

SESSION 7

EFFLUENT STACK MONITORING

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T. M. Punch

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DOSE PROJECTION PROGRAM**

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**A REAL-TIME STACK RADIOACTIVITY MONITORING SYSTEM
AND DOSE PROJECTION PROGRAM**

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Abstract

At Brookhaven National Laboratory, a commercial Low- and High-Range Air Effluent Monitor has become operational at the 60 Mw (t) High Flux Beam Reactor. Its output data is combined with that from ground-level and elevated meteorological sensors to provide a real-time projection of the down-wind dose rates from noble gases and radioiodines released from the HFBR's 100 m stack.

The output of the monitor, and the meteorological sensors and the dose projections can be viewed at emergency response terminals located in the Reactor Control Room, its Technical Support Center and at the laboratory's separately located Meteorological Station and Monitoring and Assessment Center.

I. Introduction

A commercial low- and high-range monitoring system (Eberline SPING-3 and AXM-1) for the air effluent from the 60 MW(t) High Flux Beam Reactor (HFBR) at Brookhaven National Laboratory (BNL) has recently become operational. Commissioned in 1967, the HFBR is moderated and cooled with heavy water in order to optimize the thermal neutron flux at its beam ports, where most of its experimental facilities are situated. The 20,000 cfm ventilation of the HFBR's 4.9×10^4 m³ confinement building and the reactor vessel off-gas are discharged from a 100 m stack (which was originally utilized for the 100,000 cfm flow through the now decommissioned Brookhaven Graphite Research Reactor). Up to the times of the installation of this system, the routine monitoring of the HFBR air effluent has been on a passive basis, except for an installed Kanne Chamber for the detection of HTO. Standard Operating Procedures were provided for the manual acquisition and analysis of non-routine samples and for dose projection in the event of abnormal concentrations resulting from fuel damage during an incident or accident.

At full power and at the end of the HFBR's 28 day fuel cycle, in which half of the 28 fuel elements in its core of 93% enriched uranium is discharged and the other half rotated, the HFBR's inventory of noble gases would be 7.1×10^6 Ci and of radioiodines 1.02×10^7 Ci. Since the HFBR operates at a relatively low pressure (~200 psi), it would not be subject to catastrophic vessel failure and its piping arrangement precludes the possibility of a pipe-break resulting in a rapid loss of coolant accident. However, in order to establish an upper limit on the concentrations of noble gases and

radioiodines that the monitoring equipment might see, a worst case accident scenario was postulated. The resulting peak effluent concentrations were of the order of several hundred $\mu\text{Ci}/\text{cm}^3$ of noble gases and several $\mu\text{Ci}/\text{cm}^3$ of radioiodine. These concentrations are well in excess of the range of a conventional low-range stack monitor, as well as of standard analytical laboratory capabilities. Thus, it was decided to acquire both a low- and high-range monitoring and sampling capability when the decision to install a real-time monitoring capability was made.

From its inception in 1949, the Laboratory has had a meteorological capability for obtaining measurements of surface and elevated wind directions and velocities and temperatures. Currently, these measurements are made at 10 m and 88 m, respectively (with a correction of the latter for the stack release elevation of 100 m). SOPs and map overlays were provided for the determination of stability classes and making dose projections.

At the time that the decision to acquire an active stack monitoring capability was made, it was also decided to develop a computer program which would merge the stack monitoring and meteorological data on a real-time basis. This decision was made to provide "State of the Art" compliance with DOE Orders requiring that its nuclear reactors have 24 hour monitoring capability for concentrations anticipated during routine operations and during accidents⁽¹⁾ and for consequence assessment and for protection actions during emergencies.⁽²⁾

II. Monitoring System

A. SPING-3A

As shown in Table 1, the SPING component of the monitoring system includes four channels for the measurement of the concentrations of radioactivity, one each for particulate beta activity and gaseous I-131 along with a low- and a mid-range channel for noble gases. It also includes four other channels for the detection of "background" activity, some of which is subtracted from the active measurement channels. Each of the channel's detectors and its purposes are shown in Table 1. The ranges of the monitoring detectors are also shown. As also indicated in Table 1, three channels are devoted to the measurement of flow rates and one to the measurement of absolute pressure in the sample lines (used for the calculation of flow at STP).

B. AXM-1

As also shown in Table 1, the AXM component includes one channel which monitors the activity collected at a very low flow rate ($\sim 100 \text{ cm}^3/\text{min}$) on a particulate iodine collection cartridge, and two channels for the measurement noble gases in the high concentrations that would be anticipated during an accident which resulted in fuel damage or melting. One channel monitors "background," part of which is subtracted from the active measurement channels. Alarms for detector failure, loss of flow, "alarm" or "high alarm" conditions are provided for both the SPING and AXM components, along with "rate of increase" alarms.

The data from the SPING and AXM are accumulated by the individual channels, digital from radiation detectors or analog from measurement transducers (flow and pressure) and processed by these channels so that they can be displayed in any desired form. They are then sent to a control

Table 1

Radiological, Flow and Pressure Channels in the SPING-3A and AXM-1A

SPING Channel	Description/Detector	Range	Units
1	β Particulates	$6 \times 10^{-12} - 1 \times 10^{-5}$	
2	α Particulates (Rn)	Subtracted - Channel 1	cpm
3	Iodine-131 NaI-SCA	$1.2 \times 10^{-11} - 3 \times 10^{-6}$	$\mu\text{Ci}/\text{cm}^3$
4	Iodine 132-135 NaI-SCA		cpm
5	NG Low Range β Scintillation	$1.1 \times 10^{-7} - 3.6 \times 10^{-2}$	$\mu\text{Ci}/\text{cm}^3$
6	γ Area GM		mR/hr
7	NG Median Range GM	$9.2 \times 10^{-4} - 1.5 \times 10^3$	$\mu\text{Ci}/\text{cm}^3$
8	γ Background	Subtracted Channel 5-7	cpm
10	Stack Flow Rate	-	cfm
11	SPING & AXM Flow Rate	-	cfm
14	Absolute Pressure	-	psig
15	SPING Flow Rate	-	cm^3/min
AXM Channel			
1	Grab Samples GM I-131	$0.5 - 1 \times 10^6$ $1 \times 10^{-6} - 6 \times 10^1$	cpm $\mu\text{Ci}/\text{cm}^3$
2	NG Background	Subtracted - Channel 3&4	cpm
3	NG High Range GM	$6.9 \times 10^{-1} - 1.2 \times 10^5$	$\mu\text{Ci}/\text{cm}^3$
4	NG Intermediate Range GM	$1.5 \times 10^{-4} - 6.9 \times 10^1$	$\mu\text{Ci}/\text{cm}^3$

terminal (Eberline CT-1B). Control functions and data display are available at the control terminal. Various command and data readout capabilities and system status are available on four peripheral communication ports, one of which is utilized for a report generator interface (RGIF).

History files are available for twenty-four one-minute, ten-minute, one-hour and one-day periods. Through Eberline provided software, these data as well as channel parameters and system status, may be displayed and commands may be initiated from remote IBM-PC compatible computers.

III. Meteorological Measurements

Brookhaven's current meteorological capability includes the measurement of standard meteorological parameters, including the wind speed/direction and temperatures at 10 and 88 meters. These data are sampled once per second and are reported into a data logger. Averages (as well as some maxima, minima and variances) are reported once per minute as ASCII strings of 5-digit real numbers.

IV. Emergency Response Network and Terminals

Software has been developed for real-time emergency response displays of the stack monitor data and the meteorological data.⁽³⁾ A Class A plume model is utilized to provide graphical and numerical projections of the selected environmental dose rates. This software runs in a complex environment of computers and network connections to PCs configured in emergency response terminals (ERTs). The source term and meteorological data flows are shown in Figure 1.

The plume model is a simple straight line, steady state, Gaussian Plume model of transport and dispersion of a type that has been discussed extensively in the literature.⁽⁴⁾ Input to the model is the location of a source, its height above the surface, representative wind speed, wind direction, and Pasquill Gifford atmospheric stability classifications. The model calculates near surface relative concentrations as a function of distance and direction from a source. The output is a set of isopleths of (χ/Q) overlaid on a map of the BNL site or a listing of the maximum χ/Q , and other information on the spatial distribution of the ground level concentrations. The key to its utility of a Class A model is its link to real time wind directions and wind speed data and atmospheric stability and it is designed to provide those making decisions during emergencies with information on the region where action should be taken; and in conjunction with source information, the magnitude of potential threats to expose populations.

The effluent source term data is collected in Building 715 (the Stack Monitoring Facility) on the Eberline CT-1B, and distributed to Building 750 (the HFBR control room), Building 120 (the Reactor Technical Support Center), Building 703, (the backup Technical Support Center), Building 051, Room 19 (the Monitoring and Assessment Support Center), Building 515 (Communications & Computing Division) via a relay in Building 051, Room 7 (the Meteorological Forecast Room). The data from two meteorological towers and other instruments are collected in Building 051 on data loggers (Campbell Scientific Inc.) in and sent to two PCs in Building 051, a μ VAX 3100 (BNLMET) in

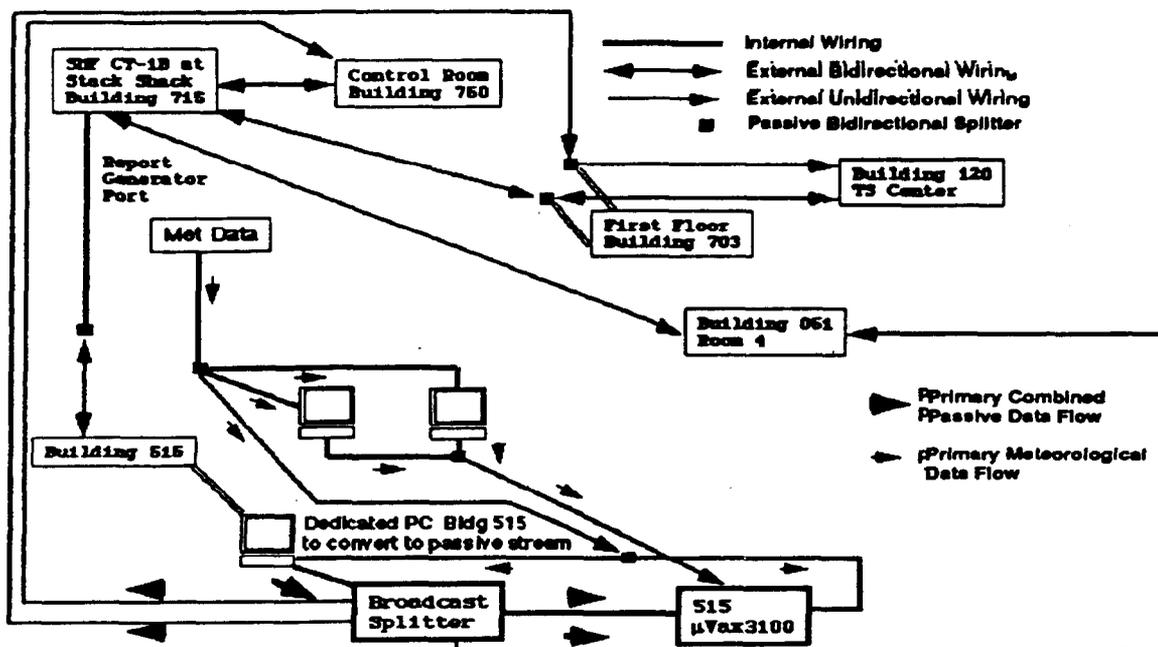


Figure 1. Effluent Source Term Data and Meteorological Data Flows for SMF

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Building 515, and to a PC (METPC) in Building 515 where it is combined with the effluent source term data once per minute. The combined data is then redistributed to BNLMET and to ERT in Buildings 750, 120, 703 and 051.

