

Conf-780508--12

TRITIUM PERMEATION THROUGH INCOLOY 800 OXIDIZED IN SITU BY WATER VAPOR*

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The in situ formation of oxide layers on the surfaces of heat exchangers in the steam system of a fusion power plant may be the most feasible way to control tritium release into the steam. Tritium permeabilities of Incoloy 800 have been determined while the downstream surface was oxidized by water vapor at 525, 660 and 720°C. The in situ formation of oxide coatings on the Incoloy 800 surface has been observed to reduce tritium permeabilities by factors of 30 to 700 depending on conditions. The effects of the in situ formed oxide coatings to impede tritium permeation are dependent on the chemical and physical compositions of the oxides, and the compositions of the oxides have been observed to depend on the history of the material.

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*Research sponsored by the Div. of Materials Sciences, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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INTRODUCTION

Environmental regulations will determine permissible rates of release of tritium from fusion power plants into the environment. Permeation of tritium from the heat transfer medium through the heat exchanger into the steam system is potentially a major mechanism for tritium release. Such permeation must be minimized to meet regulations and to ease the requirements for other parts of the fusion system. Current designs for fusion systems and current conclusions include the requirement that a heat exchanger material have a tritium permeability that is 2 to 3 orders of magnitude lower than permeabilities for common construction materials. Problems in assembly and in materials compatibility during operation prohibit the use of low permeability materials such as refractory metals or ceramic materials in the construction of heat exchangers. Therefore, designs of fusion power plants should include tritium permeation barriers on the heat exchangers that will reduce tritium permeation rates by two or three orders of magnitude without seriously reducing the heat transfer properties. Such permeation barriers must be

formed on the heat exchangers after construction, because the construction process would damage the barriers. Furthermore, the barriers should be capable of self healing during operation in the event of cracks, pin holes etc.

The in situ formation of oxide layers on the heat exchangers may be a good way to produce effective tritium permeation barriers with self-healing characteristics.

(Such oxide films were first shown to impede hydrogen permeation by Flint⁽¹⁾ who reported 400 fold reduction factors in permeation rates through 347 SS when treated with wet hydrogen. Then Huffine and Williams⁽²⁾ reported impedance factors up to 10^3 for hydrogen permeation when an oxide layer was formed on an Fe-Cr-Al alloy at 1111°C in air. They also reported that defects produced in the oxide layers by thermal stress would self-heal by continued oxidation. The Oak Ridge National Laboratory has been studying tritium permeation through clean metals and through metals while oxide coatings are formed by steam oxidation.⁽³⁻⁶⁾ This paper is an

up-to-date report of the tritium permeation-steam oxidation studies. Particular subjects include: (1) Tritium permeability of clean Incoloy 800, (2) Reduction of tritium permeability of Incoloy 800 by in situ formed oxides, (3) Effects of thermal stress on the in situ formed oxides, and (4) Chemical analysis of the oxides and variance in composition with history of the material.

EXPERIMENTAL

The apparatus and techniques for measuring tritium permeation through metal samples at 400 to 800°C with a 0 to 1 atm H₂O pressure on the downstream side were described previously.⁽⁴⁾ However, two points should be repeated. First the tritium source was a few parts per million tritium isotopically equilibrated in a 4% H₂-Ar mixture, and second, the metal samples have been tube type. The apparatus and techniques for measurements on clean metal tube samples have been similar except that the tritium source was a few parts per million of tritium in hydrogen and the downstream sweep gas was hydrogen. Water was removed from these two hydrogen streams by passing the streams through a steel ball packed column at liquid nitrogen temperature. However, this bed at -176°C did not remove traces of oxygen less than 1 ppm that could have been in the hydrogen sources.

