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Department of Nuclear Energy

March 30, 1981

Mr. Mel Silberberg, Chairman  
Peer Review Group  
Fission Product Behavior Report  
U. S. Nuclear Regulatory Commission  
Washington, DC 20555

Dear Mr. Silberberg:

My following comments apply to both the Draft Report on Technical Bases for Estimating Fission Product Behavior During LWR Accidents and to the presentations and the comments made during the two-day review session.

The review panel and the meeting participants have pointed to a number of corrections to the Draft. Most of these problems can probably be attributed to the multiple authorship and the speed with which the report was prepared. In general, I agree with most of the comments covered in the two-day meeting. In this letter my comments deal with points I feel were not made or not made adequately.

With respect to the data and theories dealing with the chemistry and physics of iodine releases:

*change*  
1.1  
1.9

1. A portion of the data in the report are contradictory, inconclusive, and incomplete. In my opinion the experiments do not suggest that the chemistry, physics, or mechanics of iodine releases are understood well enough to warrant consideration of regulatory changes at this time.
2. With the notable exception of the contribution by Wichner, Kress and Lorenz of ORNL and with the exception of a few cases of pure gas phase reactions involving no surfaces and no condensed phases, the use of equilibrium thermodynamics in this report can be unjustified and misleading, as suggested by the authors of Chapter 5.

*change*

In systems where dilute fission products are dispersed in condensed phases or where low pressure gases react to form thin surface films, the thermodynamic activities can be many orders of magnitude different from those estimated from the equilibrium

*change*

Mr. Mel Silberberg  
March 30, 1981  
Page 2.

tables. In such systems reactions that are forbidden by macroscopic equilibrium thermodynamics have been observed and recognized as resulting from large and unexpected deviations from ideal activity estimates. In addition to this source of error, surface reactions with low pressure gases may involve compounds and complexes for which there are no appropriate thermodynamic data. The use of equilibrium thermodynamics assumes that such compounds do not exist.

- Chap 4-5*
3. The assumption expressed during the review "that equilibrium thermodynamics might be justified at higher temperatures because kinetics are rapid" can be misleading. In high temperature experiments performed in the HTGR program iodine was deposited on steel surfaces. It was found that after the very rapid iodine reaction with various steel surfaces had occurred and when the system was studied with time, the iodine redistributed itself to different temperature zones from those it was first deposited on. The initial deposit was believed due to a rapid surface reaction followed by an iodine redistribution attributed to a slower diffusion controlled attempt to reach equilibrium between bulk and surface components. (Copies of the results from HTGR-NRC progress reports are enclosed.)

*Deposit*

Whether or not the above explanation is correct is, I believe, not important for this problem. What is important is the experimental observation that iodine deposited during the early stages of a release may redistribute itself without a change in the gaseous environment. This is not a conclusion deducible from the assumption of thermodynamic equilibrium.

In reviewing the report and presentations there appear to be contradictory experiments and experiments that bear directly on the level of understanding of fission product releases.

*Chap 14*

No specific example from an important report (referenced in this NRC document) "Fission Product Release From Highly Irradiated LWR Fuel by R. A. Loren, J. L. Collins, A. P. Malinauskas, O. L. Kirkland and R. L. Towns, NUREG CR-072 ORNL/NUREG/TM-287/R1."

The report deals with several release experiments in which elemental iodine was a major form of the iodine released. In explaining the results the authors assumed that equilibrium thermodynamics could be used to imply that the unexpected elemental iodine resulted from extraneous side reactions of the predicted CsI with surfaces or by reactions with oxidizing impurities in the gas streams. Again, after using equilibrium concepts to justify formation of CsI, on page 125 of the report the authors note "At first approximation we

Mr. Mel Silberberg  
March 30, 1981  
Page 3.

*1.7*  
would be tempted to calculate concentrations from the vapor pressures of probable species (e.g., CsI or CsOH), but we have discovered that the experimentally observed concentrations are much lower." Continuing in this vein on page 127 the report states "...it was shown that the measured cesium and iodine concentrations in the vented gas were one to two orders of magnitude less than would prevail in equilibrium with bulk CsI and CsOH. ....The reason for the low observed values is probably a combination of different species existing (see Section 5.1) and the effect of sorption by fuel and cladding surfaces..."

The cyclic use of invoking then denying equilibrium concepts to modify observed facts pervades the literature on iodine and cesium releases. If anything, it is strong testimony to the fact that the physics and chemistry of the release reactions are poorly understood.

*1.7*  
Several speculations used in the report and in the literature cited in the report have been actually tested and then published in literature not cited in the report. For example, a paper can be found in the Journal of Inorganic Chemistry on the generation of I<sub>2</sub> by CsI reaction with steel (performed under NRC funding in the HTGR program). A second study on Cs, I<sub>2</sub> and CsI deposition along with other studies of Cs and CsI reaction with quartz are enclosed. All of the results bear on speculations in the report.

*1.9*  
For the reasons cited above, I do not believe the report clearly identifies what is known and what is not known in the area of chemistry of the fuel. I also believe that the report in its present form requires careful revision if it is to be a useful resource for future research in the area of chemistry. Many of the explanations of observed effects are controversial and may even be incorrect.

*1.1*  
I feel that development of the technical report has been a worthwhile effort. I believe the report does, in fact, present fairly strong circumstantial evidence that although the processes involved in fission product release experiments are not understood they seem to involve releases that are lower than the estimates used to develop regulatory guidelines. Nevertheless, I feel the NRC cannot consider changing regulatory criteria on the basis of limited observations of phenomena that are not adequately understood.

Sincerely,

*Donald G. Schweitzer*  
Donald G. Schweitzer, Associate Chairman,  
Head, Nuclear Waste Management Division

DGS: gfs  
Enclosure

**PROCEEDINGS  
OF THE  
JAPAN - U.S. SEMINAR ON  
HTGR SAFETY TECHNOLOGY**

**HELIUM TECHNOLOGY  
VOLUME II**

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WASHINGTON, D.C. 20555**

**CONTRACT NO. EY-76-C-02-0016**



A STUDY OF FISSION PRODUCT TRANSPORT AND  
DEPOSITION USING THERMOCHROMATOGRAPHY\*

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J. M. Dickey and F. B. Growcock  
Brookhaven National Laboratory  
Upton, New York, 11973

ABSTRACT

A simple band theory is proposed to describe the thermochromatographic technique with which trace quantities of semi-volatile substances present in a flowing gas may be separated on the walls of a temperature gradient tube. It is shown that the speed of a moving band of a substance becomes essentially stationary at a temperature characteristic of the heat of vaporization of the substance. The thermochromatographic technique is well suited for studying the chemical state of fission products released from heated specimens of reactor fuels into simulated HTGR environments. Data are presented for the chemical stability of CsI at high temperatures and in helium containing various oxidizing impurities.

INTRODUCTION

The potential release of radioactivity into the environment is one of the major hazards always associated with nuclear reactors. When making reactor safety analyses, it is often necessary to estimate the extent of fission product release and the ultimate distribution of these radioactive materials within and/or beyond reactor primary circuits. Such a consideration requires not only a large data base for making computations, but a thorough understanding of the fundamental processes governing the transformation and transport of fission products under a variety of postulated accident conditions.

The present paper describes an experimental technique with which the chemical state of fission products released from HTGR fuels may be investigated. In addition, the thermodynamic stability, potential chemical reactions with the contaminants in the helium coolant, and the transport and deposition behavior of the released fission products are readily studied. The technique, known as thermochromatography, was originally developed at the Brookhaven National Laboratory<sup>1</sup> and has since been employed at BNL<sup>2,3</sup> and elsewhere<sup>4</sup> for fission-product studies related to the LWR and LMFBR programs. Essentially, the thermochromatograph is an apparatus for separating trace quantities of semi-volatile chemical species by the differences in their mobilities along a tube which is held in a temperature gradient. In the present work, a simplified theory of thermochromatography is proposed. In addition, since CsI has frequently been regarded as the most likely chemical form for fission product cesium and iodine in high burnup ceramic fuels<sup>5,6</sup>, data on CsI deposition on quartz and metallic surfaces and its stability at high temperatures and in oxidizing atmospheres are presented.

\*This work was performed under the auspices of the United States Nuclear Regulatory Commission.

## EXPERIMENTAL METHOD

The thermochromatographic technique has previously been described in detail.<sup>1</sup> Since the apparatus employed in the present study is a new setup incorporating several modifications, a brief account of the technique is given here.

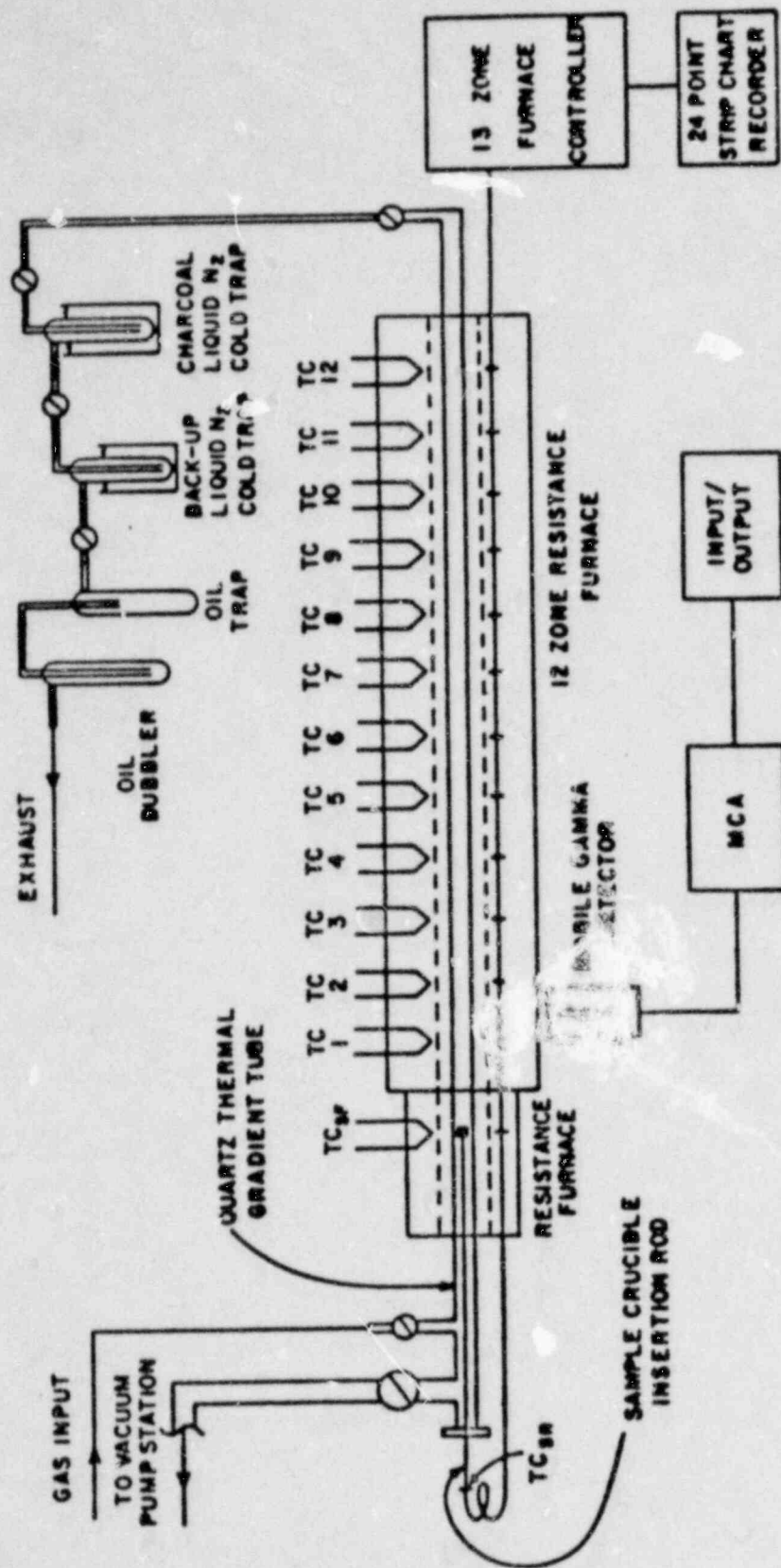
A schematic diagram of the apparatus is shown in Figure 1. A quartz tube, usually 30 mm in diameter, is placed in a custom-built 48-inch Marshall furnace with a split core made up of 12 separately wired heating sections, each equipped with a temperature controller actuated by thermocouples numbered 1 through 12 as shown in the diagram. This furnace is capable of producing a temperature gradient linearly descending from 1200°C to ambient along the length of the quartz tube. A thin-walled metal tube may be inserted inside the quartz tube to change the deposition surface, if necessary. For release temperatures below 1000°C, the sample crucible is heated by a separate resistance furnace placed adjacent to the hot end of the gradient furnace. For higher temperatures, induction heating is employed.

The inert carrier gas, usually helium, is purified by passage through cold traps containing molecular sieve and charcoal and subsequently over copper turnings at 500°C. The helium can be mixed with oxygen, CO<sub>2</sub>, or other gases in all proportions by using gas proportioning units. Water vapor is introduced, when necessary, into the carrier gas over a range of partial pressures by passing through a water bubbler held at a desired temperature; the concentration of water vapor is monitored with a dew-point meter.

