or Los Alamos reports and presented their work at professional meetings. Supplemental funds and in-kind contributions, such as staff time, instrument use, and work space, were also provided to TDEA-funded projects by organizations external to ESH Division.

Previous reports in the unclassified series are LA-13191-PR, LA-13264-PR, LA-13438-PR, and LA-13579-PR.

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*Technology Development, Evaluation,
and Application (TDEA)
FY 1999 Progress Report*

Environment, Safety, and Health (ESH) Division

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Introduction

The public expects that the Los Alamos National Laboratory (LANL, Laboratory) will operate in a manner that prevents negative impacts on the environment and protects the safety and health of its employees and the public. To achieve this goal within budget, the Department of Energy (DOE) and the Laboratory must develop new and improved environment, safety, and health (ES&H) technologies and implement innovative, more cost-effective ES&H approaches to operations.

The Environment, Safety, and Health Division (ESH) is a multifaceted division with activities and responsibilities that require technology development and application in addition to the technical and operational support of Laboratory activities. Protecting the health of Laboratory workers and the public is a major effort involving expenditures of over \$60 M a year. In fiscal year (FY)95, the Division established the Technology Development, Evaluation, and Application (TDEA) Program. The program emphasizes cost effectively improving worker health and safety by becoming more efficient, making better use of resources, and addressing special needs and problems. Now in its fifth year, the program's success can more clearly be evaluated by comparing its accomplishments with the initial TDEA Committee priorities. In the body of this report, the reader will find a miniprogress report for each ES&H discipline represented in the TDEA.

The program concentrates on five topical areas: 1) dosimetry, 2) hazards protection, 3) instrumentation, 4) monitoring, and 5) neutron measurements. However, the committee considers funding other topics that have compelling justification or significant immediate impact. Several projects fit into more than one category. Of the ten projects funded in FY99, two projects fit into the dosimetry category, three in hazards

protection, two in instrumentation, five in monitoring, and one in neutron measurements.

In its first year, the TDEA Committee allocated \$300 K to support five projects for six months. Over the past five years, ESH has increased this annual allocation to \$500 K, supporting approximately 10 projects each year. From the beginning, the committee decided to limit the duration of any one project's funding to three years. Much of the technology that has been developed from TDEA-funded projects is applied not only within the Laboratory and throughout the DOE complex, but nationally and internationally through government organizations and industry. The TDEA Committee maintains the following program priorities.

Improve ES&H protection to Laboratory workers and the public.

Although all funded projects contribute to protecting workers and the public, three projects in particular have the potential to reduce worker exposure to radioactive material in Laboratory facilities where historically significant exposures to workers have occurred. Those projects—a ventilation study and two studies that develop improved, specialized workplace airborne-monitoring methods—have the potential to reduce internal exposures to workers. A fourth project, a method for evaluating pressurized drums, can reduce the risk of injury to emergency workers at the Laboratory and be readily applied to emergency responses that occur worldwide in industrial societies.

Support Laboratory mission objectives. The Laboratory's central mission is reducing the danger of nuclear weapons and nuclear materials worldwide. Whether or not the benefits of TDEA-funded projects accrue to stockpile stewardship and management, nonproliferation, or environmental stewardship, they all support this central mission by developing instruments,

equipment, methods, and processes to improve ES&H operations.

Respond and build on the unique expertise of the Laboratory and Laboratory requirements. Investigators for TDEA-funded projects have

- developed lightweight, more sensitive instrumentation to measure worker exposure to neutrons;
- applied sophisticated analytical chemistry techniques to bioassay sample-measurement methods;
- determined the impacts on the environment with regard to wildlife interaction within the Laboratory;
- determined pressure-deformation-correlation criteria to allow emergency responders to evaluate the hazards from pressurized drums;
- identified methods to reduce worker exposure to internally deposited radioactive material, developing methods to determine the properties of respirable beryllium associated with chronic beryllium disease; and
- evaluated the reusability of organic vapor air-purifying respirator cartridges.

Achieve success within three years. This annual report summarizes progress during the fifth year of this program, which is demonstrated by the implementation in the workplace of early TDEA-funded project products. We discuss successful implementation of these products in more detail in the body of this report.

Find potential to transfer technologies to other DOE sites. Information and methods generated by TDEA-funded projects are transferable to other DOE organizations with the same ES&H concerns. The developed technology has also been sought by other government organizations, universities, and private industry.

Introduction

The FY99 projects listed by discipline include

Environment

A Wildfire Behavior Model for the Los Alamos Region and an Evaluation of Options for Mitigating Fire Hazards

Health Physics

Detection and Internal Dosimetry of Insoluble Metal Tritides

Determining and Monitoring the Inhalable Fraction of Plutonium Aerosols in an Accident

Implications of Room Ventilation and Containment Design to Minimize Worker Exposure to Plutonium Aerosols

PRESCILA: Proton Recoil Scintillator Los Alamos Neutron Dose Meter

Rapid Discrimination of Personnel Contamination Due to Radon Versus Other Alpha-Emitting Radionuclides

An XRF Continuous Air Monitor (CAM) for Metal Tritide Aerosols in the Workplace

Industrial Hygiene/Safety

Development of Methods for Determining Physicochemical Properties of Respirable Beryllium Aerosol Materials

Associated with Chronic Beryllium Disease

Pressure Effects and Deformation of Waste Containers

Service-Life Modeling for Using Organic Vapor Air-Purifying Respirator Cartridges and Setting Change-Out Schedules

The TDEA Committee evaluates TDEA Program success according to the following measures: publications and presentations, cost savings, new technologies, and external support. Peer review is an important part of confirming the validity of the work. The interest from organizations external to ESH Division, especially financial support, also is a measure. However, the primary factor illustrating success is the actual application of the results of a project toward better protection of workers and the environment. Measures of success, including applications of TDEA-funded project results, are discussed in front of each topical section of this report.

Projects listed under FY95 are documented in LA-13191-PR, for FY96 in LA-13264-PR, for FY97 in LA-13438-PR, and for FY98 in LA-13579-PR.

Environment

A Wildfire Behavior Model for the Los Alamos Region and an Evaluation of Options for Mitigating Fire Hazards

Studies to date

FY96

Seasonal Movements, Activity Patterns, and Radionuclide Concentrations of Rocky Mountain Elk (*Cervus elaphus nelsoni*) and Mule Deer (*Odocoileus hemionus*) Inhabiting the Pajarito Plateau

FY97

Development and Evaluation of a Radio-Frequency Identification System to Measure Time Spent by Medium-Sized Mammals at Contaminated Sites at Los Alamos National Laboratory (LANL)

Seasonal Movements, Activity Patterns, and Radionuclide Concentrations of Radio-Collared Rocky Mountain Elk (*Cervus elaphus nelsoni*) and Mule Deer (*Odocoileus hemionus*) Inhabiting the Pajarito Plateau

FY98

Comparison of Two Permanent Plots within the 1977 La Mesa Fire and Observations from the Oso Fire

Development and Evaluation of a Radio-Frequency Identification System to Measure Time Spent by Medium-Sized Mammals at Contaminated Sites at Los Alamos National Laboratory (LANL)

Seasonal Movements, Activity Patterns, and Radionuclide Concentrations of Rocky Mountain Elk (*Cervus elaphus nelsoni*) Inhabiting the Pajarito Plateau

Summary of progress

Investigators for the FY99 environmental TDEA Program generated five papers and presentations. The program has received \$140 K additional external funding from collaborating institutions. Those organizations include the US Forest Service, Rocky Mountain Research Station, the University of Arizona, and Stephen F. Austin State University. The methods and models developed from this study are applicable to similar ecosystems throughout the southwestern United States. Since 1996, the total number of papers and presentations generated by TDEA-funded environmental projects are 35.

A Wildfire Behavior Model for the Los Alamos Region and an Evaluation of Options for Mitigating Fire

Principal Investigators: Randy G. Balice and Steven W. Koch, Ecology Group (ESH-20)

Coinvestigators: Patrick Valerio and Sam Loftin (ESH-20); Jeff Baars, Air Quality Group (ESH-17)

Funding: FY99, \$93.5 K; FY00, \$95.5 K; FY01, \$93.9 K. During FY98 and FY99, ESH-20 or collaborating institutions (University of Arizona and Stephen F. Austin State University) received \$140 K from the US Forest Service Rocky Mountain Research Station to provide support in the form of fire-hazard inventories and fire-hazard mapping.

Introduction

Los Alamos National Laboratory (LANL, the Laboratory) has been increasingly threatened by catastrophic wildfires in recent years. Several severe wildfires have already occurred in the region, and as the forests continue to develop and add fuels to the landscape, the wildfire threat increases. Catastrophic wildfires have the potential to destroy major facilities at the Laboratory and, in spite of heroic efforts by fire fighters, they are difficult or impossible to suppress. The present and future risks of catastrophic wildfires at the Laboratory can only be mitigated through purposeful environmental intervention and active land management. However, the development of optimal land management and mitigation action strategies require a detailed knowledge of the potential behavior of wildfires and their impacts.

The potential for the destruction of Laboratory facilities from wildfires is not constant from place to place. Some Laboratory areas are at greater risk than others. Variable risk is a function of the conditions of the vegetation, soils, topography, and proximity to facilities and urban or industrial developments. As part of this project, we are developing an objective instrument for

- evaluating these relative risks to Laboratory facilities from wildfire,
- assessing the potential effectiveness of selected mitigation action strategies, and
- providing assurances that related amenities, such as soils, will not be disturbed in the process.

Primarily, this research project will provide information for the development of LANL forest management and wildfire hazard reduction plans. Moreover, completion of the proposed work in conjunction with subsequent planning and management activities will ensure that the Laboratory is compliant with applicable regulations and National Fire Protection Association (NFPA) codes and standards, as required by the University of California contract with the Department of Energy.

The Laboratory will also benefit financially from the results of this project. Optimal mitigation action strategies for reducing the overall fire hazard in the LANL region will be recommended that will incorporate relative implementation and maintenance costs. The cost analysis will ensure that subsequent LANL forest management and wildfire hazard reduction plans are implemented cost effectively.

Objectives

To partially meet the Laboratory's need to protect its facilities from catastrophic wildfire, we will develop an objective instrument for evaluating the risks to LANL facilities from catastrophic wildfire. This will be done by accomplishing the following major objectives:

- construct a database of relevant environmental information,
- develop a computer model for evaluating relative risks from wildfire,
- estimate LANL's long-term expected

loss from wildfire,

- perform an experiment to contrast the potential efficacy of selected wildfire hazard reduction treatments, and
- propose a system of optimal, cost-effective mitigation action strategies.

Methods

Database development. We defined a database for a region that includes portions of LANL and adjacent land tracts, such as Bandelier National Monument, US Forest Service lands, and Los Alamos County, which manage dense forests in the vicinity of the Laboratory. We compiled data layers in a geo-referenced ARC/INFO format. The data layers contain information pertaining to the fuels inventories and other aspects of the natural vegetation, as well as US Geologic Survey digital elevation models, topography, weather, geologic structures, and soils contaminants. These soil data were synthesized into weather data layers and eight model input data layers: elevation, slope, aspect, fuel model (Anderson 1982), canopy cover, crown height, height from the ground to the base of the live crown, and crown bulk density. The last five of these data layers incorporated summarized field data collected during ongoing fuels inventories and fire hazard analyses (Balice et al. 1999a, 1999b).

Model development and validation. We combined an existing fire behavior model, FARSITE (Finney 1998) with the ARC/INFO system. As part of this system, we are defining weather data layers according to the regional weather conditions observed during recent

wildfires. Our definition captures severe and extreme weather conditions expected during the Los Alamos fire season. Given these input weather conditions, the FARSITE system will be validated by simulating historic wildfires. We are also evaluating the model for its sensitivity to the range of model inputs. To complete the modeling system, we will use existing data for lightning strikes during the fire season to produce a data layer that represents ignition probabilities. The probability space of lightning ignitions will be used to generate random fire starts. FARSITE is also being linked to soil erosion and soil volatility submodels, and these submodels are being validated and subjected to sensitivity analyses.

Simulate LANL's expected losses from wildfire. We will simulate fires from each of the randomized ignition points. Each simulation will assume that suppression is authorized and, given this assumption, the simulations will be allowed to proceed from ignition to crown fire or suppression endpoints. The paths and the expected extent of any crown fires will be monitored, and the predicted damage or destruction of LANL facilities within the study area (X) will be recorded. Over the course of many simulations (N), the values of these affected facilities, including costs related to suppression and potential radiological emissions, will be incorporated into an average expected loss (AEL) function which will take the form

$$AEL = \frac{1}{N} \left\{ \sum_{n \in N} S(n) + \sum_{n \in N, x \in X} I_{n,x} (F(x) + R(x)) \right\} \quad (1)$$

where AEL = the average expected loss from wildfire,

$S(n)$ = cost of wildfire suppression activities,

$I_{n,x}$ = indicator variable of damage or severe destruction to facility x from wildfire n ,

$F(x)$ = value of facility x , including its contents, and

$R(x)$ = social costs of radiological emissions.

Experimental comparison of selected wildfire hazard reduction treatments. We will modify the vegetation layers in the ARC/INFO database to mimic the application of selected silvicultural treatments to portions of the landscape. The treatments will include

- low thinning or removal of fuel ladders and trees less than 8 in. in diameter,
- uniform thinning or tree removal that is proportional to the size distribution, and
- fuel breaks or removal of nearly all trees and most of the large shrubs.

This range of treatments will be implemented with and without prescribed fire. With these alterations of the landscape, the fire simulations and AEL calculations will be repeated. The change in expected loss after each treatment will be calculated as

$$REL_t = AEL - (AEL_{t,post} + C_t) \quad (2)$$

where REL_t = the reduced expected loss from treatment t ,

$AEL_{t,post}$ = the posttreatment average expected wildfire loss, and

C_t = the cost of applying treatment t .

This equation reflects the reduced expected loss from wildfire after implementation of treatment t .

Compilation of optimal mitigation action strategies. We will evaluate the reduced expected loss functions and contrast them with potential impacts on soils and other environmental amenities. These results will be summarized in optimal mitigation action strategies. The strategies will be incorporated in forest management and fire hazard reduction plans that are currently being developed for the Laboratory.

Progress and Results

Database development. We have defined the initial area of interest for this study to include the southwestern portions of the Laboratory, continuing west to the crest of the Sierra de los Valles. From the north side to the south

side, the study area is bounded by Pajarito Canyon and by Frijoles Canyon. Several LANL facilities and clusters of facilities are located in the study region. The prominent vegetation types include ponderosa pine forests, mixed conifer forests, spruce-fir forests, aspen forests, and montane grasslands (Balice 1998). To distinguish among fuel conditions within vegetation type, we have defined three topographic settings: canyon, mesa, and mountain.

We used combinations of vegetation types and topographic settings to subdivide the study region into relatively homogeneous units. Then for each of these combinations, the fuels inventory and fire hazard analysis data were used to define the fuel model, percent canopy coverage, height of the overstory canopy, height from the ground to the base of the live crown, and crown bulk density (Table 1).

Model development and validation

Weather data development. To model fire behaviors, we defined weather data layers for the time periods approximating the Dome Fire (April–May 1996) and the TA-40 fire (March 21–22, 1996). Variables of interest, including air temperature, air humidity, wind speed, and wind direction, were constructed from basic meteorological data collected and archived by the LANL weather-monitoring system at TA-6 (Bowen 1990). We did this by calculating hourly averages from the original 15-min data. Then, these values were converted to units required by FARSITE.

We did not directly measure percent cloud cover using the Laboratory's weather-monitoring system. Instead, we estimated this parameter by comparing the average hourly incoming solar radiation with the maximum value that had been recorded during that month and calculating a percentage of the maximum value. We assumed skies to be clear during nighttime periods.

Model validation. The FARSITE-ARC/INFO system was partially validated against the TA-40 fire, which burned for 8 h on March 22, 1996. The

approximate boundary of the actual fire is shown in Figure 1. Fire fighters used extensive suppression measures to keep the fire from burning LANL facilities immediately to the southeast of the ignition point and from spreading into the canyon that borders TA-40 to the north. As a result, the fire burned in an east-west direction along the ridgeline.

Figure 1 also shows the hourly results of the simulation of the TA-40 fire. The output fire size was 4.9 hectares, compared with the actual fire size of 3.4 hectares. The simulated fire is approximately 44% larger than the actual fire, and about 50% of the simulated fire boundary overlaps the actual fire boundary. In spite of the confounding fire suppression that occurred during the actual fire but not the simulated fire, the results appear to compare well.

Sensitivity analysis. We began testing the sensitivity of the model to heavy fuel conditions. The heights from the ground to the base of the live crowns were varied from 0.5 m to 8.5 m, while all other parameters were kept constant. FARSITE produced an inflection point at 0.85 m (Figure 2). Up to this level, flame length and heat per unit area decreased exponentially with increasing crown base height. Above this level, the output values were constant. This parameter also influenced intermittent crown scorching, as it occurred below crown base heights of 0.85 m, but not above. The arrival times of the fire and its spread rates did not change throughout the range of crown base heights.

Soil erosion and contaminant volatility. Several soil-erosion models were evaluated for application to postfire conditions. Although we identified no quantitative models that had been developed specifically for this purpose, we did identify two models that can be adapted to meet our needs. We will be using the universal soil loss equation (USLE), which was developed for agricultural applications but has been modified for use under local conditions (Nyhan and Lane 1986). The USLE is a quantitative model based on rainfall, soil characteristics, vegetation, and manage-

ment factors. The second model is a soil-erosion risk model developed for postfire applications (MacDonald et al. 1999). This model is based on estimates of postfire soil hydrophobicity, soil erodibility, and rainfall probability. These models will be implemented independently, and the combined results will be used to identify high-risk sites.

Volatilization of soil contaminants could be an undesirable result of wildfire.

We have identified potential contaminants and their boiling points (volatilization temperatures). The boiling points of these contaminant compounds range from 56.2°C (uranium tetraiodide) to 4000°C (chromium sesquioxide). Some of these temperatures are within the range that could be generated by wildfire. We will use the FARSITE model to generate estimates of soil-surface temperature and compare that with contaminant compounds in potential release sites to evaluate the potential for volatilization.

Table 1. Values for selected fire behavior model parameters¹

Vegetation Type	Topography	Fuel Model	Can Cov (%)	Can Ht (m)	G-C Ht (m)	Crn BD (kg/m ³)
Ponderosa Pine	Canyon	Shrub-grass	41.2	17.7	3.96	0.14
Ponderosa Pine	Mesa	Pine litter	64.3	17.2	5.82	0.20
Ponderosa Pine	Mountain	Pine litter	68.4	12.1	4.18	0.20
Mixed conifer	Canyon	Shrub-forb	73.9	16.0	6.80	0.26
Mixed conifer	Mountain	Timber-shrub	76.7	16.9	5.03	0.26
Spruce-Fir	Mountain	Spruce litter	78.9	19.8	5.30	0.25
Aspen	Mountain	Shrub-grass	78.8	16.7	8.41	0.16
Montane grass	Mesa	Shrub-grass	19.1	1.0	0.21	0.09
Montane grass	Mountain	Grass	0.5	6.4	0.06	0.10

¹Vegetation types and topographic conditions are adopted from Balice et al. (1999a). Fuel models are adopted from Anderson (1982). Can Cov = Canopy cover, Can Ht = Canopy height, G-C Ht = the distance from the ground to the base of the live tree crown, and Crn BD = Crown bulk density.

Figure 1. Validation test for the TA-40 wildfire.

Figure 2. FARSITE results for fireline intensity versus height from the ground to the base of the crown. Similar results were obtained for flame length and heat per unit area. Error bars are standard deviations.

Summary

We have successfully concluded the first year of a three-year study to develop a wildfire behavior and wildfire impact model for the Los Alamos region. The first objective of this project, database development, is complete. The second phase, model development and validation, is partially complete. Several key elements of the final three objectives, including the definition of the sampling frame of LANL facilities and selection of mitigation actions, are also under way.

Acknowledgments

Portions of the study region are on Bandelier National Monument and US Forest Service lands, as well as on the Laboratory. As such, the work conducted for this study is done in close cooperation with these agencies. Supporting information, including field data, was generated as a result of cooperative agreements with the US Forest Service Rocky Mountain Research Station, Stephen F. Austin State University, and the University of Arizona. The results of these collaborations and the results of this project are that proposed fire hazard mitigations can be coordinated and optimized across these agencies.