An additional apparatus was used for oxidizing tab type metal samples under identical conditions for the permeation-steam oxidization experiments. Tab samples were suspended in a reaction chamber inside a furnace at selected temperatures between 400 and 800°C. A constant ratio of H₂O/Ar flowed



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RESULTS AND DISCUSSION

The compositions and the oxidation potentials of the components in Incoloy 800 have been tabulated in Table 1. It was very difficult to obtain and maintain oxide free Incoloy 800 at temperatures in the 400 to 800°C range because of the low oxidation potentials for silicon, manganese and chromium. Permeation measurements showed that this alloy oxidized under experimental conditions of 780 torr hydrogen with only 0.5 ppm water at temperatures below 550°C, and that an oxide formed as such was reduced at temperatures above 600°C. The Arrhenius plot of the tritium permeability of Incoloy 800, Figure 1, showed the effects of small amounts of oxidation at the lower temperatures. An activation energy of 19.75 kcal/g at. was calculated from the data for temperatures greater than 550°C. A linear plot considering the data over the complete temperature range would have led to a large error in the activation energy. This implies only that one must avoid the smallest amounts of surface oxidation when measuring permeability parameters.

Incoloy 800 is 21% chromium with less than 1% manganese and silicon, and the oxidation potentials, Table 1, indicate that only these three components could have oxidized in a medium with the H_2O/H_2 ratio of less than 10^{-6} . Thermodynamics for the formation of Cr_2O_3 , MnO and SiO_2 indicate that MnO and SiO_2 would have formed over the entire range of experiment temperatures but Cr_2O_3 could have formed only at the lower temperatures. Thus the effects observed here probably were because of the oxidation and reduction of chromium and the formation of manganese and sili-



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Five experiments have observed the permeabilities, DK_s , of Incoloy 800 with steam oxidation at two temperatures and three water pressures. Data and results from the first two experiments were presented previously, and a typical plot of $\ln DK$ versus the square root of time has been included, Figure 2. The permeability dramatically decreased

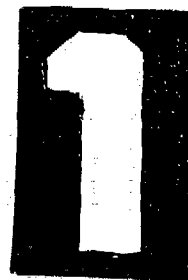


over the early stages of the oxidation and then more slowly decreased at the longer times. The trends were in accord with a model where the surface was effectively covered in the early part of the experiment, and the slower decrease in permeability occurred with and because of an increase in the oxide thickness. Experiments typically continued for 150 to 190 days and the results to reduce tritium permeabilities have been summarized in Table 2. The barrier effects of the oxides formed at 660°C increased with time and with the water pressure. The samples in experiments 3 and 4 were identical except that the Incoloy 800 surface of sample number 3 had been electropolished. These two sets of data indicated that the electropolished surface produced an oxide coating with ^{somewhat} lower barrier effects. From these data we have derived an empirical expression for the oxide barrier effects on Incoloy 800 at 660°C showing the dependence on time in days, t , and on the water pressure in atmospheres, P_{H_2O} ,

$$\frac{(DK)_0}{(DK)_{t, P_{H_2O}}} = 1 + 45 t^{1/2} \cdot P_{H_2O} .$$

This equation should not be used for calculating barrier effects at other temperatures and/or for high water pressures.

The formation of the oxide coating at 520°C had a much smaller effect on reducing tritium permeation, Table 2. The tritium permeation rate through the sample almost leveled off after 50 days, Figure 3. This indicated that oxidation had almost ceased, and we surmised that the diffusion of the bulk metal components was not



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The formation of the oxide coating at 520°C had a much smaller effect on reducing tritium permeation, Table 2. The tritium permeation rate through the sample almost leveled off after 50 days, Figure 3. This indicated that oxidation had almost ceased, and we surmised that the diffusion of the bulk metal components was not sufficient to maintain the oxidizing materials at the metal-oxide interface. An increase in temperature to 650°C restarted the oxidation process and the decreasing trend in permeability. After 80 days at 650°C, the temperature was decreased back to 520°C, and the permeability was 274 times lower than the initial permeability.



Another 60 days at 520°C further reduced the permeability by a factor of only 1.3.

