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HANDLING TECHNIQUES FOR RUBIDIUM

H. E. McCoy, Jr.
E. E. Hoffman

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METALLURGY DIVISION

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HANDLING TECHNIQUES FOR RUBIDIUM

H. E. McCoy, Jr. E. E. Hoffman

ABSTRACT

Experience in handling and purifying rubidium metal, prior to high-temperature corrosion testing, has been obtained. Some of the physical and chemical properties of this metal are listed. Distillation and filtration experiments are described, and the analysis of samples following such purification procedures are given. Stripping procedures following corrosion testing are discussed briefly. Results of preliminary corrosion experiments indicate that Inconel is a satisfactory container material for boiling rubidium at temperatures up to 1520°F.

INTRODUCTION

The handling procedures described in this report were developed in the course of purifying the metal and investigating its corrosive properties. The work was performed by the General Corrosion Group of the Metallurgy Division in cooperation with an Oak Ridge School of Reactor Technology summer research project group.

When this work was initiated, no rubidium metal was commercially available, principally because of its high cost and chemical activity and because there are few uses for the metal at the present time. Five pounds of rubidium were obtained from a chemical firm at relatively small cost, as compared to the $6.50 per gram quoted in the literature.[1] If the demand increases, the cost of the metal will be reduced appreciably.

Many difficulties were encountered during both the production and subsequent handling of the rubidium on account of lack of experience and information. The problems encountered in handling the metal are reported with the intention that assistance might be rendered anyone desiring to work with it.

PROPERTIES OF RUBIDIUM

The physical properties of rubidium are tabulated below.

Molecular weight	85.48
Density	See Fig. 1
Melting point	39°C (102.2°F)
Boiling point	688°C (1270°F)
Vapor pressure	See Fig. 2
Natural isotopic abundance, %	
Rb^{85}	72.8
Rb^{87}	27.2
Specific heat[2] at 20°C, cal/g/°C	0.080
Heat of fusion,[2] cal/g	6.1
Coefficient of linear thermal expansion[2] near 20°C, μin./°C	90
Electrical resistivity[2] at 20°C, μohm-cm	12.5
Crystal structure[2]	Body-centered cubic

Rubidium metal is gray, and soft; and it is silvery, and lustrous when freshly cut.

[1] E. H. Covey, *Availability and Sources of Ninety-Six Elements in High-Purity Form*, UCRL-266 (March 1, 1949).

[2] *Metals Handbook*, p 20, Am. Soc. Metals, Cleveland, Ohio, 1948.

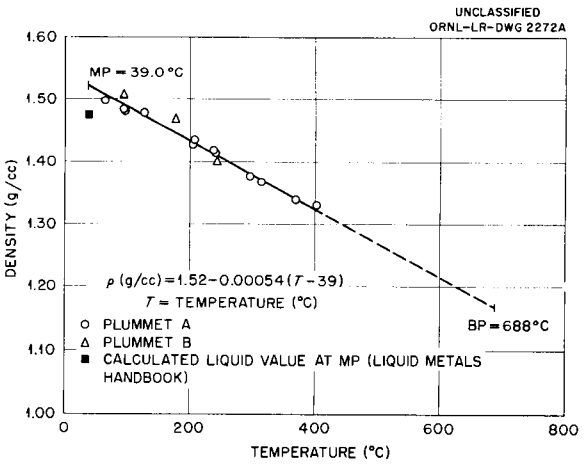

Fig. 1. The Influence of Temperature on the Density of Rubidium.