In a typical experiment, the sample, which is tagged with appropriate radioactive isotopes, is heated and the volatilized material carried in the gas stream through the temperature gradient tube, where successive stages of condensation and vaporization take place. The release, usually completed in 20 to 30 minutes, is followed by an additional 30 minutes of helium flow. At the end of an experiment, the split furnace is opened to quench the temperature gradient tube quickly to room temperature. The deposition of the material is established by a gamma scan along the tube length. Figure 2 shows a typical deposition profile obtained with CsI tagged with <sup>137</sup>Cs and <sup>131</sup>I.

## THEORETICAL CONSIDERATIONS

The thermochromatographic technique (TC) is particularly suited for separating substances which become volatile only at high temperatures. As in conventional gas chromatography (GC) the movement of a substance down the tube (or a packed column) is due to a frequent exchange of molecules back and forth between mobile and stationary phases. Whereas in the GC the partition of a substance between phases is fixed by the solubility or adsorption isotherm at a given temperature, in TC it is the variation of vapor pressure with temperature that determines the probability of a molecule being in the vapor phase at a particular location. Thus, the speed of the impurity band in GC is constant and independent of the position along the column. In TC the band travels at a high speed in the high temperature region and slows down very sharply with decreasing temperatures; the location at which the band becomes almost stationary depends only slightly on the carrier gas flow rate and the total quantity of the substance in the band, but very strongly on the vapor pressure of the substance.



SCHEMATIC OF THERMOCHROMATOGRAPH

Figure 1



DEPOSITION OF CsI IN He FLOW INSIDE A TEMPERATURE GRADIENT TUBE

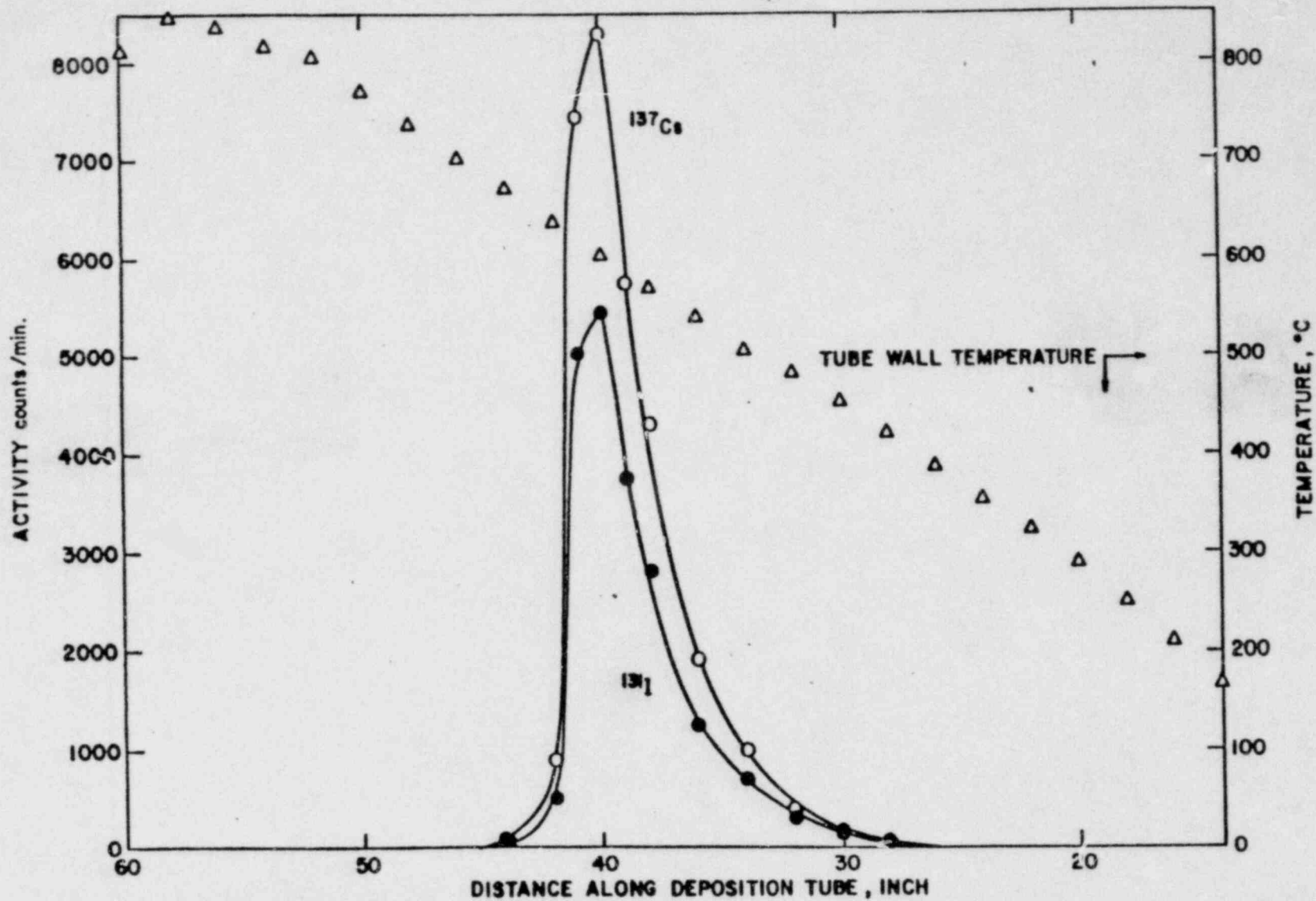


Figure 2



Although a detailed mathematical analysis of the thermochromatography is possible by considering non-equilibrium transport processes in a well-defined boundary and flow regime, only a much simplified theory is given here to illustrate the usefulness, as well as the limitations, of the technique when applied to studies of fission product release. A more general theory is being developed and will be published elsewhere.

Consider the flow of a carrier gas at an average velocity,  $v_g$ , inside a tube, the wall temperature of which decreases linearly with distance,  $x$ . Let the temperature of the tube wall at position  $x$  be represented by the equation,

$$T = T_0 - \beta x \quad (1)$$

where  $T_0$  and  $\beta$  are constants. Suppose that at time  $t=0$  a puff of  $N$  moles of an impurity is released instantaneously into the carrier stream at  $x=0$ . The following assumptions are made:

- (1) The impurity travels down the tube as a narrow band of constant width  $l$  with a speed  $v_b$ .
- (2) At any distance  $x$  the impurity maintains its vapor pressure  $p^0$  at the tube wall temperature. The vapor pressure is expressed in the usual form:

$$\ln p^0 = A - \frac{B}{T} \quad (2)$$

- (3) The system behaves like an ideal gas at constant pressure.
- (4) Convection and diffusional processes are ignored.

Following the treatment of conventional chromatography<sup>8</sup>, the band speed is proportional to the mobile phase velocity and to the probability that the impurity molecules are found in the gas phase. Thus,

$$v_b = \frac{dx}{dt} = v_g \left( \frac{n}{N} \right) \quad (3)$$

where  $n$ , the amount of the impurity present in the gas phase at  $x$ , is given by  $p^0V/RT$ .  $V$  is the total volume occupied by the band. It follows that

$$v_b = \left( \frac{v_{g0} A}{NRT_0} \right) e^{-B/T} \quad (4)$$

where  $v_{g0}$  is the carrier gas velocity at  $T_0$ . The ratio  $v_{g0}/T_0$  is constant throughout the temperature gradient tube.

Eq. (4) shows that the band velocity changes exponentially with temperature, the extent of change being determined by the constant  $B$  which is related to the heat of vaporization. Thus, two substances having different heats of vaporization will become stationary at two different temperatures, thereby effecting a separation along the temperature gradient tube.

Taking the vapor pressure of CsI,<sup>9</sup> the band velocities were calculated as a function of temperature. The results are shown as Curve b in Figure 3. A slight variation of the band theory is the convection model shown as Curve a in Figure 3. Essentially, in the convection model the restriction of a fixed band width is lifted, and, instead, local equilibrium is assumed to be established at all temperatures along the tube wall. The true picture in which there will be some variation in density of the vapor along the tube will be between these two extreme cases. A detailed analysis is in progress. Nevertheless, both models show that in the case of CsI deposition the band becomes essentially immobile at temperatures below ~600°C, in good agreement with the experimental data. Figure 4 shows calculated curves of deposition temperatures vs. time for CsI, Cs, and I<sub>2</sub>, clearly predicting an effective separation of these chemical species in a temperature gradient tube.

#### CHEMICAL STABILITY OF CsI

Based on fission yields and thermodynamic considerations, CsI has often been inferred as the compound likely to form in high burnup oxide and carbide fuels. Recent electron microprobe work<sup>10</sup> has indicated the possible presence of CsI in the pyrocarbon coatings of uranium carbide fuel particles. CsI has also been identified<sup>11</sup> as a product formed from a synthetic mixture of (U,Pu)O<sub>2+x</sub>, Cs<sub>2</sub>O and PdI<sub>2</sub> heated to 1150°C in the hot end of a sealed stainless steel (s.s.) temperature gradient capsule. A knowledge of the stability and reactivity of CsI is needed for calculating the distribution of fission product cesium and iodine released into the environment from a potential accident.

Experiments were performed with chemically pure CsI (tagged with <sup>137</sup>Cs and <sup>131</sup>I) vaporized at high temperatures in the thermochromatograph. The released CsI was deposited on the surfaces of either quartz or Type 304 s.s. It was found that CsI is stable in purified helium up to 1550°C and deposits on quartz or s.s. surfaces in the temperature region 630°-530°C. The effect of various contaminants introduced in helium on the stability of CsI was investigated both during its release at high temperatures and after deposition. A summary of the results to date is given in Table 1. Although the results are still preliminary, some interesting conclusions may be drawn from the experimental observations.

(1) The presence of up to 1% water vapor in helium did not affect the stability of CsI upon release at 800°C; however, partial dissociation of CsI occurred when it was heated to 1500°C in helium containing 2% water vapor. The dissociation product iodine was carried by the gas flow to the charcoal trap located at the cold end of the temperature gradient tube, while cesium was found to have reacted with quartz surfaces on the hot end of the gradient tube where it was collected.

(2) CsI deposited on quartz surfaces at 550°C was not oxidized by passing over it helium containing 2% water vapor, 15% CO<sub>2</sub> + 15% CO, 30% O<sub>2</sub> or air containing 2% water vapor. However, CsI deposited on Type 304 s.s. surfaces, although resistant to water vapor oxidation, was found to decompose quickly and completely in a helium stream containing 10% oxygen. Figure 5 shows the thermochromatogram of a decomposed CsI deposit: Cs remained in the same deposition region, while iodine was carried down the tube and collected in the charcoal trap.