The effects of three kinds of thermal stress have been observed. A 30 minute thermal cycle of 663 to 637 to 663°C had no noticeable effects on the formation of the oxide and its barrier properties. A temperature change of 660 to 560°C in five minutes apparently destroyed the barrier characteristics of the oxide. However, the defects in the oxide immediately began to heal, and five days after the temperature was raised back to 660°C, the permeability had decreased to the projected value had the thermal shock not been imposed. This healing of defects in the oxide was similar to that reported for the air oxidation of an Fe-Cr-Al alloy at 1111°C.⁽²⁾ At another time, an equipment failure required that the permeation sample be cooled from 660°C to room temperature. The temperature was decreased slowly to room temperature and the sample sat for three days under dry argon. Then the temperature was raised slowly back to 660°C, and 12 days later the permeability was at the projected level had the equipment not failed or the sample not been cooled. This 12 days to reestablish the barrier characteristics on the oxide compares to 130 days required to initially establish the oxide.

Activation energies for tritium permeation through two of the oxide coated samples were determined, and they appear to be dependent on the conditions under which the oxides were formed. The activation energies were 30 and 15.3 kcal/g·atom, respectively, for permeation through samples four and five with formation of the oxides, respectively, at 660°C for 109 days and 520°C for 26 or for 210



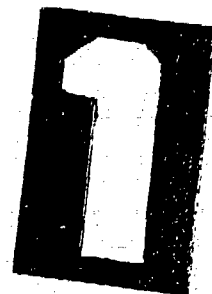
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Ion microprobe techniques have been used to determine the relative quantities of Incoloy 800 components in the oxide coatings. Analyses of the



oxides on the first four permeation samples have shown almost equal quantities of manganese and chromium even though the bulk content ratio of Cr/Mn is about 30. Relative quantities of the alloy components in the oxide will be determined primarily by the relative bulk compositions, the relative oxidation potentials, and the relative diffusion rates in the bulk alloy and in the oxide. The ratio of bulk concentrations times the inverse ratio of oxidation potentials for chromium and manganese indicated that the manganese oxide in the oxide coating would be about 0.75 times the chromium oxide when bulk diffusion rates for these components are high relative to the oxidation rates. Figure 4 showed the relative compositions of the oxide formed on Incoloy 800 after 150 days at 660°C in 0.94 atm water. The percentages of the metal components in the oxide have been plotted against the depth of the oxide. The composition of the oxide is predominantly chromium and manganese oxides. However, there are significant quantities of aluminum, titanium and silicon oxides, and the relative concentrations are not uniform with depth in the oxide. The maximum amounts of the various metals seemed to be ordered according to the oxidation potentials, i.e. aluminum is the easiest oxidized at 660°C and the aluminum peak appeared at about 1.2 μ . Then there were peaks for titanium and silicon, respectively, at 0.8 and 0.5 μ . This ordering of the maximum quantities with oxidation poten-



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suggested that some oxygen actually diffused into the metal.

There appeared to be three material regions for the steam oxidized samples. First, the outer oxide region was composed of the various oxides. Second, the center or perturbed metal region appeared to have some diffused oxide in the bulk metal. And third, the bulk metal region.

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Table 1. The elemental composition on Incoloy 800 and the oxidation potentials of the elements

Element	Atom percent	Oxidation potentials*	
		793°K	923°K
Iron	46.9	0.6	0.8
Nickel	30.4	88	250
Chromium	22.0	1.8×10^{-7}	2.9×10^{-6}
Manganese	0.76	1.8×10^{-8}	1.4×10^{-7}
Silicon	0.63	4.8×10^{-13}	1.1×10^{-10}

*

$$\frac{P_{H_2O}}{P_{H_2}} = \exp(-\Delta G/RT)$$

ΔG is the free energy for the formation of Fe_3O_4 , NiO , Cr_2O_3 , MnO , or SiO_2 from the metals and H_2O .

Table 2. The effects of steam oxidation to decrease the permeabilities, DK, of Incoloy 800

Experiment	Temp. (°C)	P_{H_2O} (atm)	$\frac{DK(\text{clean})}{DK(15 \text{ days})}$	$\frac{DK(\text{clean})}{DK(150 \text{ days})}$
1	660	0.32	65	250
2	660	0.70	87	304
3	660	0.94	159	494
4	660	0.94	210	699*
5	520	0.94	31	42*