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Health Physics

Internal Dosimetry for Inhalation of Insoluble Hafnium Tritide Aerosols

Determining and Monitoring the Inhalable Fraction of Plutonium Aerosols in an Accident

Implications of Room Ventilation and Containment Design to Minimize Worker Exposure to Plutonium Aerosols

Proton Recoil Scintillator Los Alamos Neutron Dose Meter (PRESCILA)

Rapid Discrimination of Personnel Contamination Due to Radon Versus Other Alpha-Emitting Radionuclides

An XRF Continuous Air Monitor (CAM) for Metal Tritide Aerosols in the Workplace

Studies to date

FY95

Optimization of Placement of Workplace Continuous Air-Monitoring (CAM) Instrumentation

High-Energy-Neutron Dosimetry

FY96

Applications of Thermal Ionization Mass Spectrometry to the Detection of ^{239}Pu and ^{240}Pu Intakes

High-Energy-Neutron Dosimetry and Spectroscopy

Development and Implementation of the LANL Neutron Extremity Dosimeter

Optimization of Continuous Air-Monitoring (CAM) Instrument Placement

FY97

Applications of Thermal Ionization Mass Spectrometry (TIMS) to the Detection of ^{239}Pu and ^{240}Pu Intakes

Development and Implementation of the LANL Neutron Extremity Dosimeter

High-Energy-Neutron Dosimetry and Spectroscopy

Optimization of Continuous Air-Monitoring (CAM) Instrument Placement

Resuspension of ^{238}Pu from Surfaces

FY98

Characterization of Photon Radiation Fields in a Los Alamos National Laboratory (LANL) Plutonium Facility

Detection and Internal Dosimetry of Insoluble Metal Tritides

Determining and Monitoring the Inhalable Fraction of Plutonium Aerosols in an Accident

Implications of Room Ventilation and Containment Design to Minimize Worker Exposure to Plutonium Aerosols

PRESCILA: Proton Recoil Scintillator Los Alamos Neutron Dose Meter

Summary of progress

The investigators for the health physics projects funded by TDEA have generated 65 papers and presentations since the start of the TDEA Program in FY95. TDEA has provided funding for 11 health physics projects since FY95. The greater number of projects funded in the health physics discipline reflects the unique and diverse radiation protection required at LANL. Many of the projects are applicable across the DOE complex.

Internal Dosimetry for Inhalation of Hafnium Tritide Aerosols

Investigators: W. C. Inkret, Nuclear and Radiochemistry (CST-11); M. E. Schillaci, Radiological Dose Assessment (ESH-12); M. K. Boyce (ESH-TSE); Y. S. Cheng, Lovelace Respiratory Research Institute (LRR), D. W. Efurd (CST-11); T. Tadfor Little and G. Miller (ESH-12); J. A. Musgrave, Environmental Systems and Waste Characterization (CST-7); and J. R. Wermer, Tritium Science Engineering (ESA-TSE)

Funding: FY98, \$99 K (ESA-TSE matched staffing funds at \$20 K); FY99, \$26 K; 00 \$49 K

Introduction

After human lungs inhale tritium in the oxide form, the tritium is rapidly exchanged throughout the body's water components (Pinson and Langham 1957, Osborne 1966, ICRP 30 1979, ICRP 54 1988). Biological distribution of tritium oxide in body water is nearly uniform within several hours of inhalation, ingestion, or skin absorption (Pinson and Langham 1957, Osborne 1966). In addition to physical decay by beta emission with a physical half-life of 12.35 yr, tritium leaves the body via transpiration, exhalation, and urination as tritium oxide with an average biological half-time of 10 days (Butler and Leroy 1965). The committed effective dose, $E(T)$, is determined by integrating the total number of decays over $T = 50$ yr, multiplying by the average energy absorbed per decay (at 6 keV), multiplying by a quality factor ($w_R = 1$), and dividing by the average total body soft-tissue mass (63 kg) (ICRP 1975, ICRP 1977, 10 CFR 835 1994, NCRP 1993). The biokinetic behavior of tritium retention in body water is adequately described by a single exponential function,

$$C(t) = C(0)e^{-t/T_B} \quad (1)$$

where, $C(t)$ is the concentration of tritium in body water at time t , $C(0)$ is the concentration of tritium in body water at time zero, 1 is the elimination rate constant ($\ln 2 / T_B$), and T_B is the effective retention half-time in the body (ICRP 1979).

During exposure to elemental tritium gas, the lungs are directly irradiated by beta particles originating from the gas' decay in the lungs. The tritium gas lung dose component is delivered within an

hour after exposure. Radiation dose to the rest of the body results from the biological distribution of tritium oxide in body water, generated by oxidation of tritium gas in the lungs and skin absorption of tritium oxide that has been produced by oxidation of tritium gas in the environment.

Metal tritides are another class of tritium compounds that may be involved in worker exposure. These tritium materials include the chemical hydrides and dihydrides of hafnium, erbium, titanium, zirconium, and other metals. Inhalation of metal-tritide-bearing aerosols results in deposition of metal tritide particles in the pulmonary regions of the lungs. Within the pulmonary environment, metal tritide particles release tritium as dissolution occurs at the particle surface. The resulting tritium oxide distributes throughout the body water. For metal tritides with small dissolution rates, residence time in the lungs can be considerably longer than the biological half-time normally associated with tritium oxide in body water.

Another factor that influences pulmonary residence time is mechanical clearance by ciliary action. The combination of particle dissolution and clearance mechanisms results in an effective pulmonary residence half-time. As the half-time in the pulmonary region increases, $E(50)$ and the committed lung dose equivalent, $H_{lung}(50)$, increase due to the long-term irradiation of the lungs by low-energy beta particles and *bremsstrahlung* x-rays.

Changes in urine tritium concentration are proportional to the solubility of metal tritide particles in the lung. The ratio of $E(50)$ or $H_{lung}(50)$ to urine tritium concentration is larger than the associated

values for inhalation of tritium oxide. The difference in these ratios explains the underestimation of $E(50)$ and $H_{lung}(50)$ if urine bioassay data are interpreted assuming that the intake is tritium oxide when the intake form is actually metal tritides.

In this report, we present and discuss results from a study organized to measure the biological dissolution rate and particle-size distribution of hafnium tritide and hydride samples, and we apply those results to tritium dosimetry models. The generalized results contained herein may be applied to other metal tritide species. The dissolution rate and mechanical clearance are major parameters determining a particle's retention, distribution, and clearance from the lung, and therefore are essential for dosimetric modeling of the inhaled particle.

Biological Behavior of Metal Tritides

The distribution of inhaled particles in the pulmonary system depends primarily on particle size. Large particles [>10 -mm activity median aerodynamic diameter (AMAD)] tend to remain in the upper respiratory tract, including the anterior and posterior nose, the oral cavity, pharynx, and larynx. Particles deposited in the upper tract are rapidly cleared via exhalation from the anterior nose and through the gut from posterior nose, oral cavity, pharynx, and larynx. Particles deposited in the anterior nose contribute little to no radiation dose. A small fraction of the particles cleared through the gut may dissolve and enter the circulatory system to contribute to the effective dose. Smaller particles (1-mm–4-mm AMAD) have a tendency to deposit in the deeper pulmonary regions, where mechanical clearance rates are

slower. For chemical forms with slow dissolution rates, the bronchial and alveolar interstitial regions of the lung deliver much of the radiation dose (ICRP 1994, Cheng et al. 1997).

The dose from inhaled metal tritide particles is from three sources: particles cleared through the gut from the lung by mucociliary action, direct irradiation of the lung tissues, and absorption of tritium into the body's water as the particle matrix dissolves in the lung. The low-energy beta particles from tritium decay have an unknown effect on lung tissue: a thin layer of lung fluid may block their short range, and the radiosensitive cells may not be reached (Balanov et al. 1984, Inkret et al. 1994). According to the current lung model of the ICRP, greater than 90% of the target cell nuclei are at least 10 mm from the beta-particle source. Tritium beta particles have a mean range in water of about 5 mm (ICRP 1994).

The compounds exposing the general body to a dose are produced during particle dissolution in the lung fluid. One of two tritiated compounds is formed—tritium gas and tritium oxide in an approximate 1:99 ratio and a metal hydroxide (Cheng et al. 1997). Much of the tritium gas and a small amount of tritium oxide vapor formed in the lung may be eliminated during exhalation. Most of the tritium oxide enters the bloodstream and is rapidly distributed throughout the body within two to four hours (Balanov et al. 1984, Inkret et al. 1994, Cheng et al. 1997).

Also formed are organic molecules containing bound tritium. These molecules are produced from the exchange of organically bound hydrogen in the lung compartment and gastrointestinal tract with the tritium from the metal tritides particle or tritium oxide (Hill and Johnson 1993, Straume and Carsten 1993). Acutely, 0.5%–4% of tritium reversibly replaces hydrogen atoms in O-H, N-N, and S-H bonds in organic molecules and 1% of the tritium is irreversibly incorporated into stable C-H bonds. For chronic exposure to tritium oxide, as may be seen with the slow

metal tritide dissolution, up to 35% of tissue-bound hydrogen has been observed to exchange with tritium (Straume and Carsten 1993). Organically bound tritium has a slower turnover rate than tritium oxide, so it contributes a larger radiation dose relative to tritium oxide in the body (Straume and Carsten 1993). The bound tritium dose is also important because the bound tritium molecules may be incorporated into cellular material, including deoxyribonucleic acid or histones. Tritium decay is close to biological target structures and may cause damage due to beta-particle ionization or transmutation of tritium to ^3He (Hill and Johnson 1993).

Also of potential concern are the metal compounds released into the body during dissolution. It has been proposed that some toxic effects from metal exposure could be seen; however, the body burdens of metal discussed in this paper are well below the recommended tolerance levels. In addition to the minute metal burden, the metal hydroxides of the class discussed in this paper (Class IV—titanium, zirconium, erbium, and hafnium) are insoluble in body fluids and do not tend to exhibit inherent toxicity. Although some accumulation of metal may be seen in target organs, such as binding of zirconium to the skeleton, much should be removed from the blood and excreted from the body (Brown and Yodama 1987).

Methods

Hafnium hydride was prepared from a direct reaction of the elements. We purchased 325-mesh hafnium powder from Alfa Chemicals. To minimize its reaction with atmospheric oxygen, we placed the hafnium powder in an argon-filled glovebag in a stainless steel tube with a Cajon VCR fitting on one end. Using a 0.5-mm stainless-steel-filter gasket between the reactor and valve to limit migration of the powder throughout the gas-handling system, we assembled the reactor with a Nupro SS-4BG bellows valve. The reactor assembly was installed on the gas-handling system and evacuated while we slowly ramped the temperature to 450°C. The reactor was allowed to cool to room temperature. We

measured a aliquot of hydrogen isotopes into the gas system to correspond to stoichiometries of 2:1 and 1:1 (hafnium ditritide, hafnium dihydride, hafnium monotritide, and hafnium monohydride). The temperature of the reactor was slowly ramped to 400°C; reaction of the hydrogen began at 150°C and was complete before reaching 400°C.

We analyzed samples of hafnium tritide to provide a biologically based particle-dissolution-rate parameter to be used in dose assessment models. The hafnium tritide particle samples were sandwiched in filters and placed in a flask with a lung simulant fluid. The system was maintained at 37°C. At predetermined sampling times, we sampled the fluid and air in the flask and counted for the presence of tritiated water and tritium, which are assumed to account for all tritium dissolved in the lung-simulant fluid (Cheng et al. 1997).

Hafnium monohydride and hafnium dihydride samples mounted on carbon-coated, double-sided tape were analyzed for particle-size distribution. The tape adheres the particles to a substrate and provides a conductive surface to dissipate the specimen current. For this particular experiment, the hafnium monohydride and hafnium dihydride particles were not carbon coated. The uncoated samples were introduced into a Tracor-Northern ADEM scanning electron microscope. We analyzed for an initial x-ray emission on each sample to confirm that the material was primarily composed of hafnium. We then scanned at an average working distance of 19 mm and an acceleration voltage of 15 kV.

Results

Particle Solubility Studies. Figure 1 contains a plot from two data sets of the measured fraction of tritium retained in the hafnium tritide complex in a simulated lung fluid. Particle-size analyses of the hafnium tritide materials used in this solubility study indicated a particle size on the order of 1 μm . Results show a remarkable break at about 40 days, after which the dissolution rate appears to have

returned to the same slope. The exponential, t , indicates two dissolution rates, a minor component with a biological half-time of 43 days and a dominant component with a biological half-time of 1.9×10^5 days.

Scanning Electron Microscopy of Hafnium Hydride Particles. We used scanning electron microscopy (SEM) to study particles of hafnium hydride. Our purpose was to determine the morphology of the particles and their size distribution. The parameters used to determine particle-size distribution were aspect ratio, maximum projection, and minimum projection.

Figure 2 contains a histogram of the number of observed particles as a function of aspect ratio. Aspect ratio is the maximum projection divided by the minimum projection, where maximum projection is determined by finding the vertices of the convex perimeter and then searching these vertices for the pair farthest apart. Figure 3 contains a histogram of the number of observed particles as a function of maximum projection length.

An aspect ratio of 1 indicates a particle that is tending towards a spherical geometry, whereas particles with aspect ratios greater than 1 approach a rectangular form. Particles with aspect ratios between 3 and 6 are prismatic to acicular (needle-like) in crystal habit.

Six hundred to seven hundred particles were counted in each of the hafnium hydride and hafnium dihydride samples to determine size distribution. Examination of the histograms for the aspect ratio of both the hafnium hydride and hafnium dihydride samples indicates that the majority of the particles have an equant to slightly elongate crystal form, i.e., 1:2 aspect ratio. Both the hafnium hydride and hafnium dihydride samples have smaller populations of prismatic crystal habits.

Results for both the hydride and dihydride samples with maximum and minimum projections plotted indicated that the majority of particles are less than 15 μm and that the greatest number of

Figure 1. A plot from two data sets of the measured fraction of tritium retained in the hafnium tritide complex in a simulated lung fluid.

Figure 2. The number of observed particles as a function of aspect ratio.

Figure 3. The number of observed particles as a function of maximum length.

particles between 2 mm and 10 mm.

Figures 4 and 5 contain scanning electron photomicrographs of the two materials. These photomicrographs show that the particles are covered by a “dust” of smaller particles. It was impossible to determine a size distribution for these particles because they lie on the surface of the larger particles, and the particle-sizing program could not distinguish these small particles.

Dosimetry Models

Mathematical Description of the Problem. If the tritium in the body were in the oxide form only, the effective dose would be given by the expression

$$E(T) = N_0 S_{ST} (I_p I) (1 - \exp(-IT)) \quad (2)$$

where S_{ST} is the specific effective energy for soft tissues (absorbed fraction = 1, $w_R = 1$, energy emitted per decay = 9.61×10^{-9} ergs, and the total body soft-tissue mass, $m_{ST} = 63$ kg), N_0 is the initial number of tritium atoms taken into the

body, and $T = 50$ y = 1.83×10^4 d. The effective rate constant, λ , is given by the sum of physical and biological rate constants

$$\lambda = \lambda_p + \lambda_b, \quad (3)$$

where the physical rate constant is

$$\lambda_p = \ln 2 / t_{1/2} = \ln 2 / (12.35 \text{ y} \times 365.25 \text{ d/y}) = 1.54 \times 10^{-4} \text{ d}^{-1}, \quad (4)$$

and the biological rate constant is

$$\lambda_b = \ln 2 / 10 \text{ d} = 6.93 \times 10^{-2} \text{ d}^{-1}. \quad (5)$$

Inserting these values, converting to rad (1 rad = 100 erg/g), and using a quality factor, $w_R = 1$, to convert to rems, we obtain the committed effective dose from tritium in body water,

$$E_{HTO}(50) = 3.38 \times 10^{-18} N_0 \text{ rem} \quad (6)$$

For the metal tritides, we assume that particles are deposited in the lungs and that tritium dissolves from the surface of these particles with a rate constant, r , and is distributed quickly throughout the body as tritium oxide (ICRP 1995).

Additionally, particles are cleared from the lungs with a rate constant, s , and these particles deliver a radiation dose to the lungs only during their residence time. For the component remaining within the lungs, we assume that tritium decays irradiate the lungs uniformly (which is not strictly true). For the component distributed throughout the body as tritium oxide, we must apply the biological rate constant, λ_b .

The committed effective dose has two components: (a) the dose to the lungs resulting from the decay of tritium in the metal tritide form and (b) the whole-body dose resulting from the decay of dissolved tritium in the oxide form, tritium oxide, which is distributed throughout the body.

(a) The committed equivalent dose to the lung is given by

$$H_{\text{lung}}(T) = N_0 S_{\text{lung}} (\lambda_p / \lambda_p + r + s) (1 - \exp^{-(\lambda_p + r + s) T}), \quad (7)$$

where S_{lung} is the specific effective energy for the lung (absorbed fraction = 1, $w_R = 1$; energy emitted per decay = 9.61×10^{-23} erg; and the lung tissue mass, $m_{\text{lung}} = 1$ kg), N_0 is the initial number of tritium atoms taken into the body, and $T = 50$ y = 1.83×10^4 d. We also assume that the entire energy of decay is deposited uniformly in the lung tissue. The contribution of this lung dose to the committed effective dose is given by

$$E_{MT}(50) = w_R \times H_{\text{lung}}(50), \quad (8)$$

where $w_{\text{lung}} = 12$ is the organ-weighting factor for including $H_{\text{lung}}(50)$ in $E(50)$ (NCRP 1993, ICRP 1991, ICRP 1997, 10 CFR 835 1994).

In the limit where both r and s approach zero, all of the dose is from decay in the metal tritide form and all energy is deposited in the lungs. In this limit, the committed effective dose is given by

$$\lim_{r,s \rightarrow 0} E_{MT}(50) = 1.08 \times 10^{-14} N_0 \text{ rem} \quad (9)$$

(b) The number of tritium atoms, $N(t)$, distributed throughout the body as tritium

Figure 4. Backscattered electron photomicrograph of HfH particles at 456 x magnification, working distance of 19.3 mm, electron acceleration voltage of 15 kV, and a specimen current of 47.2 pA. Note the apparent aspect ratio of the smaller particles, less than $5\text{ }\mu\text{m}$, is on the order of 1 to 2. The larger particles display a larger variation in aspect ratio.

Figure 5. Backscattered electron photomicrograph of HfH_2 particles at a magnification of 523 x, working distance of 19.4 mm, electron acceleration voltage of 15 kV, and a specimen current of 29.4 pA. Note the apparent coating of smaller particles on the larger particles and the remarkable angularity in particle geometries. The apparent aspect ratio of the smaller particles, less than $5\text{ }\mu\text{m}$, is on the order of 1 to 2. The larger particles display a larger variation in aspect ratio.

oxide is given as a solution to the equation:

$$-dN/dt = l N(t) - r N_{\text{lung}}(t), \quad (10)$$

$$\text{where } N_{\text{lung}}(t) = N_0 \exp\{-l(p+r+s)t\}.$$

The number of decays from tritium oxide occurring throughout the body in a time, T , is given by

$$N_{\text{body}}(T) = \{(N_0 r l_p)/(l_b - r - s)\} \{(1 - \exp^{-(l_p+r+s)T})/(l_p + r + s) - 1 - e^{-l T/l}\}. \quad (11)$$

The committed effective dose from tritium oxide distributed throughout the body is then given by

$$E_{\text{HTO}}(T) = N_{\text{body}}(T) S_{\text{ST}}. \quad (12)$$

For a small dissolution rate constant, r , on the order of 10^{-5} d^{-1} or less, practically all the committed effective dose results from tritium decays from metal tritide particles in the lungs. For a small clearance rate, s , this dose can be orders of magnitude larger than that expected if all of the tritium were distributed throughout the body as tritium oxide. On the other hand, for a large dissolution rate constant, r , on the order of 10 d^{-1} , practically all of the committed effective dose results from tritium decays from tritium oxide distributed throughout the body.

Realistically, the orders-of-magnitude increase in dose given in the preceding paragraph must be considered an upper limit because of the following considerations:

- mechanical clearance from the lungs can substantially reduce the number of metal tritide particles, thereby substantially reducing lung dose;
- not all of the decay energy is deposited in the lungs, as assumed, because some fraction of the decay energy is self-absorbed in the metal tritide matrix; and
- if the metal tritide particles are not completely insoluble, any solubility will decrease the pulmonary residence time and, therefore, the lung dose. All of these mitigating considerations are strongly dependent on particle size.

Radiation Weighting Factor. The fraction of beta energy that escapes hafnium ($Z = 72$) tritide particles should be approximately the same as that which escapes erbium ($Z = 68$) tritide particles, which for particle diameters in the range 1 mm to 5 mm has been calculated to be in the range of 0.5 to 0.1 (Kropf et al. 1998). For 5-mm AMAD particles, the average beta-particle energy is about 1 keV per decay or less. The stopping power of 1-keV electrons in water is about 12 keV/mm. If we assume that the average lineal energy in a 1-mm-diameter spherical tissue volume is given approximately by the stopping power, then the quality factor associated with these escaping beta particles is about 3 (ICRU 40 1986). This value of Q is in good agreement with the recommended value

of $Q = 2$ for unattenuated tritium beta particles (ICRP 1986). The ICRP still recommends a value of $w_R = 1$ for all beta particles, including those from tritium decay (ICRP 1991).