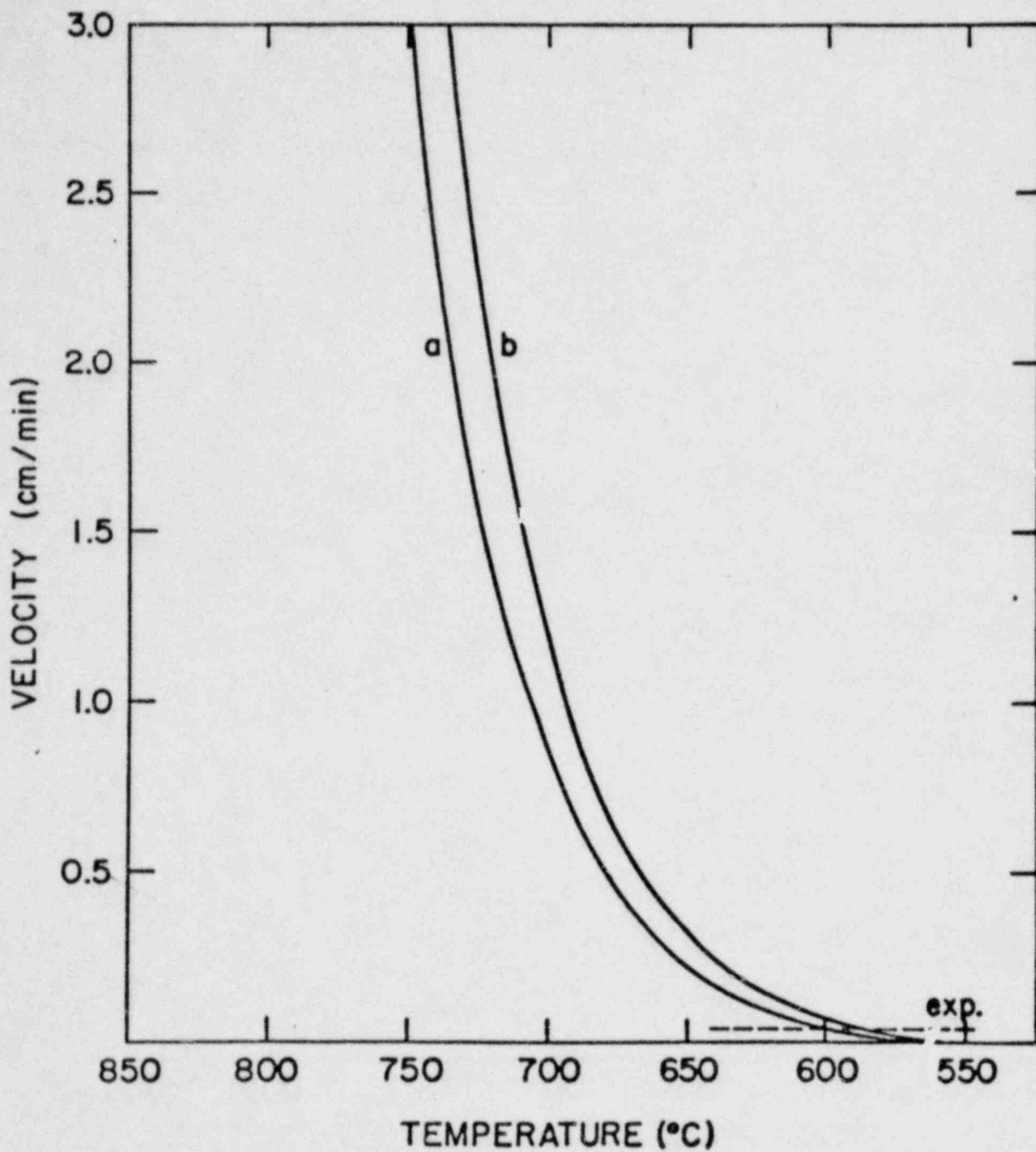
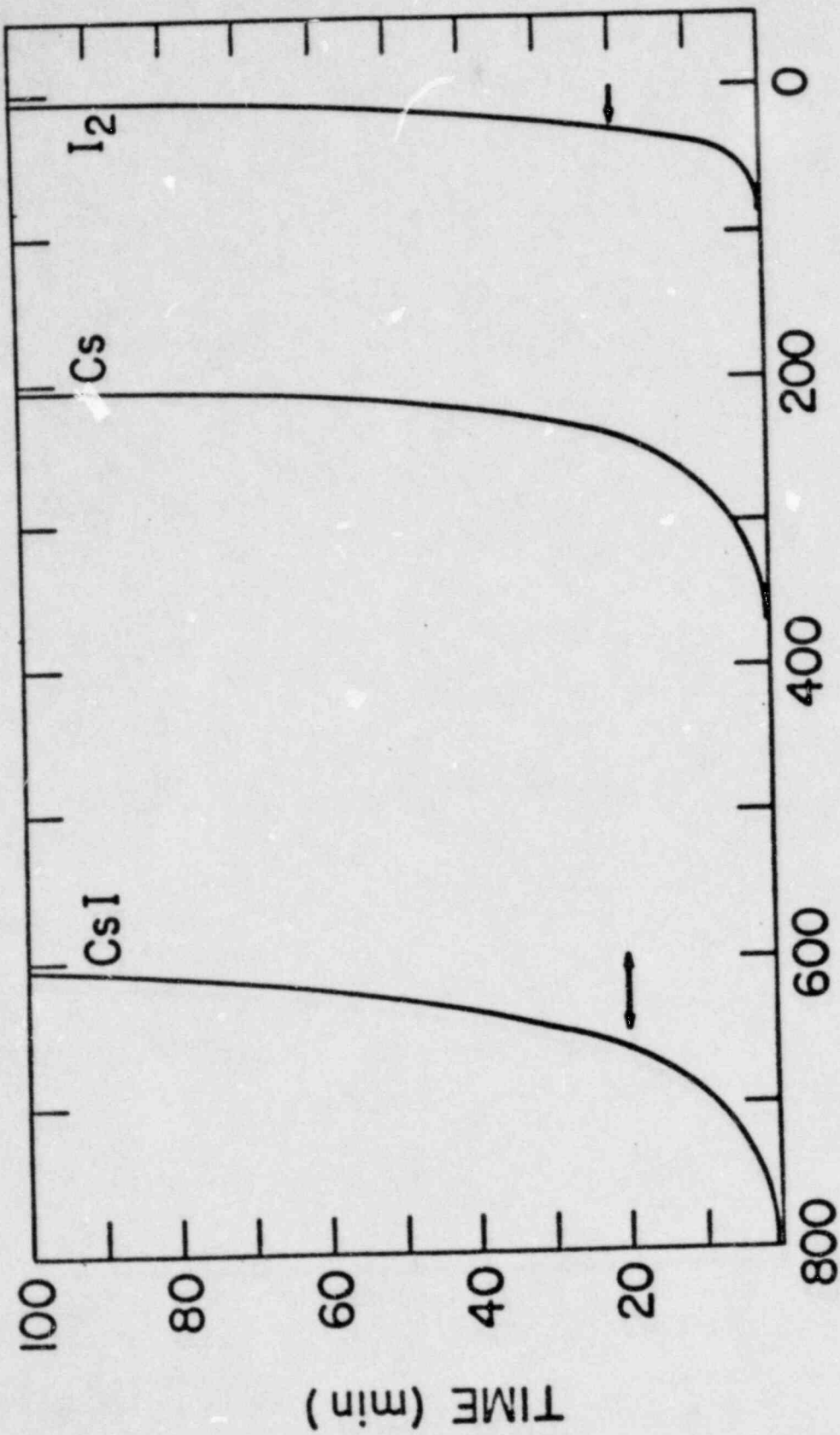


Figure 3. Velocity of the deposit along the tube for a) convection model, b) band model.



TEMPERATURE (°C)

Figure 4. Time taken to travel along the tube to the stated temperature. The temperatures at which deposits were observed are indicated by arrows.



Table 1. Summary of Results from CsI Deposition Experiments

<u>Sample Description</u>	<u>Atmosphere</u>	<u>Deposition Surface</u>	<u>Deposition Temperature</u>	<u>Comments</u>
15 mg CsI in graphite crucible at 800°C	He at 50 ml/min	s.s. 304	570-630°C	Molecular CsI was released.
15 mg CsI in Al <sub>2</sub> O <sub>3</sub> crucible at 800°C	He+0.6% H <sub>2</sub> O at 50 ml/min	s.s. 304	540-610°C	CsI was not oxidized by water vapor.
15 mg CsI in graphite crucible at 800°C	He+0.6% H <sub>2</sub> O at 50 ml/min	s.s. 304	560-610°C	CsI was not oxidized by water vapor.
CsI deposited on s.s. surfaces at 550°C	He+10% O <sub>2</sub> at 50 ml/min	s.s. 304	Cs: 490-560°C I: charcoal trap at ambient	CsI was oxidized by O <sub>2</sub> .
10 mg CsI in graphite crucible at 1550°C	He at 140 ml/min	quartz	520-570°C	CsI was stable up to 1550°C.
10 mg CsI in graphite crucible at 1500°C	He+2% H <sub>2</sub> O at 140 ml/min	quartz	CsI: 460-500°C Cs: 850-900°C I: charcoal trap at ambient	CsI was partially oxidized by water vapor.
CsI deposited on quartz surfaces at 550°C	He+2% H <sub>2</sub> O He+30% O <sub>2</sub> He+15% CO+15% CO <sub>2</sub> Air+2% H <sub>2</sub> O	quartz	CsI peak position moved from 550°C to 475°C in 9 hours at 140 ml/min	CsI remained on surfaces.

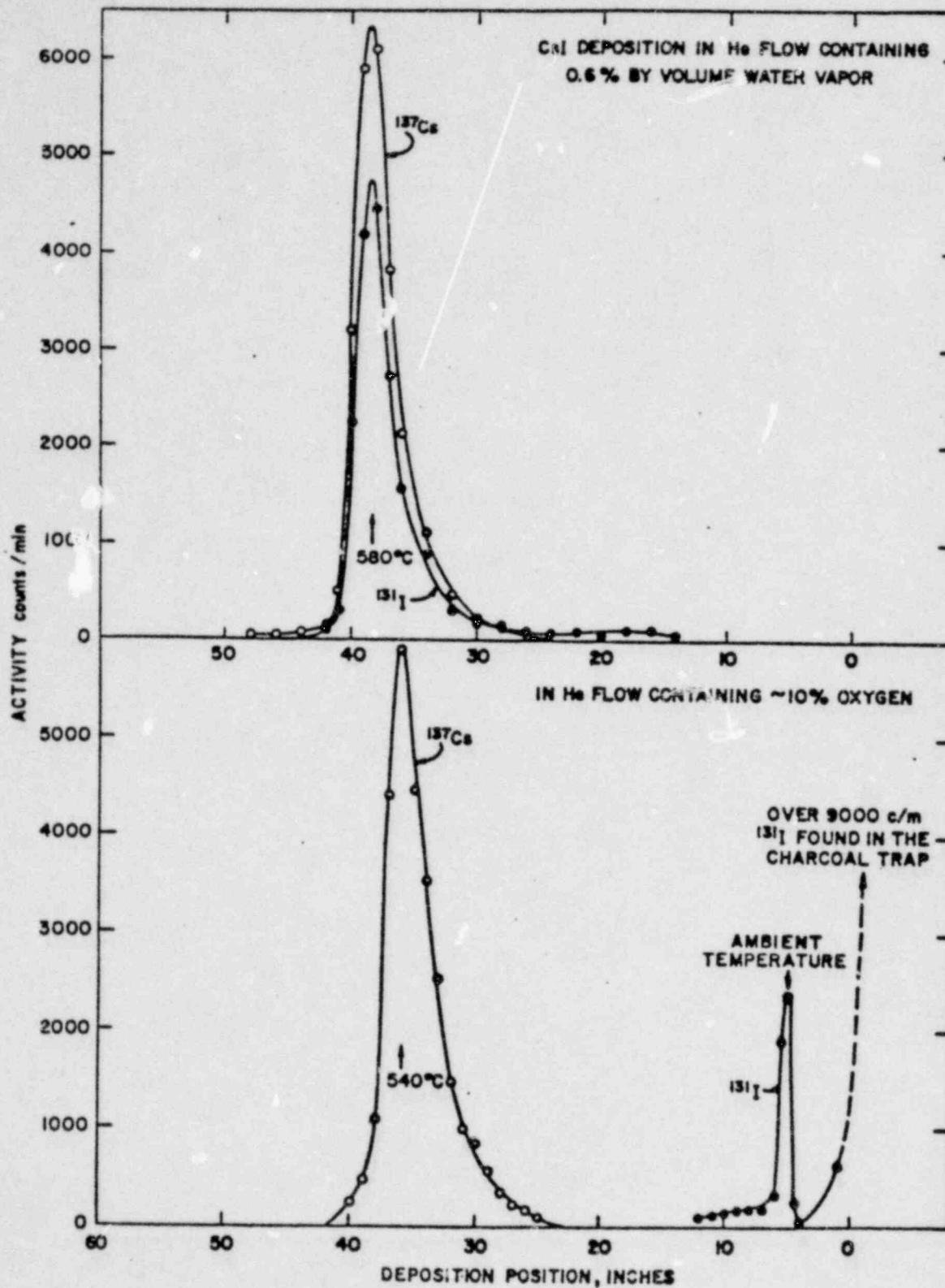


Figure 5

(3) It was found that a large fraction of the Cs residus (possibly  $Cs_2O$ ) from the oxidation of CsI deposited on s.s. surfaces would be revaporized by heating it to  $800^{\circ}C$ . This is illustrated in the thermochromatogram shown in Figure 6. While the first peak represents the fraction of  $^{137}Cs$  remaining on the surface after reheating, the second peak is the new deposit of the volatilized Cs residus.

#### CONCLUSION

It has been shown that the thermochromatograph is a useful technique for studying the chemistry of fission products which are only volatile at high temperatures. The technique is particularly suited for investigating the interaction of fission products with the contaminants in the helium coolant during their release at elevated temperatures and/or after they have deposited on surfaces of different nuclear materials. The theory of thermochromatography is currently being developed and as the theory develops, a better insight into the parameters controlling the deposition temperature, as well as the spread of the deposition band, is expected. Such information will be valuable as a guide to future refinement of the technique. It is anticipated that the thermochromatographic technique will be employed to full advantage in fission product release experiments with irradiated HTGR fuel materials in the near future.

#### ACKNOWLEDGEMENT

The assistance of R. D. Taylor in the construction of the apparatus and in performing part of the experiments is greatly appreciated.