* Extrapolated from data up to 50 days

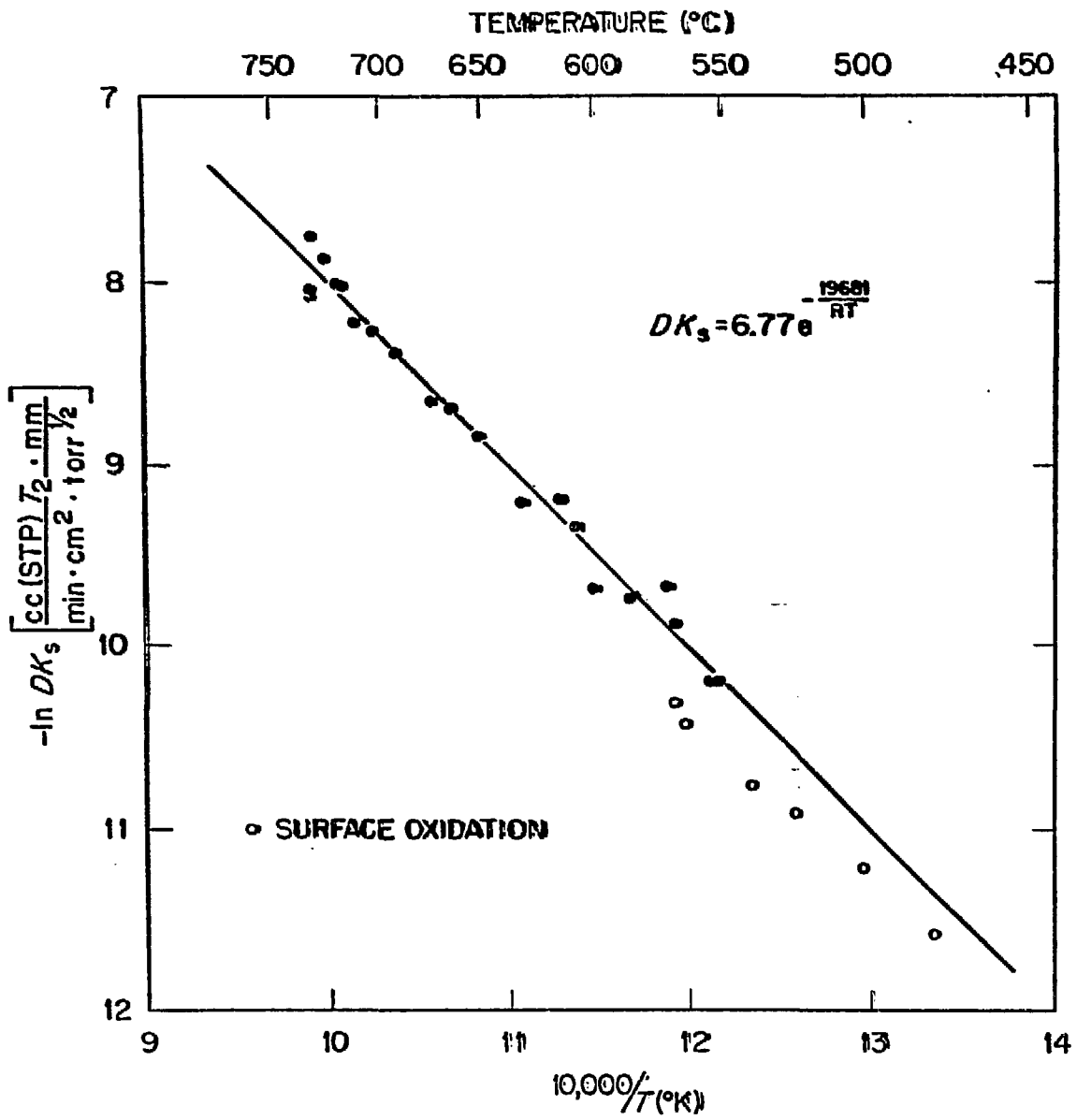
List of Figures

Figure 1: Tritium permeabilities of Incoloy 800 over the 450 to 750°C range. The open data points below 570°C were decreased by surface oxidation.