The Emergency Response Terminals (ERTs) for the Stack Monitoring Facility are specially programmed Personal Computers, either Gateway 2000 clones of IBM PCs or IBM PS/2s. The machines run the IBM OS/2 2.0 operating system, which combines the capabilities of MS-DOS and Windows with the ability to run several real-time programs at once. As shown in Table 2, "Window List," many displays can be accessed. Some of the listed programs are not for end-users, but for diagnosis of problems. The principal user displays are listed in Table 3.

Within the SHOW15R.CMD, SHOW15.CMD and SHOW60.CMD displays, screens are available for the display of instantaneous present and past plume meteorological and dispersion data, and Source (monitor channel indication and release rates) Plume and Source Data Lists for the current and nineteen previous time intervals (two minute for the 15-minute running average, 15 minute for the 15-minute fixed windows, and hourly for the 60-minute fixed window screens).

Table 2. Window List

CMD.EXE
DAILYRUN.EXE
GETRAW.EXE
SHOW15R.CMD
SHOW15M.CMD
SHOW15P.CMD
SHOW15S.CMD
PCCRT.EXE
OS/2 2.0 Desktop - Icon View
OS/2 Full Screen - OS/2 Full Screen
LOGMET.EXE
LOGMET.EXE
ERTMENU.CMD
PLPLOT.EXE

Table 3. User Displays

SHOW 15R.CMD
SHOW15.CMD
SHOW 60.CMD

These three programs show 15 minute running average text displays updated every 2 minutes (...15R...), 15 minute fixed time-window displays (...15...) updated every 15 minutes on the hour, 15 minutes after the hour, 30 minutes after the hour and 45 minutes after the hour, and 60 minutes displays (...60...) updated on the hour.

PCCRT.EXE

This is the Eberline Instrument Corporation program which can control the instruments at the Stack Shack. It can be used to reset alarms and is an alternate means of access to source term data in case of failure of the system which combines meteorological and source term data.

PLPLOT.EXE

This is a graphic display program showing an approximate map of the BNL site overlaid with contour lines of an estimated release plume.

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An example of a 15-minute running average Plume Screen for 16:01 EST on June 16, 1994 is shown in Figure 2. The wind direction and velocity are calculated for the 100 m release height of the HFBR stack on the basis of a power law extrapolation from the 88.1 m tower observations. The horizontal stability class is calculated from the 88.1 m $\sigma\theta$ (the standard deviation of the wind direction) and the vertical stability on the basis of the ΔT between 88.1 and 10.6 m. As shown, the maximum χ/Q , the distance and direction to it, and the plume half-widths at several distances are also calculated, as is the transit time to them. The 15-minute running average screen is updated every two minutes. The 15-minute fixed time window screen is updated on the hour and every 15 minutes thereafter, while the 60-minute screen is updated on the hour.

An example of the 15-minute running average Source Screen for 16:25 on the same date is shown in Figure 3. This screen shows a time post-shutdown, which is based on a user entry of the time of reactor shutdown. This time is used in the calculation of the release concentration (as Xe-133 effective) for the mixture of released noble gases and of radioiodines as I-131 effective. The 100 m release winds, stability classes and release concentrations and rates are also shown. The latter are calculated on the basis of the measured stack flow. The maximum χ/Q , as well as the direction and distance to it and to 10% of the maximum, is also shown, as are the concentrations of I-131 equivalent and Xe-133 equivalent and related dose rates at the location of the maximum. The SPING sampling flow rate and the SPING and AXM channel readings are also shown on the Source Screen to facilitate a quick review of them.

As indicated in Table 2 a Plume Display screen is also provided, an example of which is provided in Figure 4. The display is designed to be self-contained (i.e., the meteorological assumptions are listed, the definition of wind directions and the map scale and orientation are explicitly stated). The relevant meteorological parameters, the location of the ground maximum and isopleths at the 50%, 10%, 1%, 0.5% and 0.1% of maximum are shown, superimposed on some of the essential features of the Laboratory site and surrounding areas. This projection is automatically updated every fifteen minutes, and a more frequent update may be obtained manually on request, as may be its magnification factor to encompass a smaller or larger area than the standard 6 km \times 6 km.

```

PLUME SCREEN      TOWER DATA LOGGING PROGRAM  15 Min. Running Ave.
Computer Date: Jun 16,1994      Time: 15:48:34
Logger Julian Day 167.         Time: 16:01      EST
                                WIND SPEED/WIND DIRECTION
                                ( mps /deg)
      100.0 M (Release Ht):    3.1/116.
      88.1 Meter:              3.1/117.
      10.6 Meter:              3.5/123.
HORIZONTAL PG STABILITY (Winds)  D   ( .35)
VERTICAL PG STABILITY           A   ( .00)
Maximum Chi/Q                   1.92E-05
Dist/Direction TO max (km, deg) .4/296.
Dist to 10% of max (km)        1.9 @ max 1.6km 3.2km 8.0km 16 km
Plume half-widths to 10% of max: .06 .09 .00 .00 .00
Transit time (hh:mm):          0:01 0:08 0:17 0:43 1:26
Temperatures (Deg C  Deg F)   Other Data Measurements
Shelter :                    24.8  76.7  Precipitation (in): .00
10 Meter (Field)             23.7  74.6  Relative Humidity (%): 65.
10 Meter (Tower)             23.8  74.8  Pressure (in of Hg): 30.08
87.3 Meter (Tower)           22.1  71.8  Solar Radiation: .74
Delta T :                    -1.64 -2.96 88.1 Meter Sigma Theta: 10.7
Minimum Shelter :            24.7  76.4 10.6 Meter Sigma Theta: 999.0
Maximum Shelter :            24.9  76.9 QA Count (% valid data) 100.00
up/down arrows = scroll, space = +10, return = home, h = help, q = quit
    
```

Figure 2. Plume Screen, June 16, 1994

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SOURCE SCREEN      TOWER DATA LOGGING PROGRAM 15 Min. Running Ave.
Today Is Thu, Jun 16,1994 jdate 167, Time: 16:12          .0 hrs postShutdown
  Logged Thu, Jun 16,1994 jdate 167, Time: 16:25 EST      .0 hrs postShutdown
-- 100.0 METER RELEASE WINDS-----
wind speed/direction (mps/deg)      3.5/134.
horizontal PG stability (Winds)      C (.20)
vertical PG stability                 A (.00)
ESTIMATED RELEASE RATES-----uCi/cc---Ci/sec---status---
Iodine (I-131 equivalent)           5.01E-11 2.57E-10 normal
Noble Gas (Xe-133 equivalent)        2.72E-03 1.40E-02 normal
-----PLUME MAXIMUM
Concen Dose rate
Ci/m3      Rem/hr
Iodine      3.21E-15 8.20E-10
Noble Gas   1.74E-07 8.16E-05
-----
STACK FLOW: 10885.cfm      5.14 m3/s      PLUME MAXIMUM CHI/Q: 1.25E-05 sec/m3
SPING+AXM FLOW:      1.cfm      normal      Dist/Dir TO max (km,deg)      .4/314.
-----Dist to 10% of max      1.9 km

SPING flow 1.20E+00 cfm      normal      Gamma Bckgd 1.38E+00 cpm      normal
Beta part  6.66E-12 uCi/cc   normal      Abs Press.  2.81E+01 inHg A    normal
Alpha part 4.42E-01 cpm      normal      AXM GrabSmp 2.62E-02 mR/h     normal
Iodine      5.01E-11 uCi/cc   normal      AXM NG Bckg 1.06E+00 cpm      normal
I-Backgnd  8.18E+01 cpm      normal      NG hi rng   1.84E-01 uCi/cc   normal
NG low rng  5.31E-07 uCi/cc   normal      NG Intrmed  1.55E-04 uCi/cc   normal
Gamma Area  8.33E-02 mR/h     normal
NG med rng  2.72E-03 uCi/cc   normal      QA Count (% valid data)      100.00
up/down arrows = scroll, space = +10, return = home, h = help, q = quit
    
```

Figure 3. Source Screen, June 16, 1994

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CHI/Q Manual Input 24-May -1994 16:36          Ver LU
WIND from SSW, ( 212 deg) at 6.4 m/sec.
SIG y from PG D      SIG z from PG A
Source hgt 100 meters
Maximum value is 9.31E-06 at a distance of 0.35 +- 0.05 km.
Isopleths at 50.00% 10.00% 1.00% 0.50% 0.10%

North toward top of page
Small tick marks on border are 1 KM apart
    
```

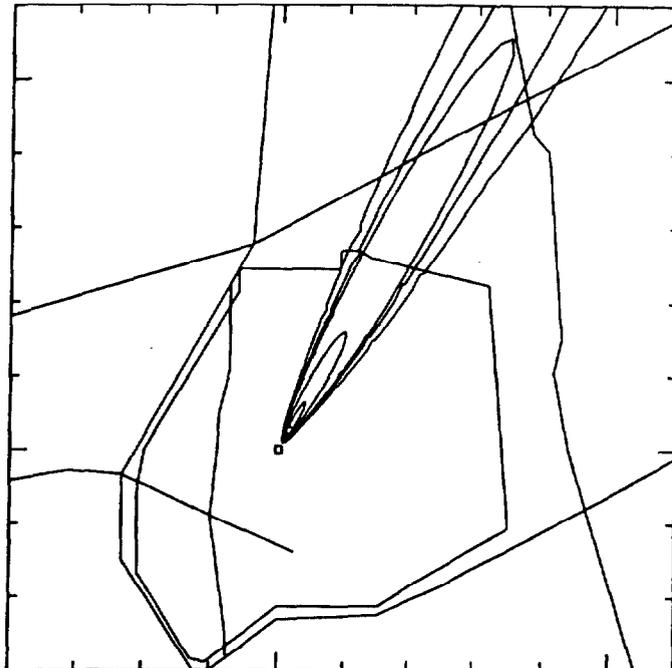


Figure 4. Plume Display

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References

1. DOE Order 5480.30 "Nuclear Reactor Safety Design Criteria", 1-19-93.
2. DOE Order 5580.3A "Planning and Preparedness for Operational Emergencies", 4-30-91.
3. H. J. Bernstein, "SMF Software Manual," Bernstein & Sons, 5 Brewster Lane, Bellport NY 11713, April 7, 1993.
4. See, for example, F. Pasquill, Atmospheric Diffusion, 2nd Edition, John Wiley and Sons, 1974.