Bremsstrahlung. For a 10-keV beta-particle slowing down in water, the fraction of its initial energy given off as *bremsstrahlung* radiation is 0.0001 (Turner 1986). This fraction depends on the atomic number of the atoms in the medium as Z^2 , so for hafnium ($Z = 72$), this value is approximately two orders of magnitude larger than for water ($Z \approx 8$). Thus, we should expect on average about 0.06 keV of *bremsstrahlung* energy. However, the average energy of escaping beta particles for a 5-mm particle is 0.6 keV per decay. Therefore, the dose due to

Table 1. Estimated annual limits on intake (ALI), derived air concentrations (DAC), and surface contamination (SC) action levels for inhalation of a 1 μm AMAD, aerosol of hafnium tritide, and lung clearance half-times (s) of 50 days, 500 days, and 5000 days for several lung dissolution rates (r). A correction for beta-particle self-absorption is not included.

s (days)	r (days)	ALI (mCi)	DAC Ci m^{-3}	SC ($10^6 \text{ dpm}/100 \text{ cm}^2$)
50	1×10^1	1.6×10^9	2.4×10^{13}	8.9×10^{11}
	1×10^1	5.7×10^8	8.8×10^{12}	3.3×10^{11}
	1×10^2	4.4×10^8	6.7×10^{12}	2.3×10^{11}
	1×10^2	3.2×10^8	5.0×10^{12}	1.8×10^{11}
	1×10^3	3.1×10^8	4.8×10^{12}	1.8×10^{11}
	1×10^3	3.0×10^8	4.6×10^{12}	1.7×10^{11}
500	1×10^1	1.3×10^9	2.0×10^{13}	7.5×10^{11}
	5×10^1	3.2×10^8	4.9×10^{12}	1.8×10^{11}
	1×10^2	1.8×10^8	2.7×10^{12}	1.0×10^{11}
	5×10^2	6.2×10^7	9.5×10^{11}	3.5×10^{10}
	1×10^3	4.7×10^7	7.3×10^{11}	2.7×10^{10}
	5×10^3	3.5×10^7	5.5×10^{11}	2.0×10^{10}
5000	1×10^3	3.4×10^7	5.2×10^{11}	1.9×10^{10}
	5×10^3	3.3×10^7	5.1×10^{11}	1.9×10^{10}
	1×10^1	1.3×10^9	2.0×10^{13}	7.4×10^{11}
	5×10^1	2.9×10^8	4.5×10^{12}	1.7×10^{11}
	1×10^2	1.5×10^8	2.3×10^{12}	8.6×10^{10}
	5×10^2	3.5×10^7	5.4×10^{11}	2.0×10^{10}
	1×10^3	2.1×10^7	3.2×10^{11}	1.2×10^{10}
	5×10^3	9.1×10^6	1.4×10^{11}	5.2×10^9
5000	1×10^4	7.6×10^6	1.2×10^{11}	4.4×10^9
	5×10^4	6.5×10^6	1.0×10^{11}	3.7×10^9
	1×10^5	6.3×10^6	9.8×10^{10}	3.6×10^9

bremsstrahlung is small relative to the beta-particle dose.

Secondary Limits. Table 1 contains estimated annual limits on intake (ALI) derived air concentrations (DAC), and surface contamination (SC) action levels for inhalation of 1- μm AMAD, poly-dispersed aerosols of hafnium tritide for several dissolution half-times and for clearance half-times of 50 d, 500 d, 5000 d, respectively. In all cases the effective ALI is listed because it is smaller than that of the lung's ALI. The SC action levels correspond to a potential exposure that would result in a committed effective dose of 1 mSv. The assumed pulmonary deposition fraction for 1 μm is 0.25. For larger particles, this fraction decreases, and the values of ALI on intake, DAC, and SC increase proportionally. For comparison, the ALI for tritium oxide is 3×10^{10} Bq, and the derived air concentration is 8×10^6 Bqm⁻³.

The values in Table 1 are based on the assumption that all the decay energy is deposited in 1000 g of lung tissue. These values do not include particle self-absorption corrections. To include this correction, these values must be scaled up by the appropriate factor (e.g., for particle diameters in the range of 0.1 μm to 5 μm , this factor is in the range of 2 to 10).

The effective ALI is determined from the sum of the dose delivered to soft tissues from tritium in the body water, with a 10-day biological half-time, after transfer from the pulmonary compartment, and the weighted lung dose ($w_{\text{lung}} = 0.12$) (ICRP 1988, 10 CFR 835 1994) from the deposited metal tritide dissolution and mechanical clearance half-times. The surface contamination action level is based on an eight-hour exposure period of light activity, 1- μm -AMAD material, detection efficiency of 0.2, and a resuspension factor from surface-to-air of 10^{-4} m⁻¹ (Brunskill 1964).

Discussion

Dissolution measurement data indicate a biological half-time in the pulmonary region on the order of 10^5 days. It is interesting to note that Cheng and coworkers have found the dominant

biological half-time in lung tissue to 1- μm -AMAD particles of titanium tritide to be on the order of 30 days (Cheng et al. 1997), significantly less than the half-times for hafnium hydrides discussed here. The dissolution rates for titanium tritide and hafnium tritide may represent extreme values for the metal tritides.

Miller and coworkers have noted that the dissolution rate of metal tritides may have high variability from one period to the next (Miller 1982). This variability was evident in the dissolution study presented here. Evidently, a small fraction of the hafnium tritide particles had a higher dissolution rate in one of the sample periods.

In this study, we assume that all of the beta-decay energy from deposited particles is delivered to the lung tissue. Corrections for self-absorption are strongly dependent on the particle-size distribution. The results presented herein would scale linearly with such a correction. Based on the current information regarding particle size and hafnium tritide solubility, it appears that the ALI and DAC for hafnium tritide (1- μm AMAD) will be two orders of magnitude lower than the corresponding values currently used for tritium oxide.

It is clear that in future work we need to focus heavily on workplace air monitoring, and because the dissolution rate is so critical, additional in vitro dissolution studies for a range of particle sizes and chemical forms are needed. In vivo studies are needed to confirm the results of the in vitro dissolution studies, as well as to determine mechanical clearance rates, which also are critical. Improved sensitivities in the assay of tritium in a urine matrix will be necessary to detect intakes corresponding to $E(50) = 5$ rem, if the pulmonary clearance rates turn out to be small. The lung dose calculation could be refined by a detailed Monte Carlo study and experimental confirmation of the decay-energy self-absorption for a range of sizes of metal tritide particles.

Another issue that should be considered in further modeling or research is in the role of alveolar macrophages in

particle removal. Macrophages are the primary lung resource for particle clearance, phagocytizing and transporting up to 90% of the particle burden from the lungs in one day (Lenert et al. 1987). If this process occurs with inhaled metal tritide particles, the distribution and dose received would be very different from those modeled in this paper.

The photomicrographs in Figures 4 and 5 indicate the "dust" of smaller particles covering the larger particles. It was impossible to determine a size distribution for these particles because they lie on the surface of the larger particles, and the particle-sizing program could not distinguish these small particles. It is clear that this dust is significantly smaller than the measured 5–20- μm AMAD particles. A possible solution to this problem would be to sonicate the samples to dislodge and disperse the smaller particles before scanning electron microscope measurements.

Deliverables

This study produced the following deliverables:

- Air-sample and surface-swipe workplace-monitoring techniques and action levels.

Status: Contamination action levels have been calculated for hafnium tritide materials.

- Bioassay schedule protocol and intake estimation.

Status: biokinetic model complete, bioassay response estimates complete.

- Internal dosimetry model.

Status: Basic biokinetic response functions have been developed and benchmarked, dose coefficients have been estimated, associated committed organ dose and committed effective dose models have been developed and benchmarked.

Publications and Presentations

Poster 1999 ESH DRC review

Presentation to DOE Metal Tritide Working Group, January 1999, Mound, Ohio

Presentation to LANL Tritium Users Group, July 1999

Poster 2000 CST DRC Review

Presentation to DOE-EH, Headquarters, April 1999

Presentation to DOE-EM, Headquarters, April 1999

Presentation to ESH-TDEA Committee July 1999

Manuscript submitted to *Rad. Protect. Dosimetry*; in press June 2000

In addition, the work with LRRI (initiated by the TDEA Project) has led to two larger collaborations between ESA and LRRI and NMT and LRRI.

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Determining and Monitoring the Inhalable Fraction of Plutonium Aerosols in an Accident

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Introduction

In nuclear laboratories where significant quantities of plutonium are handled in gloveboxes, both retrospective and real-time radiological air monitoring are routinely conducted. Real-time monitoring is conducted with alpha-continuous air monitors (CAMs), while retrospective monitoring is carried out by continuous sampling with filter air samplers (FASs). In the latter case, laboratory analysis for plutonium is made after allowing for decay of radon progeny collected along with whatever plutonium aerosol may have been present. These samples are assumed to be representative of worker breathing-zone air by virtue of monitor proximity to worker locations around a laboratory space. When the laboratory analysis of FAS data is complete, if exposure conditions warrant, the results may be used to support analysis of worker dose and interpretation of separate bioassay data. In this use, some estimate must be made of the activity median aerodynamic diameter (AMAD) of the particles associated with the release. Whereas in the past a very conservative assumption has been made that the AMAD is 1 mm, more recent studies of data obtained in the nuclear industry suggest that most radioactive aerosols are likely to have AMADs closer to the new default ICRP 66 assumption of 5 mm (ICRP 1994). Unfortunately, due to the challenges and costs associated with obtaining particle-size-distribution data by traditional methods, relatively little is known about plutonium-accident-aerosol distributions. The objective of this project has been to build a relatively simple and inexpensive FAS-type of aerosol-size spectrometer that would be a

practical addition to workplace monitoring. Then there would be an incentive to begin to build a database on accident aerosols that would be of great value to dose estimation.

Approach

The approach taken in this project has been to design a multistage size-fractionating sampler based on refinements of the 1970s concept of sampling with stacked nuclepore filters. As a result of the project studies, a sequential set of filters based on both nuclepore-type-sieve filters and newer nylon-mesh-type filters has been selected that should provide good separation of the larger size fraction ($> 10\text{-mm AD}$) in the particle distribution from the smaller sizes. Both computational fluid dynamics analysis and experimental testing have been used to select filters for this application and determine the filtration efficiency versus particle size for each filter type. After an exposure incident, the stack of filters can be disassembled and counted for plutonium activity. The interpretation of the resultant set of activities associated with particular filter responses is carried out by a deconvolution process called "expectation maximization" (Maher and Laird 1985). The strategy is to find the most likely particle-size distribution that will produce the observed distribution of plutonium activity on the several filters.

Progress

The Los Alamos National Laboratory's (LANL's) stacked-filter-array sampler for determining the particle-size distribution of plutonium aerosols that might be released into workroom air following an accidental

release has been successfully completed. The unit consists of a special filter-air-sampler open-faced holder, a stacked sequence of filters of selected mesh size to capture different portions of the polydispersed aerosol being sampled, a cartridge to hold the filter stack, a critical flow venturi to control flow through the stack at the design rate, and a solenoid valve to control when the sample is collected. The FAS holder, cartridge, and typical array of filters and filter separators are shown in Figure 1.

Figure 1. FAS holder (left), cartridge (center), and stacked filters (right).

We contracted with the URG Corporation to manufacture an updated version of the special FAS case for the Laboratory's Canberra Quick-Change-Cartridge filter holder, which is used in the project to hold the selected sequential filter array. A set of these URG-manufactured units, consisting of the cartridge holder and a critical flow venturi, was delivered in late August. Certain design modifications and URG vendor support problems had resulted in a much-delayed completion of the order.

The URG-finished piece is a considerable improvement over the earlier test FAS units manufactured locally. The new

FAS has a heavier sidewall that supports the use of a larger, sturdier hinge, which results in more stable cartridge loading and unloading. The entire assembly was manufactured out of aluminum stock and then finished with an electrodeless nickel metal plating that allows better fitting, nongalling assembly of the threaded parts, and permits more effective decontamination should a unit be exposed in a contaminated atmosphere. A vendor for a suitable 115-VAC solenoid valve that can be interfaced with the alarm relay contacts of an alpha CAM was identified, and a set was purchased for evaluation. With such a solenoid valve in line with the special FAS unit, it is possible to operate the sequential-filter-array size-fractionating sampler in a conditional mode, which means that only during those events resulting in a CAM alarm would a sample of the particulates be taken (valve switched on). This mode of operation avoids accumulations of unwanted background dusts and ensures that filter alpha-count analysis will be carried out only when activity is expected to be present.

Deliverable

An example of a complete plutonium particle-size-monitoring setup consisting of an assembly of an alpha CAM (Canberra Alpha Sentry), a FAS holder containing a cartridge with sequential filter array, a critical flow venturi for locking flow at the design specification, and a solenoid valve controlled by the CAM is shown in Figure 2.

Figure 2. FAS with sequential filter array controlled by an alpha CAM (background) via solenoid valve (left).

The red electrical cable connects the solenoid vacuum valve to the CAM relay contacts that will be programmed to close only in a radiation alarm condition (e.g., 4 DAC-hr exposure) as detected by that particular CAM. The cartridge in the CAM in the background is the same as the one holding the filter array in the FAS device. Other than the new, inexpensive FAS/venturi elements, no new parts and supplies are needed to implement this procedure. Although the CAM filter should be changed out on a regular basis (weekly), the sequential filter array cartridge may only be opened and counted in the rare event of a CAM alarm, thus minimizing the support costs of this additional form of air monitoring.

We conducted tests of a counting system for the filter array, a Model 7404 Canberra Quad Alpha Spectrometer detection system multiplexed to a Canberra AccuSpec MCA card in a PC. The radioactive particulates we used for the test were radon progeny collected on the filters in the ESH-4 radon chamber. The tests successfully demonstrated that such a counting system provides simultaneous alpha-spectral-counting capability for a set of filters from a sequential filter array. Such a procedure leads to high-sensitivity counts without long delays for decay of radon progeny because background compensation may be used. Alternative alpha-counting systems in use in the Laboratory's health physics analysis laboratories may also be used.

Planned tests of the effects of solid-particle bounce on the predicted size distribution when sampling dry particulates with this device were not completed as planned because certain FAS parts were unavailable and a source generator of a suitable solid-test aerosol was not available. However, it is expected that these tests will be completed as part of plans to apply the sequential filter array concept to a monitoring application in a related project.

Impacts

Although the concept is too new to have been implemented at present, there is interest in a trial of a FAS-type of aerosol-size spectrometer in a laboratory workroom. There has also been interest in applying this device to the problem of determining the particle-size distribution of other radioactive particulates such as stable tritiated particulates associated with decontamination and demolition operations in tritium laboratories. Again, as in the case of plutonium particles, the size of the inhaled radioactive tritium particulate has significant dosimetric consequences, so deploying a number of particle-sizing instruments such as the FAS-type of aerosol-size spectrometer around a work environment could provide much needed input to tritium dosimetry. A proposal has been submitted to the Department of Energy for funding a study that would include possible application of the stacked-filter-array FAS instrument.

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Implications of Room Ventilation and Containment Design for Minimization of Worker Exposure to Plutonium Aerosols

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Introduction

In work environments where toxic or radioactive materials are handled, a possibility exists for accidental airborne releases of toxic or radioactive aerosols or gases. This possibility requires that safety professionals and engineers design effective warning systems and countermeasures to minimize a worker's exposure. Computer simulations that use computational fluid dynamics (CFD) modeling of airflows and aerosol transport combined with tracer experiments can provide critical information. With this information, we can better determine where to place early warning and monitoring instruments and how to minimize transport of hazardous materials in the worker's breathing zone.

The amount of a harmful material inhaled by a worker depends on the temporal and spatial dispersion patterns in a room, the time-dependent concentrations in the worker's breathing zone, and the achieved level of protection from alarming air monitors. Aerosol dispersion patterns are driven by complex interactions of room ventilation rate and design, room furnishings, airflow characteristics, human presence and activity, and characteristics of the material (particle size, release rate, release location, etc.). Safety professionals often assume an instantaneous and perfectly uniform (well-mixed) concentration field when estimating exposures. This assumption can lead to large underestimates of exposure. For example, research shows that complete mixing is often not attained (Nicas 1996) or that it can take up to several hours for complete mixing (Buchanan et al. 1995). In addition, steep, time-dependent concentration gradients can exist in the vicinity of the release, an area often occupied by the worker(s) who

caused the release and where s/he could get large exposures (Dresher et al. 1997, Whicker et al. 1997).

Buchanan (Buchanan et al. 1995) demonstrated that airflows can be significantly altered by simply partitioning a room and that mixing improves as the airflow disruption increases. This disruption depends on the interplay of the obstruction's size, shape, and placement relative to convective flows. Nielsen (1998) showed the influence of furniture on air velocities in occupied areas and that the influence seemed greater at the higher room-air exchange rates. Because in the Los Alamos National Laboratory Plutonium Facility glovebox sections can be added, removed, or modified, and ventilation rates can fluctuate, it is important to investigate how changes in these parameters can influence general airflow characteristics and aerosol transport.

The goals of this study were to investigate changes in airflow characteristics such as velocity and direction, turbulence intensity, and subsequent aerosol dispersion as they are affected by changes in ventilation designs (rate and diffuser design), interior room furnishings, and human presence. Ultimately, strategies for enhanced worker protection can be realized through better understanding and accurate prediction of transport of released aerosols as influenced by ventilation-induced airflow patterns, containment structures, and interactions with a worker positioned in front of a containment structure.

Materials and methods

Experimental Room. The simulated plutonium workroom we used in this study is a free-standing structure located in a larger building. The room is a

modular metal-wall structure with dimensions of 6.1 m x 4.8 m x 2.4 m ($V = 70.3 \text{ m}^3$). This interior space is furnished with two mockup glovebox lines and an overhead passbox (a sealed tunnel used for moving radioactive samples between gloveboxes in a plutonium facility). The gloveboxes, made of aluminized foam board, were removable so three different configurations could be arranged: 1) two full rows of gloveboxes and passbox (FB); 2) half of the gloveboxes removed and passbox (HB); and 3) all gloveboxes and passbox removed (NB). Schematic cross-sections of the room configurations are presented in Figures 1a, b, and c.

The room is supplied with close-looped HEPA¹-filtered air using a portable HEPA-filtered blower² that passes incoming air passing through four 0.2 m-diameter inlet nozzles with 0.3 m-diameter horizontal baffle plates that were located in the ceiling (Figure 1). Four 0.2-m-diameter adjustable-flow exhaust registers are located in the room corners 0.3 m above the floor. The nominal volumetric air exchange rate was set to approximately 6 h⁻¹ LV (low ventilation) or 12 h⁻¹ HV (high ventilation) by adjusting the baffle plate on the air-blower outlet line. Because the experimental room is located indoors and has a thermally insulated floor, no significant (less than 0.5°C) temperature gradient was detected between opposite walls (including ceiling and floor), as measured with fine wire thermocouples³. The room openings (e.g., sampling or cable ports) were sealed to make the structure as airtight as possible.

¹ High-efficiency particulate air filter.

² Model SP-700, Radiation Protection Systems, 10 Vista Dr, Old Lyme, CT 06371-1541.

³ Model FW05, Campbell Scientific, Inc., Logan, UT, USA.

Figure 1. Schematic diagram of the test-room facility with three different configurations of simulated gloveboxes: a) full set of gloveboxes (FB), b) half of gloveboxes removed (HB), c) no gloveboxes or trolley (NB).

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Air-velocity measurements. We used a commercial three-dimensional sonic anemometer⁴ to characterize room airflow. Sonic anemometers measure the time of flight of pulsed sound waves across a fixed-measurement path. To measure air velocity on each axis, two ultrasonic signals are pulsed in opposite directions; times of flight of the first signal (out) and second signal (back) are measured; and air velocity is calculated from the time difference. From these measurements, we determined the three orthogonal air-velocity components using a programmable sampling rate. Wasiolek (1999) presents a detailed description of air-velocity measurements in rooms using sonic anemometry.

⁴ CSAT Sonic Anemometer, Campbell Scientific, Inc. Logan, UT, USA.

We mounted the sonic anemometer head on a mobile cart for ease of transport and leveled it after every change in sampling location. The mounting arrangement allowed for changes in the sampling height. The sonic anemometer head (Vogt 1997) and the mobile cart were designed to minimize local airflow disturbance.

Sampling frequency of the sonic anemometer was set to 1 Hz, and data were collected over a sampling interval of 600 s. We converted the raw, binary data files containing air-velocity individual components to ASCII text format, corrected them for offset, and rotated them to align orientation of the sonic sampling head with common room coordinates.

By vector summation of individual air-velocity vector components u_x , u_y , and u_z , the absolute air velocity was calculated for every sample, i , with the equation

$$u_i (\text{cm s}^{-1}) = \sqrt{u_{ix}^2 + u_{iy}^2 + u_{iz}^2} \quad (1)$$

The time average velocity for a 10-min run was calculated as

$$\bar{u} = \frac{1}{N} \sum_{i=1}^N u_i$$

Turbulence Measurements. A statistical measure of the dispersion of data of a variable A about the mean $\bar{A}$ is the unbiased variance σ_A^2 defined as

$$\sigma_A^2 = \frac{1}{N-1} \sum_{i=0}^{i=N-1} (A_i - \bar{A})^2 \quad (2)$$

Figure 2. Locations of sonic anemometer measurements in the experimental room.

However, any turbulent variable, A , can be split into a mean and turbulent part as $A = \bar{A} + a'$, and the substitution of a turbulent part $a' = A - \bar{A}$ into the definition of variance gives (Stull 1988)

$$\sigma_A^2 = \frac{1}{N-1} \sum_{i=0}^{i=N-1} (a'_i)^2 = \overline{a'^2} \quad (3)$$

Therefore, since the standard deviation is interpreted as a measure of the magnitude of the spread or dispersion of the original data from its mean, it can be used as a measure of the level of turbulence.

The level of turbulence might be expected to depend on the air speed, so it is often normalized to the mean air

velocity. Several definitions of turbulence intensity are used in the literature. Hanzawa et al. (1987) defined turbulence intensity as standard deviation, s , of air velocity, u , divided by local mean velocity, $\bar{u}$:

$$Tl_t = \frac{\sigma}{\bar{u}} \quad (4)$$

We selected the 19 locations marked in Figure 2 for air-velocity measurements. As the experimental room in two of the glovebox configurations has a ceiling-mounted passbox, the sampling heights varied depending on location. At locations 7, 8, 9, we sampled heights at 60 cm and 120 cm; for all 19 sampling

locations, we measured at approximately 60 cm, 120 cm, and 180 cm above the room floor. In the NB room configuration, we sampled at all three heights. The sonic anemometer was positioned 50 cm from glovebox faces and the room walls. We measured under steady-state conditions, which were established by waiting for at least 5–10 min (one nominal air exchange) after closing and sealing the room door.