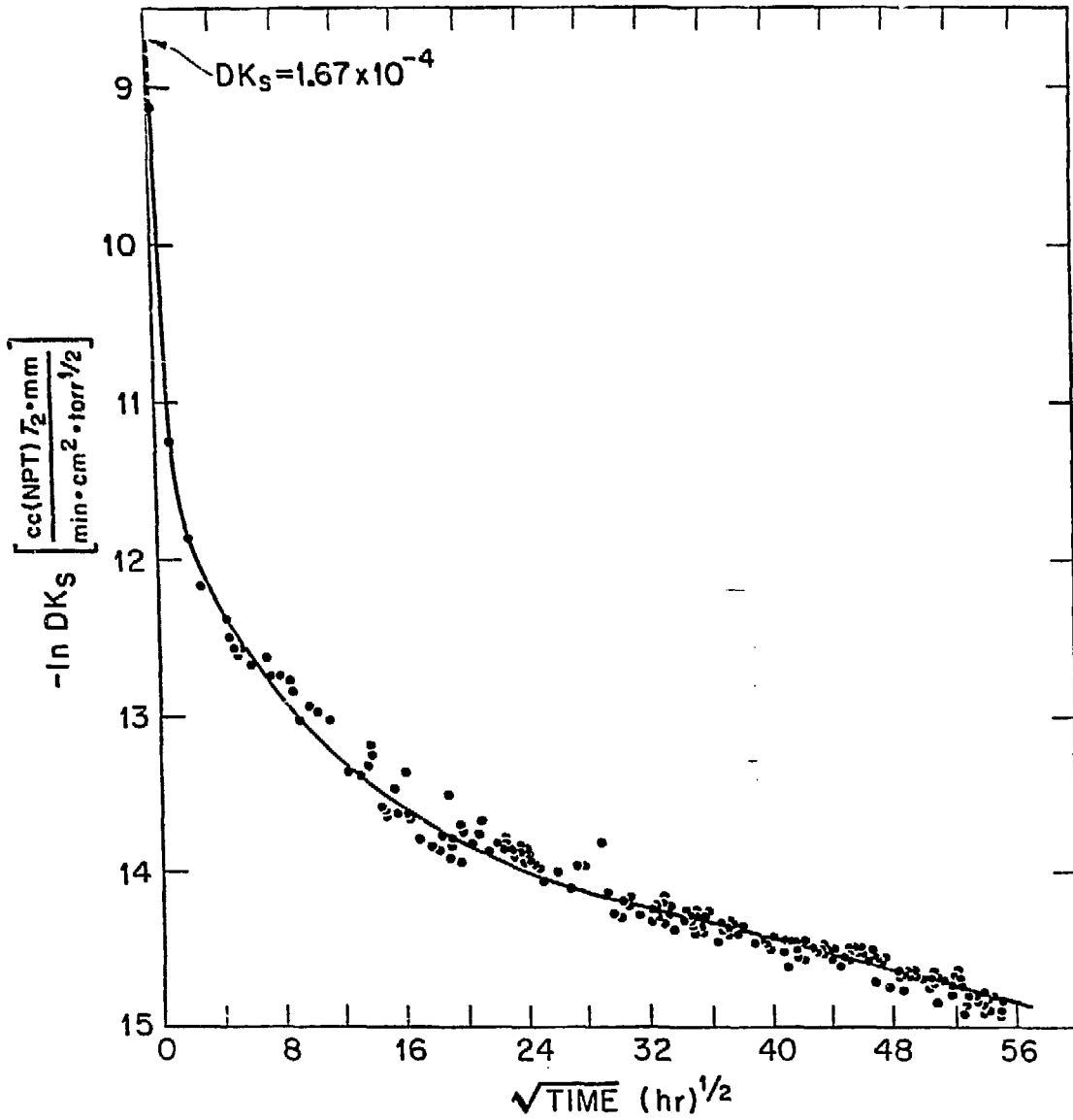
Figure 2: Tritium permeabilities of Incoloy 800 as an oxide layer was formed by the reaction with 0.94 atm H₂O at 640 to 660°C.

Figure 3: Tritium permeabilities of Incoloy 800 as an oxide layer was formed by the reaction with 0.94 atm H₂O first at 520°C, then at 657°C, and then at 519°C.