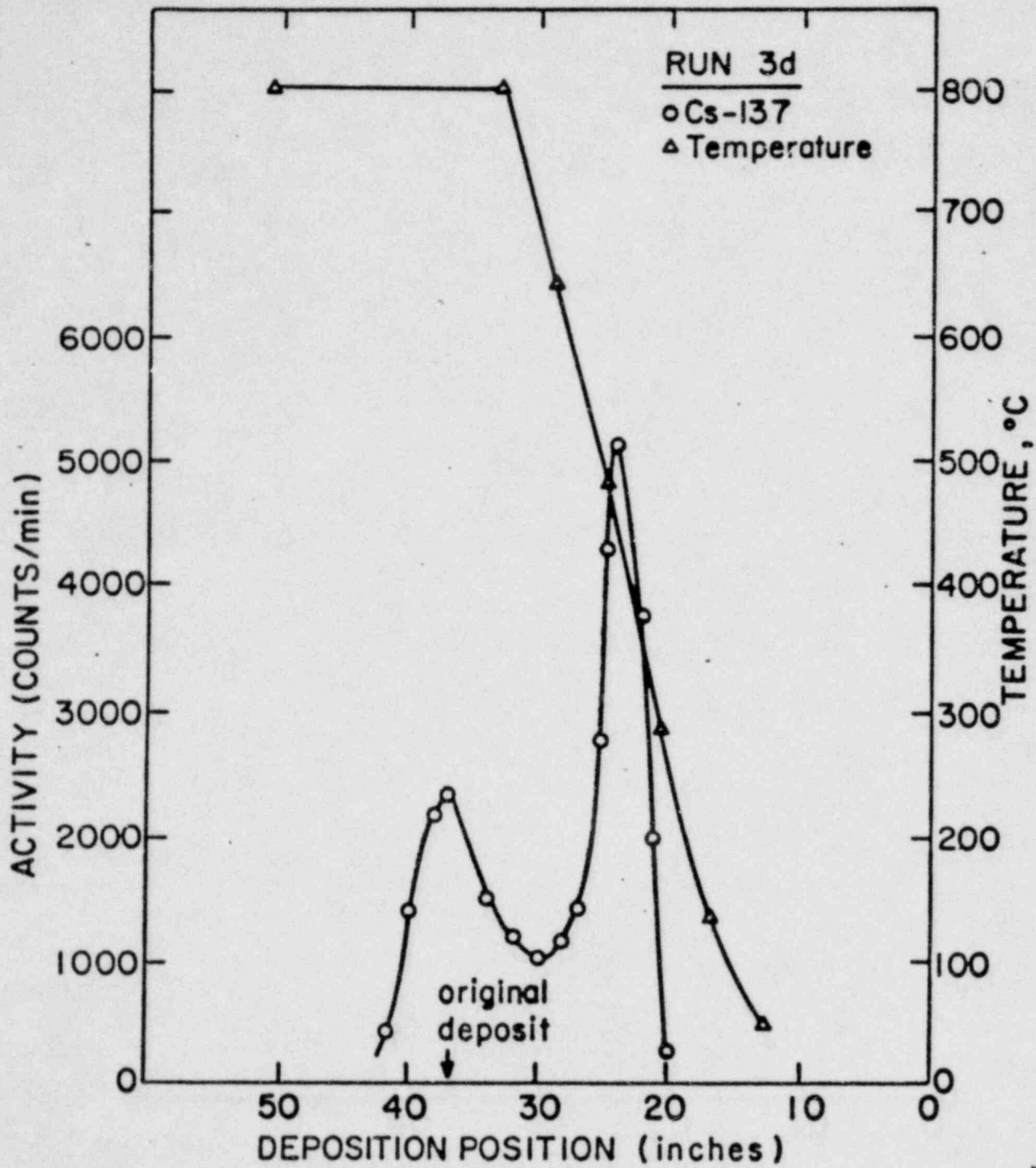


Figure 6



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## DISCUSSION

Q. Is there any carry over of material?

A. We have a series of traps at the end. We have a charcoal trap at liquid nitrogen temperature, so that we should be able to catch all the radioactive materials.

Q. What is the amount of material trapped?

A. We find no activity whatsoever in the trap. When you have CsI deposit at a clear peak, there is 100 percent collection in the tube.

Q. In the test you did with cesium and graphite at 1500 degrees C, you show a cesium peak at about 800 degrees C.

A. Right.

Q. How do you know that it was not some type of compound formation from interaction?

A. The crucible material is graphite. We have water vapor flowing over the graphite. The decomposition products should be cesium oxide or hydroxide. However, cesium oxide, you can see from the latest studies, deposits somewhere around 450 degrees C; also cesium oxide thermodynamically is not stable at the temperatures above 800 degrees C. So, you wouldn't expect to find cesium oxide or hydroxide in that temperature region because of the thermodynamic considerations. They are not stable. If they were, they should be carried down to about 450 degrees C. And also we find it is very hard to get rid of the cesium deposit on the wall. You have to leach with HF to remove it. It penetrates the glass.

Q. Once the material is deposited on the wall, it is governed more or less by the equilibrium vapor pressures of the materials. I would think that it is a very complex situation. You've got to take into account chemical reaction of the materials with the wall, whether the material or the vapor has the high or low condensation coefficient.

A. That is true. However, this is the only case where we present cesium iodide. We use the heat of vaporization which gives a good prediction. If there is some heat absorption, we have this data we can incorporate into the theory. There is nothing special about the heat of vaporization term. That term can be a sum of many terms as long as it is in the exponential term. It is a very simplified theory. Normally you should work in the diffusion processes or convection process into it. That will allow you to predict a spread of the deposition profile.

Q. Can you obtain the constants A and B?

A. The constants A and the B, if you believe this model, can be derived from experiments. However, we assumed that we know all this information and tried to predict where this temperature deposit is.

reaction on CsI + carbon steel in quartz

1978d) This unexpected result has prompted speculation on the source of iodine evolution and necessitated repeating the experiment. A schematic of the apparatus is shown in Figure 1.7. The result of the carbon steel/air/CsI experiment is shown in Figure 1.8. When air was replaced with pure O<sub>2</sub>, no effect on the rate of I<sub>2</sub> evolution was observed; however, when O<sub>2</sub> was replaced with He, the rate decreased substantially and probably would have reached a negligible level given sufficient time. The zero-order dependence of the rate on O<sub>2</sub> concentration is indicative of virtually complete reaction of the CsI or of a diffusion controlled reaction which is relatively independent of the O<sub>2</sub> concentration. The high rate of I<sub>2</sub> evolution confirms the previous result that CsI can attack carbon steel in the presence of O<sub>2</sub>. The reaction of CsI with high purity iron in the presence of O<sub>2</sub> is currently being investigated to elucidate the nature of the carbon steel reaction.

NO! Later experiments showed that CsI was actually attacking the quartz

The effect of flow rate on the reaction CsI/O<sub>2</sub>/S.S. 304 was explored also. The data from 2 experiments are shown in Figures 1.9 and 1.10. Limiting I<sub>2</sub> partial pressures were obtained, which indicate that the equilibrium reaction is 2CsI + 5/4 O<sub>2</sub> + 1/2 Cr<sub>2</sub>O<sub>3</sub> = Cs<sub>2</sub>CrO<sub>4</sub> + I<sub>2</sub>.

This project is being concluded before the end of April 1979.

1.3 High Temperature Vaporization Studies of HTGR Fuel Components and Fission Products (S. Aronson, P. Epstein - Brooklyn College)

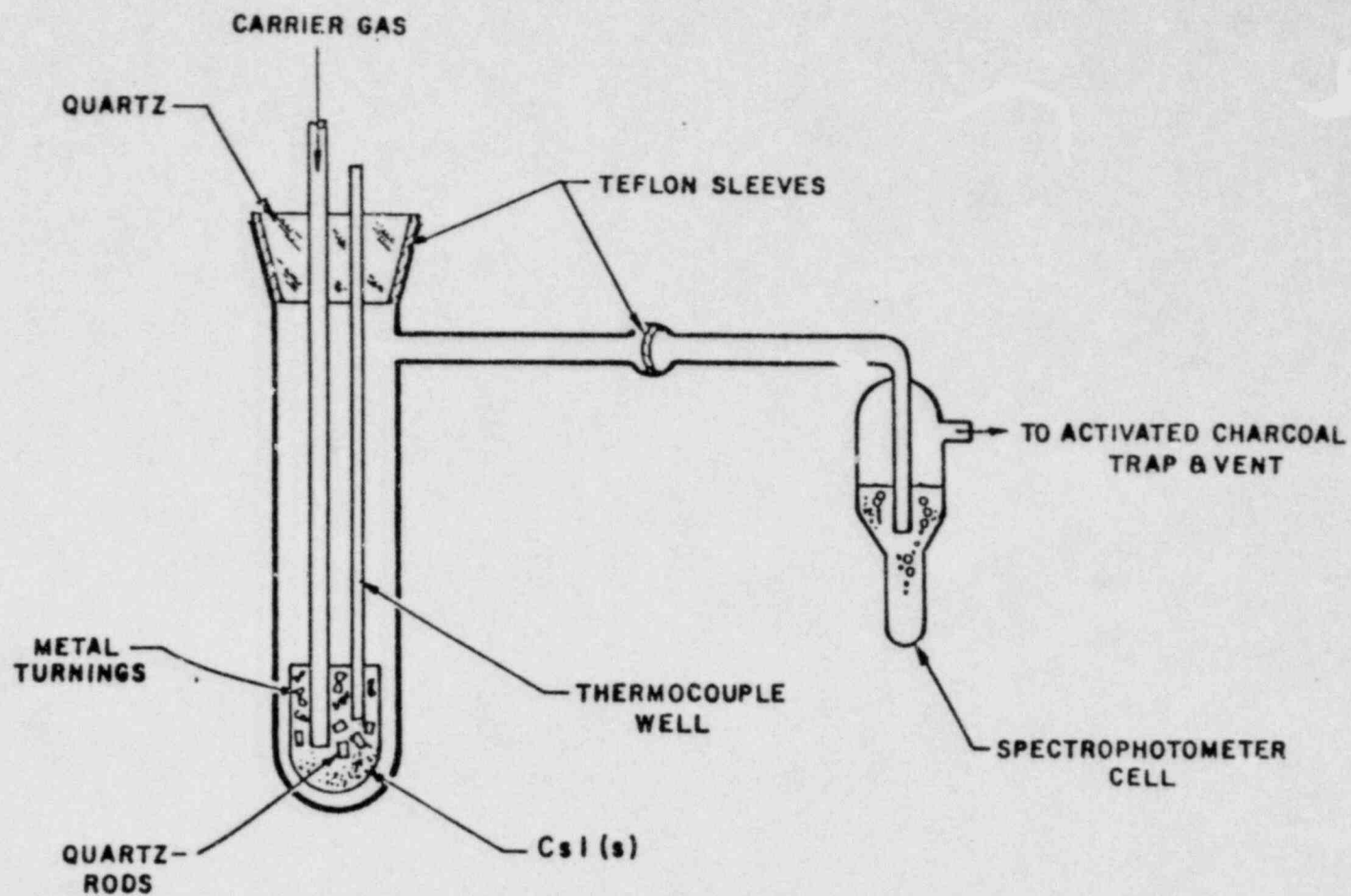
An experimental program has been initiated to investigate gas formation (primarily CO and CO<sub>2</sub>) resulting from the high temperature reaction of mixtures of graphite, UO<sub>2</sub>, ThO<sub>2</sub>, SiC and simulated fission products. UO<sub>2</sub>, ThO<sub>2</sub> and graphite powders have been procured. Graphite crucibles are being fabricated. A 7 kW high frequency induction heating unit is being readied for use and a fused quartz reaction system is being fabricated.

In a continuation of the study of the interaction of cesium with fused quartz, a sample of the quartz tube exposed to cesium vapor at 730°C (Aronson, 1978b, Experiment II) was examined by SEM to gain information about the nature of the attack. A photomicrograph is shown in Figure 1.11. In Figure 1.11a, circular regions of attack with small central nuclei are observed. One of the circular regions is magnified in Figure 1.11b. Superimposed on the photomicrograph is a trace representing the concentration of cesium. Cesium is present throughout the region with the highest concentration occurring in the nucleus.

The long term test on the interaction of fused quartz with cesium vapor was continued. The temperature of the liquid cesium reservoir was 40°C corresponding to a cesium vapor pressure of 10<sup>-8</sup> atm. The temperature of the fused quartz tube ranged from 40°C in the vicinity of the cesium reservoir to 740°C at the center of the furnace. No attack was observed visually after a total exposure of 3,720 hours. A long term test was run on the interaction of fused quartz with tellurium. The tellurium reservoir was at 300°C (10<sup>-6</sup> atm). The temperature of the fused quartz ranged from 300° to 740°C. No attack was observed after 1,875 hours of exposure.

This program on the interaction of volatile fission products with fused quartz has now been terminated.





FLOW APPARATUS FOR MEASUREMENT OF  $I_2$  EVOLUTION

Figure 1.7

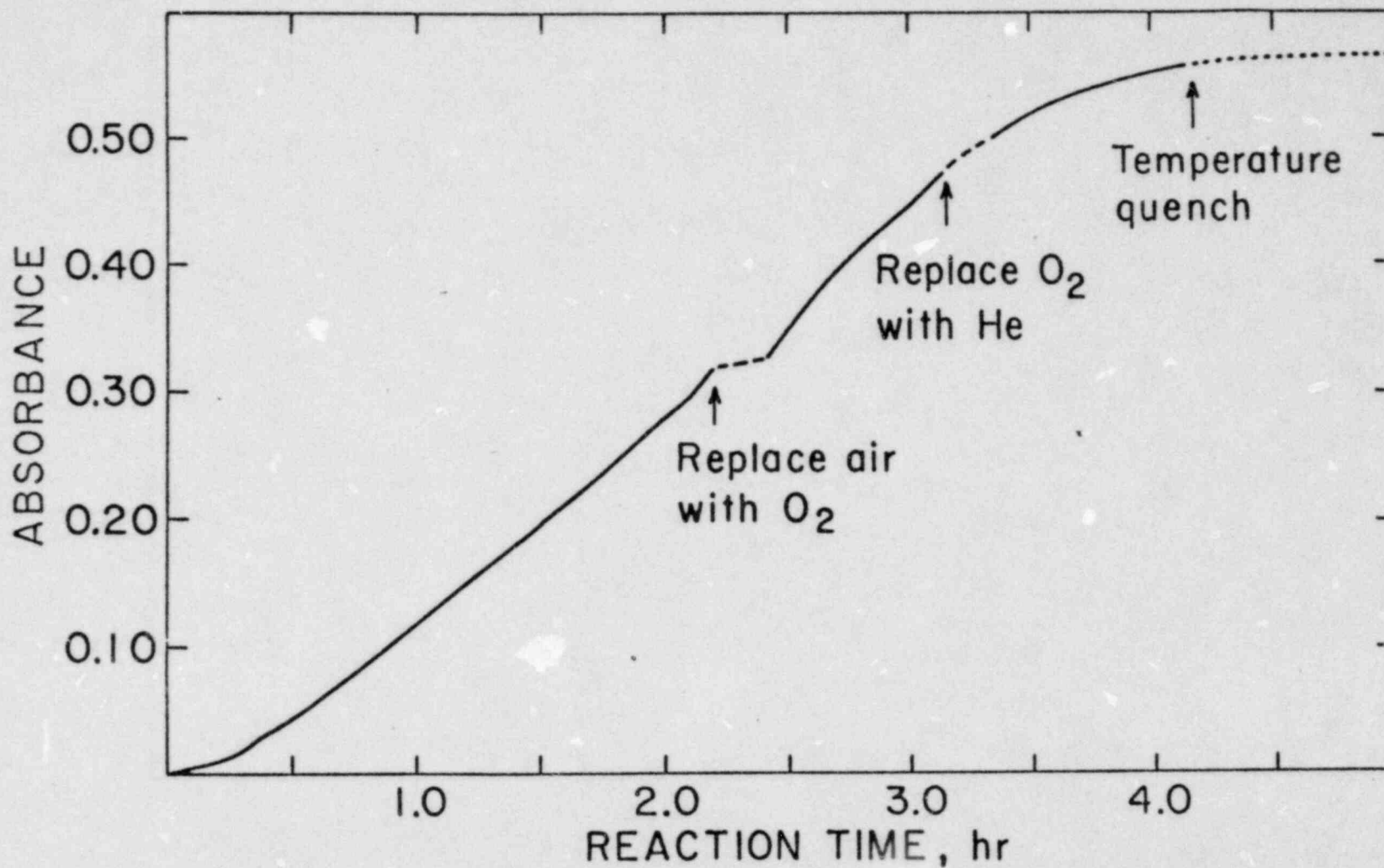


Figure 1.8. Iodine evolution during the reaction of CsI(g) with No. 1018 carbon steel and air at 600°C.