DISCUSSION

EVANS: I am curious about how you come up with the correction factors to get your ratio of iodine to noble gases. Is this based on some type of measurement or is it based on a release rate?

HULL: We do not do it by ratios, we do it by the assumption that there is a fixed mixture of noble gases (xenon and krypton) and a given mixture of iodine 131-135, which has been worked out for default accident scenario purposes. The very short life krypton and xenon are so short-lived that we do not put them in the calculation; they are not dose contributors at any distance away, at any time after shutdown. We start with the assumption of this mixture at shutdown and just correct it on the basis of decay of each of the individual constituents with time. We also throw in the dose factors, the effective energy of the mix for the gases and the iodides. A lot of the accident projection schemes work on the assumption of iodine-to-gas ratio. We do not do that, we operate on studying the shutdown mix.

EVANS: Maybe it is not a fair question to address to you, but you have assumptions of releases from the core for a given accident scenario, plus volatilities, etc. Has somebody else done these calculations to come up with the ratios that are going to become airborne in time? What sort of values go into this? You have assumptions there about what fraction of the iodine is going to volatilize.

HULL: There is a default assumption on the accident scenario as to the form of iodine. The 20,000 CFM effluent is continuously filtered by high efficiency filters for particulates. And the effluent also goes through an iodine adsorbent bed, so the assumption is that most of what gets out is in the form of methyl iodide.

HAYES: Is this particular monitoring system also utilized to report normal effluents?

HULL: We have this in mind, but it turns out, we have discovered, that we have to work around to get the instrumental backgrounds down to the point where we can see them. When we got the backgrounds down to the lowest predictable level, sensitivity was sufficient so that it turns out that we are putting out about 1×10^{-7} $\mu\text{Ci/cc}$ of argon-41 on a continuous basis. Until we had the monitor, we could not see it. So, the answer is, yes, I think we will be utilizing it for routine effluents, too. But then you can not make assumptions about the mix, you have to do some grab sampling to establish the constituents.

HAYES: With respect to your normal effluents, would you be likely to change the program so that your mix would be based upon a weekly grab sample?

HULL: We haven't thought about it seriously, but I think we will probably continue to have it interpret the accident situation, because that is really what we developed it for. We do not want to have to change it the minute we have an accident, we want to perform in that mode. We will probably just do grab sampling to say we have so much in iodine-131 equivalents or so much in xenon-133 equivalents. We would reinterpret it, in terms of what we think is the principal constituent in the routine releases, and that will

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be established by grab sampling.

OOSSENS: How do you reckon with the presence of noble gases that might be emitted?

HULL: I am not sure I understand your question because major components of what we are monitoring are the noble gases that are routinely released, in very small quantities, so small that we can not measure them on an everyday basis. Our intention is to monitor the noble gas releases that might be expected after any damage to the reactor fuel. I should have said while I am with the Safety and Environmental Protection Division, our Reactor Division has sponsored this installation. The idea was that, sooner or later, somebody from the DOE was going to come around and say that our monitoring was insufficient in terms of industry practice and the precedents that were established by NUREG-737. So, we decided to stay ahead by doing it on our own. The Reactor Division paid for it and I should have expressed my appreciation to them. The meteorological component is very user friendly, it can be tailored for other elevations in the release and for other locations than the reactor stack that you saw in the last slide. At present, it assumes that the point of release is the top of the reactor stack at 100 m. In the future we will be trying to make it a little more flexible in terms of emergency response for other facilities and release heights.

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POTENTIAL RADIONUCLIDE EMISSIONS FROM STACKS ON THE HANFORD SITE, PART 2: DOSE ASSESSMENT METHODOLOGY USING PORTABLE LOW-RESOLUTION GAMMA SPECTROSCOPY*

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Abstract

In September 1992, the Westinghouse Hanford Company began developing an *in situ* measurement method to assess gamma radiation emanating from high-efficiency particulate air filters using portable low-resolution gamma spectroscopy. The purpose of the new method was to assess radioactive exhaust stack air emissions from empirical data rather than from theoretical models and to determine the potential unabated dose to an offsite theoretical maximally exposed individual. In accordance with Title 40, Code of Federal Regulations, Part 61, Subpart H, "National Emission Standards for Hazardous Air Pollutants", stacks that have the potential to emit $\geq 1 \mu\text{Sv y}^{-1}$ (0.1 mrem y^{-1}) to the maximally exposed individual are considered "major" and must meet the continuous monitoring requirements. After the method was tested and verified, the U.S. Environmental Protection Agency, Region 10, approved its use in June 1993. Of the 125 stacks operated by the Westinghouse Hanford Company, 22 were targeted for evaluation by this method, and 15 were assessed. (The method could not be applied at seven stacks because of excessive background radiation or because no gamma emitting particles appear in the emission stream.) The most significant result from this study was the redesignation of the T Plant main stack. The stack was assessed as being "minor", and it now only requires periodic confirmatory measurements and meets federally imposed sampling requirements.

I. Introduction

In September 1992, the U.S. Environmental Protection Agency (EPA), Region 10, concurred with a Westinghouse Hanford Company (WHC) proposal to develop a test method to measure radioactive particulate emissions [particularly gamma emitters from high-efficiency particulate air (HEPA) filters] in stack exhaust systems across the Hanford Site. Its intended purpose was to show the compliance status of potential unabated stack emissions and the estimated dose to the offsite maximally exposed individual (MEI) through the use of empirical data. A nondestructive assessment, *in situ* method was developed, tested, and implemented using portable low-resolution gamma spectroscopy instrumentation (Microspec-1**) to evaluate gamma emissions from operating HEPA filters. This method has become commonly known as the nondestructive assessment (NDA) method.

* Work conducted for the U.S. Department of Energy under contract number DE-AC06-87RL10930.

** Microspec-1 is a registered trademark of Bubble Technology Industries, Inc., Chalk River, Ontario, Canada.

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Guidance for the developed method comes from Title 40, Code of Federal Regulations (CFR), Part 61, Subpart H⁽¹⁾ and Appendix B, Method 114⁽²⁾.

On May 19, 1993, the Microspec-1 was taken to the B Plant and used to measure gamma emissions from the 296-B-13 stack HEPA filters to test the NDA method and to provide concrete results to the Region 10 EPA office. This location was chosen because it is readily accessible, and gamma counting may be performed without difficulty. Data acquired from the experiment was used to determine an offsite effective dose equivalent (EDE) to the MEI over a 1-y period assuming no filtration of the exhausted air. The results were presented, and a demonstration of the NDA method was given on June 10, 1993 to the EPA, Region 10. The method was accepted as an alternative to the other approved EPA methods for determining potential offsite doses, and implementation began across the Hanford Site where applicable.

The NDA method provides a technical basis for empirically measuring potential emissions, and it uses low-resolution portable gamma spectroscopy to collect *in situ* spectra from HEPA filters. By calibrating the instrument to the same geometry as that observed in the field, data acquired from field measurements may be decay corrected for filter lifetime to determine the potential annualized activity release to the atmosphere. Several assumptions made regarding the activity calculation make the reported value conservative: (1) filters otherwise considered to have zero activity are assigned the minimum detectable activity (MDA); (2) the total activity is placed on the filter at the time of installation; and (3) alpha and beta emissions are established based on known relationships to the gamma emitters. Dose conversions from the activity determination are made from EPA-approved dose conversion factors. Stacks with resultant dose estimates less than $1 \mu\text{Sv y}^{-1}$ (0.1 mrem y^{-1}) to the offsite MEI are considered "minor" and do not require continuous monitoring for radionuclide emissions. High radiation near or emitted from HEPA filters limits the application of this method.

II. Objective and Scope

The objective of this test method is to identify gamma emitting radionuclides collected on HEPA filters, in a quantitative manner, over a discrete time period at the Hanford Site facilities managed by WHC using portable gamma spectrometry. Portable gamma spectrometry may also be used qualitatively to confirm the presence of gamma radiation. These data, in conjunction with process and plant history records, are used to determine an empirical potential unabated source term that has the potential for release to the atmosphere. As a result of determining the unabated source term, a dose to the MEI may be calculated, which will determine if the emissions from the stack are greater than the EPA threshold of $1 \mu\text{Sv y}^{-1}$. Alpha and beta emitting radionuclides may not be measured using the NDA method but are established using known facility ratios. Volatile nuclides and other nonradioactive materials are also beyond the scope of this method.

III. Test Method

The Microspec-1 is used, and data may be collected with or without a lead sleeve [i.e., a collimated shield over the NaI(Tl) detector]. Before each field use, the instrument is calibrated to the in-field HEPA filter geometry under controlled conditions. A background spectrum is collected at the test site, and

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several HEPA filter spectra are collected. The setup, results, and offsite dose calculations are discussed for the method.

Sampling was initially conducted on 9 of the 84 WHC stacks registered with the Washington State Department of Health⁽³⁾. All 84 stack assessments were completed by December 17, 1993⁽⁴⁾. Beginning in 1994, unregistered WHC stacks were evaluated for potential emissions greater than the EPA threshold of $1 \mu\text{Sv y}^{-1}$; all reporting was completed by August 31, 1994.