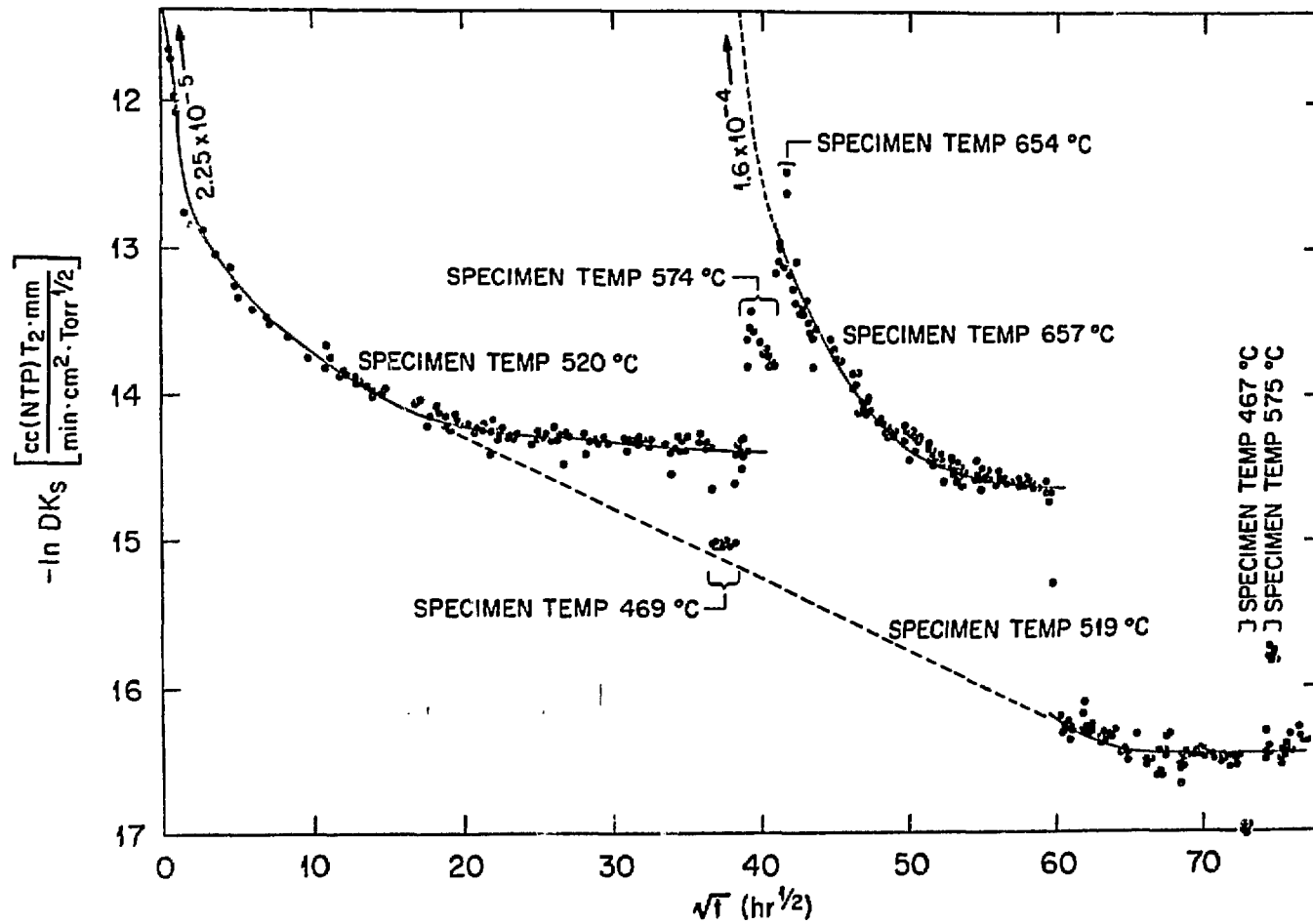
Figure 4: Metal composition of an oxide formed on Incoloy 800 by the reaction of 0.94 atm H₂O at 640 to 660°C.



Tritium Permeation Through Clean Incoloy 800.