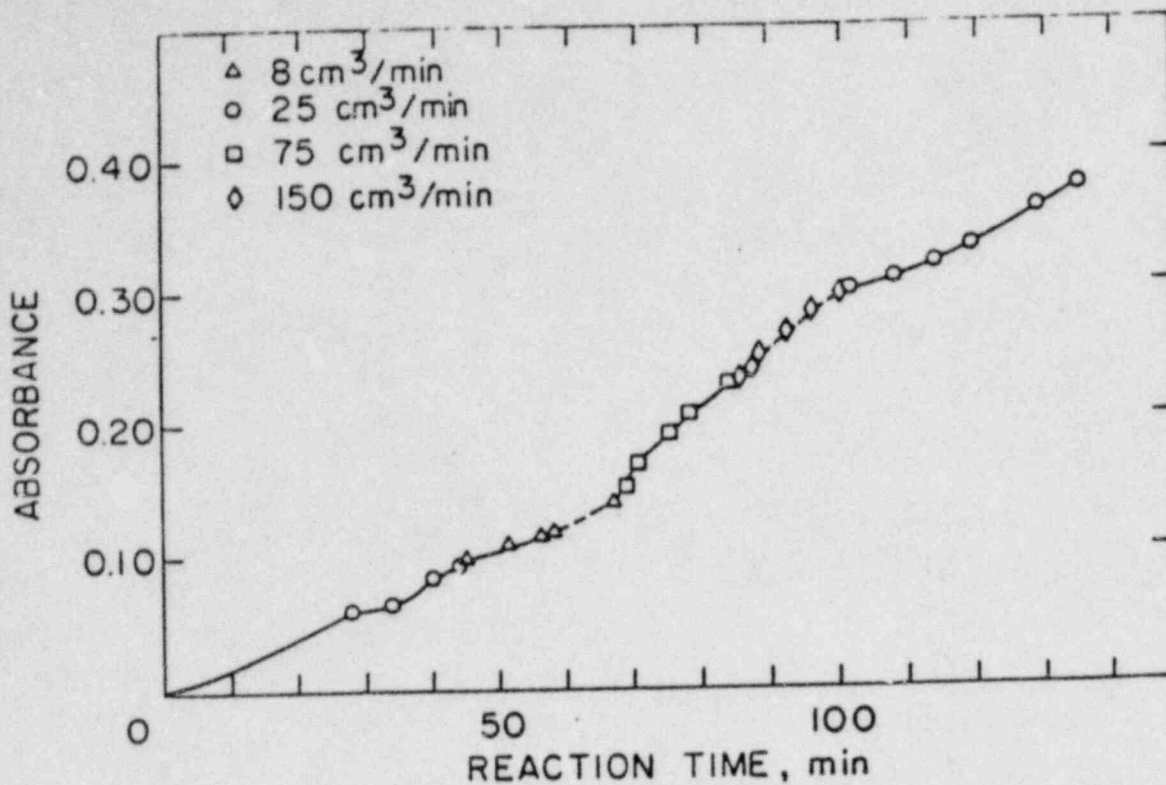


Figure 1.9. The effect of flow rate on iodine evolution during the reaction of CsI(g) with stainless steel 304 and air at 600°C.

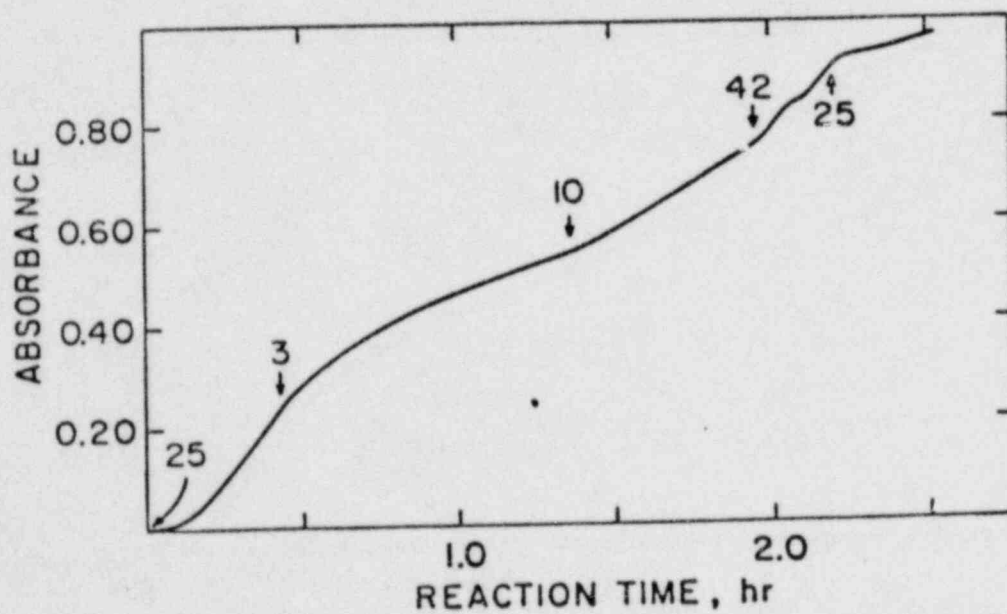
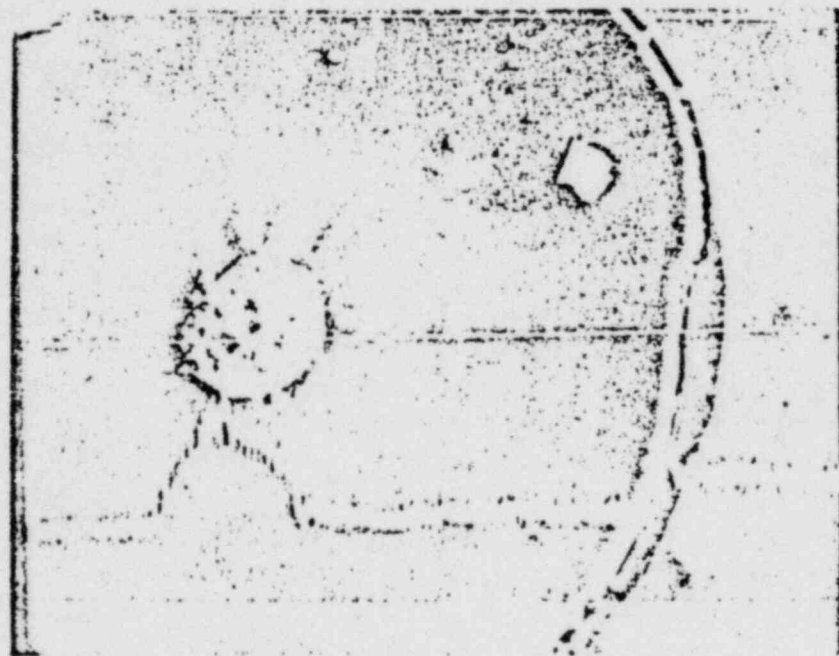


Figure 1.10. Repeat of experiment on the effect of flow rate on iodine evolution during the reaction of CsI(g) with stainless steel 304 and air at 600°C.



(a)

50X



(b)

500X

Figure 1.11. Cesium attack on fused silica.



that they are more than 3 orders of magnitude greater than the diffusion coefficient, D, as calculated using the correlation used in the SORS code,

$$-\log_{10} D = A + \frac{B \times 10^3}{T} \quad (\text{Schwartz, 1974})$$

where for Mo: A = 1.0, B = 19.2 and T is in °K.

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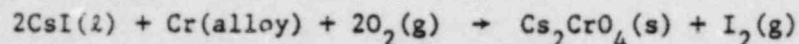
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Jan - March 73

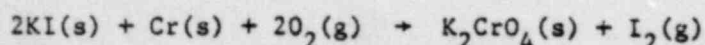
1.3 Interaction of CsI With Stainless Steel, Incoloy 800 and Hastelloy X  
(S. Aronson, M. Friedlander - Brooklyn College)

Experimental evidence was presented (Aronson, 1978) that the interaction of CsI in air or oxygen at 600°C with 304 stainless steel, Incoloy 800 and Hastelloy X is related to the oxidation of chromium to the VI state. Additional evidence has been obtained by rinsing the reacted metal turnings in water and measuring the visible spectra of the resulting yellow solutions. In addition, samples of Na<sub>2</sub>CrO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and CrO<sub>3</sub> were dissolved in water and their spectra were measured.

The spectrophotometric data are shown in Figure 1.9. It is observed that the absorbance maxima for the three alloys occur at the same wavelength, 372 nm, as the absorbance maximum for Na<sub>2</sub>CrO<sub>4</sub>. CrO<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> have absorbance maxima at 347 nm. Thus, it is likely that CsI reacts with chromium-bearing alloys in the presence of oxygen to form Cs<sub>2</sub>CrO<sub>4</sub>. A reaction of the type



probably occurs. It is also possible that formation of CrI<sub>2</sub> or FeI<sub>2</sub> occurs. Thermodynamic data on Cs<sub>2</sub>CrO<sub>4</sub> are not available. However, potassium and cesium compounds have similar thermodynamic properties. It is, therefore, instructive to look at the corresponding reaction of KI to form K<sub>2</sub>CrO<sub>4</sub>.



The standard enthalpy change at 25°C for this reaction is highly negative, -159 kcal. Therefore, the postulated reaction of CsI with the alloys seems quite reasonable even taking into account the substitution of cesium for potassium, the lower activities of chromium (in stainless steel) and oxygen (in air), the difference in temperature (600°C vs. 25°C) and the use of enthalpy instead of free energy.

Additional experiments are under way to investigate the disposition of the iodine in the reaction.

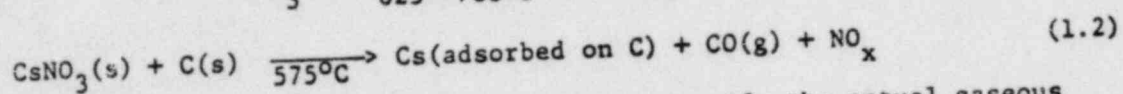
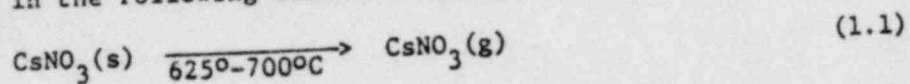
1.4 Interaction of Cesium With Fused Silica (S. Aronson, M. Friedlander, J. Mittelman - Brooklyn College)

The U-tube apparatus for studying the interaction of elemental cesium with fused silica described previously (Aronson, 1978) was used in an experiment in which the cesium was held at 140°C (Cs vapor pressure 6 x 10<sup>-6</sup> atm) and the small-bore quartz tubing was kept at 840°C. After 60 hours, no transfer of radioactive cesium from the cesium reservoir to the small-bore tubing was observed. However, the tubing had turned grey and translucent indicating that some attack had occurred. To check the maximum rate of transfer of cesium from one leg of the U-tube to the other, the leg containing the small-bore quartz tubing was immersed in liquid nitrogen. Even after several hours no cesium transfer was observed. It is not clear whether the lack of transfer was



due to difficulties in vaporization, the presence of impurity gases or the adsorption of cesium in other parts of the system. An additional preliminary experiment is under way in which non-radioactive cesium is being vaporized in a quartz tube placed in a temperature gradient.