Aerosols Measurements. The method used in the present aerosol study is similar to the one described by Whicker et al. (1997). Because most releases in Laboratory workrooms are acute “puff” releases (McAtee 1990), our study focused on this type of short-duration release (60 s). In addition, the data analysis in the present study emphasizes the time-dependent nature of aerosol dispersion. The time resolution of concentration measurements in this study is 10 s. This resolution allowed analyses of the time progression of an aerosol cloud.

To simulate an accidental release, we generated polydisperse dioctyl sebacate (DOS) oil aerosols with a custom-made orifice nozzle. Operation of the nozzle was adjusted for releases so that aerosols exited the nozzle at low velocity (approximately 1 cm s^{-1}) and quickly accommodated to local airflow conditions. The particle-size distribution was approximately log normal with the count median diameter of 0.52 μm and geometric standard deviation of 2.0. From analysis of historical accident data, we concluded that most releases took place as a result of some worker action and not a random event; therefore, we positioned the aerosol release nozzle 120 cm above floor (approximately chest high, the height of glovebox gloves) to simulate a glovebox glove-failure-type release, which is the most common cause of airborne releases (Whicker 1993).

An array of 16 laser particle counters⁵ (LPCs) was established in the test room to make aerosol measurements resolved in time and space. Figure 3 shows the

⁵ Models 3755 and 7550, Particle Measuring Systems, 5475 Airport Blvd., Boulder, CO 80301.

Figure 3. Locations of aerosol releases (Roman numerals) and laser particle counters (LPCs) in the experimental room.

aerosol release and LPC locations in the test room. The LPCs were suspended 120 cm above room floor. Location and height of LPCs were selected to be close to the breathing zone of a worker at a glovebox workstation. The airflow rates of the LPCs were controlled by a critical-flow orifice with a sampling rate of about $50 \text{ cm}^3 \text{ s}^{-1}$. All LPCs were coupled to a multiplexer⁶, and the raw data were recorded every 10 s using commercial software⁷. Raw concentration data were corrected for LPC-specific airflow rates and for particle coincidence counting. A 60-s release at every location was

repeated three times for quality control, and we present the results as averages of the three releases.

For this study, the lag time was used as the metric for comparison among changes in the ventilation rates and room configurations. Lag time was defined as time from the start of the release until the time that an aerosol concentration at the

⁶ Model 3701, TSI Inc., 500 Cardigan Rd., St. Paul, MN 55164-0394.

⁷ Model 390040 Advanced Cleanroom Software, TSI Inc., 500 Cardigan Rd., St. Paul, MN 55164-0394.

sample location exceeded three standard deviations above background on two consecutive 10-s measurements.

Data Analysis

The metrics of lag time, air velocity, airflow direction and turbulence intensity were stratified by ventilation and room configuration. We then compared them with one another using nonparametric tests because the measurement distributions were not normally distributed. The Sign Test was used for the paired comparisons of air velocity, turbulence intensities, and lag times. To look for the effects of room configuration and ventilation rates on the variation of lag times across all sampling locations, we compared coefficients of variations in the mean lag times using a dependent t-test.

We measured changes in airflow direction by the angle (in radians) between the flow vectors for each ventilation and room geometry condition. We paired direction vectors for each sampling location with the direction vector at the same location but measured under either a different ventilation rate (same room configuration) or a different room configuration (same ventilation rate). This angle in radians was determined by Equation 5.

$$\cos^{-1} \theta =$$

$$\frac{x_1 x_2 + y_1 y_2 + z_1 z_2}{\sqrt{x_1^2 + y_1^2 + z_1^2} \times \sqrt{x_2^2 + y_2^2 + z_2^2}} \quad (5)$$

We created histograms, which measured the effects of each of the variables of changes in airflow direction as ventilation rate changed (holding the room configuration constant) and altered room configuration (holding the ventilation rate constant).

CFD Analysis. We made significant progress during the last fiscal year by using computer-aided CFD tests of the effects of alternative ventilation designs on room airflow patterns. Along with ESH-1, NMT-8, and ESA-DE, we identified three alternative designs to test against the baseline design (similar to that in the Plutonium Facility). These

three alternatives were designed based on two important criteria: first, airflow directed in a downward direction at the faces of the mock gloveboxes; and second, a cost-effective and easy-to-install alternative design. The three tested alternative designs included a cone-shaped diffuser and a ceiling with deflector plates and an air shower design. Figure 4 shows the designs of the supply diffusers. In addition, the impacts of humans on the airflows were studied (Figure 5).

Figure 4. Various supply diffuser designs that were tested for downward airflow in the breathing zone using CFD analysis. Schematic (a) the current diffuser design, (b) a cone-shaped diffuser, and (c) the air-shower design.

Results

Air velocity. Figure 6 shows that the average air velocities for different configurations were similar as they scaled up with increased ventilation rate. The increase in mean flow velocities between LV and HV rates were by factors of 2.71 for the full set of gloveboxes (AB); 2.83

Figure 5. UHTREX geometry with simulated humans.

for half gloveboxes removed (HB); and 2.41 for the empty room (NB). The velocities ranged from a low of 1.6 cm s^{-1} under LV conditions up to 12 cm s^{-1} under HV conditions.

Figure 7 shows the effects of variations in room geometry and ventilation rates on the direction of airflows as

Figure 6. Plot of U_T (the standard deviation) turbulence intensity, and lag time under different ventilation and room configuration conditions.

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Figure 7. Changes in airflow direction with changes in (a) glovebox configuration, (b) ventilation rate.

Table 1. Mean square values of the fluctuating velocity components for different room setups and ventilation rates

	σ_x^2	σ_y^2	σ_z^2
ABLV	2.79	3.16	2.61
ABHV	17.63	16.47	16.86
HBLV	2.92	3.04	3.35
HBHV	18.74	19.07	18.24
NBLV	2.95	3.02	2.94
NBHV	18.57	17.37	16.87

calculated using Equation 5. These histograms show that changes in direction are mostly less than 90° (1.57 radians) across the variations. The median change in angle over the variation in air exchange rate was 0.94 radians with a quartile range of 0.6 to 1.4 radians. The median change in direction for variations across changes in room configuration was 0.92 radians with a quartile range of 0.47 to 1.54 radians.

Turbulence. The measurement of turbulent eddy size with a sonic anemometer is restricted by the volume averaging of the sensor caused by the 10-cm spacing between transducers. The sampling frequency used in our study was only 1 Hz, which is below typical sampling frequencies used in thermal anemometry.

The average values of TI were very similar for all configurations and ventila-

tion rates. Because CFD simulations often assume isotropic turbulence (i.e., at any point in the flow the mean square values of the three fluctuating components are equal $\overline{\sigma_x^2} = \overline{\sigma_y^2} = \overline{\sigma_z^2}$), we checked the validity of this assumption for the studied room configuration and ventilation rate. We present the results in Table 1. The variances of air-velocity components averaged for all 19 sonic anemometer locations for a particular room geometry and ventilation rate are very similar, suggesting that the turbulence was approximately isotropic for each room and ventilation condition.

Aerosols. One of the primary objectives of the study was to obtain data on aerosol dispersion, especially in regard to transport time. The metrics used for this purpose were the lag time and the lag time to maximum concentration. The response time is the critical parameter in placement of air monitors in a work place. Figure 4 shows the decrease in mean lag times with increasing ventilation rate, and Figure 8 compares the distributions of lag times categorized by room and ventilation configuration.

The two-fold increase in ventilation rate resulted in the decrease of the lag time by a factor of 2.0 for AB, 1.7 for HB, and 1.9 for NB. It is interesting to notice the difference in lag time to the beginning of an aerosol cloud to lag time to maximum aerosol concentration by a factor of about 2.5. This finding could provide data for revision of some common assumptions used in industrial hygiene, e.g., instantaneous mixing of particulate air pollutants or the times needed for evacuation of a contaminated facility. There was also a strong dependence of average lag time on the release location. For example, for the ABLV release at Location 3, the average lag time was 83 s versus 223 s for release at Location 1.

We studied the influence of ventilation rate on aerosol dispersion (mixing) rate in more detail by comparing the variation of lag times across all sampling locations for each release. Figure 9 shows the effects of room configuration and

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Figure 8. Box-and-whisker plot of lag times under various room and ventilation conditions.

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Figure 9. Box-and-whisker plot of the coefficient of variation among lag times categorized by room and ventilation conditions.

Figure 10. CFD result for flat-plate diffuser (baseline PF-4 type).

Figure 11. CFD results for air-shower diffuser and under glovebox exhausts.

ventilation rate on the coefficient of variation of mean lag times as measured across all LPCs in the room for each release location. Statistical comparisons showed that there was a general decrease in the coefficient of variation (COV) as glovebox lines were removed. This decrease suggests that complete aerosol mixing throughout the room is more rapid when there are fewer furnishings in the room. We found no significant differences in the COV when the ventilation rate varied and the room configuration remained the same.

CFD Results. After all the supply diffuser types we had analyzed with CFD, the results suggested that the air shower with an exhaust located under the glovebox provided the most protective airflow patterns that would sweep aerosols downward and away from the breathing zones. Figures 10 and 11 show the predicted airflow velocities in the vertical direction at the breathing zone height for the current design and the air shower, respectively. The colors represent a velocity scale with positive velocities in the upward direction. The velocity vectors for the air shower were generally downwards at each of the workstations, with the exception of under the trolley. However, the CFD model of each of the designs assumed seven room air exchanges per hour and this resulted in low air velocities (a few centimeters per second) with the air-shower design. Therefore, it was important to see the effects of human presence at the workstation. Airflow around a human figure was modeled for both an unheated human (to look at flow blockage only) and a heated human. Preliminary results suggest that humans create significant alterations in local airflow patterns, which could have significant implications for trying to estimate worker exposure. However, the effects of a worker's presence could be localized and may not significantly affect the general airflow patterns in the room.

Discussion

The objective of our study was to investigate how changes in room geometry and ventilation rates influence airflow and aerosol dispersion. Changes in these variables are observed to occur quite often in many research facilities that contain toxic materials. Studying the effects of these changes is important when we evaluate the level of worker protection provided by a distribution of air monitors in a room or when trying to accurately interpret air sample results under varying conditions.

We found that ventilation rate (for the same room configuration) significantly affected lag times and airflow velocities, but not turbulence intensity. As ventilation rates increased, lag times decreased, which is probably tied directly to the increase in airflow velocities. Turbulent eddies also affected the rate that aerosols were transported through the rooms. We found that as the airflow velocities increased, velocity deviations also increased proportionally, resulting in relatively constant turbulence intensity across all strata of ventilation rate and room configuration. The constant turbulence intensity suggests that the rate of aerosol dispersion, as reflected by the lag time, is affected by the airflow velocities in a room and also by a turbulent diffusion rate. Our observations confirm the findings of Siurna and Bragg (1986), who showed that the velocity field and turbulence fields are of fundamental importance in contaminant dispersion by room ventilation. We did find that turbulence intensity appeared to be linearly related to airflow velocity, which may also suggest a nonlinear relationship between aerosol dispersion rates and ventilation rate because the dispersion rates are affected by both airflow velocity and turbulence. Finally, changes in ventilation rate, while affecting airflow velocities, did not seem to completely alter the direction of the airflows. We found that over 75% of the changes in direction were less than 1.4 radians (80°) when changes in ventilation alone were considered.

In addition, our results suggest that changes in the room configuration (for the same ventilation rate) have significant effects on the mean lag times and their COV but generally had little effect on the direction of the airflow vector, mean airflow velocities, or the turbulence intensity. In general, there was a trend for lag time to decrease with removal of the mock glovebox sections. The data suggest that room structure has a tendency to slow down mixing by creating areas of relatively stagnant air or air pockets. If furnishings are removed, the aerosol mixes more rapidly. Changes in room configuration have no significant effect on airflow velocities, except between HBLV and NBLV experimental setups when the HBLV resulted in higher velocities. We found it difficult to determine if this is because of experimental uncertainty or perhaps the presence of the structure in the room that increases the air exchange rate and consequently the airflow velocities.

It is also possible that there is an effect not only of adding a structure in a room, but also of placing of the structure relative to the airflow direction and velocity. Buchanan et al. (1995) suggests this effect as they found an increase in mixing with an increase in the airflow disturbance. However, the effects of room furnishings and airflow characteristics on worker exposure are complex. Flynn et al. (1996) found that under certain airflow conditions the presence of an object could impede contaminant removal from the breathing zone of a worker unless the airflow was from the side of a worker and swept the airborne material out of the space between the worker and the furnishing.

Deliverables

The deliverables included

- Evaluating a number of possible ventilation and containment configurations designed to create favorable airflow patterns and upon which recommendations will be based;
- Obtaining valuable information on CFD model validation along with a sensitivity analysis to help determine the important variables influencing the capture efficiency of slot-boxes and local airflow patterns;
- Making the larger audience of safety professionals and facility owners aware of our findings through technical presentations and peer-reviewed articles.

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PRESCILA: Proton Recoil Scintillator Los Alamos Neutron Dose Meter

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Funding: FY99, \$15K

Introduction

Neutron meters currently in use at Los Alamos National Laboratory (LANL, Laboratory) and elsewhere are based on 1960s technology that relies on a large neutron moderator assembly surrounding a thermal detector to achieve an accurate dose response. Typically, a BF₃ gas-filled detector tube is positioned in the center of a heavy (e.g., 20 lb) polyethylene moderator. The only commercial exception is the HPI Inc. Model Rem 500, an instrument that weighs 5 lb, but is severely limited in sensitivity (only 8 counts per minute per mrem/h), offers no thermal response and is very expensive (\$6 K).

In general, current dose meters are not only heavy and bulky but possess a poor high-energy response above 10 MeV, which makes them inaccurate for applications at high-energy accelerator facilities (e.g., Los Alamos Neutron Science Center [LANSCE]). Other disadvantages are high cost (as much as \$6 K) and poor ergonomics for field surveys.

Our goal was to develop a practical proton recoil scintillator (PRESCILA) of low-weight (< 5 lb) with good sensitivity and gamma rejection and enhanced high-energy response. PRESCILA offers the potential of replacing thousands of neutron rem meters in field applications around the world with a lightweight and more accurate design.

Benefits

The Radiation Protection Group (ESH-1) has requested a lightweight alternative to the standard rem meter to facilitate field surveys. The weight of the PRESCILA prototype detector is less than 5 lb versus the 20 lb of a standard rem meter.

The cost of maintenance of the current inventory is driven by the need to periodically replace the BF₃ detector tube (\$300 each). Over the life of the inventory (130 rem meters), these costs are estimated to be \$60 K. Maintenance costs for PRESCILA should be about 50% lower, for a saving of \$30 K.

The poor energy response at high-neutron energies limits the ability of a standard rem meter to accurately measure dose around accelerator facilities such as LANSCE. Standard rem meters with a pure polyethylene moderator seriously underestimate (by up to a factor of 10) neutron dose around accelerator facilities. Two recent designs use lead and tungsten inserts to improve the high-energy response via spallation neutron generation but at a serious weight penalty, which pushes the moderator assembly to over 30 lb.

As PRESCILA-type rem meters are accepted throughout the DOE complex, cost savings and improved performance will be realized within every radiation protection program where neutron exposure is present.

The possibility of patenting this detector means royalty income to the Laboratory via licensing agreements with instrument vendors. For example, Eberline Instruments, Inc., has expressed strong interest in commercializing the PRESCILA technology.

Objectives and methods

During FY99, the project team investigated a Generation II PRESCILA probe design with the following objectives:

- identify the optimum operating point,
- characterize the probe's energy response, and

- develop a Generation III design based on test and evaluation results.

Progress and results

Optimum Operating Point.

PRESCILA was operated with the Eberline E600 counter during all data collection. The E600 counter's functionality provides for definition of both gamma-and neutron-channels-based pulse-height discrimination. In addition, a real-time algorithm allows subtraction of a fixed percentage of one channel from the other. This feature makes it possible to implement a dynamic gamma compensation scheme to correct for gamma spillover into the neutron channel by subtracting a small fraction of the gamma-channel-count rate from the neutron channel.

The gamma spillover was measured in pure gamma fields using both ¹³⁷Cs and ⁶⁰Co sources. The photomultiplier high-voltage and the upper discriminator setting were varied to determine the spillover as a function of instrument parameters. Monte Carlo calculations of the expected electron-energy-track distributions in the plastic scintillator made it possible to calculate a relationship between electron energy and upper discriminator voltage. For ¹³⁷Cs photons, a maximum of 0.4 MeV is deposited in the scintillator. The corresponding upper discriminator setting was determined to be about 16 mV. For ⁶⁰Co, the maximum deposition is 0.8 MeV, and a discriminator setting of 32 mV is required for effective photon rejection. The light output function for a plastic scintillator is nonlinear for proton recoils because of a pronounced dE/dx effect. Relative to electrons, protons produce about one-third less light in the range below 0.5 MeV. Therefore, pulse-height discrimina-

tion for photons introduces a much higher threshold for proton recoils. For ^{137}Cs discrimination, the corresponding cutoff for neutrons is about 1.2 MeV, and for ^{60}Co discrimination the neutron cutoff is 2.5 MeV. An upper discriminator setting of 16 mV at a photomultiplier high voltage of 635 V (4% spillover for ^{137}Cs) was selected for energy-response testing.

Probe Energy Response. PRESCILA was irradiated at the German Bureau of Standards (PTB) Accelerator Facility during July 1999 to a series of monoenergetic neutron beams over the energy range from 0.144 MeV to 19 MeV. These beams are produced by accelerating protons or deuterons onto a variety of targets. The beams have been well characterized by spectral measurements, including time-of-flight techniques. The probe was irradiated at each technique with and without a shadow cone to determine the room return. The room return was subtracted from the gross measurement to obtain the net count. The results of these measurements are shown in Figure 1.

The detector response in counts per minute (cpm) per unit dose is given as a function of incident neutron energy. The ideal rem meter response is a uniform response with energy. The measured high-energy response is excellent above 8 MeV. At 1.5 MeV, the detector response is near zero because all of the proton recoils are produced below the gamma discriminator setting. At and below a neutron energy of 0.25 MeV, the signal response rises slightly because of the thermal signal from the ZnS(Ag). These measurements highlight the need to improve the detector's response at intermediate energies.

Generation III Probe Design. Based on the energy response measurements collected at PTB, the PRESCILA probe was redesigned to incorporate a thermal detector element. This dual-scintillator design will improve on the energy response of earlier designs.

Conclusion and deliverables

Much information has been obtained about the underlying physics and performance capabilities of the Generation II probe. Gaps have been identified in the energy response, and means to address these gaps have been incorporated into the original design. The Generation III probe design will be assembled and tested during the FY 2000 phase of this project. The concept continues to be viable and promises to meet the following performance benchmarks:

- lightweight (< 5 lb),
- capability for both neutron and gamma dose measurements,
- neutron sensitivity of 100 cpm/mrem/h (about twice the neutron response of an Eberline NRD rem meter), and
- gamma rejection to 100 mR/hr.

Figure 1. Prescila energy response.

Rapid Discrimination of Personnel Contamination Due to Radon Versus Other Alpha-Emitting Radionuclides

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Funding: FY99, \$22.2 K; FY00, \$18 K. The collaborators contributed \$25 K in FY99 and \$12 K in FY00.

Introduction

Personnel, clothing, and other items may become contaminated with unknown radioactive isotopes. Naturally occurring radon and thoron affect the ability to determine the source of contamination because they collect on electrostatic surfaces—plastic items and synthetic clothing—then transfer to personnel or clothing.

The present available methods for determining if contamination is due to radon or other radionuclides include the following:

- alpha-to-beta ratio determination (accomplished with hand-held alpha-beta friskers in the field or by counting smears with gross alpha-beta laboratory counters),
- sample recount after a short decay period to confirm short-lived or long-lived isotopes,
- alpha spectroscopy, and
- gamma spectroscopy.

These methods take time and may prove inconclusive. Investigation time results in lost productivity and varies according to what is learned about the unknown contaminant. Also, while the worker and the surveyor(s) make a determination, the worker may become anxious because an uptake has the potential to affect his/her health and safety and medical treatment may be necessary.

Approximately 150 contamination events each year are due to radon progeny. Any personal or clothing contamination other than that from radon must be reported in an radiological

incident report (RIR). Each year, approximately 300 RIRs are written for personal and/or clothing contamination incidents at the Laboratory. A simple RIR may cost \$10 K in person-hours per incident (300 incidents times \$10 K = \$3 M/yr). The determination that these are radon contamination events may cost as much as \$2 K for each event in person hours (150 events times \$2 K per event = \$300 K/yr).

Rapidly ruling out radon progeny as the contaminant allows investigation of the cause of contamination to proceed more efficiently. Being able to identify the contaminant as radon also allows timely resumption of normal operations and minimizes worker concerns about radiological safety. Being able to identify the specific isotope allows the investigation into the causes of the incident to be directed to only those operations and locations where that specific isotope is present. In addition, this rapid identification of the isotope assists the Occupational Medicine Group's response to personnel contamination events.