Instrument Calibration

In the laboratory, the spectrometer is energy calibrated using the two peaks obtained from a ^{22}Na check source placed in a representative HEPA filter geometry. ^{22}Na is preferred for an energy calibration because it has both a low-energy (511 keV) and a high-energy (1274.5 keV) gamma emission. National Institute of Standards and Technology (NIST) traceable radioactive check sources are placed in the center of the calibration HEPA filter. Because of the distance from the detector to the source, the point source is approximated for calibration, even though the activity in a HEPA filter to be monitored is widely deposited. For all measurements of the same geometry, the detector head is placed up to the clean HEPA filter or housing at a location similar to where the actual measurement will be taken. After the energy calibration, a region of interest (ROI) is established for each isotope expected to be found during measurement for the given HEPA filter geometry using NIST traceable gamma check sources implanted in the clean HEPA filter. Typical isotopes include ^{54}Mn , ^{60}Co , and ^{137}Cs . The absolute efficiency is given by Equation 1.

$$\eta = \frac{\left[\frac{\text{counts}}{t(1-DT)} \right]_{\text{source}} - \left[\frac{\text{counts}}{t(1-DT)} \right]_{\text{background}}}{A_0 e^{-\lambda \Delta t}} \times 100 \quad [\%] \quad (1)$$

where:

- η = absolute efficiency in percent
- counts = gross counts in region of interest
- t = count time of source, background (min.)
- DT = instrument dead time i.e., fractional time instrument does not respond
- A_0 = initial check source activity (dpm)
- λ = decay constant of check source (y^{-1})
- Δt = time elapsed since check source manufacture date.

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Data Collection

Before sampling begins, background measurements are collected. The background spectrum is collected within 10 to 20 m of outdoor systems; for indoor systems, the background spectrum is collected within the room or facility. The minimum detectable activity for a particular ROI is given by Equation 2⁽⁵⁾.

$$MDA = \frac{4.66 \sqrt{\left[\frac{\text{counts}}{t^2(1-DT)} \right]_{\text{background}}}}{2.22\eta} \quad [\text{pCi}] \quad (2)$$

where:

- MDA = minimum detectable activity for given ROI
- 4.66 = the value used to determine the instrument reading with a difference from background that is large enough to be statistically significant at the 99% confidence level
- 2.22 = the conversion from counts per minute to picocuries.

Each stack evaluation is governed by an individual WHC test plan. In the field, *in situ* measurements are made of the gamma radiation emanating from the HEPA filters and prefilters. Instrument data are logged, and the resultant spectra are recorded electronically. The instrument is placed near the HEPA filter in the same geometry as during calibration. This method eliminates the risk of radiation dose from HEPA filter changeout and the resultant disruption of the exhaust system. Count times vary between three and five minutes during which a gamma spectrum is collected. For the specific ROI(s), the collected counts (corresponding to a gamma ray) are converted to a particular activity. Stacks that cause excessive instrument dead time ($\approx > 70\%$) cannot be assessed using this method.

Measured activities are decay corrected and annualized. The HEPA filter activity is given by Equation 3. In systems that have them, prefilters are included in the analysis for the total activity calculation. Each resultant value is compared to the MDA. If the value is below the MDA, the MDA is assigned as a measure of conservatism. Additionally, activity estimates are made for alpha and beta emitters from ratios derived from the gamma emissions. Dose conversions from the activity determination are made from EPA-approved dose conversion factors. Summing the reported annual isotopic emissions and the derived average annual potential emissions from the HEPA filters results in the annual total potential emissions. Stacks with resultant dose estimates less than $1 \mu\text{Sv y}^{-1}$ to the offsite MEI are considered minor stacks needing only periodic confirmatory measurements.

$$A_{i_{HEPA}} = \frac{\left[\frac{\text{counts}}{t(1-DT)} \right]_{i_{HEPA}} - \left[\frac{\text{counts}}{t(1-DT)} \right]_{\text{background}}}{2.22\eta e^{-\lambda t_{i_{HEPA}}}} \quad [\text{pCi}] \quad (3)$$

where:

$A_{i_{HEPA}}$ = activity of i th HEPA filter (pCi)
 $t_{i_{HEPA}}$ = time elapsed from HEPA filter installation to measurement date (y).

Potential Dose Calculation

The Hanford Site employs the CAP-88 dose model⁽⁶⁾ to demonstrate compliance with 40 CFR 61.92. This model calculates a unit dose factor for each radionuclide discharged from the Hanford Site by discharge area to predict an EDE for the offsite MEI. The EDE is multiplied by the activity of each isotope, and the results are summed to produce the offsite potential dose to the MEI as shown in Equation 4^(7, 8).

$$\dot{H}_{total} = \sum (EDE_{(i)} \times A_{(i)}) \quad [\text{mrem } y^{-1}] \quad (4)$$

where:

\dot{H} = potential unabated dose to the MEI
 $EDE_{(i)}$ = effective dose equivalent for each radioisotope.
 i = each applicable radioisotope

IV. Results

Calibration of the Microspec-1 2 x 2 NaI(Tl) well detector has consistently yielded for the ¹³⁷Cs ROI an intrinsic efficiency ranging from 11% to 16%. The calculated detector resolution using ¹³⁷Cs for a typical HEPA filter geometry is 8.5%.

Although the background radiation may vary with location, the Hanford Site typically has a natural background on the order of 10 to 15 $\mu\text{R hr}^{-1}$. Using the

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in-field background data collected, the average MDA is about 100 nCi. MDA values range from about 50 nCi to 200 nCi.

Of the 84 registered WHC stacks, 14 were considered for NDA; however, only 9 were evaluated using the NDA method. Although one stack was readily accessible, the background and HEPA filter radiation emanating from the area rendered the instrument useless because of the excessive instrument dead time. Four of the available stacks could not be assessed with this method because the source term was solely alpha contamination. Figure 1 compares the results of the NDA assessment with the back calculation method (i.e., $3,000^n \times$ emitted dose, where n is the number of HEPA filter stages) for the registered stacks. Without using the NDA method, all nine stacks assessed would have been subject to full compliance with the NESHAP requirements, which would have subjected them to upgrades.

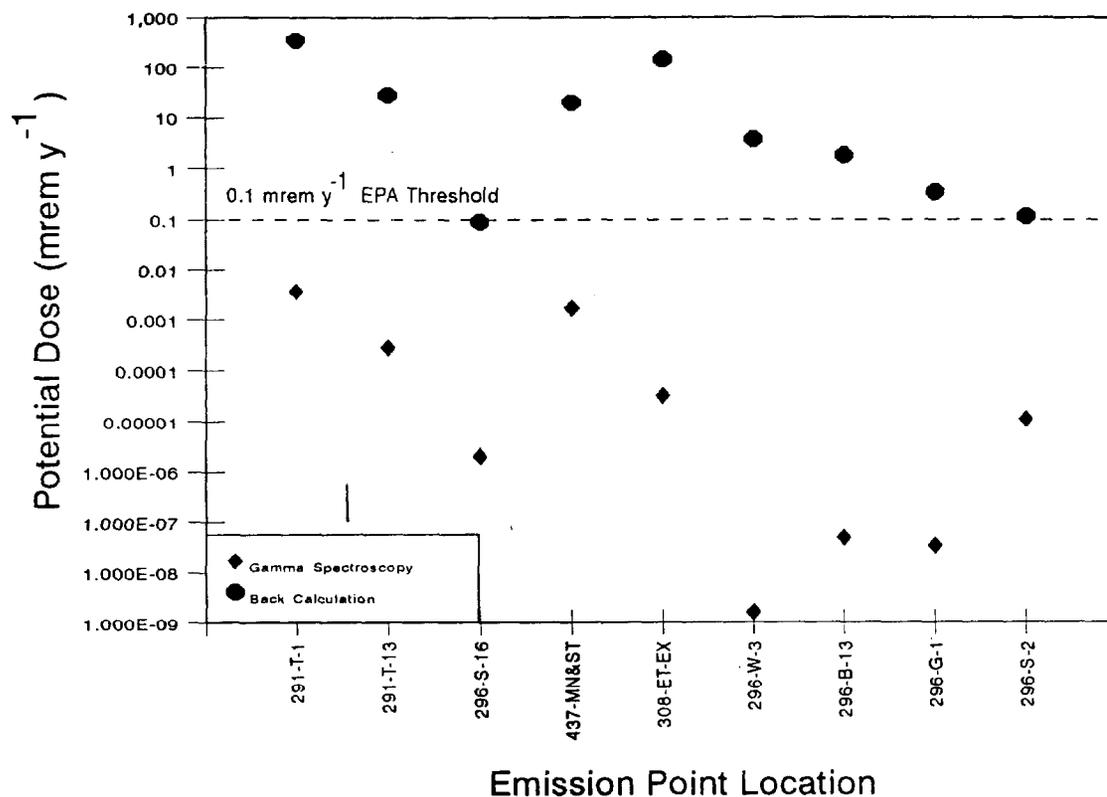


Figure 1 Comparison of the empirical results obtained from portable gamma spectrometry versus the theoretical back calculation model⁽⁸⁾.

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A significant result was obtained for the T Plant main stack. This is a 60 m (200 ft) stack and had been considered a "major" source of potential radioactive emissions. It had been designated in 1991 by the EPA, Region 10, as requiring upgrades to meet all of the NESHAP and Clean Air Act requirements. However, the empirical results using the NDA method showed conclusively that the potential emissions were not only below the $1 \mu\text{Sv y}^{-1}$ EPA threshold but also five orders of magnitude below the theoretical estimated potential. As a result, a petition for redesignation was submitted to the EPA, Region 10⁽⁹⁾, and the EPA, Region 10, accepted the proposal in a letter transmitted January 3, 1994. All actions for this stack are now considered complete, and it only requires periodic confirmatory measurements as specified in 40 CFR 61.93.

There were 41 WHC unregistered stacks assessed for potential emissions in 1994. Eight stacks were considered for NDA, and six of the unregistered stacks were assessed for potential unabated emissions using the NDA method. None of the NDA sampled stacks were above the EPA threshold. Two stacks could not be assessed because the background radiation interfered with the gamma radiation coming from the HEPA filter system.

V. Discussion and Conclusions

The data confirm the ability to measure *in situ* environmental, low-level concentrations of gamma radiation emanating from HEPA filters using portable low-resolution gamma spectrometry. Increasing the count time decreases the instrument dead time, resulting in better counting statistics. Using the collimated shield reduces the instrument dead time and also increases the data reliability. Using a point source within the HEPA filter to calibrate the instrument and establish the ROI is sufficient and enables specific and repeatable geometries; this is important considering the many stack geometries on the Hanford Site. Results have shown NDA to be as much as nine orders of magnitude below the theoretical back calculation model.