Additional experiments in the quartz spring balance system were performed on the decomposition of  $\text{CsNO}_3$ . Data on the vaporization of  $\text{CsNO}_3$  in helium are shown in Figure 1.10 at temperatures of  $625^\circ\text{C}$  to  $750^\circ\text{C}$ . The  $\text{CsNO}_3$  sample weights were approximately 200 mg. It is observed that the rate of weight loss is very low at  $625^\circ\text{C}$  and increases sharply with increasing temperature. Some molecular decomposition occurs at  $750^\circ\text{C}$  but not at  $700^\circ\text{C}$  or below since only the residual sample from the  $750^\circ\text{C}$  vaporization experiment gave a basic solution when dissolved in water. The weight loss at  $575^\circ\text{C}$  for  $\text{CsNO}_3$  is compared to the weight loss on a mixture of  $\text{CsNO}_3$  with graphite in Figure 1.11. It is apparent that graphite is instrumental in decomposing  $\text{CsNO}_3$ . The weight loss of almost 50 milligrams corresponds approximately to the decomposition of  $\text{CsNO}_3$  to elemental cesium. The aqueous solution obtained by dissolving the remaining sample in water was basic. The results of the experiments can be tentatively summarized in the following chemical equations:



Additional experimental work would be required to identify the actual gaseous reaction products. Confirmation is also required for the production of adsorbed cesium rather than elemental cesium or cesium oxide.

#### 1.5 Mass Spectrometric Study of Volatile HTGR Fission Products (S. Nicolosi, I. Tang, H. Munkelwitz)

High temperature mass spectrometry is being used to determine the identity and stability of species present in the gas phase over volatile HTGR fission products. A quadrupole mass spectrometer is being utilized in conjunction with a Knudsen-type cell. The system has been greatly improved with the replacement of induction heating by radiative heating of the cell. This has eliminated troublesome r.f. interference and has made more precise temperature control possible. This was necessary since r.f. radiation was interfering with the quadrupole mass filter causing a severe loss of resolution at high heater power.

$\text{Cs}_2\text{O}$ ,  $\text{CsOH}$ , and  $\text{CsOD}$  systems have been studied to verify spectrometer operation and to settle upon an optimum crucible material. Most of our previous work has been performed in Ta cells with Au, Ni, or Pt orifice foils. It has been determined that  $\text{Cs}_2\text{O}$  reacts with Ta and Ni resulting in suppression of the  $\text{Cs}_2\text{O}$  species in the gas phase and abnormally high Cs pressures. Preliminary work with a crude Pt foil crucible has given results qualitatively in agreement with those of previous investigators. We are currently awaiting completion of fabrication of Pt liners for use in stainless steel crucibles. The preliminary data



April - June '70

Figure 1.10. This profile was verified with the recently installed Ge(Li) detector. This result indicates that  $FeI_2$  formed on a well oxidized surface is relatively immobile if the gaseous environment is inert.

Sufficient data is not yet available to justifiably reconcile all of the results on iodine sorption. Iodine and  $FeI_2$  appear to behave similarly when exposed to carbon steel. Iodine which interacts with carbon steel can be as mobile as other species deposited on inert substrates if the gaseous environment is such as to alter the nature of the surface or maintain it in a reduced state. Temperature excursions imposed on reduced surfaces bearing iodine can also cause the adsorbate to move as expected on an inert surface.

### 1.3 Interaction of Cesium with Fused Silica (S. Aronson and J. Mittelman - Brooklyn College)

The interaction of cesium with fused quartz was studied in 3 sealed tube experiments. In each experiment, a small sample of cesium metal ( $\sim 0.1$  gram) was placed in a fused quartz tube in a helium filled glove box. The quartz tube (13 mm o.d.) was evacuated to  $10^{-6}$  torr, was sealed off (28 cm long) and was positioned in a tube furnace so that the cesium was near the end of the furnace. The other end of the quartz tube was at the center of the furnace at a temperature of  $\sim 750^\circ C$ . The experimental conditions employed for the 3 experiments are given in Table 1.1.

Table 1.1

<u>Experiment</u>	<u>Temp. of Cs Sample (<math>^\circ C</math>)</u>	<u>Cs Vapor Pressure at Sample Location (torr)</u>	<u>Duration of Experiment (hours)</u>
I	250	0.3	48
II	210	0.08	190
III	140	0.004	330

The appearance of the fused quartz tube after Experiment III is sketched in Figure 1.11. The approximate temperature at each location during the run is also given. It is apparent in Figure 1.11 that reaction of cesium with quartz occurred at all temperatures above  $320^\circ C$ . Assuming that the severity of attack is directly proportional to the darkness of the color formed, then the quartz at temperatures of  $420^\circ C$  to  $650^\circ C$  suffered the worst attack. It is likely that this region was exposed to cesium at the highest vapor pressure. As the cesium traveled down the tube the vapor pressure decreased as a result of interaction with the quartz walls. An increase in coloration at the hot end of the tube probably resulted from cesium molecules moving horizontally with relatively few collisions under the high vacuum conditions present in the tube.

The pattern of attack in all 3 experiments was similar. The degree of attack in all temperature regions was highest in Experiment I and lowest in Experiment III. This is consistent with the cesium vapor pressure present in each tube.

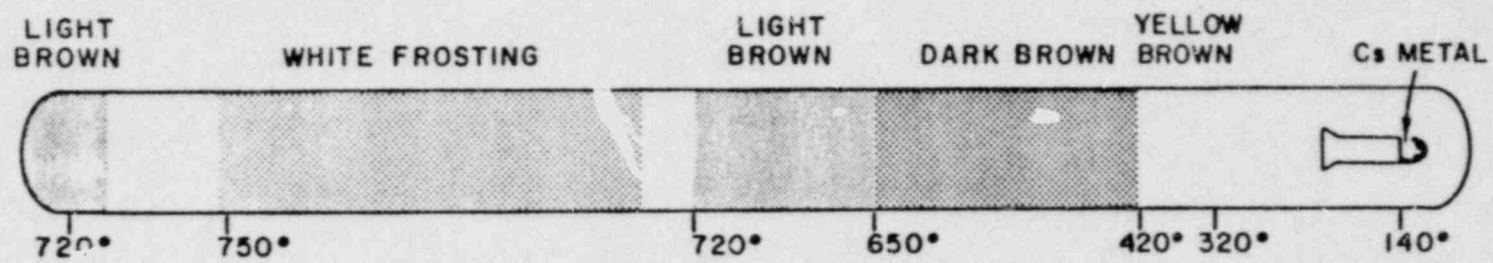


Figure 1.11. Fused quartz tube exposure to cesium in Experiment III.

These preliminary experimental results suggest that the fused quartz insulation and core support components in an HTGR which are exposed to fission product cesium will suffer attack. The nature of the interaction of cesium with fused quartz remains to be elucidated. It is likely that the interaction involves incipient devitrification (crystallization) of the amorphous glass. An experiment was performed on the quartz tube from Experiment II. The area that had been heated to approximately 700°C and was covered with a light brown frosting, was reheated, after opening the tube to air, in an oxygen-methane flame to approximately 1200°C. After removing the flame, a bending force was applied by hand to the two ends of the tube. The reheated area immediately became white, opaque and crystalline. This result suggests that fused silica in an HTGR which is exposed to cesium at high temperatures under mechanical stress may be especially susceptible to devitrification.

An additional, longer term experiment is under way in which the cesium metal will be kept at room temperature and exposure of the quartz to the vapor at temperatures up to 750°C will continue for 2 months. The vapor pressure of cesium at room temperature is  $2 \times 10^{-6}$  torr. Since depletion of the cesium occurs due to interaction with the quartz as it travels through the tube, the vapor pressure of cesium in the high temperature end of the tube may not be much higher than the estimated vapor pressure of cesium in an HTGR,  $\sim 10^{-10}$  torr. The conditions are, therefore, similar to those present in an HTGR and the information obtained should be directly applicable to HTGR operation.

#### 1.4 Mass Spectrometric Study of Volatile Fission Products (S. Nicolosi, I. Tang, H. Munkelwitz)

High temperature mass spectrometry is being used to determine the identity and stability of simulated volatile fission products. Since we are awaiting delivery of platinum crucible liners, necessary for quantitative high temperature measurements, we utilized this quarter to improve the quality and reliability of the mass spectrometer system. The Knudsen type cell was moved closer to the ionizer for greater signal intensity and an additional magion pump was installed in the quadrupole region of the vacuum system. Also, a troublesome electronic component, the mass programmer, was sent to the factory for repair and calibration.

#### 1.5 Aerosol Formation During Graphite Oxidation by Water Vapor (S. Nicolosi, I. Tang, H. Munkelwitz)

Experiments have been performed to determine the extent of aerosol formation from core graphite when the temperature is elevated above that of the normal operating regime. The flow system used is illustrated in Figure 1.12. A typical experiment begins with the establishment of a steady helium-water composition, as measured by the Model 440 EG&G optical dew point hygrometer. The temperature is then raised to the maximum temperature for that run and the system is allowed to stabilize at a constant level of condensation nuclei (CN) per  $\text{cm}^3$ . When a previously untested graphite specimen is initially heated to 1200°C, levels in excess of  $10^6$  CN/ $\text{cm}^3$  are always achieved. When the CN/ $\text{cm}^3$  level has stabilized, the temperature is gradually lowered and the CN/ $\text{cm}^3$  levels are recorded. As long as the temperature at which the system was "stabilized" is not exceeded, the data



obtained in air and oxygen, to be discussed below, were similar indicating that nitrogen does not play a significant role in the interaction of metals with CsI. The most extensive data were obtained on samples exposed to air at 620°C for 4 hours. The results are shown in Table 1.2.

We observe in Table 1.2 that exposure of Hastelloy X and Incoloy 800 to air at 620°C resulted in the formation of a blue surface film. The metal surface remained shiny. The stainless steel surface appeared to be more tarnished. The presence of CsI resulted in a dull grayish-brown tarnish film on all 3 alloys. Rinsing the turnings in distilled water imparted a yellow color to the water. A positive qualitative test for  $\text{Cr}^{+6}$  was obtained (nitric acid, ethyl ether, hydrogen peroxide, blue color in ether layer) on the rinsings from the Incoloy 800 and Hastelloy X turnings. Negative results were obtained on tests for nickel and iron ions.

The data on the alloys indicate that CsI interacts with the chromium in the presence of an oxidizing atmosphere. This observation was confirmed by exposing mixtures of CsI and either iron, nickel or nickel powders to air at 620°C for 4 hours. Only chromium interacted with CsI with the formation of some  $\text{Cr}^{+6}$  ion.

The investigation is continuing with the objective of obtaining information on the interaction of CsI with HTGR alloys in the presence of preformed surface oxide films and mild oxidizing environments (e.g. water vapor).

#### 1.4 Interaction of Cesium with Fused Silica (S. Aronson, M. Friedlander and J. Mittelman - Brooklyn College)

The apparatus for studying the interaction of elemental cesium with fused silica which was previously described (Aronson, 1977) was modified to make the preliminary experimentation more convenient. The modified apparatus is shown in Figure 1.7. A 0.3 gram sample of cesium metal was irradiated in a sealed quartz tube at BNL to a 0.3 mC level. The sample tube was opened and was inserted in the left leg of the quartz U-tube apparatus in an argon atmosphere glovebox. The other leg of the U-tube was filled with 22, 1 1/2 inch lengths of quartz tubing, 2 mm I.D. and 3 mm O.D. The apparatus was attached to an ion pump vacuum station, was evacuated to  $10^{-7}$  torr and was sealed off. The legs of the U-tube were inserted into an oil bath and a tube furnace. Measurements of cesium absorption by quartz at temperatures of 600-1100°C are currently under way.

Other experiments on the interaction of cesium with quartz will require work in a flowing mixture of helium and water vapor. It will be expedient to use a salt such as  $\text{CsNO}_3$  as the source of cesium in this type of experiment. Work was, therefore, begun on the thermal decomposition of  $\text{CsNO}_3$ . Several  $\text{CsNO}_3$  composition experiments were performed in a system containing a quartz spring balance in which sample weight changes could be observed. The preliminary results indicate that  $\text{CsNO}_3$  does not significantly decompose at temperatures up to 750°C. In contact with powdered graphite, however, rapid decomposition occurs at 570°C. This latter observation is in accord with previous observations made on graphite soaked with an aqueous  $\text{CsNO}_3$  solution and heated in vacuum.



July - Sept 77

species CsI, I<sub>2</sub> and Cs using the convection model, and the experimental peaks are indicated. It can be seen that even these simple models can predict the widely different temperatures at which different compounds should be deposited (Figure 1.7).

1.4 Interaction of Cesium with Fused Silica (S. Aronson, J. Mittelman - Brooklyn College)

The HTGR primary coolant, helium, circulates through the reactor system at relatively high temperatures, 400°C to 900°C, with transient temperatures of 1200°C possible at certain locations. Both metallic and ceramic thermal insulating materials are used to keep the PCRV at a reasonably cool temperature. The principal metallic high temperature materials are Incoloy-800, Hastelloy-X and special composition steels (Roberts, 1974). The principal ceramic high-temperature materials are fused silica block, fused silica fiber and aluminosilicate fiber (Roberts, 1974). There is relatively little information in the literature on interactions with metallic materials and almost no information on interactions with non-metallic materials.

We plan to investigate plate-out, lift-off and penetration of cesium, strontium and iodine-base substances with fused silica which is the material that will be exposed to the gaseous helium environment at the highest temperatures during normal operation, 1200°C. The chemical interactions will be studied as a function of temperature and fission product concentration in vacuo and in gaseous environments of either helium or mixtures of helium and water vapor.