Reducing the time to determine if contamination is due to radon results in a person-hour cost saving equal to the percent reduction in the time required (150 events times \$2 K times a 50% reduction in time required = \$150 K/yr). A small percentage (perhaps 10%) of those incidents of personal or clothing contamination reported in the RIRs may be due to radon, but we do not have the capability or resources to make the determination at the lower regulatory limits for personal contamination. This potential cost savings is \$300 K/yr (300 incidents/yr x 0.10 x \$10 K/incident).

The total potential cost savings of \$450 K per year is the sum of the cost saved by reducing the response time to determine if the event is due to radon progeny (\$150 K/yr) and the cost saved by not producing RIRs for the 10% of the contamination events that are due to radon (\$300 K/yr).

Objectives

We identified the following objectives:

- Detect other alpha-emitting isotopes such as ^{239}Pu , ^{238}Pu , ^{241}Am , ^{238}U , ^{235}U , and ^{234}U in the presence of interferences from radon/thoron progeny,
- Achieve a detection limit of less than 300 dpm/100 cm² for the isotopes of interest using a short count time, and
- Determine if the contaminant is one of the transuranics or if it is uranium or thorium.

Method

The radon/thoron interference in alpha contamination discrimination is due to the 7.68-MeV ^{214}Po and 6.0-MeV ^{214}Po alpha peaks from ^{222}Rn decay and the 8.78-MeV ^{212}Po and 6.05-MeV ^{212}Bi alpha peaks from ^{220}Rn decay. Radon and thoron exist everywhere in our environment and are a source of concern when personnel or their clothing are contaminated with these sources of natural radioactivity.

The typical personnel contamination response begins with a contamination alarm on a whole-body frisker such as the Eberline PCM-2. A responding radiological control technician (RCT) then uses a hand-held contamination detector to perform a whole-body frisk. The spot of

contamination or the article of clothing may be removed and allowed to radioactively decay for a short period before another measurement is taken. Radon progeny have an effective half-life of approximately 30 min while thoron progeny have an effective half-life of approximately 10.5 h. When the hand-held contamination detector shows no detectable activity and the PCM-2 does not alarm, then the activity is determined to have been radon progeny.

The determination of the alpha-to-beta ratio using the PCM-2's indication and the hand-held contamination monitor such as the Eberline E-600/SHP-380 gives further assurance that the contaminant is radon progeny if the ratio is approximately 1:2. However, this method is not absolute since a mixture of alpha and beta emitters other than radon progeny could have been encountered. The uranium isotopes have a similar alpha-to-beta ratio.

Alpha, beta, or gamma spectroscopy can sometimes be used to identify specific isotopes. Alpha spectroscopy is performed in the field using the SAIC AP-2 hand-held instrument. This instrument has an alpha-energy resolution of about 200 keV. If the alpha emitters on the spot of contamination are not attenuated, then the AP-2 can resolve the alpha energies well enough to distinguish radon progeny alpha emitters from the other alpha emitters. However, such things as clothing and hair do attenuate the alpha energies, causing the spectrum on the AP-2 to be smeared into the lower energy range. Beta spectroscopy is not routinely performed in the field, but has some potential for identifying the contamination as being radon progeny. At present there are no portable-low-cost beta spectroscopy systems commercially available. Gamma spectroscopy is performed in the field using the HPI Rainbow MCA and the 3-in.-diameter by 3-in.-thick sodium iodide detector. This instrument has a gamma energy resolution of about 10 keV. The gamma emitters may be attenuated by various materials, but the gamma energies are not shifted as is the case with the alpha-spectroscopy systems.

Isotopes and Instruments

Figure 1 shows the commonly encountered alpha emitters. Table 1 provides a comparison of thoron and thorium decay rates. Table 2 provides a comparison of radon decay rates.

Instruments

The following are illustrations and descriptions of the instruments that can be used during a personnel contamination response.

Figure 1. Commonly encountered alpha emitters.

Table 1. ^{220}Rn (thoron) decay from ^{232}Th (thorium)

Isotope & half-life	^{220}Rn (thoron) decay from ^{232}Th (thorium)		
	α Energy (MeV) & abundance	β Energy (MeV) & abundance	γ Energy (MeV) & abundance
^{220}Rn 55s (thoron)	6.29 @ 100%	No	0.550 @ 0.07%
^{216}Po / 0.15 s	6.78 @ 100%	No	Negligible
^{212}Pb / 10.64 h	No	0.346 @ 81% 0.586 @ 14%	0.239 @ 47% 0.300 @ 3.2%
^{212}Bi / 60.6 m	6.05 @ 25% 6.09 @ 10%	1.55 @ 5% 2.26 @ 55%	0.040 @ 2% 0.727 @ 7% 1.620 @ 1.8%
^{212}Po / 304 ns	8.78 @ 100 %	No	Negligible
^{208}Tl / 3.10 m	No	1.28 @ 25% 1.52 @ 21% 1.80 @ 50%	0.511 @ 23% 0.583 @ 86% 0.860 @ 12% 2.614 @ 100%

* ^{212}Bi decays 64% of the time to ^{212}Po through beta decay and 36% of the time to ^{208}Tl through alpha decay.

Table 2. ^{222}Rn (radon) decay from ^{238}U

^{222}Rn (radon) decay from ^{238}U			
Isotope & half-life	α Energy (MeV) & abundance	β Energy (MeV) & abundance	γ Energy (MeV) & abundance
^{222}Rn / 3.823 d	5.49 @ 100%	No	0.510 @ 0.07%
^{218}Po / 3.05 m	6.00 @ 100%	0.33 @ 0.019%	Negligible
^{214}Pb / 26.8 m	No	0.65 @ 50% 0.71 @ 40% 0.98 @ 6%	0.295 @ 19% 0.352 @ 36%
^{214}Bi / 19.7 m	Negligible	1.00 @ 23% 1.51 @ 40% 3.26 @ 19%	0.609 @ 47% 1.120 @ 17% 1.764 @ 17%
^{214}Po / 164 μs	7.69 @ 100%	No	0.799 @ 0.014%
^{210}Tl / 1.3 m	No	1.3 @ 25% 1.9 @ 56% 2.3 @ 19%	0.296 @ 80% 0.795 @ 100% 1.31 @ 21%
^{210}Pb / 21 y	Negligible	0.016 @ 85% 0.061 @ 15%	0.047 @ 4%
^{210}Bi / 5.01 d	Negligible	1.161 @ 100%	Negligible
^{210}Po / 138.4 d	5.305 @ 100%	No	Negligible
^{206}Tl / 4.19 m	No	1.571 @ 100%	Negligible

PCM-2. The typical personnel contamination response begins with a contamination alarm on a whole-body frisker such as the Eberline PCM-2. The PCM-2 has multiple, large-area P-10 gas flow detectors for measuring alpha and beta contamination.

Figure 2. PCM-2.

E-600/SHP-380. A whole-body frisk is then performed by the responding RCT using a hand-held contamination detector such as the Eberline E-600/SHP-380. The SHP-380 is a hand-held detector using a plastic scintillator for beta detection and zinc sulfide for alpha detection.

Figure 3. Eberline E-600/SHP-380.

SAIC AP-2. A portable instrument such as the SAIC Alpha Analyzer AP-2 or the Quantrac Sensor AP750 may be used to determine the alpha energies. These microprocessor-controlled, portable, solid-state silicon detector instruments allow for discriminating the alpha energies to a resolution of about 300 keV in field conditions. The instruments are similar in size to a typical alpha-beta frisker and are used in the same manner to locate the area of contamination. However, the active area of the detector is 2 in. in diameter, about 1/6 the surface area of the E-600/SHP-380. Then the probe is held directly over the area of highest activity while a spectrum is collected. The MCAs in these instruments give more than adequate channels of separation for discriminating the 7.68-MeV peak from a 5.5-MeV peak. Discriminating a 6.0-MeV peak from a 5.15-MeV peak is also a simple task. Discriminating the 6.0-MeV peak from a 5.5-MeV requires more care in collecting the spectrum and is more affected by any attenuation of the alpha energies.

Figure 4. SAIC AP-2.

Harwell A92A. The A92A uses a silicon solid-state detector with a surface area of 9 in.² (3 in. by 3 in.) to detect alpha emitters. The A92A does not have an MCA but uses an upper-level discriminator that eliminates the instrument's response to alpha energies above the upper-level cutoff. The upper-level discriminator is typically set just above the highest alpha expected to be encountered. This may be the 5.8-MeV alpha energy from ^{244}Cm . By eliminating alpha-energy response above 5.8 MeV, more than 90% of the typical interference from radon progeny is eliminated from the instrument's response. Also, if the contamination is due to radon progeny only, then using the upper-level discrimi-

nator on the A92A limits its response to only the 6.0-MeV alpha energy from ^{214}Po , which has a 3-min half-life. This allows for a much more rapid determination that the activity is radon by allowing for the decay of this single radon progeny isotope.

Figure 5. Harwell A92A.

HPI Rainbow MCA with sodium iodide detector. This MCA with the sodium iodide detector is used to determine gamma energies, discriminating them to a resolution of about 10 keV. The detector's active surface is similar in size to the A92A and AP-2 and is used in the same manner to locate the area of contamination. Then the probe is held directly over the area of highest activity while a spectrum is collected. The MCAs in these instruments give more than adequate channels of separation for discriminating the gamma energies from radon progeny and from some of the transuranics such as ^{241}Am . Detecting the low-abundance gamma-energy emissions from the plutonium isotopes is very difficult.

Figure 6. HPI Rainbow MCA with sodium iodide detector.

Progress

In FY99, the SAIC and Quantrad Sensor instruments were evaluated along with the Eberline SHP-330, which is a sealed gas-proportional detector. A portable MCA (HPI Rainbow) and a 3-in.-diameter by 3-in.-thick sodium iodide detector were purchased for the project during FY99. The evaluation of that portable gamma spectroscopy system is continuing. The Eberline SHP-330 was found to be unsuitable for this application because of its small detector active area and problems with alpha-to-beta and beta-to-alpha cross-talk.

Alpha-to-beta cross-talk is the term that describes the condition when a portion of the low-energy alpha emitters is being detected as beta emitters by the detector. Beta-to-alpha cross-talk is the condition when high-energy beta emitters are being detected as alpha emitters by the detector. The SAIC AP-2 was found to be much more portable and user-friendly than the Quantrad Sensor AP750. The Quantrad Alpha Liquid Analyzer was found to be unsuitable because of the potential generation of mixed waste in the measurement step. The Harwell A92A, a large-area, solid-state silicon detector (3 in. by 3 in.) was identified for inclusion in the evaluation of survey instruments. This instrument is being set up to discriminate against the higher-energy alpha emitters from radon and thoron progeny. This detector will also be connected to the portable MCA (HPI Rainbow) for alpha spectroscopy and will be evaluated as a gross alpha detector with an upper-level discriminator.

Conclusions

- In most cases of personnel contamination, if hand-held detectors are used, it is possible to rapidly discriminate between radon/thoron progeny and other alpha emitters.
- It is not possible for the present automatic personnel contamination monitors to discriminate between radon/thoron progeny and other alpha emitters.
- Using more sophisticated electronics in

the personnel contamination monitors may allow for discrimination of the different beta energies. This could make the personnel contamination monitors much more effective in discriminating between radon/thoron progeny and other alpha emitters.

- Field identification of the specific isotopes will require more sophisticated portable detectors. However, those portable detectors do not need to be expensive and the operators do not need extensive training if adequate procedures are developed.

Deliverables

We have evaluated two portable silicon-detector, alpha-spectroscopy instruments (Model AP-2), developed working procedures, made available instruments for use by the RCTs in field identification of alpha emitters. In many cases, the spectrographic resolution of these instruments is sufficient on field samples and precludes the need for on-the-spot alpha-emitter identification.

We have evaluated a portable sodium iodide gamma spectroscopy instrument, developed working procedures and made the instruments available for use by the RCTs in field identification of gamma emitters.

We have evaluated three portable silicon-detector, gross alpha-detector (Model A92A) instruments, developed working procedures, and made the instruments available for use by the RCTs. These gross alpha detectors have their upper-level discriminators set to eliminate 90% of the interference from radon and thoron. In many cases, eliminating interference has allowed rapid discrimination of radon and thoron from the other alpha emitters.

We are evaluating two portable silicon detectors (detectors are the same as in the Model A92A instrument) as alpha-spectroscopy instruments. These detectors have approximately three times more surface area than the detectors in the Model AP-2. The larger surface area provides higher counting efficiency.

An XRF Continuous Air Monitor (CAM) for Metal Tritide Aerosols in the Workplace

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FY99 Funding Level: \$38.1K

Introduction

Tritium metal hydride compounds are industrial materials used for a variety of purposes, including tritium storage. Tritides of hafnium, zirconium, and titanium are examples of stable metal tritides (SMTs) in use today. Studies of the solubility of inhalable particles of these compounds conducted at Los Alamos National Laboratory (LANL, Laboratory) (Inkret et al. 1998) and at Lovelace (Cheng et al. 1997) have found that some of these tritiated aerosols are extremely insoluble in body fluids so that the tritium is released at a very slow rate with the result that the materials are retained in the body for a very long time. This is particularly true in the case of hafnium tritide, which has a biological half-time on the order of hundreds of years.

Usual bioassay and air-monitoring strategies for worker protection and dosimetry based on direct counting of the beta emissions from tritium in such a compound would apparently be of limited use. The self-absorption of beta energy in the tritide particle itself has been found both experimentally and theoretically to be substantial for particles of stable metal tritides in the respirable size range. This implies difficulties for both beta detection and for the dosimetry of stable metal tritides. An alternative to the usual bioassay or ion chamber determination of worker exposures is needed for facilities where stable tritiated particulates may be present.

Approach

The approach we have taken in this project is to develop an SMT air monitor for a tritium laboratory or workplace that will detect the metal atom constituent of the target metal tritide. The monitor will

then infer the presence of the tritide compound and its quantity based on the chemistry of the compound. A promising technique for this purpose is x-ray fluorescence (XRF) quantification. The determination of trace levels of metals in airborne particles has been applied in air pollution studies as a laboratory method but not to the problem of inferring the presence of associated tritium in a portable air-monitoring instrument. We propose an SMT continuous air monitor (CAM) that consists of an appropriate x-ray excitation source illuminating a CAM filter. On the filter would be the SMT sample collected during monitoring, with a coaxial x-ray detector capable of sensitive, high-resolution detection of the characteristic low-energy L x-rays emitted by hafnium or other SMT particles. The x-ray source proposed for demonstration of the concept is an annular encapsulated radioisotope source that could readily be mounted in a CAM sampler head. The detector system is a small, low-energy x-ray detection system that likewise can be mounted in a CAM sampler. The preliminary design of the CAM system was developed by using a detailed Monte Carlo simulation of the source-sample-detector geometry and the Laboratory code MCNP. We assumed that the geometry of the system would conform to the detector-filter configuration of the Canberra Alpha Sentry CAM sampler head so that an existing, tested sampler design could be used without further need for sampler inlet design development.

Progress

The first stable metal tritide to be investigated in the project is hafnium tritide (HfT_2). We determined that with a K-edge energy of about 65 KeV, a ^{155}Eu or ^{153}Gd radioisotope source would

provide excitation energies (approximately 80–100 KeV) close enough to the K-edge to efficiently excite x-ray fluorescence. We contacted a vendor, Isotope Products, for the source to obtain data on the annular source geometry. The detector chosen for the development was an extremely compact cadmium zinc telluride (CZT) photodiode x-ray detection system of Amptek's design. Amptek improved performance by mounting a small ($3 \times 3 \times 2 \text{ mm}^3$) CZT photodiode on a thermoelectric cooler, together with the input field-effect transistor to the preamplifier. The entrance window is a thin beryllium film that allows very-low-energy x-ray detection. The detector assembly is mounted on a tube that projects from the rest of the preamplifier chassis and so can be brought into close proximity to the sample. Because of the compact design, it proved possible to readily retrofit the entire Amptek detector-preamplifier assembly into the Alpha Sentry CAM preamplifier housing. Once we resolved these critical geometry issues, we constructed an MCNP model of the source-filter geometry, as shown in Figure 1.

In the course of the MCNP modeling of the detection scheme as illustrated in Figure 1, it soon became evident that for an unshielded 100-mCi source, the scattered high-energy photons plus the low-energy emissions (around 40 keV) of the excitation source would swamp the detector electronics and paralyze the detector. After trying a number of strategies to deal with this problem, we decided that perhaps a useful strategy would be to place a thin, high-Z shield in front of the source that would both absorb the useless low-energy emissions and cause a wavelength shift in the primary high-energy emissions closer to the K

edge of hafnium. Lead proved to be a suitable candidate. An example of an MCNP output, shown in Figure 2, illustrates an outcome for the case of 0.5 mm of lead in front of a ^{153}Gd source of about 100 mCi.

We placed a special order with Amptek for a CZT low-energy x-ray detector system with the detector tube repositioned to a central position for coaxial mounting in the CAM. A special plastic piece was made to mount the assembly in the CAM head. The signal output of the preamplifier-amplifier was fed into a Canberra AccuSpec multichannel analyzer (MCA) card in a personal computer to obtain an x-ray spectrum for analysis. A special lead holder and shield were designed for the XRF-CAM head that would hold the annular excitation source in position centered on the detector, illuminate the sample, and also shield the detector from direct irradiation by the source (Figure 3).

At the same time that the detector hardware was being assembled and tested, we placed an order for the radioisotope source. Since the source strength was relatively large, the delivery schedule was long. Meanwhile, in order to test the functionality of the detector and MCA, we made a series of runs using a plated 30-k/dpm source of ^{241}Am . The expectation was that it should be possible to detect the 59.5-keV and multiple lower energy x-ray emissions from this source. Indeed, as shown in Figure 4, a very good spectrum was obtained. The full width at half maximum of the 59.5-keV peak proved to be only 902 eV wide (i.e., less than 1 keV), which should be important for successful detection of the hafnium x-ray fluorescence peak in a noisy background.

Unfortunately, when the ^{153}Gd source was finally manufactured and delivered in September, it was mounted with epoxy glue in a special Isotope Products lead shield, making it impossible to transfer the source to the special lead holder that was designed for the XRF-CAM. Consequently, we had to send the source back to the manufacturer for disassembly and repackaging. The manufacturer has

Figure 1. An MCNP model of the SMT CAM geometry based on an Amptek CZT detector positioned coaxially with a radioisotope source in an Alpha Sentry CAM head. The filter sample is in a filter cartridge positioned about 5 mm under the detector. Airflow during sampling passes through the annulus between the CAM body and the preamplifier can.

XRF CAM: Lead shield + .5mm Pb filter
file xrf6.r --- tally 8

Figure 2. MCNP tally/photon versus energy plot for the proposed XRF-CAM geometry. Note the K x-ray peak from hafnium in the region of 55–60 keV. There is clearly a potential for interference from scattered photons having energies within the energy range of interest.

Figure 3. Layout of the XRF-CAM prototype. The CZT detector-preamplifier assembly is shown (left) inserted in a modified Canberra Alpha Sentry CAM head. Sample filters are mounted through the hatch at the bottom center of the CAM head. Signals from the preamplifier are passed to an external amplifier in the center chassis. This unit also provides power for the thermoelectric cooler. The amplified signal then is passed to the MCA in the personal computer (right) for multichannel analysis and display.

Figure 4. Multichannel spectrum (counts versus channel) of photon emissions from ^{241}Am obtained with an ^{241}Am -plated source mounted in the XRF-CAM head in the standard filter sample geometry. The high-energy spike on the right edge of the spectrum is a sum channel count representing all pulses higher than about 70 keV and thus is essentially noise.

since returned it. However, the delay meant that planned tests of the XRF excitation and detection process in the CAM had to be postponed until the next fiscal year. Problems also surfaced in obtaining the x-ray spectrum analysis program, Win-AXIL. In addition to many delays in shipping the code, when the package arrived, the compact disk proved unreadable, apparently because of the recording mode. A set of floppy disks containing the code is scheduled for shipment.

Deliverables

During FY99, we studied and resolved a number of critical design issues for development of an XRF CAM concept. By using of MCNP modeling of the excitation and detection process in fully analog form, we were able to relatively quickly consider and test a number of design possibilities before committing to a specific hardware configuration. Fortunately, it proved possible to use the existing Alpha Sentry CAM sampling head as the foundation for the new CAM sampler design. This possibility occurred because the miniaturized Amptek CZT x-ray detector package could fit in the Alpha Sentry preamplifier can geometry. Amptek was very cooperative in providing the necessary package modification to move the detector into a coaxial position. An x-ray spectrum for ^{241}Am was obtained from the completed XRF CAM hardware configuration that demonstrates the system will work as expected.

Impacts

Although a fully functional prototype XRF CAM for hafnium tritide was not available by the end of the fiscal year, sufficient progress has been made to demonstrate that the LANL team is near a proof-of-concept test of the proposed approach to metal tritide particle monitoring. The proposed approach has attracted the attention of Department of Energy (DOE) headquarters, where tritide-monitoring issues are of immediate concern. The LANL team was invited to participate in an information meeting at the Miamisburg Environmental Management Ohio Field Office, where the many

technical issues associated with stable metal tritide monitoring were discussed.