Conservative measures were used to calculate the potential unabated dose to the MEI. The first of these includes assigning the MDA to a filter that shows an activity less than the MDA. This assignment may represent greater than 25% of the actual measured activity; indeed in some cases it is 100% of the measured activity. The second conservative influence involves back-calculating the deposited activity to the date of the HEPA filter installation. This assumes all the activity accumulates on the HEPA filter the day it is installed instead of accumulating over time, as actually occurs. Third, the prefilter contribution to the potential dose is derived from empirical data. Fourth, although no alpha or beta activity is measured by this method, alpha and beta contributions are established based on known ratios of these emitters to the measured gamma emitter (e.g., ^{137}Cs). The alpha and beta components may account for as much as 70% of the potential unabated dose to the MEI.

This method clearly demonstrates the ability to use NDA for ascertaining the collected gamma-emitting isotopes on HEPA filters. Guidance for the method development comes from 40 CFR 61, Appendix B, Method 114, the intent of which was followed as much as possible. However, unlike Method 114, which requires taking a sample from the HEPA filter and sending it to a laboratory for analysis, the method developed uses nondestructive, *in situ* sampling. Advantages include reduced exposure and dose to personnel, time savings over laboratory analysis, and cost savings gained from reduced labor time and analytical laboratory

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analyses. However, the variety of systems at the Hanford Site prevent applying this method universally, among other reasons, because of difficulties encountered with higher radiation areas, limited access into radiation zones, and restricted proximity to the HEPA filters.

VI. Acknowledgements

The author thanks Ms. Barbara Boucher, Victoreen, Inc., without whose help this project would not have been completed in a timely manner, and Mr. Jack Mizner who spent many hours learning the method and working on the T Plant main (291-T-1) stack redesignation petition. Additional thanks go to Mr. Larry Diediker, Manager of Effluent and Emission Monitoring (WHC), and the dedicated WHC air emissions cognizant engineers, facility operators, health physics technicians, and publication services editors.

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DISCUSSION

WREN: You are looking at other parameters besides cesium-137, is that correct?

BARNETT: That is correct.

WREN: Because the viewing volume of the gamma spectrometer is quite small, you are looking at a very small fraction of the HEPA filter. Do you see any changes in total activity, depending on where you are? Does the composition of the trapped particles change depending on where you are looking along the HEPA filter?

BARNETT: We have looked at that and have determined efficiency and activity based on a point source calibration. We found that moving sources around, i.e. implanting sources in one of nine locations on a grid on a clean HEPA filter, did not change efficiency significantly. This has resulted in a point source calibration approximation.

DUVALL: It seems as though you have some very large correction factors, particularly the geometry correction factor, because you are assaying the entire concentration of radionuclides on the HEPA filter. Therefore, you are measuring a fraction of that and you have to correct for four-pie geometries to assess the entire filter. In addition to corrections for alpha and beta contributions, which are a significant fraction of the activity, you are taking a correction factor for geometry that may also be large, and applying them to your overall result. How do those two factors impact your measurements in terms of the uncertainty of the overall results?

BARNETT: First, the instrument is calibrated to the particular geometry that we are looking at i.e., one HEPA filter, so geometry is taken into consideration at the point of making the efficiency determination. Second, we have used the geometry calibration to determine what the alpha and beta contribution is going to be. It can vary somewhat, based on laboratory results, and there are errors associated with it also. When you combine them to make a final dose estimate, the error, typically, is on the order of 30%. The alpha and beta contributions are assessed; they add about 5% to the total error. In some locations, because of the types of activity, errors can be on the order of 50%, but, typically they are 25-30%.

HULL: I do not understand why all this attention is given to what is on the HEPA filters. If you monitor the stack, and know what is going on at that monitoring point, why would you be concerned about what did not get out?

BARNETT: We are looking at the potential for emissions from the stack, as required by NESHAPS. What we did was to look at what is on the filter and use that to determine our potential release in a year. We take that value and develop what the maximally exposed individual would receive as a dose from a particular stack.

HULL: I am not familiar with NESHAPS; is "potential" defined by the regulation?

BARNETT: Yes, "potential" is the theoretical stack emission in a year under normal operating conditions without filtration. The potential is considered unabated. We are looking at

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the filters to see what has been collected.

KARHNAK: Perhaps I can offer a little clarification. If a stack can potentially discharge more than 0.1 mrem/y, it requires continuous monitoring. If it is below that, it does not require continuous monitoring. That is the reason for measuring what is upstream in the filter.

HAYES: Have you determined what isotopes are collected on the HEPA filter on a routine basis, or is the historical data sufficient? Have you taken upstream samples to test the assumption utilized in your evaluation that the mix would not change?

BARNETT: Before we go into a facility, we do a characterization. We also have the facility's environmental monitoring plans and other documents that tell us what types of activity we can expect to see. If that changes from one year to the next, or the mission of the facility changes, we are able to go back and make changes based on the new isotopes and the new activities that we would expect to see. The portable gamma spectrometer has an isotope identification capability. Therefore, gamma emitting isotopes collected on HEPA filters may be tagged. Upstream samples can be taken to establish radioactive material present in a system. I haven't done this, but have relied on recent and historical publications to determine the radioactive materials in the exhaust stream.

THE RETENTION OF IODINE IN STAINLESS STEEL SAMPLE LINES

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Abstract

Following an accident in a multi-unit CANDU nuclear generating station, decontamination of air vented from containment, by the emergency filtered air discharge system (EFADS), would play a critical role in minimizing the release of iodine to the environment. The concentration of gas phase iodine in containment air would be measured using the post accident radiation monitoring system (PARMS), requiring that air samples be passed through a considerable length of tubing to a remote location where the desired measurements could safely be made. A significant loss of iodine, due to adsorption on the sample line surfaces, could greatly distort the measurement. In this study, the retention of I₂(g) on stainless steel was evaluated in bench scale experiments in order to evaluate, and if possible minimise, the extent of any such line losses.

Experiments at the University of Toronto were performed using 6" lengths of 1/4" type 316 stainless steel tubing. Air, containing ¹³¹I labelled I₂(g), ranging in concentration from 10⁻¹⁰ to 10⁻⁶ mol/dm³ and relative humidity (RH) from 20 to 90 %, was passed through tubing samples maintained at temperatures ranging from 25 to 90 °C. Adsorption at low gas phase iodine concentrations differed substantially from that at higher concentrations. However, in general, the rate of deposition was proportional to the gas phase concentration, giving support to the concept of a first order deposition velocity. The surface loading increased with increasing relative humidity, particularly at low RH values, while the deposition rate decreased with increasing temperature, in contradiction to the behaviour expected based on an Arrhenius type relationship. It is speculated that surface water on the steel may play an important role in the deposition process.

Measurements using XPS and SEM at Whiteshell Laboratories revealed that the chemisorbed iodine was located primarily in areas of corrosion. Furthermore, water used to wash the steel contained Fe, Mn and iodine in the form of iodide, suggesting that I₂ reacted to form metal iodides. The deposition of I₂ was also found to depend on the initial surface condition, such as the degree and type of oxidation present. Pretreatment with nitric acid reduced the retention as did electropolishing.

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The results to date suggest that extensive loss of $I_2(g)$ would likely occur in the PARMS and that corrections for the extent of such loss will be unreliable, given the apparent complexity of the phenomena involved.

Introduction

Following an accident in a multi-unit CANDU nuclear generating station, decontamination of air vented from containment, by the emergency filtered air discharge system (EFADS), would play a critical role in minimizing the release of iodine to the environment. It is important that the concentration of gas phase iodine be measured, in order to estimate the potential radiological impact of any iodine released to the surrounding population. This requires that air samples be passed through a considerable length of tubing to a remote location where the desired measurements can safely be made. The equipment required for this sampling and measurement is referred to as the Post Accident Radiation Monitoring System (PARMS). The vented air may contain gaseous iodine in various forms such as $I_2(g)$ and $CH_3I(g)$, particulates and noble gases. A significant loss of iodine during the passage through the tubing, due to adsorption on surfaces, could greatly distort the measurement.

Previous work has established that $I_2(g)$ can readily be adsorbed by stainless steel under some conditions⁽¹⁾. Both physical and chemical adsorption appears to be involved, with the chemical sorption being related to corrosion of the steel surface^(1,3) and the formations of metal iodides⁽²⁾. However, large differences exist in the deposition rates and iodine loadings that have been reported^(1,4). Furthermore, most of the previous work has involved higher temperatures and gas phase concentrations than those relevant to the PARMS.

In this study, the retention of $I_2(g)$ on stainless steel was evaluated in bench scale experiments. The overall objective was to evaluate, and if possible find methods to minimize, iodine deposition under conditions relevant to the PARMS. Specific objectives included evaluating the impact of operational conditions, such as air flow rate, temperature, humidity and gas phase concentration, and identifying chemical transformations occurring on the steel surface. Even though this study is still ongoing, some useful trends have already been identified suggesting tentative conclusions. However, further work is required in order to test properly and support these conclusions and to understand more fully the underlying phenomena.

Experimental

Studies at the University of Toronto

The rate and extent of iodine adsorption on stainless steel tubing was investigated for a range of gas phase concentrations, surface temperatures and relative humidities, in an apparatus at the University of Toronto (Figure 1).

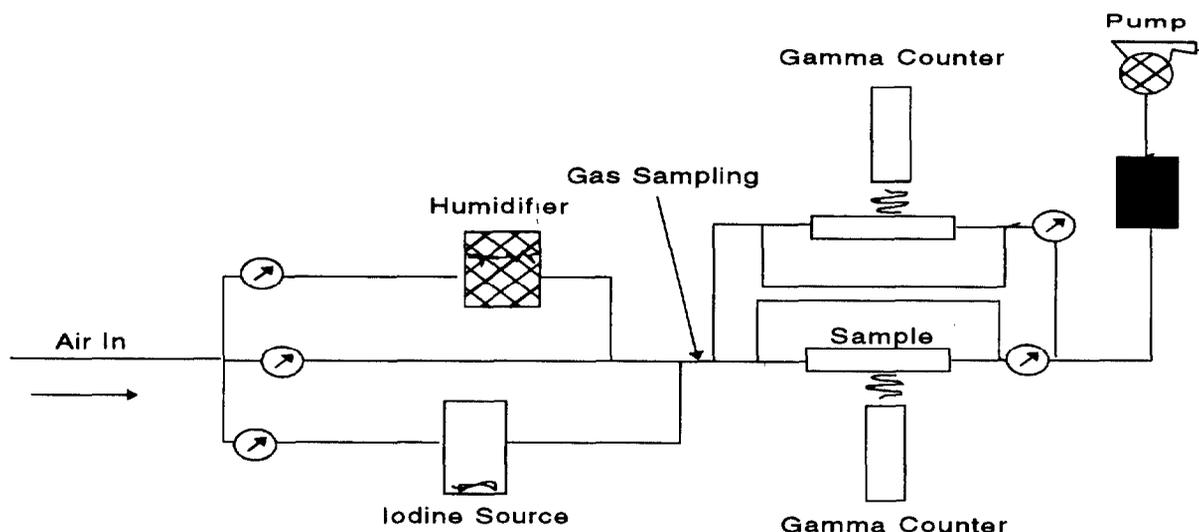


Figure 1: Apparatus used for the experiments performed at the University of Toronto

Laboratory air was drawn into the apparatus and divided into three streams. Most of the air passed through the first two streams, the second of which passed through a water bubbler before rejoining the first stream. Varying the relative flow of air in these two streams allowed the relative humidity of the air to be controlled. The relative humidity and temperature of the air was measured at the point where the two streams combined using a Cole Parmer™ Relative Humidity and Temperature probe.