The apparatus shown in Figure 1.8 will be used to study the interaction of elemental cesium with fused silica in vacuo. This system is similar to that used by Milstead and Zumwalt (Milstead, 1966) to study cesium interactions with steels. Elemental cesium tagged with <sup>134</sup>Cs will be vaporized by the furnace at the left of Figure 1.8 to achieve cesium vapor pressures of 10<sup>-2</sup> to 10<sup>-6</sup> torr. The cesium vapor will interact with fine quartz rods (~2 mm diameter) positioned in a second furnace at a temperature of interest in the range of 600°C to 1100°C. Absorption of cesium by the quartz in cesium vapor and desorption of cesium from the quartz in vacuo will be followed with a γ-scintillation detector focused on the quartz rods. Construction of the apparatus is now under way.

A study which is under way of the release of cesium from graphite in mixed adsorbates containing cesium and strontium has been temporarily suspended. This investigation requires the doping of graphite with cesium and strontium salts (e.g., CsNO<sub>3</sub>, Sr(OH)<sub>2</sub>) which would presumably decompose at elevated temperatures to yield elemental cesium and strontium co-adsorbed on graphite. Some preliminary experiments on the volatilization of CsNO<sub>3</sub> performed in the thermochromatographic apparatus at BNL have indicated that the decomposition of CsNO<sub>3</sub> in the presence and absence of graphite is more complex than expected. The decomposition processes for other cesium and strontium salts are equally obscure. Experimental work will, therefore, be deferred until a reliable method is found to co-adsorb cesium and strontium on graphite.

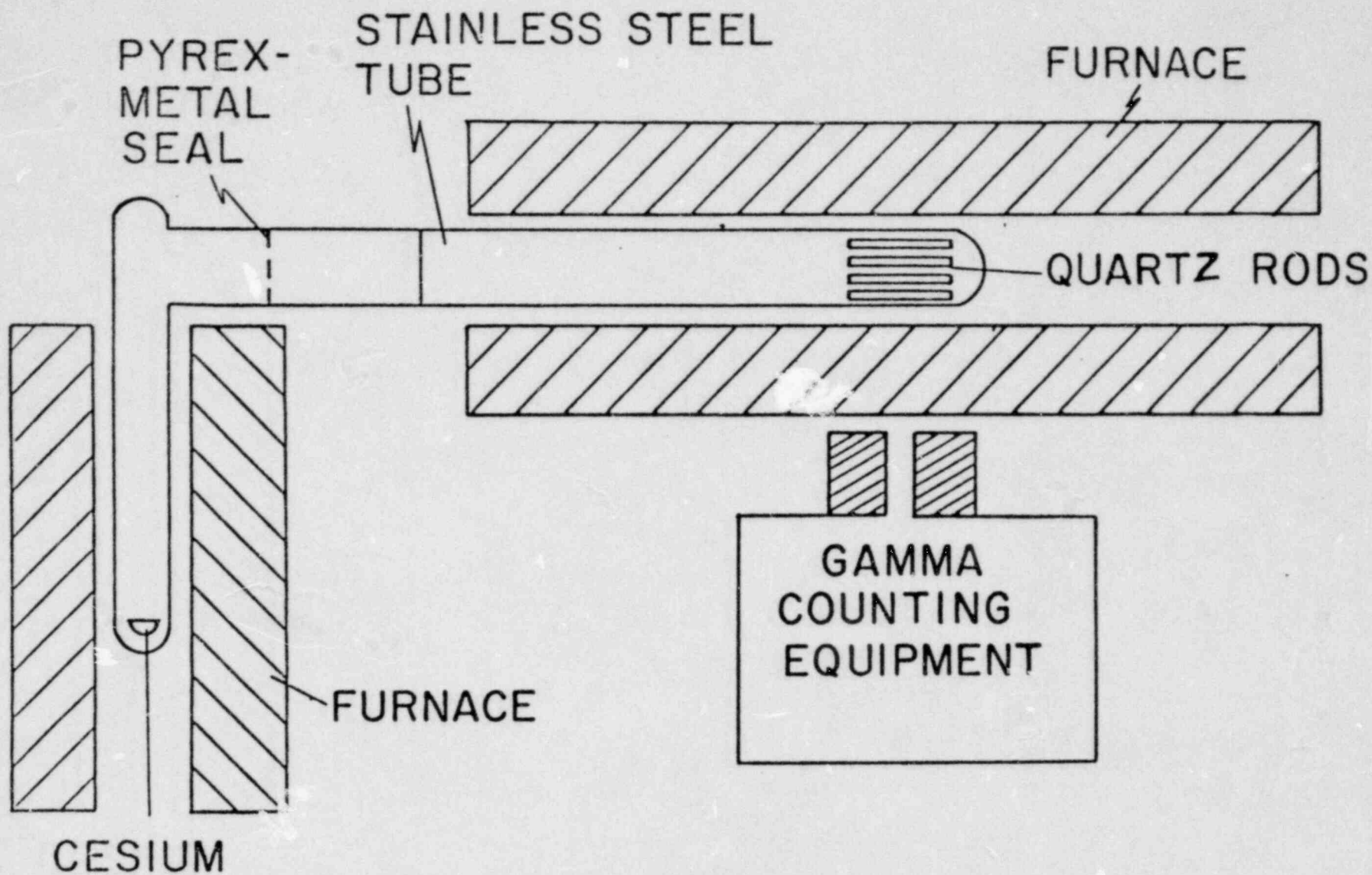


Figure 1.8 Apparatus for studying the absorption of cesium by silica in vacuo.

periods ( $\sim 2$  to 3 days) to allow the transport phenomenon to reach a steady state. The count rates obtained were plotted as a function of time (Figure 1.16). From this plot, the slope for the linear-most sections corresponding to a given flow rate was obtained.

A plot of the slope as a function of flow rate is shown in Figure 1.17. The plot shows a linear behavior up to a helium flow rate of 950 ml/min. Beyond this flow rate there is a large deviation from linearity. This leads us to conclude that helium passed over the tagged iodine crystals is saturated with iodine for flow rates up to about 950 ml/min. Lower flow rates were employed in all of our sorption and permeability experiments; accordingly, saturation can be assumed in estimating the vapor pressure of iodine to which concrete samples were exposed.

#### 1.6.4 High Temperature Sorption Experiment

The high temperature sorption experiment was started in the second week of September. For sorption experiment procedures refer to Quarterly Reports January through June 1977. The only difference in this experiment is that the concrete samples are being held at 100°C instead of room temperature ( $\sim 20^\circ\text{C}$ ).

To date, two samples have been exposed to  $^{131}\text{I}$ -tagged iodine vapor for 9 days and 3 days, respectively. These samples were subsequently sectioned to obtain iodine concentration profiles. The data from these samples are being analyzed.

Currently, a third sample is being exposed. The planned exposure period for this sample is 27 days.

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## NOTES

### The interaction of CsI with high-chromium alloys in the presence of oxygen†

(Received 13 October 1978; received for publication 11 January 1979)

Based on fission yields and thermodynamic considerations, CsI has often been inferred as a compound likely to form in high burnup oxide and carbide nuclear fuels. Recent electron microprobe work [1] has indicated the possible presence of CsI in the pyrocarbon coatings of uranium carbide fuel particles. CsI has also been identified [2] as a product formed from a synthetic mixture of (U, Pu)O<sub>2-x</sub>, Cs<sub>2</sub>O and PdI<sub>2</sub> heated to 1150°C in the hot end of a sealed stainless steel temperature gradient capsule. A knowledge of the stability and reactivity of CsI is needed for calculating the distribution of fission product cesium and iodine released into the environment from a potential accident.

The stability of CsI volatilized at temperatures above 700°C and passed through a temperature gradient furnace has been studied by the High Temperature Gas-Cooled Reactor (HTGR) Safety Group at Brookhaven National Laboratory [3]. It was observed that CsI volatilized at 800°C and transported in a flowing helium atmosphere (50 ml STP/min) deposited on a quartz or 304 stainless steel tube at temperatures of 540-630°C. The addition of water vapor as an impurity in the helium during volatilization had no effect on the deposition characteristics.

In the particular experiment shown in Fig. 1(a), CsI tagged with <sup>137</sup>Cs and <sup>131</sup>I was vaporized in a helium-0.6% water vapor carrier gas and was deposited at 580°C on a 304 stainless steel tube. The carrier gas composition was then changed to helium-10% oxygen. As is observed in Fig. 1(b), the CsI deposit lost its iodine which travelled downstream and redeposited on the 304 stainless steel tube at room temperature and in a charcoal trap at liquid nitrogen temperature. However, in subsequent experiments using quartz tubes, it was observed that while CsI deposited at the same temperature on quartz as on stainless steel, decomposition of CsI did not occur when a helium-10% oxygen atmosphere was introduced.

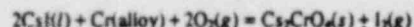
An experimental program was undertaken to elucidate the reasons for the different behavior of CsI on quartz and on 304 stainless steel (70% Fe, 30% Cr, 10% Ni) and to obtain information on the interaction of CsI with the potential HTGR alloys [4] Incoloy 800 (50% Fe, 30% Cr, 30% Ni) and Hastelloy X (18% Fe, 22% Cr, 50% Ni, 9% Mo).

Mixtures of CsI with 304 stainless steel, Incoloy 800 and Hastelloy X turnings as well as with Fe, Ni and Cr powders were heated either in air, oxygen or in helium for periods of several hours at temperatures of 550-650°C. In helium, no corrosion of the metals occurred either in the presence or absence of CsI. The data obtained in air and oxygen, to be discussed below, were similar indicating that only oxygen played a significant role in the interaction of metals with CsI. The most extensive data were obtained on samples exposed to air at 620°C for 4 hr. The results are shown in Table 1.

We observe in Table 1 that exposure of 304 stainless steel, Hastelloy X and Incoloy 800 to air at 620°C resulted in the formation of a blue surface film. The metal surface remained shiny. The presence of CsI resulted in a dull grayish-brown tarnish film on all three alloys. Rinsing the turnings in distilled water imparted a yellow color to the water. A positive qualitative test for Cr<sup>6+</sup> was obtained (nitric acid, ethyl ether, hydrogen peroxide, blue color in ether layer) on the rinsings from the Incoloy 800, Hastelloy X and 304 stainless steel turnings. Negative results were obtained on tests to identify nickel and iron ions.

The data on the alloys indicate that CsI interacts with the chromium in the presence of an oxidizing atmosphere. This observation was confirmed by exposing mixtures of CsI and either iron, nickel or chromium powders to air at 620°C for 4 hr. Only chromium interacted with CsI with the formation of some Cr<sup>6+</sup> ions.

Additional information was obtained by measuring the visible spectra of the yellow aqueous solutions. The spectra of aqueous solutions of Na<sub>2</sub>CrO<sub>4</sub>, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> and CrO<sub>3</sub> were also obtained. The spectrophotometric data are shown in Fig. 2. The significant feature in each curve in Fig. 2 is the wavelength of maximum absorbance. The absorbance maxima for the three alloys occur at the same wavelength, 372 nm, as the absorbance maximum for Na<sub>2</sub>CrO<sub>4</sub>, CrO<sub>3</sub> and K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> have absorbance maxima at 347 nm. Thus, it is likely that CsI reacts with chromium-bearing alloys in the presence of oxygen to form Cs<sub>2</sub>CrO<sub>4</sub>. A reaction of the type



†This work was performed under the auspices of the U.S. Nuclear Regulatory Commission under subcontract 336644-S.

probably occurs. Thermodynamic data on Cs<sub>2</sub>CrO<sub>4</sub> are not available. However, potassium and cesium compounds have

Table 1. Data obtained on metal-CsI samples exposed to air at 620°C

Material	CsI	Appearance	Aqueous solution	Positive test for
304 Stainless steel	Absent	Blue film	Colorless	—
304 Stainless steel	Present	Tarnish	Yellow	Cr <sup>6+</sup>
Incoloy 800	Absent	Blue film	Colorless	—
Incoloy 800	Present	Tarnish	Yellow	Cr <sup>6+</sup>
Hastelloy X	Absent	Blue film	Colorless	—
Hastelloy X	Present	Tarnish	Yellow	Cr <sup>6+</sup>
Iron powder	Absent	—	Colorless	—
Iron powder	Present	—	Colorless	—
Nickel powder	Absent	—	Colorless	—
Nickel powder	Present	—	Colorless	—
Chromium powder	Absent	Green powder (Cr <sub>2</sub> O <sub>3</sub> )	Colorless	—
Chromium powder	Present	Green powder (Cr <sub>2</sub> O <sub>3</sub> ) Yellow powder (Cr <sup>6+</sup> )	Yellow	Cr <sup>6+</sup>