As a result of the Miamisburg meeting, DOE invited the Laboratory team to submit a proposal for direct funding of further developments in the area of tritide monitoring. Discussions with potential collaborators at Lovelace Respiratory Institute and Lawrence Livermore National Laboratory led to a proposal to investigate two additional approaches to detection besides the ongoing XRF concept. One approach is based on detection of *bremsstrahlung* x-ray radiation from tritium-beta interactions in tritide particles using essentially the same CZT detector configuration and the other on detection of beta scintillation from near-surface emissions from the particles. Funding for these proposals is still under review.

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Industrial Hygiene/Safety

Development of Methods for Determining Physicochemical Properties of Respirable Beryllium Aerosol Materials Associated with Chronic Beryllium Disease

Pressure Effects and Deformation of Waste Containers

Service-Life Modeling for Using Organic Vapor Air-Purifying Respirator Cartridges and Setting Change-Out Schedules

Studies to date

FY95

Pilot Program for the Risk-Based Surveillance of Lung Cancer in Los Alamos National Laboratory Workers

A Polymeric Barrier Monitor to Protect Workers

Evaluation of a Real-Time Beryllium Detection Instrument and the Implications of its Use

FY96

A Polymeric Barrier Monitor to Protect Workers

Evaluation of Commercial Air-Purifying Respirator Cartridges for Protection against Vapors of Nitric Acid

FY97

Reusability of Organic Vapor Air-Purifying Respirator Cartridges

FRHAM-TEX II Cool Suit Material Testing for Water (and Therefore, Tritium) Protection

A Polymeric Barrier Monitor to Protect Workers

FY98

Pressure-Deformation Correlation in Waste Containers (PDCWC)

Reusability of Organic Vapor Air-Purifying Respirator Cartridges

Summary of progress

Industrial hygiene and safety projects have produced 25 professional papers and presentations since the TDEA Program was started in FY95. The primary focus of projects has been evaluations of commercial products for purposes other than the original design specifications. Implementing the recommendations of these studies has the potential to generate significant cost savings.

The Pressure Effects and Deformation of Waste Containers Project has received praise from industrial safety and hazardous material response communities from throughout the country. The project produced information that can be used immediately by any organization dealing with the potentially deadly hazard of pressurized drums. The project also produced a device that will allow workers to determine the severity of the hazard.

Development of Methods for Determining Physicochemical Properties of Respirable Beryllium Aerosol Materials Associated with Chronic Beryllium Disease

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Funding: FY99 \$88 K; MST-6 \$90 K

Introduction

To date, efforts to eliminate occurrence of chronic beryllium disease (CBD) in workers through control of the work environment have not been successful (Eisenbud 1998). Recent epidemiological studies (Kreiss et al. 1997, Eisenbud 1998) and exposure assessments (Kent 1997, Kent et al. 2000) indicate that investigation into exposures indices other than beryllium aerosol mass concentration may be needed to control exposures. Development of such indices requires information on the physical and chemical properties of beryllium aerosol exposures that may affect occurrence of disease. The objective of this study is to adapt methods for evaluating these properties in actinides and other hazardous materials to evaluations of respirable beryllium aerosol materials.

Epidemiologic studies find that exposure to insoluble beryllium aerosol materials is associated with development of CBD in workers (Eisenbud and Lisson 1993, Kreiss et al. 1993, Stöber et al. 1989, Kreiss et al. 1996a, Kreiss et al. 1997). At the cellular and molecular level, it is thought that a dissolved beryllium species is the beryllium input to the immunopathologic process that results in disease (Newman 1993). This project is focusing

Figure 1. Drawing of a macrophage showing a hypothetical pathway for cellular conversion of beryllium particles to a dissolved species that is presented to a T-cell. [ESH 99-381a (11/99)].

on physical and chemical properties of beryllium particles that control conversion from particle to dissolved species. The study hypothesis is that the rate of dissolution and dissolution life-time of particles deposited in the alveolar region of the lung may influence the disease process and that exposure indices based on physicochemical properties that govern dissolution may lead to protection of workers.

This is a report of progress for the first year of the project, FY99. During this year, we made progress in four areas:

- method development,
- beryllium work authorization,
- methods for analysis and interpretation of experimental results, and
- collection of respirable study materials.

Progress made in each of these areas is described below.

Method Development

Fate of Beryllium Particles Deposited in the Pulmonary Alveolar Space. Insoluble aerosol particles are expected to be phagocytized by pulmonary alveolar macrophages (PAMs) within hours of deposition in the alveolar region of the lung (Stöber et al. 1989, Nyberg et al. 1989). The particles remain within macrophages during their residence in the alveolar space, possibly being passed from one phagocyte to another (Benson et al. 1995). Inside the phagocytes, particles are found initially within phagosomes and later in phagolysosomes (Figure 1). The phagolysosomes are the likely sites where dissolved beryllium

species are produced (Eidson et al. 1991, Kreyling 1992) and where the hapten involved in CBD immunopathology is formed.

The fluid in these cellular vacuoles, phagolysosomal solvent, composes the dissolution medium for phagocytized particles. This solvent is made up of extracellular fluid engulfed along with the particle during phagocytosis and constituents selectively introduced into the vacuole across the phagolysosomal membrane. The saline portion of the extracellular fluid is an isotonic solution with a pH of 7.4. On the membrane of the phagolysosome (Figure 2) is a hydrogen ion pump, which, through the conversion of adenosine triphosphate to adenosine diphosphate, reduces the pH within the phagolysosome to approximately 5 (Nyberg 1992). Table 1 shows the expected pH and chlorine ion concentration within phagolysosomes.

In vitro simulants of this solvent have been developed by Finch (Finch et al. 1988) and Helfinstine (Helfinstine et al. 1992). Review of the chemistry of these simulants found that they might not be appropriate for dissolution of beryllium particle materials based on findings of Hill (Hill et al. 1998) for electrochemical dissolution of beryllium metal and on findings of Berry (Berry et al. 1997) for transformation of phagocytized metal oxides.

The pH and chlorine ion concentrations of the simulants are listed in Table 1, along with expected values in phagolysosomes. Both Finch and Helfinstine used aqueous HCl solutions to simulate phagolysosomal solvent. The Finch simulant matches the expected chlorine ion concentration but has a pH much lower than the expected phagolysosomal pH. The Helfinstine simulant matches the expected pH range but has a chlorine ion concentration lower than that expected in phagolysosomes. Work by Hill (Hill et al. 1998) found both pH and chlorine ion concentration to be important in the electrochemical dissolution of beryllium metal.

Figure 2. Depiction of a phagolysosome showing two possible mechanisms for phagolysosomal dissolution of beryllium particles.

Table 1. Composition of Phagolysosomal Solvent

	Finch	Helfinstine	Phagolysosomal Solvent
pH	1	4-6	5
Cl ⁻ Concentration	0.1 M	10 ⁻⁴ –10 ⁻⁶ M	0.12 M

Comparison of results from Finch's study of beryllium metal aerosol particles and Hill's corrosion rate measurements on polished beryllium metal specimens revealed a major difference in measured dissolution rates. Finch's measurements were two orders of magnitude below those of Hill for the same dissolution environment (pH 1 in 0.1 M chlorine ion aqueous solution). Such specimen size effects have been reported by Burstein and Ilevbare (1996).

Also found in the phagolysosomal solvent are various enzymes that serve to break down proteins into peptide chains as part of the major histocompatibility complex (MHC), Class II restricted process (Abbas et al. 1997). This process has been implicated in CBD

immunopathogenicity (Newman 1993) (Figure 1). One of these enzymes is an acid-activated enzyme called acid phosphatase. This enzyme has been associated with the intracellular conversion of metal oxide particles to metal phosphate structures (Figure 2) through a cytochemical reaction called the Gomori reaction (Berry et al. 1997). The conversion has been observed for a variety of metal oxides, including aluminum oxide, but has not been observed for beryllium oxide. However, the chemical similarity between aluminum and beryllium suggests that beryllium oxide may undergo such a conversion within phagolysosomes to produce a beryllium-phosphate species (Figure 3).

Figure 3. Micrograph showing phagolysosomal conversion of UO_4 particles (black granular particles) to uranium-phosphorous needles (used with permission of Marie-Hélène Hengé-Napoli).

The evaluation of phagolysosomal solvent simulant chemistry raised questions about the appropriateness of existing simulants for beryllium metal particles. A clear alternative to these simulants would be a 0.12-M NaCl solution buffered to a pH of 5. However, simulation of the potential enzyme involvement in the dissolution of beryllium particles may be difficult and is

beyond the scope of this project. As an alternative, cellular methods for evaluation of particle dissolution (André et al. 1987, Kreyling et al. 1990) are being investigated. This investigation will provide information on the mechanisms of phagolysosomal dissolution important in evaluating the feasibility of developing in vitro methods of dissolution analysis relative to cellular methods.

The investigation will also be useful in evaluating adaptation of cellular methods to measurement of beryllium particle dissolution.

Possible Mechanisms of Beryllium Particle Dissolution. Typically, particle dissolution is assumed to be a surface-area limited reaction with the rate of dissolved species production from a particle expressed as

$$\frac{dl}{dt} = ks, \quad (1)$$

where k = chemical dissolution rate constant,

s = particle surface area = $\alpha_s d_p^2$,

α_s = surface shape factor, and

d_p = particle diameter (Me67).

This dissolution mechanism is characterized by uniform attack over the entire particle surface.

For beryllium metal, localized electrochemical dissolution or “pitting” may occur under the expected dissolution environment within phagolysosomes (Hill et al. 1998). This dissolution mechanism is characterized by preferential dissolution along specific planes in the crystalline beryllium metal lattice (Figure 4). Hydrogen gas may also be evolved in this process through the cathodic reduction of hydrogen ion.

As described earlier, beryllium oxide may undergo a conversion to a beryllium-phosphorus compound within phagolysosomes. For other metal oxides, ingrowth of amorphous metal-phosphorus structures, referred to as “needles” or “spherules,” has been observed using electron microanalytical techniques (Berry et al. 1997, Hengé-Napoli et al. 1998).

Analytical Plan. A set of analyses is planned to examine the physical and chemical properties of respirable beryllium materials before and after phagocytosis. The J774 monocyte cell line has been selected as an initial cell line for this work. We have practiced cell culture

Figure 4. Micrograph of beryllium metal electrochemical pitting showing preferential dissolution along specific crystalline planes (used with permission of Mary Ann Hill).

Figure 5. Micrograph showing phagocytized polystyrene latex microspheres inside J774.1A monocytes.

techniques and sample analysis using surrogate materials (polystyrene microspheres and Al_2O_3 powder). A micrograph of phagocytized polystyrene microspheres is shown in Figure 5. Cell culturing, dosing, and initial fixing of cell pellets were completed in collaboration with B-5 (formerly LS-5) at Los Alamos National Laboratory (LANL, Laboratory), Los Alamos New Mexico. Final cell-pellet section preparation and microtoming were performed by LRRI. Electron microscopy was performed by Center for Materials Science staff. Review of the micrographs by LRRI and Laboratory cell biologists indicates that cell preparations were successful in maintaining cell homeostasis and normal phagocytic activity through the culturing period.

Our analytical plan calls for analysis of particle materials pre and postcell culture. Planned analyses include x-ray diffraction and specific surface area analysis of powders and single-particle analysis using transmission electron microscopy techniques of microelectron diffraction and electron-energy-loss spectroscopy (Berry et al. 1997). Scanning electron microscopy is to be used to evaluate morphological changes in phagocytized particles associated with electrochemical dissolution (Hill et al. 1998). A Coulter counter is being used to determine particle-count concentration of liquid test material suspensions. Inductively coupled plasma, atomic emission spectroscopy (ICP-AES) analysis is planned to determine beryllium mass in specific dissolved and particulate fractions of cell cultures. Other potential analytical paths being developed include

- chemical speciation of beryllium moieties in liquids from specific cell culture fractions using such techniques as nuclear magnetic resonance spectroscopy (CST-18) and
- analyses of colloidal-sized-particle distributions using a laser-particle-size spectrometer (E-ET).

Analyses are planned on aerodynamic-size fractions of laboratory and process ventilation materials. The laboratory materials include beryllium metal and

beryllium oxide. The process materials come from air samples collected from the ventilation systems for selected operations at a beryllium production facility. Operations were selected based on CBD prevalence rates found in an epidemiologic study of beryllium facility workers (Kreiss et al. 1997). Details of the materials collected and the methods of collection follow in the section on Collection of Respirable Study Materials.

X-Ray Diffraction. X-ray diffraction analysis is planned to determine crystalline and amorphous constituents of material samples using the instrument in the MST-6 Powder Analysis Laboratory. Similar analysis of uranium materials showed stratification of particle composition with particle size (Scripsick et al. 1984, Scripsick et al. 1985). Such stratification could lead to a particle-size dependence of k , the chemical dissolution constant, and translate into a particle-size dependence of the hazard index for respirable beryllium aerosols.

Our literature review found no references to x-ray diffraction studies of respirable beryllium aerosol materials. We are adapting the x-ray diffraction technique developed in the study of uranium materials to the study of beryllium materials (Scripsick et al. 1984, Scripsick et al. 1985). The major obstacle in this adaptation is that gram quantities of materials are needed because the low atomic number of beryllium results in a low-x-ray-scattering efficiency. In many cases, this sample requirement is greater than the amount of size-segregated materials available. A nondestructive sample preparation method is being developed in conjunction with MST-6. This method should enable recovery of a large portion of the x-ray diffraction sample material for use in other analyses. Because of the sample mass requirement, no postculture x-ray diffraction analysis is planned.

Specific Surface Area Analysis. Measurement of surface area is needed to determine k from dissolution rate experiments (Equation 1). A method developed for actinide materials (Rothenberg et al. 1984, Mewhinney et

al. 1987) and used in uranium materials studies (Scripsick et al. 1984, Scripsick et al. 1985) is to be adapted for the determination of the surface area of beryllium aerosol materials. The gas adsorption instrument in the MST-6 Powder Analysis Laboratory is to be used for these measurements.

The method is expected to require gram quantities of powders which, again, are in some cases greater than the amount of material we have. Fortunately, the method is not destructive and we expect to recover a large portion of the sample materials after analysis.

A major problem with this method of surface area determination is that it is not chemical-species-sensitive. Consequently, measurement results represent the surface area of the entire powder sample, and no information is available on the surface area of specific chemical components. This nonselectivity is expected to be less of a problem for the laboratory materials than for the process ventilation materials. Development of a chemical-selective surface area analytical method is beyond the scope of this project. Our plan is to use a combination of particle-size measurement methods and chemical electron microscopy methods to make estimates of particle surface area.

Transmission Electron Microscopy (TEM). We plan to use TEM methods to analyze powder samples, samples in suspension, and cell section samples. Electron diffraction will be used to assess crystalline chemical composition. Broad-field electron diffraction will be used to examine powder properties. Microelectron diffraction will be used to assess single-particle makeup. Electron-energy-loss spectroscopy will be used to determine elemental makeup of solid amorphous materials in the different sample media. Differential analysis before and after cell culturing, will help isolate changes attributable to phagocytosis and support development of hypotheses on phagocytic mechanisms of particle dissolution.

Beryllium Work Authorization. Beryllium materials being studied in this

project are selected to be respirable and come from processes associated with the development of CBD in worker populations. Consequently, precautions in working with these materials are needed to protect worker health and to prevent environmental release of materials. We have been coordinating project activities with appropriate Laboratory Environment, Safety, and Health Division professionals from the beginning. In this first year of the project, we have completed requirements needed to commence our work with beryllium materials in a laboratory at TA-59 and to collect materials at a commercial beryllium production facility. Some of these requirements include air-emissions-control approval (LANL Air Quality Group [ESH-17]), respiratory protection qualification (LANL Occupational Medicine Group [ESH-2]) and Industrial Hygiene [ESH-5]); beryllium medical surveillance qualification (ESH-2, LANL ES&H Training Group [ESH-13]), HRL site/work training (B-DO, B-5); development of hazard control plans (HCPs); work with surrogate materials; US Department of Transportation requirements for transport of hazardous materials; and management of waste in accordance with Laboratory policies.

Three HCPs were completed and authorized in FY99. These include

- an HCP for work with surrogate materials,
- an HCP for work with beryllium materials, and
- an HCP for collection of materials at a commercial beryllium production facility.

The surrogate materials HCP pertains to work with polystyrene microspheres and Al_2O_3 powder. Work with surrogate materials is important to develop and practice study techniques with low hazard materials. Also, because study materials are only available in very limited quantities, work with surrogate materials helps to conserve these limited supplies. In the first year of the project, we have completed the surrogate materials studies.

Both the HCP for work with beryllium materials and the HCP for collection of

beryllium materials had a residual risk in the "low" to "minimal" range and required authorization at the group-leader level. All training and worker qualifications required by these HCPs were completed, and group leader authorization of the work was obtained.

Methods for Analysis and Interpretation of Experimental Results

As previously discussed, a material property likely to be important in characterizing intracellular transformation of beryllium particle materials is the chemical dissolution rate constant, k . Mathematical methods of interpreting values of this parameter relative to potential mechanisms of CBD are being developed. Starting with Equation 1 and an expression for the time-dependent particle surface area (Scripsick et al. 1985, Scripsick and Rothenberg. 1986):

$$s(t) = \alpha_s d_0^2 \left(1 - \frac{\alpha_s k t}{3 \alpha_v \rho} \right)^2, \quad (2)$$

where, d_0 = diameter of particle at $t = 0$,

t = dissolution duration,

α_s = volume shape factor, and

α_0 = mass density of particle.

The rate of production of dissolved beryllium species was estimated for aerodynamic particle sizes expected to deposit in the pulmonary alveolar space. Estimates of particle lifetimes (time for particles to completely dissolve) were also made from these expressions. Results of these calculations are shown in Figure 6 for $k = 1.5\text{e-}9$ g Be/($\text{cm}^2\text{-day}$).

This analysis shows that, depending on the value of k ,

- lifetimes of larger particles (e.g., $>1\text{-}\mu\text{m}$ aerodynamic diameter) can be comparable to the latency and term of CBD and
- the dissolution rate of these larger particles can be orders-of-magnitude

greater than the rate for smaller particles. At smaller values of k , particle lifetimes for the smaller particles will extend further into the time range of CBD latency and duration, but their dissolution rates will decrease.

Under nonpathological conditions, macrophage-mediated clearance of insoluble particles from the pulmonary alveolar region has a half-time of approximately 100 days (Stöber et al. 1989). From the current understanding of the beryllium-induced immunopathogenic response, there is a likelihood of a stage in the CBD process where this particle clearance is stopped. Under this condition, the effective local dissolution rate may approach that indicated by the above analysis, and the particle residence time may be bounded by the particle dissolution lifetime.

Collection of Respirable Study

Materials. Two categories of study materials are being used in this project. For initial method development, laboratory-prepared sample materials of beryllium metal powders and beryllium oxide powders were obtained from LRRRI in July 1999. The second category of materials is those collected from process ventilation systems at beryllium-handling facilities. The first set of process materials will come from a commercial facility, where epidemiologic studies found cases of CBD associated with specific processes. Preparation for collection of these materials was completed in FY99. The second set of these materials is to be obtained from Laboratory processes. Collection is planned for early FY01.

Laboratory-Prepared Materials.

The laboratory-prepared materials were generated by LRRRI staff from commercial bulk powders obtained from Brush Wellman, Inc. The beryllium metal bulk powder is Brush Wellman designation I-400, and the beryllium oxide powder is designation UOX-125. The powder was suspended and collected using the LRRRI apparatus shown in Figure 7 (Hoover et al. 1989).

Bulk powder was generated as an aerosol using a DeVilbiss Model 175 dry

Figure 6. The time course of dissolution rate for individual respirable particles having a chemical dissolution rate constant of 1.5×10^{-9} g Be/(cm²-day).

Figure 7. Diagram of system used to collect laboratory-prepared study materials.

Table 2. Aerodynamic Diameter Size Range Fractions for Five-Stage Cyclone

Stage	Aerodynamic Diameter Range (μm)
1	$d_{ae} > 5.9$
2	$2.5 < d_{ae} \leq 5.9$
3	$1.5 < d_{ae} \leq 2.5$
4	$0.74 < d_{ae} \leq 1.5$
5	$0.50 < d_{ae} \leq 0.74$
Backup-ESP	$d_{ae} \leq 0.50$

powder blower (DeVilbiss, Inc., Somerset, Pennsylvania). Material was collected in six aerodynamic size fractions using a five-stage aerosol cyclone described by Smith (Smith et al. 1979) and, as a backup collector, a concentric electrostatic precipitator (ESP) manufactured by Mine Safety Appliances, Inc. (Model 02-1700, Pittsburgh, Pennsylvania). The cyclone was operated at 24 actual liters per minute (aLpm). The aerodynamic-particle-diameter ranges for each size fraction at a gas temperature of 20°C were calculated using regression equations determined by Parsons and Felix (Parsons and Felix 1980) from fits to cyclone calibration data. Results of these calculations are shown in Table 2. The mass of beryllium metal powder obtained for each size fraction was approximately 0.1 g. The mass of beryllium oxide obtained was approximately 1 g for each size fraction.

Process Ventilation Materials Associated with Cases of CBD. Brush Wellman offered to provide beryllium materials for the study. A sample material collection campaign to the Brush Wellman plant in Elmore, Ohio, is planned for early FY00. Our plans are to collect materials from processes, including an epidemiologic evaluation of workers where a range of CBD prevalence was found. Materials are to be collected from ventilation systems associated with the selected processes.