The third stream was connected in parallel to a 350 mL Teflon vessel containing a solution of ^{131}I labelled I_2 . The gas phase I_2 concentration could be controlled by varying the fraction of the third stream that passed through the vessel using a needle valve. The ^{131}I labelled I_2 solutions were prepared using two methods. For many of the experiments 5 mL 30% H_2O_2 and 1 mL H_2SO_4 was added to 1 mL of 0.5 mol/dm^3 CsI containing 7.4 to 37 MBq of ^{131}I . This produced a saturated I_2 solution with most of the I_2 formed precipitating. The premise was that as I_2 was lost from solution through volatilisation, it would be replenished through dissolution of the solid I_2 . Unfortunately, the $\text{I}_2(\text{g})$ concentration produced using this technique was found to drop substantially over the duration of the experiments. It is suspected that the rate of dissolution of the $\text{I}_2(\text{s})$ varied due to differences in the size of the crystals.

In more recent experiments, an alternate method was used: An aqueous solution of saturated I_2 was added to a 2 mol/dm^3 NaI solution to produce a solution containing 1.6 mol/dm^3 I_3^- in equilibrium with I_2 and I^- . A small volume of the prepared stock solution, typically 15 to 20 mL, was then labelled with 37 to 74 MBq of ^{131}I . As the I_2 was removed it was instantaneously replenished through the rapid

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equilibrium between I_2 and I_3^- . Gas phase I_2 concentrations produced using this technique were found to be more reliable.

The three streams were recombined and then split into two, each of which was passed through a section of 1/4" ID type 316 stainless steel tubing, typically 15 cm in length. The tubing was trace heated and its temperature was set using a Cole Parmer DigiSense™ temperature controller. Duplication of the system allowed any variations between the sections of tubing to be observed. Also, this arrangement facilitated doing experiments at two different temperatures.

A 2x2 NaI scintillation detector was placed in close proximity (within 3 cm) of each of the tube sections. This allowed the accumulation of iodine on the tubing to be continuously monitored. The two detectors were coupled to Aptec™ multichannel analyzers (MCA) placed in an Intel™ based 80386-40 MHz personal computer. The ^{131}I activity on the tube surface was measured every 30 minutes. This counting interval was later decreased to 10 minutes. The counting efficiency was determined after every experiment by cutting the tube and counting the pieces in a well characterised LKB Compugamma™ system equipped with a 3x3 well type NaI detector.

The gas phase iodine concentration was determined using three methods. Usually a known volume of the air stream, upstream of the stainless steel tubing, was temporarily diverted through a short (5 cm) piece of Tygon tubing containing TEDA impregnated charcoal which was subsequently counted in the LKB Compugamma™ system. Air samples were also collected downstream of the stainless steel sections in order to ensure that the gas phase I_2 concentration did not vary significantly over the length of the sections. In some tests, tubing containing charcoal was present downstream of the steel sections throughout the test, in order to provide a mass balance. These results confirmed that only a small portion of the I_2 was retained by the stainless steel. Finally, in a few tests, one of the stainless steel sections was replaced by a tube containing charcoal to allow the gas phase iodine concentration to be monitored continuously.

Air flow rates in each of the three incoming streams was measured using variable area flowtubes as was the flow rate leaving both sections of stainless steel tubing. The flow through each piece of tubing was typically on the order of 1 - 3 L/min giving velocities on the order of 100 cm/s. This high flow was used to ensure rapid gas phase mass transfer within the system. The gas phase mass transfer coefficient was estimated based on a standard engineering correlation for flow through a tube⁽⁵⁾ to be 1 - 2 cm/s. This value was confirmed in experiments involving tubing coated with an epoxy paint known to rapidly adsorb I_2 .

A charcoal trap was used to decontaminate air leaving the apparatus, which was drawn using a GAST™ fluid pump placed at the end. Using a vacuum ensured that should any leakage occur it would be inward, thereby minimising the potential for release of radioiodine from the apparatus. All the tubing, fittings and valves used in the apparatus were made of Teflon™ and the entire apparatus was located in one of the fume hoods of a medium level radioisotope laboratory.

Studies at Whiteshell Laboratories

The adsorption, desorption experiments used 304-L stainless steel coupons with the dimensions of 1.25 cm in diameter by 0.32 cm in thickness. All the coupons were prewashed in 2-propanol and deionized water, and then air dried. Electro-polish samples were treated in an acid bath (H₂SO₄, H₃PO₄, H₂O) for 30 min. at 3 amps. and 4 volts, then washed in deionized water, acetone, methanol and dried at 700 °C for 30 min.

The experiments were carried out in a closed, circulating system. The system consisted of a 1 L Teflon vessel in which I₂ was generated by the addition of HCl and H₂O₂ to a solution of ¹³¹I labelled CsI. The generated gas was circulated through Teflon lines and the sample chamber using a recirculating pump, capable of flows of between 1 to 5 L/min. The gas phase I₂ concentration was measured by trapping on TEDA Charcoal, which was then removed and counted.

After placing a coupon in the sample chamber, the chamber was valved into the circulating gas system. When the adsorption was complete, the coupon was removed and counted in an LKB 1282 Compugamma, then returned to the sample chamber. Ultra pure air was passed through the sample chamber and the desorption was followed using a NaI gamma detector. Following desorption, the coupon was removed and again counted in the LKB counter.

Results and Discussion

The Role of Surface Conditions and Chemistry

Scoping experiments were performed at Whiteshell Laboratories to investigate the impact of surface condition on the retention of iodine. The rate of adsorption and the amount of surface loading achieved was dependent upon the degree and type of oxidation present on the metal. Heating caused surface oxidation, and also extensive contamination of the surface with a thick layer containing carbon. Coupons that were heated in this manner with no subsequent polishing, absorbed relatively small quantities of iodine, likely due to protection by this layer (Table 1).

Table 1 Loading and removal of iodine on stainless steel coupons after various treatments

Treatment	[I ₂ (g)] nmol/L	Loading (ng/cm ²)	After desorption (ng/cm ²)	After washing (ng/cm ²)
Heat (500°C) polished	3-7 >10	150-4000 10000	100-600 1500	12-40
Heat (500°C) unpolished	3-5	20-30	15-20	3 - 10
Acetone	2-4	200-1000	100-500	
Nitric Acid	2-5	35-100	30-50	10-15

In contrast, coupons heated with subsequent removal of the carbon layer by polishing, adsorbed large quantities of iodine. The loading observed was reasonably similar to that for a control sample that was only washed with acetone, or untreated stainless steel tubing (Table 2), suggesting that heating with subsequent polishing did not substantially affect the deposition of iodine. Treatment with nitric acid reduced the loading, possibly due to enrichment of the surface with chromium oxides. Similarly, electropolishing was found to greatly reduce the retention of iodine by the tubing.

Table 2: Loading and removal of iodine on stainless steel tubing after various treatments

Treatment	[I ₂ (g)] nmo/L	Loading (ng/cm ²)	After desorption (ng/cm ²)	After washing (ng/cm ²)
untreated	0.3	45		
	3	9525		
	20	25400		
electropolished	2-8	11-33	10-30	0.5-1.5
nitric acid	2-8	18-50	14-36	2-31

Insight into the nature of the adsorbed iodine was provided by evaluating the removal of iodine due to desorption into air, washing with water and surface analysis using scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). A large portion of the iodine on the unpolished coupons, or those treated with acetone, could be removed by desorption into air. Analysis of the desorbed iodine using gas chromatography and species selective adsorbents⁽⁶⁾ indicated that this iodine was predominantly in an inorganic form, likely I₂, rather than being present as an organic iodide. This suggests that for these coupons part of the iodine on the surface was physically (reversibly) bound I₂.

Water was found to be very effective in removing the iodine remaining on the surface following desorption into air. This suggested that the majority of the "chemically" bound iodine on the surface was in a water soluble form. Radiochemical solvent extraction of the wash solution⁽⁶⁾ indicated that almost all (>95%) of the iodine removed was in the form of iodide. Furthermore, Fe and Mn were observed in the wash solution using Atomic Absorption Spectroscopy. These results suggest that the chemically bound iodine on the surface was predominantly in the form of metal iodides, possibly FeI₂ and MnI₂, consistent with observation of others. For example, Rosenberg et al⁽¹⁾ observed extensive removal of iodine, through washing with either water or an I₂ solution of identical specific activity. However, little iodine was lost through washing with FeI₂ solutions of identical specific activity, suggesting that the iodine on the surface was in the form of FeI₂. The lack of Cr in the wash is surprising given the large amount of Cr in stainless steel. However, Rosenberg et al found that although Fe readily adsorbed I₂, Cr did not, achieving no more than monolayer coverage. This finding is consistent with the lower retention of iodine observed following pretreatment with nitric acid in the present work.

Analysis of the coupons by SEM and XPS, indicated that iodine was retained in localised deposits, presumably oxide scale, whereas adjacent un-corroded regions contained no iodine. Fe and Cr were also detected in the corroded regions however no Mn was observed. The absence of Mn was surprising given that it was observed in the wash solutions.

The relationship between iodine deposition on steel and corrosion has long been established although the relevant mechanism remains uncertain. Recently Tsukaue et al have related corrosion to the adsorption of I_2 by water droplets on the surface, reaction with I^- to form I_3^- , oxidation of Fe to form more I^- , leading to further adsorption of I_2 . Such a mechanism, involving corrosion due to I_2 or I_3^- reduction to I^- is consistent with the conclusion by Tyler that iodine is present as a metal iodide on the surface, based on binding energy measurements using XPS.

The Role of Operating Conditions

The impact on deposition of operating conditions such as the $I_2(g)$ concentration, relative humidity, and temperature of the steel was studied using the apparatus at the University of Toronto. These experiments were performed using 316 stainless steel with no prior treatment, as it was felt that this would be more representative of the tubing in the existing PARMS. To remove any loose contamination, air was blown through the tubing samples before use.