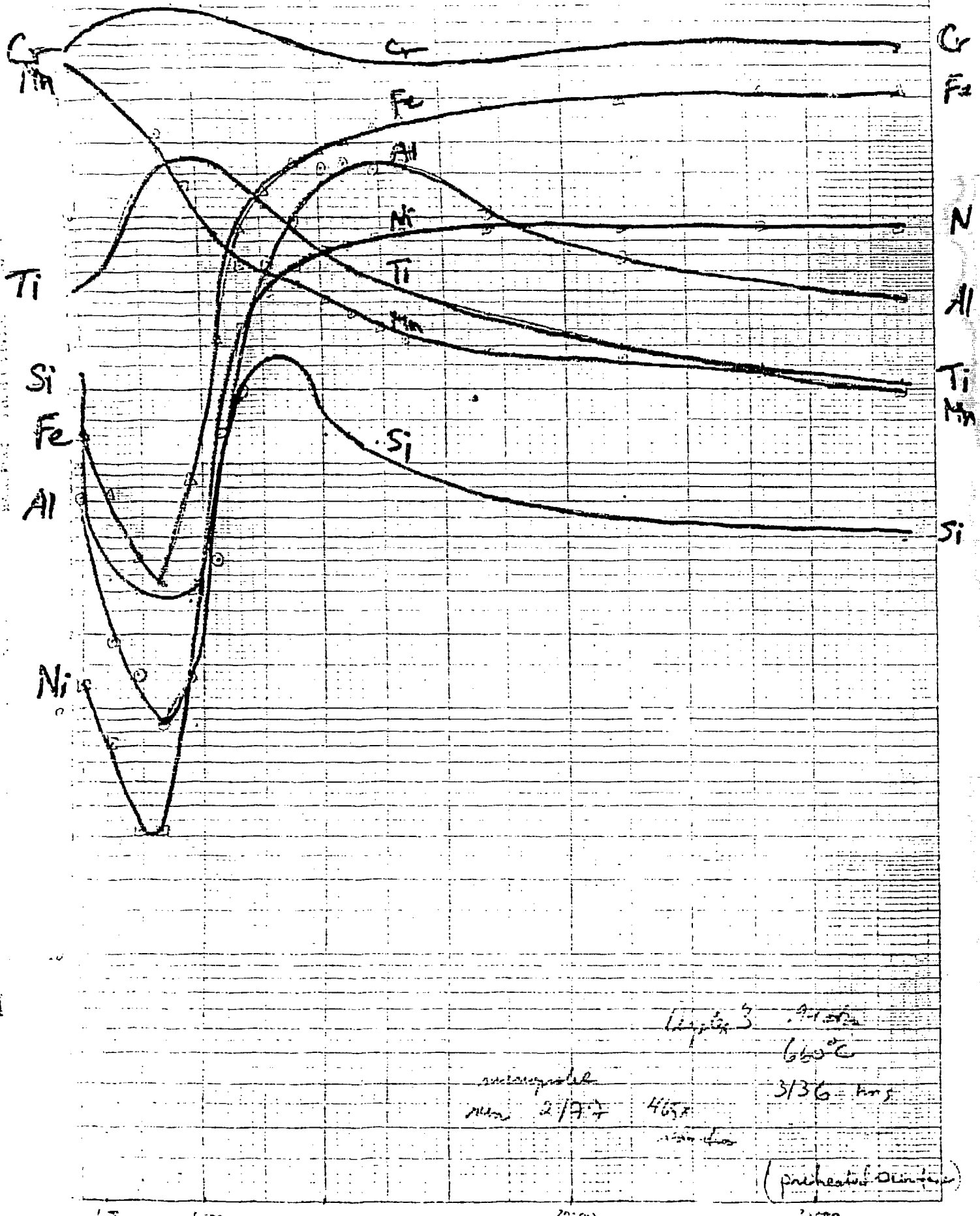


Permeation of Tritium Through Incoloy-800 Exposed to Steam of 0.94 Atmospheres and Temperature Cycling Between 640 and 660°C.



Permeation Through Incoloy 800 at 520° and 657 °C Exposed to 0.94 Atmospheres of Steam.

Rad. num 2/15/77 photo...
9th Feb



Sample 3
 660°C
 3136 hrs
 4657
 (preheated element)