Selection of Processes for Material Collection. Process selection was based on results of prevalence estimates made by Kreiss (Kreiss et al. 1996b, Kreiss et al. 1997) from study of workers at the Brush Wellman Plant. Results of this study showed a range of sensitization and disease prevalence, depending on the process to which individual workers were assigned in the study. From the prevalence results, processes that represented the full range of observed prevalence were selected. Table 3 shows the selected processes, along with prevalence results for sensitization and CBD. Observed prevalence for sensitization ranges from almost 6% to over 13%. CBD prevalence ranges from 2% to almost 7%. The ranking of processes was the same for

both medical conditions. Selection of these processes was reviewed with Dr. Kriess at the National Institute of Occupational Safety and Health and with our collaborator at Brush Wellman. The selected processes coincide with those selected for a study of workplace aerosols (Kent et al. 2000).

Aerosol Material Collection System.

To collect the process ventilation study materials, we developed an aerosol collection system similar to the LRRI collection system (Figure 8).

The collection system is designed to collect aerosol materials through a port in

ventilation ducting. A sampling probe fitted with a isokinetic sampling nozzle is inserted through the port so that the nozzle is pointed into the ventilation gas stream. A nozzle set (Model 280N, Graseby-Andersen, Smyrna, Georgia,) was used to accommodate gas velocities from approximately 600 to 10,000 ft/min when the sampler is operated 1 ft³/min (28.3 aLpm). A five-stage-aerosol cyclone sampler (Model 285, Graseby-Andersen) of the same design as that used in the LRRI collection system is used to collect size-segregated samples. Material passing the last stage of the cyclone sampler is collected with the same model

Table 3. Processes Selected for Material Collection and Associated Prevalence Results (Kreiss et al. 1996b, Kreiss et al. 1997)

Selected Process	Sensitization (%)	CBD (%)
Fluoride and Reduction	12.8–13.4	5.2–6.7
Oxide	9.8	4.9
Alloy and Casting	6.2–8.8	2.8–4.6
Master Alloy	5.8–7.1	2.0–4.3

Figure 8. Diagram of system used to collect process ventilation materials.

ESP used in the LRRI system and a backup thimble filter. Flow rate in the system was measured using a laminar flow element (Model C1026, Validyne Engineering Corp., Northridge, California). A photograph of the assembled system is shown in Figure 9.

The system was mounted on a two-wheeled handcart to facilitate moving the system between process sampling sites. Methods for checking system operation, performing leak tests, calibrating sampler flow rate, and unloading collected materials were

Figure 9. Photograph of assembled system used to collect process ventilation materials.

developed. A bubble-flow meter was used in the flow-rate calibration.

Summary

In FY99, we made progress in understanding the fate of beryllium particles deposited in the lung alveolar space and linking this understanding to available analytical methods for evaluating beryllium's physical and chemical properties. Limitations found in available phagolysosomal solvent simulants for in vitro dissolution analysis of beryllium aerosol materials resulted in an examination of cell culture method alternatives.

Because of the hazards associated with handling beryllium materials, significant effort was directed at obtaining authorization for beryllium work. By the end of the year, all authorizations needed for project activities had been obtained.

Development of mathematical methods for interpreting dissolution results allowed us to determine that particle lifetime and dissolution rate depended on initial particle size and the chemical dissolution rate constant (k). Results thus far suggest a prominent role for the largest particles (>1- μ m aerodynamic diameter) capable of depositing in the alveolar region. Particles of this size combine a relatively high dissolution rate with a lifetime comparable to the time course of CBD. Smaller particles come into this lifetime range at lower values of k, where the dissolution rate is correspondingly lower.

Laboratory-prepared, size-segregated, respirable beryllium aerosol materials were obtained from LRRI for use in initial method development studies. The materials were generated from bulk powders of beryllium metal and beryllium oxide.

Results of an epidemiologic study (Kreiss et al. 1996b, Kreiss et al. 1997) of beryllium workers at a beryllium processing facility were used to select processes for collecting respirable beryllium materials from process ventilation systems. A system to collect these materials was developed, tested, and calibrated. The collection system was mounted on a cart for easy transport in

beryllium process areas. These materials are to be used in the second phase of method development.

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Pressure Effects and Deformation of Waste Containers

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Funding: \$24.6 K

Introduction

Since 1992 there have been 123 occurrences within the Department of Energy (DOE) involving incompatible chemical mixing and pressurization of drums to unknown levels. Failure of a pressurized metal drum can cause a rapid release of pressure, possibly ejecting the drum top or bottom and resulting in flying debris and release of internal drum contents that could result in personnel injury and environmental contamination.

Pressurized drums present several personnel hazards, including

- possible injury from expelled debris, a pressure release, or burst drum;
- exposure to radioactive or hazardous contents of the drum;
- exposure to pyrophoric, flammable, or combustible materials, which can ignite and burn; and
- environmental contamination.

Pressurized drum incidents occur frequently across the United States in the public, private, and government sectors. Hazardous materials (HazMat) teams have little or no training on how to respond to or approach bulging drum incidents. Furthermore, there are many unknowns when working with pressurized drums. Previously, there was no quick, inexpensive, and reliable method for determining pressures inside drums. Research conducted at Los Alamos National Laboratory (LANL, Laboratory) has explored the effect of pressure on new closed- and open-head 55-gallon metal and plastic drums, 30-gallon metal and plastic drums, 20-gallon plastic drums, and 85-gallon metal overpacks. From the research, a pressure-indicating device has been developed for use on bulging drums.

Before this study, personnel who responded to bulging drum incidents did

not know the internal pressures of the drum. They could not visually determine if the drum was safe for installation of a pressure-relieving device, safe for removal of the bung or for puncture of the lid to relieve pressure, or even if it was safe to approach the drum at all. With the invention of the drum pressure device and the availability of its associated data, responders have the added capability of determining the risks associated with approaching 55-gallon metal drums that are under pressure.

The objectives of our continuing project to study the pressure effects and deformation of waste containers are to

- test and confirm the effectiveness of the drum pressure device,
- determine the failure characteristics between drum types of multiple manufacturers and design specifications,
- include drums of different capacities (i.e., 5-gallon and 85-gallon plastic),
- present the data in a technical report

and incorporate new findings into the emergency response video, and

- distribute the information to pertinent professionals in the field. The long-term goal is to develop safer procedures and training for responses to pressurized drum incidents.

Method

In an attempt to develop a safe and reliable method for determining the internal pressures inside metal and plastic drums, we developed a gauge using the drum pressure data in Figure 1. The gauge measured the top deformation of metal drums, which was correlated with a pressure reading by using Figure 1.

We considered two prototype gauges: 1) a quantitative gauge that used a laser to mark the top center of the drum and produced a deformation reading and 2) a qualitative mechanical gauge, which can be directly read. Both were originally intended for use on metal drums, but the qualitative mechanical gauge could be

Figure 1. Open-head versus closed-head drum top deformation averages.

used on both plastic and metal 55-gallon drums, metal 85-gallon drums, and metal and plastic 35-gallon drums. During testing, we learned that drum designs differ significantly between drum manufacturers and model numbers; therefore, we found it necessary to calibrate the gauge for specific models, types, and manufacturers. The gauge was calibrated, and we determined that it would work on models that LANL currently purchases through its suppliers. Figure 2 illustrates the laser and mechanical gauges.

The qualitative gauge was calibrated against metal and plastic 85-, 55-, and 30-gallon drums. The gauge provided accurate readings on all drums for which it was calibrated. A pamphlet entitled “The First Responders’ Pressurized Container Field Guide” was created to aid first responders in categorizing bulging drums by making comparisons with photographs and gauge readings. The use of the gauge in concert with the photographs in the field guide allows the responder to approximate the internal pressures and determine the existing hazards. Drum failure data were used to determine a safe-working envelope for responders who must mitigate pressurized drum situations.

We calibrated the gauges by pressurizing drums to a known pressure using two in-line pressure gauges and an air compressor. We measured deformation of the drum in a drum test cage and compared it with the reading on a gauge. We calibrated the gauge to 40 psig maximum. We then determined a safe working envelope to be 0–35 psig internal pressure. The HazMat team at LANL determined that a drum with greater than 35 psig internal pressure presents a significant hazard to employees; therefore, if a drum at the Laboratory is encountered and found to hold greater than 35 psig, alternative mitigation techniques are used.

Progress and Results

The pressure-indicating device or gauge works as intended and has been incorporated into procedures at LANL for

Figure 2. We determined that the quantitative laser device was difficult to use (left). The qualitative mechanical device was user-friendly and provided a direct pressure range on the instrument (right).

responding to bulging drum incidents. The gauge, pamphlet, and drum data will aid emergency responders in responding to bulging drum incidents and provide a safe working envelope. The authors are currently pursuing the patent process with legal counsel. David Volz recently received a patent on the Remote Possibly Hazardous Container Sampling Device which remotely punctures and samples pressurized or suspect containers. The video has been distributed to over 400 organizations and has provided the Laboratory with extensive community outreach. The Commercial and Industrial Trade Division has expressed an interest in promoting and selling the video.

Conclusions and Recommendations

Deformation of a drum indicates that the drum has been subjected to internal pressure, not that it is under pressure at the time of inspection. The design of these containers makes them capable of violent rupture, and caution should be taken in approaching deformed drums. We assumed that the experimental method of pressurization at increasing 5.0-psig intervals was representative of real pressurized drums in the field, although the speed and method of pressurization may be different. Also, we assumed that the deformation observations correspond to real-world pressurized drum deformations in the field.

The results of this study indicate that significant differences exist among the failure characteristics of drum types and materials. The 85-, 55-, and 30-gallon drum data were sufficient to support the development of a device for estimating internal pressures in 55-gallon metal drums because of the similarity between pressure versus deformation curves. The gauge was calibrated for 30-, 85- and 55-gallon metal drums and 30- and 55-gallon plastic drums. The gauge shows promise, and calibration shows that the gauge works as a qualitative indicator of danger.

The safe discovery and repair of a pressurized drum can make the difference between a minor incident with limited and controlled consequences and a major one with the potential loss of life and significant property damage. With the information contained in this report, DOE personnel, private and municipal fire departments, HazMat teams, hazardous device teams, and other emergency responders can make educated decisions during bulging drum incidents.

We were able to make many observations in the course of study. These observations constitute indicators of danger when an individual is approaching a bulging drum. The following indicators and observations are considered to be of extreme importance for emergency responders and waste workers:

- the distortion of the chime on 55-gallon metal closed-head drums at approximately 5 psig before failure;
- intermittent pinging of 55-gallon open- and closed-head metal drums at 15–25 psig;
- rapid and intense pinging of 55-gallon metal closed-head drums immediately before drum failure;
- a strong potential exists for closed-head 55-gallon and closed- and open-head 30-gallon metal drums to fail explosively, making the entire drum a projectile;
- all the 85-gallon and 55-gallon open-head drums that were tested self-vented;
- 30-gallon metal closed-head drums can hold and maintain in excess of 120 psig;
- a strong potential exists for closed-head plastic drums to fail out of the side of the drum;
- sealed containers of all types have the potential to become pressurized.

Based on the conclusions of this study, we recommend the development of training criteria using the data contained in this report. The training criteria should include the following information:

- indicators of drum pressurization;
- inherent hazards associated with drum incidents and chemical properties such as flammability, corrosiveness, and reactivity;
- failure characteristics and differences between types of drums;
- pressurized drum mitigation techniques such as remote venting, direct cooling (ice bath), or shooting with a projectile (water cannon or disrupter);
- inappropriate mitigation techniques;
- use of the qualitative pressure-measuring device to determine associated hazards.

Deliverables

This study produced the following deliverables:

- a tool for approximating pressures inside bulging 85-, 55-, and 30-gallon

metal and plastic drums;

- a guidebook for identifying the pressures associated with bulging drums;
- Pressurized Container Field Guide;
- presentations at national conferences and journal publications;
- DOE Green Alert Bulletin publication;
- a method for recognizing hazardous conditions of pressurized waste containers;
- information for safer responses to pressurized drums;
- training video and papers requested by and distributed to over 400 organizations;
- community outreach to a national and international audience;
- six-hour training course;
- contacts with emergency response and hazardous waste personnel.

The project provides critical information and a tool for emergency responders to assess bulging drum situations. The HazMat Response Group at LANL expects the number of bulging-drum responses to increase with the excavation, inspection, and packaging of waste drums for the TWISP (Transuranic Waste Inspection Project) project and the subsequent transportation of the drum to the Carlsbad, New Mexico, storage facility. The research and information are invaluable in protecting personnel from pressurized drums and their associated hazards.

Feedback

The principal investigators received a *Los Alamos Achievement Award* for “outstanding research and development as recognized by the ESH Division Review Committee in April 1998 for the study of pressure effects and deformation of waste containers, which contributed significantly to the safe handling and disposal of hazardous waste containers.”

The video titled “Bulging Drums—What Every Responder Should Know,” received three Aegis Awards of Excellence and two Telly Awards.

“Truly Outstanding...An excellent application of science and technology to solve a problem.”

—1998 ESH Division Review Committee, Los Alamos National Laboratory

“I commend you on your promptness in getting this useful information to the public.”

—Joseph M. Harrison, MPH, CIH, Russell Corporation

“We have never seen such a video. This is information emergency responders can use.”

—Garland Hanson, CSP, Arizona Safety Center

“This is an area that not too many of us are familiar with, and your work fills a big gap. Let your bosses know that people are benefiting from your work.”

—Jeff DeBell, Consolidated Fire District #2 (Kansas)

“Our emergency response teams will benefit greatly from this information.”

—Floyd Cobb, Intel Corporation

“This is much needed information for the emergency response and HazMat community.”

—Bobby Clark, Commonwealth of Virginia, Department of Emergency Services

“We can really use this for training and education courses.”

—Dr. Ron K. Bhada, New Mexico State University

“We are going to use this information as the core for one of our training sessions.”

—Chuck Rives, Cedar Rapids Fire Department

“The paper and video are very informative and good tools for our hazardous waste team.”

—Marty Sosby, CIH, Huntsman Corporation

“Excellent project and pertinent information.”

—Larry Borgelt, PE, CSP, Oklahoma State University

Service-Life Modeling for Using Los Alamos National Laboratory Organic Vapor Air-Purifying Respirator Cartridges and Setting Change-Out Schedules

Principal Investigator: Gerry Wood, Industrial Hygiene and Safety (ESH-5)

Funding: FY 1999, \$45 K; US Army, \$35 K; FY 2000, \$49 K; Industry Task Force, \$50.5 K

Introduction

At Los Alamos National Laboratory (LANL, Laboratory) and elsewhere, one way we protect workers from inhaling toxic vapors is by having them use commercial organic vapor (OV) cartridges with negative pressure, air-purification respirators. The cartridges contain activated carbon, an efficient and high-capacity adsorbent for condensable vapors of organic compounds such as solvents. A critical question when using these cartridges for worker protection is, "How long will a cartridge last?" Framing the answer to this simple question is complex. How long a cartridge lasts depends on use conditions (workload, vapor types, vapor concentrations, humidity, temperature, etc.) and cartridge characteristics (size, number, carbon properties, etc.).

Since October 5, 1998, the Occupational Safety and Health Administration (OSHA) has required evidence (other than odor or anecdotal history) that air-purifying respirators are not being used past their protective service life (29 CFR 1910.134). Even the Laboratory's usual practice of one-time, short-term usage of cartridges needs to be substantiated. The alternative to extensive workplace testing of respirators or use of end-of-service-life detectors (which exist for only five specific vapors) lies in the development and application of computer-based predictive models.

Computer-based predictive models, which are based on data and theories of adsorption, can predict service lives for actual use conditions of vapor type, concentration, humidity, temperature, work rate, etc. One model, developed at LANL and described in a paper published in 1994 (Wood 1994), has received considerable attention and use. However, all the proposed models are limited to dry

(< 50% relative humidity) conditions, no vapor mixtures, and no gases.

For LANL applications, we need a user-friendly computer program with a database that includes types and characteristics of cartridges used (e.g., Mine Safety Appliances, Inc., [MSA], GMC-H, and GMC-E types), chemical vapors commonly encountered, and typical use conditions. The program should also allow for expanding the input options to include new cartridge designs and new applications that may arise at the Laboratory.

The ultimate objective of this project is an easy-to-use, documented, customized computer program that will allow Laboratory industrial hygienists to estimate the service lives of organic vapor air-purifying respirator cartridges used in local applications. The benefits to the Laboratory are in the areas of improved worker protection and regulatory compliance. When quantitative guidance specific to Laboratory conditions can be provided, supervisors, industrial hygienists, and workers will be more certain that the respiratory protection they choose can provide the protection required for the period of use. Change-out schedules can be established based on quantitative service-life estimates, and safety factors can be applied according to professional judgment. The Laboratory can then be in compliance with OSHA requirements and what is becoming standard practice for industrial hygienists in the United States.

Our approach has been to

- review all available models of vapor adsorption on activated carbon,
- evaluate their usefulness and accuracy,
- examine their implementations as computer programs, and

- develop better models and computer applications.

The model reviews and developments focus on single vapors at dry conditions, single vapors at high-humidity conditions, and mixtures of vapors.

Review of Single-Vapor (Dry) Models

The objective of any service-life model is to predict a breakthrough time when the air-purifying cartridge effluent reaches a concentration that makes the air provided unacceptable for the user to breathe. Consequently, we use a service-life model to describe or predict a breakthrough curve (effluent vapor concentration versus time) or a point on it. An equation model for predicting breakthrough time of a packed carbon bed or service life of a carbon-filled cartridge requires these submodels:

- an adsorption isotherm equation with at least two input parameters,
- a breakthrough curve shape term as a function of breakthrough fraction, c/c_0 and
- an adsorption rate coefficient k_v value or equation.

In addition, these submodels are desired for better description of actual breakthrough curves:

- a way to incorporate asymmetry (skew) in the breakthrough curves,
- temperature effects for the adsorption isotherm,
- temperature effects for the adsorption rate coefficient,
- relative humidity (RH) effects on both capacity and adsorption rate, and
- effects of other vapors in mixtures in air.

We discuss the latter two subjects in detail in later sections of this report.

Typically, various authors have selected from the first group of three items listed above to put together breakthrough-time equation models. We can make a distinction between a predictive model and a correlative model. A predictive model provides the necessary equations and either input parameters or sources to obtain the needed input parameters. Some parameters, such as temperature or breathing rate, will have to come from the application; but ideally the others, such as molecular weight of the vapor, can be found in reference handbooks or may be calculated from data in such resources. The range of applicability of the model depends on the availability of input parameters. Table 1 lists six predictive equation models found during our review that have potential for estimating cartridge service lives.

A correlative model differs from a predictive model in that it requires the experimenter to obtain some of the parameters needed to extrapolate to an application. Table 2 lists three correlative models that have been proposed and used to extrapolate from data for one or more conditions to breakthrough times or curves for other conditions.

An experimental database of OV cartridge service lives or test carbon-bed breakthrough times is needed to test the predictive models. Our review of published and unpublished sources has resulted in the list of candidate databases, which are shown in Table 3. The more types of vapors in the reference database, the better the testing of models will be; therefore, we chose a minimum of nine vapors. The table shows other desirable parameters—concentration and relative humidity—that will influence the final selection of a reference database.

Figure 1 shows how such a reference database is being used. We used four of the models from Table 1 to estimate service lives of 32 compounds with three types of OV respirator cartridges. One of the candidate databases (Nelson et al. 1976) reports cartridge characteristics

and experimental breakthrough times. Figure 1 compares the model predictions with experimental values. Three of the models overestimate breakthrough times, particularly at low vapor concentrations (<125 ppm); the fourth, the Wood Model, sometimes underestimates breakthrough times. If estimates cannot be exact, it is better for worker protection to underestimate service lives. We need to analyze more models, data, and comparisons before we can make final recommendations.

Another example of a model test is shown in Figure 2. An important parameter (β) in the Dubinin/Radushkevich (D/R) adsorption isotherm (capacity) equation has been shown to be proportional to vapor molar polarizability, P_e , an easily obtained molecular property, to the 0.9 power (Wood 1992). We calculated values of β for 23 compounds from unpublished isotherm data provided by the US Army. When we plotted the 0.9 power of molar polarizability, β , against this easily obtained molecular property, we confirmed the predicted linear relationship—even the slope of this graph matched the prediction.

Review of RH Effects and Models

There are two ways of incorporating effects of RH on OV cartridge service lives:

- provide correction factors to be applied to dry-air estimates or
- use models that incorporate water vapor as one of the vapors in air.

There are also two applications to be considered:

- begin with a relatively dry carbon in a cartridge or
- begin with a cartridge that has been equilibrated at the use (or testing) RH.

Many studies of humidity effects on equilibrium adsorption capacities and/or adsorption rates have been reported. In some cases, theoretical and correlation models were developed, and the data were tested against data. The difficulty in using equilibrium capacity models for breakthrough time estimates is that for

fresh respirator cartridge applications, water adsorption equilibrium is probably not attained within the service life for the organic vapor. Also, rapid adsorption of large amounts of water vapor (high-humidity air on dry carbon) produces heating effects that affect the isotherm.

We have found few reports of the effects of humidity on breakthrough times. None of them take into account all the critical parameters that affect breakthrough times: vapor type and properties, vapor volatility, vapor concentration, temperature, vapor solubility in water, carbon bed size and capacity, carbon starting condition, RH of exposure, and time of exposure. However, taken together, they may provide enough information to account for the effects of many of these parameters.