The lack of any pretreatment resulted in some variability in the behaviour observed under any given condition, likely due to variation in the initial condition of the surfaces. The use of the duplicated system, such that two sections of tubing could be investigated simultaneously, allowed this variability to easily be evaluated. In general, the duplicate tube samples agreed to within a factor of two. In the few cases there were larger discrepancies between the samples, and some runs had to be repeated or rejected.

Additional problems with reproducibility were caused by variations in the $I_2(g)$ concentration during experiments, which sometimes decreased by up to a factor of 10 over the course of a twenty hour experiment. Usually most of this decrease occurred during the initial hours of the test. This variability could be accounted for to some extent in calculations, using the numerous $I_2(g)$ measurements that were collected throughout an experiment. However, the variation in $I_2(g)$ caused uncertainty in the interpretation of some results. Consequently, the method for producing $^{131}I_2(g)$ was changed, as described in the experimental section, resulting in far more consistent $I_2(g)$ concentrations.

The variation between the duplicate samples was relatively small compared to that due to the parameters investigated. The errors caused by the variability in the gas phase was somewhat larger. Although these sources of error may have obscured some phenomena, many important trends were still clearly evident. For example, the results of two experiments performed with the same temperature ($70^\circ C$) and similar gas phase concentrations but different relative humidities (6% and 60%) are shown in Figure 2. In both these tests, the gas phase iodine concentration decreased from 2×10^{-7} to 2×10^{-8} mol/dm³ within the first four hours. The duplicate tubes differed by 10% at the low humidity and by up

to a factor of three at the higher humidity. Despite these variations, there was a clear difference between the loadings achieved at the two humidities which differed by a factor of 200.

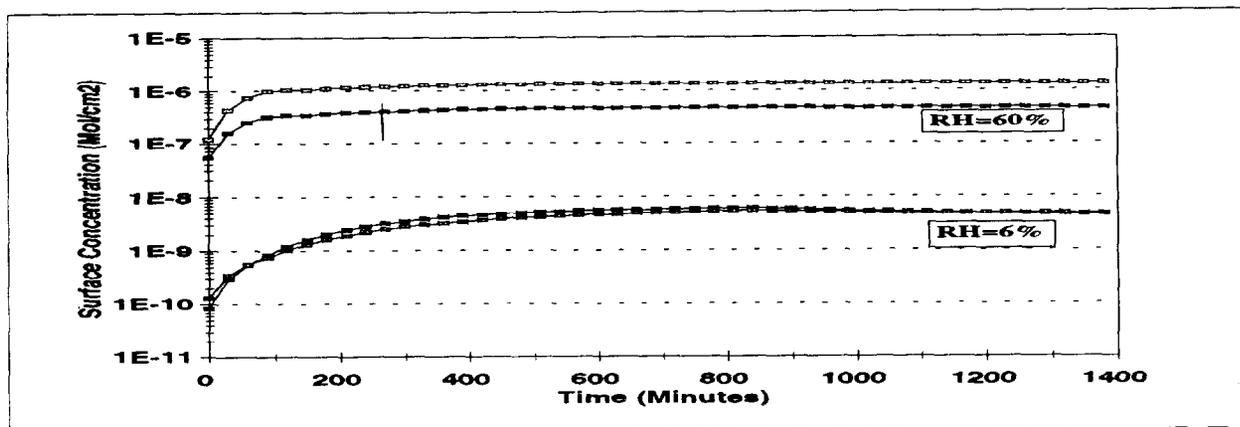


Figure 2: Dynamic surface concentrations as a function of relative humidity for 316 stainless steel at 70 °C exposed to 2×10^{-8} mol/dm³ I₂(g)

In general, the surface loading increased with increasing relative humidity. The dependence on relative humidity was particularly strong at low RH values (Figure 3). It should be noted that this trend is in conflict with any suggestion that water and I₂ are competing for sites on the steel surface. However, the observed dependence on relative humidity could be considered consistent with I₂ deposition being related to corrosion of the steel. According to Rosenberg et al.⁽¹⁾, a number of authors have reported that I₂ induced corrosion of steel is inhibited at low moisture contents. One of the authors referenced by Rosenberg et al proposed that at ambient temperatures, I₂ only corrodes iron at humidities above 30%.

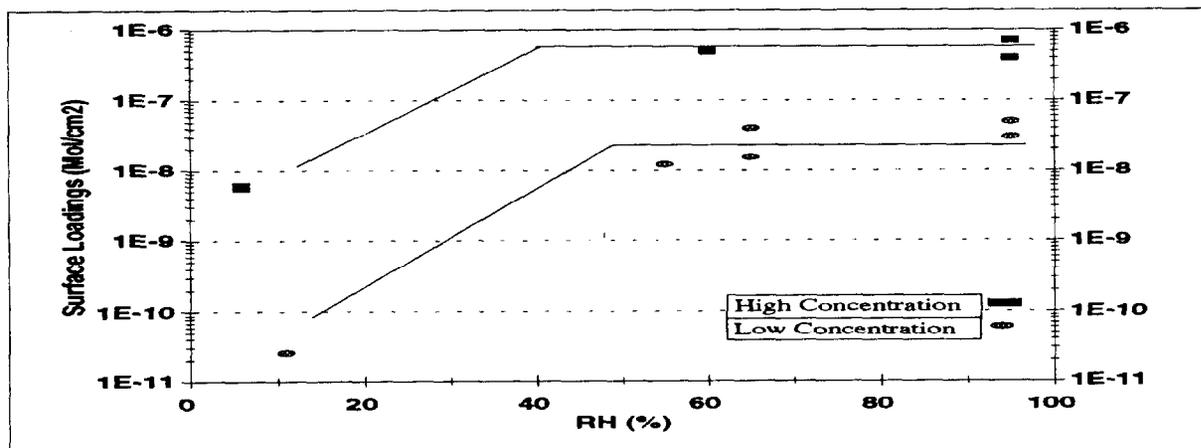


Figure 3: Surface loading as a function of relative humidity for 316 stainless steel at 70°C exposed to high (1×10^{-7} mol/dm³) and low (1×10^{-9} mol/dm³) concentrations of I₂(g)

Experiments were performed using I₂(g) concentrations ranging from 10^{-10} to 10^{-6} mol/dm³. This range encompassed the low gas phase concentrations that might be expected following a reactor accident, the intermediate concentrations that have been used for in-plant testing of the PARMS and the relatively high concentrations that were used in previous studies^(1, 4). The behaviour at low concentrations differed substantially from that at higher concentrations. In particular, at low I₂(g)

concentrations, the surface loading tended to increase throughout a test whereas at high concentrations what appeared to be asymptotes were observed (Figure 4).

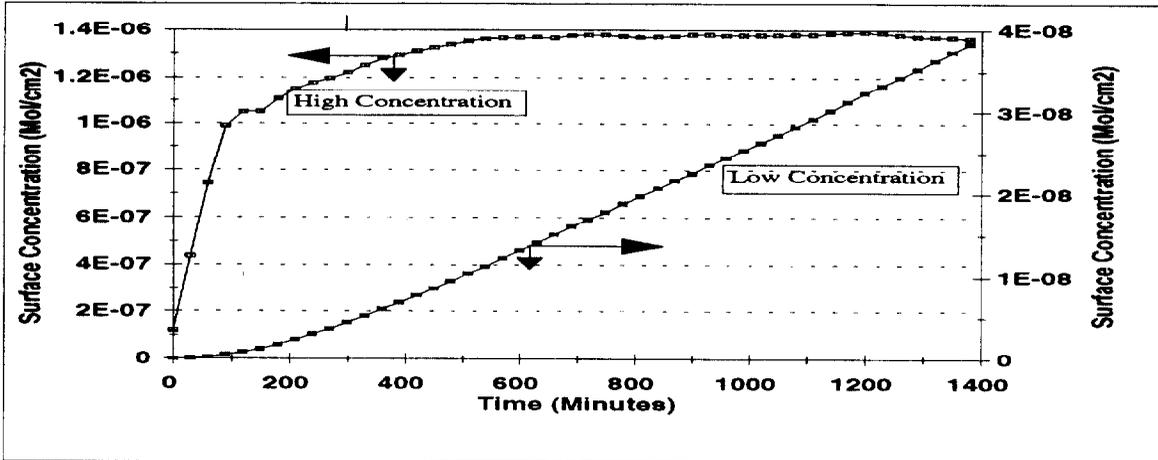


Figure 4: Different behaviour when 316 stainless steel at 70°C is exposed to 60% RH air containing a high (2×10^{-7} mol/dm³) or a low (10^{-9} mol/dm³) concentration of I₂(g)

Gas phase concentration had a substantial impact on the initial rate of surface deposition (Figure 5). The rate depended on the gas phase concentration to the first power, giving support to the concept of the deposition velocity. In some experiments the deposition rate was initially quite slow but then suddenly increased by up to a factor 10. The reason for this change in deposition rate, which typically occurred during the early stages of a test, is unclear. Often this transition occurred once a surface loading on the order of 10^{-9} moles/cm² was achieved (Figure 4), suggesting some critical loading was required in order to initiate the corrosion mechanism. It should be noted that in their study on steel corrosion in triiodide solutions, Tsukaue et al⁽³⁾ observed a delay between exposing a sample and the onset of corrosion which they accounted for using an incubation time for pit formation.