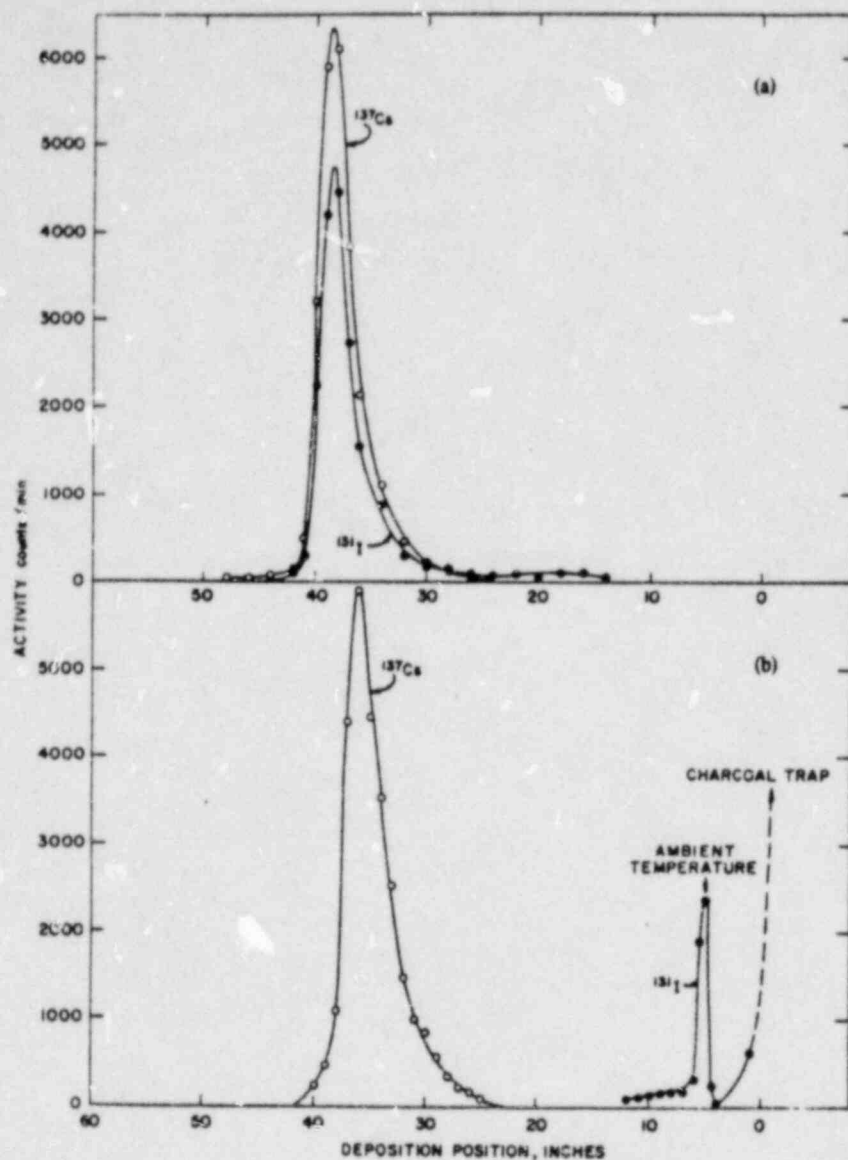


Fig. 1. O,  $^{137}\text{Cs}$ ; ●,  $^{131}\text{I}$ : (a), upper figure, CsI deposited at 580°C on 304 stainless steel in He-0.6%  $\text{H}_2\text{O}$ ; (b), lower figure, iodine transported in He-10%  $\text{O}_2$  to ambient temperature and charcoal trap. Most of the decomposed  $^{131}\text{I}$  (over 9000 counts/min) was retained in the cold trap.

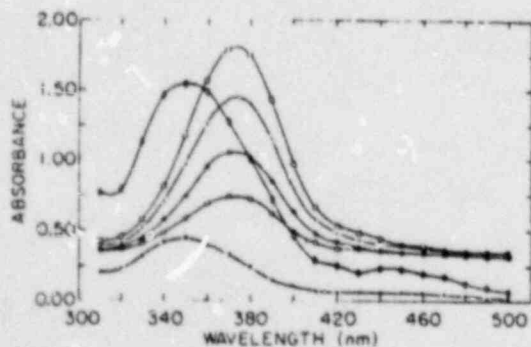
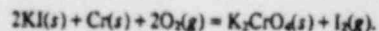


Fig. 2. Visible spectra of yellow solutions: O, 304 stainless steel; Δ, Hastelloy X; +, Incoloy 800; □,  $\text{Na}_2\text{CrO}_4$ ; x,  $\text{CrO}_3$ ; ○,  $\text{K}_2\text{Cr}_2\text{O}_7$ .

similar thermodynamic properties. It is, therefore, instructive to look at the corresponding reaction of KI to form  $\text{K}_2\text{Cr}_2\text{O}_7$ .



The reaction is highly exothermic. The standard enthalpy change at 25°C is -159 kcal/[5]. Therefore, the postulated reaction of CsI with the alloys seems quite reasonable even taking into account the substitution of cesium for potassium, the lower activities of chromium (in the alloy), the difference in temperature (600 vs 25°C) and the use of enthalpy instead of free energy.

Additional experiments were performed to verify the formation of elemental iodine. Samples of Hastelloy X, Incoloy 800 and 304 stainless steel turnings were heated with CsI at 600°C in the presence of oxygen. After the oxygen was passed over the sample, it was bubbled through absolute ethanol. Elemental iodine dissolved in ethanol gives a brownish-red solution with an absorption maximum at 360 nm. Elemental iodine was identified as a reaction product. The rate of production of iodine was

measured by inserting the exit tube into a spectrophotometer sample cell containing ethanol. The increase in absorbance with time was followed. The rate of production of iodine was high for the first few minutes and then tapered off rapidly. This type of behavior is typical for a chemical reaction occurring at a solid surface.

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## Polarographic study on dihydroxobisbiguanide manganese(IV) hydroxide

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It is well known that the stability of a metal complex is related to its polarographic half-wave potential, the later becoming more negative with increasing magnitude of the former[1]. A large amount of work has been done on the polarographic reduction of manganese(II) and manganese(III) compounds at the DME[2]. In order to study the reduction of manganese(IV) at the DME, the present complex was chosen as it is the only cationic complex of manganese(IV) which is soluble in water and stable under ordinary conditions[3].

## EXPERIMENTAL

The compounds, dihydroxobisbiguanide manganese(IV) hydroxide[3] and dihydroxibisbiguanide manganese(III) hydroxide[4] were prepared by the methods of Ray and Ray and the purity of the compounds was checked by elemental analysis.

A Cambridge pen-recording Polarograph was used for recording the polarograms, the experimental procedure being same as described earlier[5]. The solutions were made by dissolving the requisite amount of the complex in 0.1 M potassium hydroxide and then the maximum suppressor (0.01% gelatine) was added, the polarograms were recorded immediately after making up the volume.

## RESULTS AND DISCUSSION

Figure 1 shows the polarograms of fresh 0.0005 M aqueous solutions of manganese(IV) (curve a) and manganese(III) (curve b) complexes along with the polarogram of the supporting electrolyte with maximum suppressor (0.1 M KOH + 0.01% gelatine, curve c).

The polarogram of the manganese(IV) complex shows three distinct polarographic waves. The diffusion currents and the half-wave potentials corresponding to each wave were deduced from the polarogram obtained by subtracting the residual current (curve c) at each point of curve a. Half-wave potentials for each wave were obtained from the  $-E_{DME}$  vs  $\log i(i_4 - i)$  plots and are given in Table I along with respective diffusion currents. The waves are diffusion controlled and reversible, except the second one, for which only the initial portion indicates a reversible nature. In aqueous solution, this complex suffers progressive hydrolysis on dilution and it is difficult to obtain reliable data for the ionic mobility at infinite dilution. For this reason the number of electrons involved "n" corresponding to each wave, could not be obtained from diffusion coefficient data but were obtained from the slopes of the plot of  $-E_{DME}$  vs  $\log i(i_4 - i)$ [6] and are also given in Table I.

The first wave starts around  $-0.13$  V. The slope of  $-E_{DME}$  vs  $\log i(i_4 - i)$  plot gives a value of 2.2 for "n" ( $E_{1/2} = -0.232$  V), indicating a two electron reduction as this stage, so that  $Mn(IV) \rightarrow Mn(II)$ . Most Mn(III) compounds, in the presence of various supporting electrolytes, are reduced around zero volts with respect to the SCE[2]. In the case that the reduction of Mn(III) to Mn(II) occurs at a less negative voltage than the reduction of Mn(IV) to Mn(III), the reduction of Mn(IV) at the DME would give only one wave, including the reduction of Mn(III) to Mn(II) and the product would be Mn(II), the result of a two electron reduction step. Whether the reduction of Mn(III) to Mn(II) occurs at a less negative voltage was tested by measuring the polarogram of the corresponding Mn(III)-biguanide complex under the same conditions. The half-wave potential for the first wave of this polarogram is  $-0.237$  V, which is almost the same as for the Mn(IV) compound. The value of "n" for this wave indicates a one electron reduction step. The second wave of the polarogram "a" starts like a reversible wave and the initial points of the  $-E_{DME}$  vs  $\log i(i_4 - i)$  plot indicate a "one electron reduction step", but at later stage the slope of the plot changes to a higher value giving a fractional value for "n" and this is characteristic of the irreversible nature of this wave.

Table I. Half-wave potentials and diffusion currents for the polarographic reduction of dihydroxobisbiguanide manganese(IV) and manganese(III) complexes

Complex 0.0005 M		m = 6.708 mgm Diffusion current for waves, $\mu$ amps	$E_{1/2}$ volts	$t - 2.965$ sec temp 30° "n"
Manganese(IV)	1st	1.52	-0.232	2(2.20)
	2nd	1.36	-0.543	1(1.12)†
	3rd	2.94	-1.740	1(0.83)
Manganese(III)	1st	1.55	-0.237	1(1.27)
	2nd	0.72	-0.57	—
	3rd	1.62	-1.720	1(0.89)

†Obtained from the initial portion of the wave.

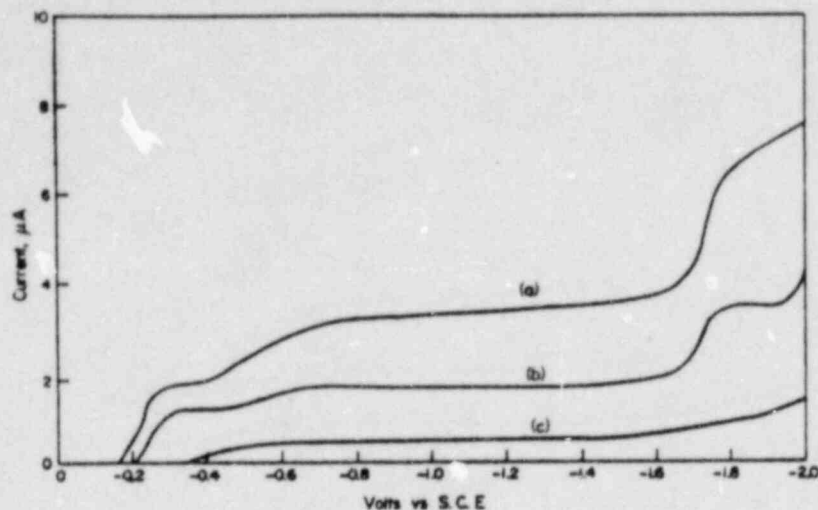


Fig. 1. Polarograms of dihydroxobisbiguanide complexes of manganese in presence of 0.1 M KOH and 0.01% gelatine  $m = 6.708$  mgm  $t = 2.965$  sec temp.  $30^\circ$ , sensitivity 1/50 damping 5; (a) 0.0005 M manganese(IV) complex; (b) 0.0005 M manganese(III) complex; (c) blank, without any complex.

Some side reactions interfere with the electrode process at this stage, the nature of which could not be identified. The second wave for the Mn(III) compound also gives a straight line for the  $-E_{1/2}$  vs  $\log i/(i_0 - i)$  plot, but the value of "n" derived from this line again gives a fractional value. Half-wave potential values of the second waves in both the compounds are very near to each other and it is very likely that similar processes occur. At this stage the reduction of Mn(II) to Mn(I) takes place. The third wave in both the compounds again gives similar  $E_{1/2}$  values, and each one indicate one electron reduction giving Mn(I) to Mn(0). Thus although Mn(III)-biguanide compound shows all the three stages of reduction indicating the formation of each lower oxidation states, the first step for the reduction of Mn(IV) is a two electron step giving Mn(II) with a half-wave potential almost equal to that for the reduction of Mn(III) to Mn(II).

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### Isomeric cross section ratios for the $(n, 2n)$ reactions on $^{45}\text{Sc}$ and $^{113}\text{In}$

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The measurement of isomeric cross-section ratios is of interest for a number of reasons. They can be used to study the transfer of angular momentum in nuclear reactions and the spin dependence of the nuclear level densities in the final nuclei. A knowledge of the ratios may also be useful for reactions which are to be used for activation analysis or neutron detection.

We have measured the isomeric cross-section ratios  $\sigma_m/\sigma_g$  for the reactions  $^{45}\text{Sc}(n, 2n)^{44m}\text{Sc}$  ( $T_{1/2m} = 2.4$  d,  $T_{1/2g} = 3.9$  h) and  $^{113}\text{In}(n, 2n)^{113m}\text{In}$  ( $T_{1/2m} = 21$  min,  $T_{1/2g} = 14.5$  min). The method used relied on the analysis of the time behaviour of the decay of the ground state. Since only the ground state activity was measured many of the sources of error present in methods which depend on observing the decay of the isomeric and ground states separately were avoided.

#### $^{45}\text{Sc}(n, 2n)^{44m}\text{Sc}$

Samples of a few grams of natural scandium oxide in powder form were irradiated with fast neutrons for periods of about three hours. The neutrons were derived from the D-T reaction using deuterons accelerated to 300 keV in a Van de Graaf accelerator. The samples were placed in different positions with respect to the tritium target and the beam direction in order to obtain a range of neutron energies. A number of runs were made at each sample position.

After irradiation each sample was transferred to a  $3 \times 3$  in<sup>2</sup> NaI detector. The intensity of the 0.511 MeV annihilation radiation arising from the  $\beta^+$ -decay of  $^{44m}\text{Sc}$  was followed for a period of a few days after irradiation. The count rate of the photopeak was observed and, after correction for the contribution from  $^{42}\text{K}$