Table 4 lists breakthrough time RH correction factors in several computer implementations of service-life estimation models. Most of these rules-of-thumb consider only exposure RH as a parameter; the Nelson table also takes into account prehumidification (Nelson 1976). The other parameters listed above are ignored.

Several equation models for reduced organic vapor capacities have been developed from capacity or breakthrough time data. By assuming capacity reduction to be the only effect of high humidity, they can be used to calculate or correct estimated service lives. The Laboratory published a correlative model in 1987 that describes both preconditioned and dry bed data (Wood 1987). It also includes vapor concentration as a parameter. While it is useful for interpolating or extrapolating data, the model has not been applied to enough data to qualify it as predictive; some parameters are still unknown functions of carbon and vapor properties. Lodewyckx (Lodewyckx and Vansant 1999) has provided the most recent empirical models for RH effects on carbon bed capacity. His approach requires knowing the water adsorption isotherm on the carbon used but has many possibilities.

The unusual shape of the water adsorption isotherm makes it difficult for the experimenter to treat water as just another vapor in a mixture with organic vapors. At low RHs, water adsorption on

Table 1. Predictive Models Used to Estimate Breakthrough Times (Service Lives)

Designation	Capacity Equation	Rate Equation	Shape Term
Mecklenburg	Dubinin/Radushkevich with β calculated from molar volume, molecular parachor, or measured.	Gameson et al., external mass transfer.	$\ln(C/Co)$.
Modified Wheeler	Dubinin/Radushkevich with β calculated from molar volume or molecular parachor.	Jonas/Rehrmann, maximum external mass transfer rate, $k_v = 111.6 v_L^{1/2} d_p^{-3/2} \text{ min}^{-1}$.	$\ln(C/Co)$.
Nelson Empirical	Boiling point correlations plus Freundlich with $C^{-2/3}$. Parameters tabulated for 10 classes of compounds.	Included in capacity term, i.e., rate term is proportional to capacity term and k_v is inversely proportional to bed contact time.	Included in capacity term model for 10% break through only.
Statistical Moments	Polanyi plot characteristic equation expressed as a polynomial.	Internal pore diffusion rate per Grubner and Underhill.	Normal distribution function with 2 moments.
Wood	Dubinin/Radushkevich with β calculated from molar polarization $P_e^{0.9}$ and the carbon structural constant from micropore volume by correlation data.	k_v an empirical function of molar polarization, flow velocity, and breakthrough fraction.	$\ln\{C/(Co-C)\}$.
Xiang	Dubinin/Astakhov with β calculated from molecular parachor.	Reduced Gameson for external mass transfer, fit to only one carbon.	$\ln(C/Co)$.

Table 2. Correlative Models Used to Estimate Breakthrough Times (Service Lives)

Designation	Capacity Equation	Rate Equation	Shape Term
Yoon/Nelson	Freundlich with parameters empirically determined by measuring breakthrough curves. Values for nine vapors from Gary Nelson data are reported.	k_v and asymmetry parameters empirically determined by fitting equations to breakthrough curves. Capacity and rate fit parameters are reported for 121 compounds from Gary Nelson data.	$\ln\{C/(Co-C)\}$ with asymmetry incorporated by an equation for capacity change with time.
Balleu	Langmuir with parameters empirically determined by measuring breakthrough curves at different concentrations.	k_v empirically determined by fitting equation to breakthrough curves. k_v proportional to $v_L^{1/2}$.	$\ln\{C/(Co-C)\}$.
Residence Time	Freundlich with Nelson's average power of 0.67.	Breakthrough time determined experimentally as a function of bed residence time for one size bed is applied to another.	

Table 3. Candidate Single-Vapor Breakthrough Time Databases for Evaluations of Service-life Models

Data Resource	Number of Organic Vapors	Concentration Varied?	Flow Velocity Varied?	Relative Humidity Varied?
MSA (1999)	15	Yes	No	Yes
Smith (1996)	12	Yes	No	Yes
Smoot (1977)	12	No, 1000 ppm	No	Yes
Xiang (1998)	23	No, 2000 ppm	Yes	No
Tanaka (1993)	46	No, 300 ppm	No	No
Freedman (1973)	29	No, 1000 ppm	No	No
Nelson (1980)	20	No, 10 TLVs	No	No
Nelson V (1974)	121	No, 1000 ppm	No	No
Nelson VI (1976)	9	Yes	Yes	Yes
Nelson VII (1976)	36	Yes	Yes	Yes
Nelson VIII (1976)	32	Yes	No	Yes

Table 4. OSHA and Commercial Implementations of Service-life Estimation Models

Source	Model Used as Basis	Relative Humidity Correction Factor Guidance *	Mixtures Calculation Guidance
OSHA (1998)	Wood	0.5 at 65% RH; testing or modeling above 85% RH.	Two rules-of-thumb suggested: add ppm for compounds of similar breakthrough times; or, ignore the most retained compound when very different (x 100) breakthrough times.
3M (1998, revised 1999)	Wood	A graph of correction factors (divisors) for five compounds of varying volatility and concentrations at 85% RH and 1% breakthrough.	OSHA rules-of-thumb.
AO Safety (1999)	Wood	0.94 for 50–65% RH; 0.72 for 65–80% RH; 0.5 for 80–90% RH; do not use above 90% RH.	None.
North (1999)	Wood	1.0 for <65% RH; 0.9 for 65–80% RH; 0.8 for >80% RH.	OSHA rules-of-thumb.
MSA (1999)	Proprietary with Freundlich isotherms.	From 1.27 at 0% RH to 0.15 at 100% RH, based on a quadratic function of RH.	Add concentrations and use for the lowest molecular weight component.
Scott (1999)	Tabulations based on 1000 ppm data adjusted for cartridge size and vapor concentrations.	1.0 for <65% RH; 0.9 for 65–80% RH; 0.8 for >80% RH.	None.

* Multipliers for estimated service lives at 50% RH unless otherwise indicated

Figure 1. Example of use of reference database.

Figure 2. Example of a model test.

activated carbon is unfavorable, and the corresponding equilibrium loadings are very low. It is only above 50% RH that significant water adsorbs into the carbon micropores. Organic vapor adsorption on activated carbon is favorable at all vapor concentrations.

Review of Covapor (Mixture) Effects and Models

Two or more vapors in air flowing through a packed, activated carbon bed, e.g., an OV cartridge, compete for the available adsorption volume. Much attention has been given to competitive adsorption of mixtures of vapors at equilibrium (without airflow). Our reviews have turned up many data and many theoretical models for equilibrium adsorption of mixtures. These models and related data are essential if we are to construct predictive models of breakthrough times of mixture components. However, in a dynamic (flowing air) situation, the following other factors must be considered:

- displacement of a more weakly adsorbed vapor by one more strongly adsorbed;
- subsequent higher concentration of the former in bed effluent than in incoming air (rollover);
- movements of adsorption wavefronts through the bed at different rates; and
- effects of one vapor on the adsorption rate of the other; etc.

We have located several reports of studies and models of mixture breakthrough curves. However, there is a common tendency to try to predict the entire breakthrough curves of the components, including displacement and rollover effects. The region of small (<10%) breakthrough fractions of importance for respirator applications has been largely ignored. Also, complete displacement is sometimes assumed; but this is a valid approximation only for vapors with very different adsorption strengths.

We have found only a few studies of effects of covapors on vapor adsorption rate coefficients; yet, these provide some

useful clues to be incorporated into mixture-effect models.

The few rules-of-thumb we have found for estimating the effects of covapors on breakthrough times (Table 4) have a fundamental flaw. They use parts per million (ppm) as the concentration units for calculations. In reality, activated carbon is a volumetric adsorbent for condensable vapors. It has a fixed micropore volume (cm^3/g), so that an adsorption capacity depends on the liquid molar volume (cm^3/g) of the vapor, not on its molar vapor concentration (ppm, moles per million moles of air, moles per liter, etc.).

New Service-life Predictive Models

From the above discussions, one can observe that there is plenty of need for improved service-life predictive models. By improved, we mean service-life predictive models that include more parameters and are more theoretically based. Whether the models are also more accurate remains to be demonstrated. For the single-vapor (dry) case a second-generation Wood-Lodewyckx Model with Lodewyckx's better adsorption rate coefficient correlation appears to be a good prospect. We have derived, but not thoroughly tested, an empirical RH-effect model, incorporating the major parameters. Also, we have begun to develop a mixtures model that involves partial volumetric displacement and includes time of exposure. Covapor effects on adsorption rates remain to be added.

Deliverables for Laboratory Applications

We have replaced the original BRKTHRU computer program written in MS-DOS BASIC. It implemented the Wood Model. The new BREAKTHROUGH is a Visual BASIC program

that performs the same calculations, but adds a graphic interface, easier data input screens, and more flexibility for changing input parameters. We have also added databases that automatically enter OV cartridge parameters and vapor parameters needed for calculations of service lives. Improved temperature compensation has resulted from including Antoine vapor pressure parameters in the database and calculations. The user can expand these databases.

The vapor pressure parameter database in BREAKTHROUGH already includes over 120 compounds. We will add more vapors from an exposure sampling database being developed independently in the Laboratory's Industrial Hygiene and Safety Group. The cartridge database includes MSA cartridges used at the Laboratory with critical parameters (micropore volume, bed geometry, etc.) measured here.

Several spreadsheet versions of breakthrough models have also been developed. These have the advantage of smaller size, more portability to users, and the ability to be distributed with fewer licensing concerns. Some of the spreadsheets allow benchmarking of the models to known data, which should improve the accuracy of predictions.

We have acquired a cartridge breakthrough time database developed by MSA and are examining it for usefulness in confirming or testing service-life predictions. We are also evaluating a service-life prediction model distributed by MSA in June 1999.

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Publications and Presentations Resulting from TDEA Projects

The publications and presentations listed below have received full or partial funding from the TDEA Program. In some instances, a project has been ongoing, and TDEA contributed support toward its progress.

Balice

Publications

Yool, S. R., J. D. Miller, R. G. Balice, B. P. Oswald, C. Edminster, "Mapping fuel risk at the Los Alamos urban-wildland interface," in *Proceedings of the Crossing the Millenium: Integrating Spatial Technologies and Ecological Principles for a New Age in Fire Management Conference and Workshop* (1999).

Presentations

Balice, R. G., "Progress in management of forests and protection from wildfire at the Los Alamos National Laboratory," presented at *Environmental Monitoring and Surveillance Meeting at LANL*, Los Alamos National Laboratory, Los Alamos, NM (1999).

Balice, R. G., S. W. Koch, P. Valerio, S. Loftin, "Spatial distributions of fuels and wildfire hazards in the Los Alamos region: The status of our knowledge," poster presented at the *ESH Division Review* (April 6, 1999) and at the *UC President's Council ES&H Review Panel* (August 11, 1999), Los Alamos National Laboratory, Los Alamos, NM (1999).

Balice, R. G., B. P. Oswald, S. W. Koch, S. R. Yool, "Fuels inventories and spatial modeling of fire hazards in the Los Alamos region," Presented at the *Crossing the Millenium: Integrating Spatial Technologies and Ecological Principles for a New Age in Fire Management Conference and Workshop*, June 16, Boise, ID (1999).

Koch, S. W. and R. G. Balice, "Input data development for the FARSITE fire area simulator for the Los Alamos National Laboratory region," poster

presented at the *ESRI User Conference* (July 26, 1999), San Diego, CA, and at the *UC President's Council ES&H Review Panel* (August 11, 1999), Los Alamos National Laboratory, Los Alamos, NM (1999).

Inkret et al.

Publications

Manuscript submitted to *Radiation Protection Dosimetry*; in press June 2000.

Presentations

Poster 1999 ESH DRC review

Presentation to DOE Metal Tritide Working Group January 1999, Mound, Ohio

Presentation to LANL Tritium Users Group, July 1999

Poster 2000 CST DRC Review

Presentation to DOE-EH, Headquarters, April 1999

Presentation to DOE-EM, Headquarters, April 1999

Presentation to ESH-TDEA Committee, July 1999

In addition, the work with LRRI (initiated by the TDEA program) has led to two larger collaborations between ESA and LRRI and NMT and LRRI. The work on particle solubility in this project in collaboration with LRRI allowed LANL to collaborate with LRRI in determining particle size and solubility in a recent TA-55 exposure.

Larrañaga

Publications

Larrañaga, M. D., "Green alert: bulging drum video and research data," DOE Technical Bulletin 1999-LA-LANL-ESH7-0004 (March 1, 1999).

Larrañaga, M. D., and D. L. Volz, "Pressurized drum mitigation," Los

Alamos National Laboratory report LA-UR-98-2542 (1998).

Larrañaga, M. D., D. L. Volz, and F. N. Bolton, "Pressure effects on and deformation of waste containers," *Fire Engineering* (July 1999).

Volz, D. L., K. E. Edwards, M. D. Larrañaga, "The first responder's pressurized container field guide," Los Alamos National Laboratory, 1999.

Presentations

Larrañaga, M. D., and D. L. Volz, "Pressure effects and deformation of waste containers," Los Alamos National Laboratory, 1999, podium presentation at the *American Nuclear Society—7th Topical Meeting on Emergency Response*, Santa Fe, NM, September 1999.

Larrañaga, M. D., and D. L. Volz, "Associated hazards and mitigation of pressurized drum incidents," Los Alamos National Laboratory, 1999, technical demonstration at the *American Nuclear Society—7th Topical Meeting on Emergency Response*, Santa Fe, NM, September 1999.

Community Outreach

Combinations of the papers and video were distributed to the following requesting organizations.

Federal Facilities and Indian Nations

San Ildefonso Pueblo, New Mexico; Navajo Nation, New Mexico; Centers for Disease Control & Prevention; National Institute for Occupational Safety and Health; US Army Department of Bio-environmental Engineering; Air National Guard; Kalama Services, Johnston Atoll; Bettis Atomic Power Laboratory; Bureau of Indian Affairs, Navajo Nation; NASA Lewis Research Center

State

California Environmental Protection Agency—Department of Toxic Substances Control, State of California; Wisconsin Department of Transportation;

Commission on Fire Prevention and Control; Connecticut Fire Academy; Commonwealth of Virginia Emergency Services Unit; Oklahoma Fire Service Training; Florida Department of Environmental Protection; Florida Department of Emergency Services; California Department of Industrial Relations; University of Nevada—Reno, Fire Protection Training Academy; Utah Fire and Rescue Academy; California Specialized Training Institute; South Florida Regional Planning Council

Department of Energy

Hanford Site Fire Department, Oak Ridge National Laboratory Fire Department, Los Alamos National Laboratory, Department of Energy—Albuquerque, Idaho National Engineering and Environmental Laboratory, Kaiser-Hill Rocky Flats Facility, Department of Energy ES&H Information Center

Academic

New Mexico State University, Waste-management Education & Research Consortium, Fire Protection Publications, Oklahoma State University, International Fire Service Training Academy, University of Pennsylvania, North Carolina Education & Research Consortium, University of North Carolina at Chapel Hill, Midwest Center for Occupational Health & Safety, The University of Arizona, University of Alabama at Birmingham, University of California—San Diego, University of Nebraska—Lincoln, Harvard University, University of California—Los Angeles, University of New Haven, Mesa Community College—Arizona, J. Sargeant Reynolds Community College—Virginia, Stanford University Fire Marshall's Office, Utah Valley State College, Mississippi State University, University of California—Berkeley, University of Houston—Clear Lake

Industrial

Akzo Nobel Chemicals; RAMFAN, Marathon Oil Company; Refinery Terminal Fire Company—Texas; Hygienetics Environmental; Roche Bioscience; Allied Signal Aerospace; QST Environmental, Incorporated;

Ground Engineering Consultants; Westinghouse Electric Corporation; Phoenix OHC, Incorporated; URS Operating Services, Incorporated; Rohm & Haas Company, Elvin Safety Supply, Eastman Kodak, Motorola, Mayo Clinic, Environmental Investigations, DuPont Imaging Systems, pH2 Environmental, Incorporated; MedImmune, Incorporated; Nexstar Pharmaceuticals, Incorporated; Occupational Health & Safety; Morton International, Incorporated; Huntsman Corporation; Clean Harbors Services; Abbot Laboratories; ManTech Environmental Technology, Incorporated; Electric Boat Corporation; General Dynamics; Metcalf & Eddy; ERP; Elf Atochem; Bay West Engineering; Conoco; Merck & Company; Arizona Safety Center; Aon Risk Services; Celanese; Occidental of Oman; Texaco E&P; Texas Instruments; Duke Engineering; SJO Consulting Engineers; Caltex Petroleum; Zurich-American Insurance—Engineering; Wassau Insurance; ARCO Prudhoe Bay Fire Department; Lockheed Martin Engineering; Intel Corporation; Russell Corporation; Huntsman Corporation; Mobil Oil; Shell Oil; ARCO—China; Hewlett Packard; Science Applications International Corporation; Johnson Controls-Northern New Mexico; International Union of Operating Engineers—International Environmental Technology and Training Center; Chemical Manufacturers Association—Lending Library

Municipal—City and County

Elmira City School District (NY), City and County of San Francisco (CA), Cedar Rapids Fire Department (IA), Dallas Fire Department (TX), El Paso Fire Department (TX), Lowell Fire Department (AR), Winter Park Volunteer Fire Department (CO), Bradford Fire Department (NH), Austin Fire Department-Hazardous Materials Section (TX), Reykjavik City Fire Department (Iceland), Phoenix Fire Department (AZ), Chillicothe Fire Department (IL), East Charles Parish Fire Department (LA), Jacksonville Fire Department (NC), Central Jackson County Fire Protection District (MO), Aurora Public Schools (CO), Cordelia Fire Protection District

(CA), Mason Deerfield Joint Fire District (OH), Aiken County HazMat Team (SC), Rio Rancho Department of Public Safety (NM), Santa Fe Fire Department (NM), Exeter Fire Department (NH), Palatine Fire Department (IL), Poudre Fire Authority (CO), Consolidated Fire District #2 (KS), Devils Lake Fire Department (ND), Broward-Miami Dade-Monroe Local Emergency Planning Committee (FL)

Voss

Publication

Voss, J. T., Los Alamos Radiation Monitoring Notebook, Los Alamos National Laboratory report LA-UR-99-3735 (July 1999).

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Peer-reviewed publications

Rodgers, J. C., J. J. Whicker, J. T. Voss, "Comparison of continuous air monitor utilization: a case study," *Rad. Prot. Manag.*, May/June:56–64 (1998).

Wasiolek, P. T., J. J. Whicker, H. Gong, J. C. Rodgers, "Room airflow studies using sonic anemometry," *Indoor Air*, 9:125–133 (1999).

Wasiolek, P. T., J. J. Whicker, R. Tavani, "Influence of room geometry and ventilation rate on aerosol dispersion," submitted to *Indoor Air* (1999).

Whicker, J. J., G. Baker, P. T. Wasiolek, "Quantitative measurements of airflows in a plutonium laboratory," submitted to *Hlth. Phys.* (1999).

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Whicker, J. J., J. C. Rodgers, P. T. Wasiolek, "Implications of room ventilation and containment design to minimize worker exposure to plutonium aerosols," in *Technology Development, Evaluation, and Application (TDEA) FY 1998 Progress Report*, Los Alamos National Laboratory report (LA-13579-PR) (1999).

Baker, G., "Air Flow Pattern Studies Using Sonic Anemometry," Master's thesis, University of New Mexico (1999).

Presentations

Konecni, S., L. M. Parietti, J. J. Whicker, and R. A. Martin, "Computation and measurement of turbulent dispersion of toxic aerosols and gases in enclosures," Los Alamos National Laboratory report (LA-UR-99-2330), presented at the *Third Biennial Tri-Laboratory Engineering Conference on Modeling and Simulation* (1999).

Whicker, J. J., P. T. Wasiolek, C. Ammerman, J. C. Rodgers, R. Martin, R. Tavani, "Studies on the effects of air distribution on aerosol mixing in rooms," Los Alamos National Laboratory report (LA-UR-99-803), presented to the DOE Air Monitor User's Group Meeting, Santa Fe, NM (1999).

Martin, R., J. J. Whicker, "HVAC design and tritium sensor placement evaluations using experiments and CFD,"

Los Alamos National Laboratory report (LA-UR-99-5871), invited technical seminar at the Savannah River Site, SC (1999).

Wood et al.

Publications

Wood, G. O., "Desorption of organic vapors from stored C2A1 gas mask canisters," presented at and submitted for publication in the *Proceedings of the 1998 ERDEC Scientific Conference on Chemical and Biological Defense Research*, Aberdeen Proving Ground, MD (November 1998).

Moyer, E. S., S. J. Smith, and G. O. Wood, "Carbon tetrachloride replacement compounds for organic vapor air-purifying respirator cartridge testing—a review," under review for publication in the *American Industrial Hygiene Association Journal* (May 1999).

Wood, G. O., "Chemical cartridge respirators and gas masks," Chapter 8,

submitted to the American Industrial Hygiene Association for publication in "*Respiratory Protection: A Manual and Guideline*" (under revision), Craig Colton, ed. (November 1998).

Presentations

Wood, G. O., "Respirators: OV Cartridge Breakthrough—A Search for Objective Information," presented by invitation at the Carolinas Section of the American Industrial Hygiene Association, Charleston, SC (October 1998).

Wood, G. O., "Respirator Cartridge Replacement Schedules," copresented in Professional Development Course #438 at the 1999 American Industrial Hygiene Conference and Exposition, Toronto, Canada (June 1999).

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