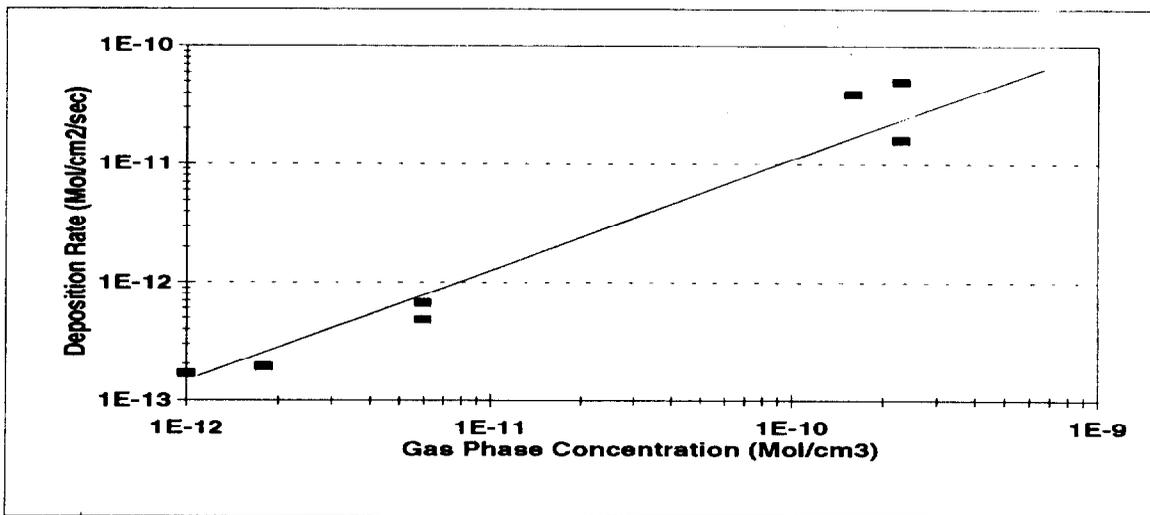


Figure 5: Variations in deposition rates with gas phase concentration for 316 stainless steel at 70°C exposed in air with 60% RH

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The rate of iodine deposition decreased with increasing temperature (Figure 6), decreasing by a factor less than 5 over the temperature range for high gas phase concentrations, and for low gas phase concentrations by a factor of 100, finally dropping below detection at 90 °C. Deposition velocities, calculated from these deposition rates and the measured gas phase concentrations varied from 1 cm/s at 25°C to 0.1 cm/s at 70 °C for high gas phase concentrations. Clearly, other than at 25°C, the rate of deposition was slower than gas phase mass transfer (1- 2 cm/s) and hence was limited by reaction on the surface. This limitation may have been a combination of pore diffusion and chemical reaction.

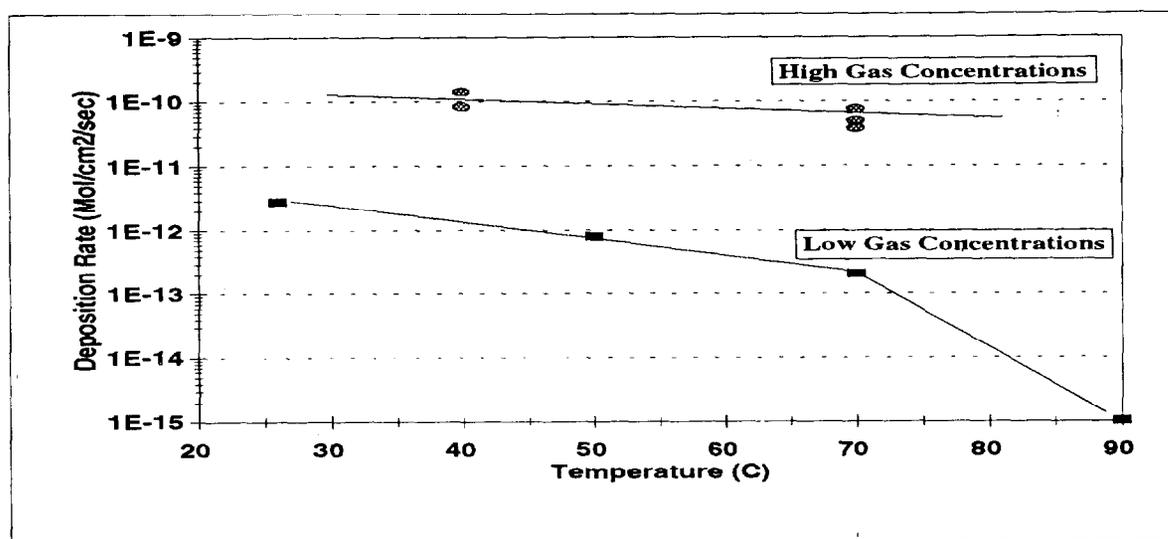


Figure 6: Decrease in deposition rates with increasing temperature at medium relative humidities and low and high I₂(g) concentrations of 10⁻⁹ mol/dm³ and 10⁻⁷ mol/dm³ respectively.

Rosenberg et al⁽¹⁾ observed a similar trend in experiments performed at temperatures above 100°C. However in the current work, the rate of deposition at 90°C was below detection and the implicit deposition velocity was far lower than that reported by Rosenberg et al at 115°C. One possible reason for this difference is that in the present work, the reported temperature was that of the stainless steel; the air was not heated and passed through the tubing so rapidly that it essentially remained at ambient temperature. In the study by Rosenberg et al, the air was heated rather than the steel. In theory, the loading of physically adsorbed I₂ on steel in contact with cooler air would be lower than that on steel in contact with air at the same temperature. Perhaps more importantly, the loading of surface water would be lower on steel in contact with cooler air.

Rosenberg et al⁽¹⁾ interpreted the temperature dependence in terms of an Arrhenius plot and thereby calculated an activation energy for the adsorption reaction. However, it should be noted that the temperature dependence observed here, and by Rosenberg et al is the opposite of that expected based on an Arrhenius type relationship for irreversible chemisorption; in theory, the reaction rate should increase not decrease with increasing temperature. Furthermore, the rates of gas phase mass transfer and diffusion within any pores on the surface would also be expected to rise with increasing temperature. Clearly, the steady state loading of I₂ on the surface at higher temperature would be expected to be lower given that adsorption is exothermic. However, this trend is usually attributed to more rapid desorption rather than slower adsorption. It is speculated based on the observed dependence on temperature and relative humidity, that localised water on the surface plays an

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important role in the deposition process. Less surface water would be expected at lower relative humidity and higher temperature. Furthermore, if deposition was mostly occurring on localised areas of the surface, rather than in a homogeneous manner, the rate of deposition would be slower than that expected based on gas phase mass transfer. This would be the case even if physical adsorption as opposed to chemisorption was the main process.

Conclusions

This study is still at an intermediate stage however, some useful trends have been identified and tentative conclusions proposed. Experiments were performed using $I_2(g)$ concentrations ranging from 10^{-10} to 10^{-6} mol/dm³ and the behaviour at low concentrations differed substantially from that at higher concentrations. In general, the rate of deposition was proportional to the gas phase concentration, giving support to the concept of a first order deposition velocity. The surface loading increased with increasing relative humidity, particularly at low RH values, while the deposition rate decreased with increasing temperature, in contradiction to the behaviour expected in theory. It is speculated that surface water may play an important role in the adsorption process.

The deposition of I_2 occurred through a combination of physical and chemical adsorption and the extent was dependent upon the initial surface condition. Pretreatment with nitric acid reduced the loading as did electropolishing. Examination of the steel surface following exposure to $I_2(g)$ revealed that the chemisorbed iodine was located primarily in areas of corrosion. Furthermore, water used to wash the steel contained Fe and Mn and iodine in the form of iodide, suggesting that I_2 reacted to form metal iodides.

Considerable further work is required in order to properly test and support these conclusions and to more fully understand the underlying phenomena. However, it is already clear that extensive loss of $I_2(g)$ would likely occur in the PARMS. Furthermore, reliable correction for the extent of such loss is likely near impossible, given the large number of parameters that could have an impact. Future work will focus on modification of operating or surface conditions leading to reduced iodine deposition rates, in order to provide recommendations regarding methods for enhancing iodine recovery in the PARMS.

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Acknowledgements

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DISCUSSION

- WREN:** I have a few comments. First, you said that the dissolution rate is higher than you expected from the mass transfer rate. That was based on a smooth surface area, but the stainless steel surface probably is not smooth, so the surface area is not quite the same as what you calculated. Thus, comparison of deposition rate vs. mass transfer rate is not very useful. I do not know how it affects the mass transfer calculation.
- EVANS:** I said the deposition rate was slower than the mass transfer rate. It is about 0.1-0.8 whereas gas phase mass transfer is 1-2 cm/s. The observed deposition velocity may exceed the mass transfer coefficient if the true surface area for deposition is greater than the geometric area. However, in this study the deposition rate was slower than that based on gas phase mass transfer indicating that gas phase mass transfer was not the limiting step or that the area on the tube surface involved in deposition was smaller than the geometric area.
- WREN:** The second comment is that your Arrhenius-type plot has a negative slope. If you are only looking at the adsorption rate, you should always have a positive Arrhenius plot (activation energy is always positive). The negative Arrhenius plot indicates that significant desorption occurs during your adsorption rate measurement, or that water adsorption-desorption has significant impact on iodine adsorption. Did you look at the the temperature effect at 0% RH on the Arrhenius type plot to see whether there is a different Arrhenius behavior?
- EVANS:** I think that is a good question. I do not think we have yet plotted the temperature dependence at very low relative humidity. The plot I showed you was for 60% RH. We observed that the deposition rate, not just the surface loading, decreased with increasing temperature. Based on an Arrhenius relationship for chemisorption or diffusion in the boundary layer, or pores for physisorption, the deposition rate would be expected to increase with increasing temperature. If, as suggested in the presentation, sorption involved water droplets on the tubing surface, then this trend could be due to

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less water on the surface at higher temperatures. Looking at the temperature effect at low humidity would be a good way to investigate this hypothesis.

WREN: Did you perform the desorption of iodine following loading? That will tell what fraction of iodine is physically adsorbed vs. chemically adsorbed.

EVANS: Desorption was performed in some experiments. However, results have not yet been compiled so I can't comment at this time. Establishing what fraction of the iodine is physisorbed is certainly important.

WREN: That will tell you the fraction of adsorption due to physical and chemical adsorption?

EVANS: That is right.

GLISSMEYER: What size stainless steel tubing was used in the PARM system?

EVANS: The PARMs differs between stations but typically involved 1/4" or 1/2" lines approximately 20 m in length.

GLISSMEYER: What kind of tubing are you going to use for the PARM system?

EVANS: The main objective of the work over the next year or so is to see whether we can recommend a way to get the existing system to work. Ontario Hydro has no desire to rip out the existing systems in three nuclear stations. It would be very nice to get the existing system to work at a level that we have confidence in. If it appears that this will not be possible, we will look at different types of tubing, and we have to look at how the tubing ages over time. We showed some possible treatments that would reduce deposition. However, we do not know whether the effects of such treatments are permanent. So I cannot answer your question.

GLISSMEYER: You might want to consider a larger diameter tubing, or separating the iodine sampling system from the particulate system and using teflon or polyethylene tubing for your iodine system.

EVANS: The apparatus we use is entirely constructed of teflon. I find teflon tubing is very good, but teflon fittings are a nightmare for adsorbing iodine. I really do not think teflon has the right properties. Glass would be very nice to use, except there's no way to get seismic qualification. These options should certainly be considered if we reach the point of recommending to Ontario Hydro that the existing lines be replaced. However, we would prefer to find a way to improve the performance of the existing lines. The experimental apparatus was constructed of teflon and, clearly, iodine is not retained significantly on teflon tubing. However, we have noticed that it is retained on teflon fittings and solid pieces of teflon.