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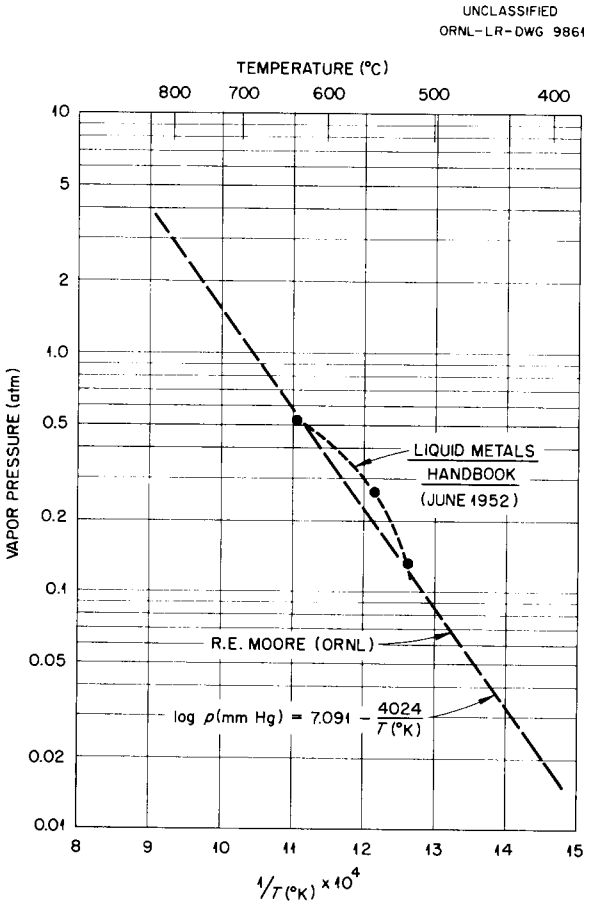

Fig. 2. Vapor Pressure of Rubidium at Various Temperatures.

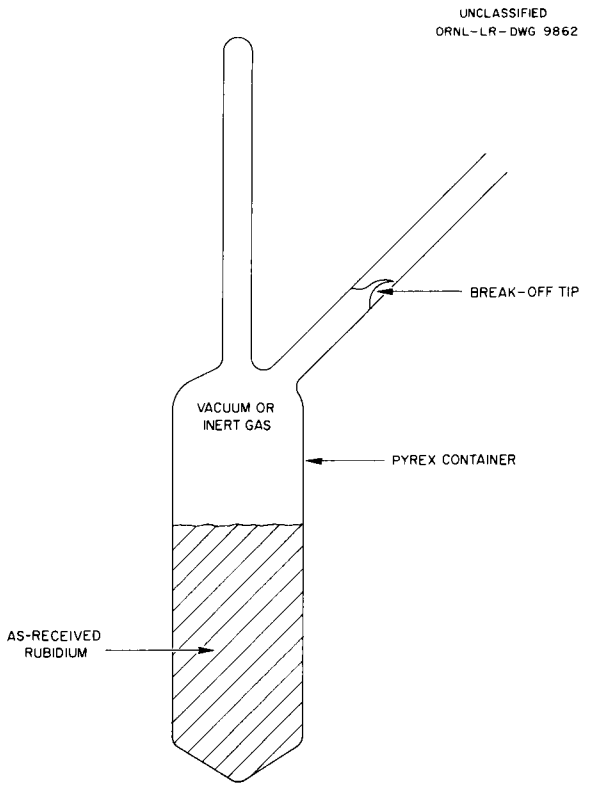

Fig. 3. Container of As-Received Rubidium.

There are two chemical properties[3] of rubidium that are of particular concern because special precautions must be observed; namely, rubidium decomposes H_2O violently and burns, and it must be stored under liquids which do not contain oxygen.

OPENING CONTAINERS RECEIVED FROM SUPPLIERS

Glass Containers. – The rubidium metal that was received in glass containers (similar to the one shown in Fig. 3) was by far the least difficult to handle. The break-off tip made it possible to seal the container of rubidium to a glass vacuum system without any danger of the rubidium igniting. Accessibility to the rubidium was then easily gained by dropping a steel ball against the break-off tip.

Pyrex was found to be essentially unattacked by molten rubidium metal at temperatures as high as 360°C; therefore, the purification procedures which were attempted were performed in pyrex systems. It was necessary to develop a satisfactory procedure for transferring the rubidium into the purification system. These operations were performed inside a helium-atmosphere dry box (Fig. 4). The vertical arm of the as-received container (Fig. 3) was broken; the container was heated; and the contents were poured into the desired container. The ends of this vessel were sealed by means of vacuum hose and clamps, and then the vessel was removed from the dry box.

Metal Containers. – The initial shipments were received from the vendor in metal containers in which the rubidium was stored under petroleum ether; in later shipments the metal was covered with hexane. The top was cut from the metal container, and the excess petroleum ether or hexane was poured off. The rubidium metal was then transferred to another vessel and placed in the entrance chamber of the dry box. The entrance

[3] *Merck Index*, p 838, Merck, Rahway, N. J., 1952.

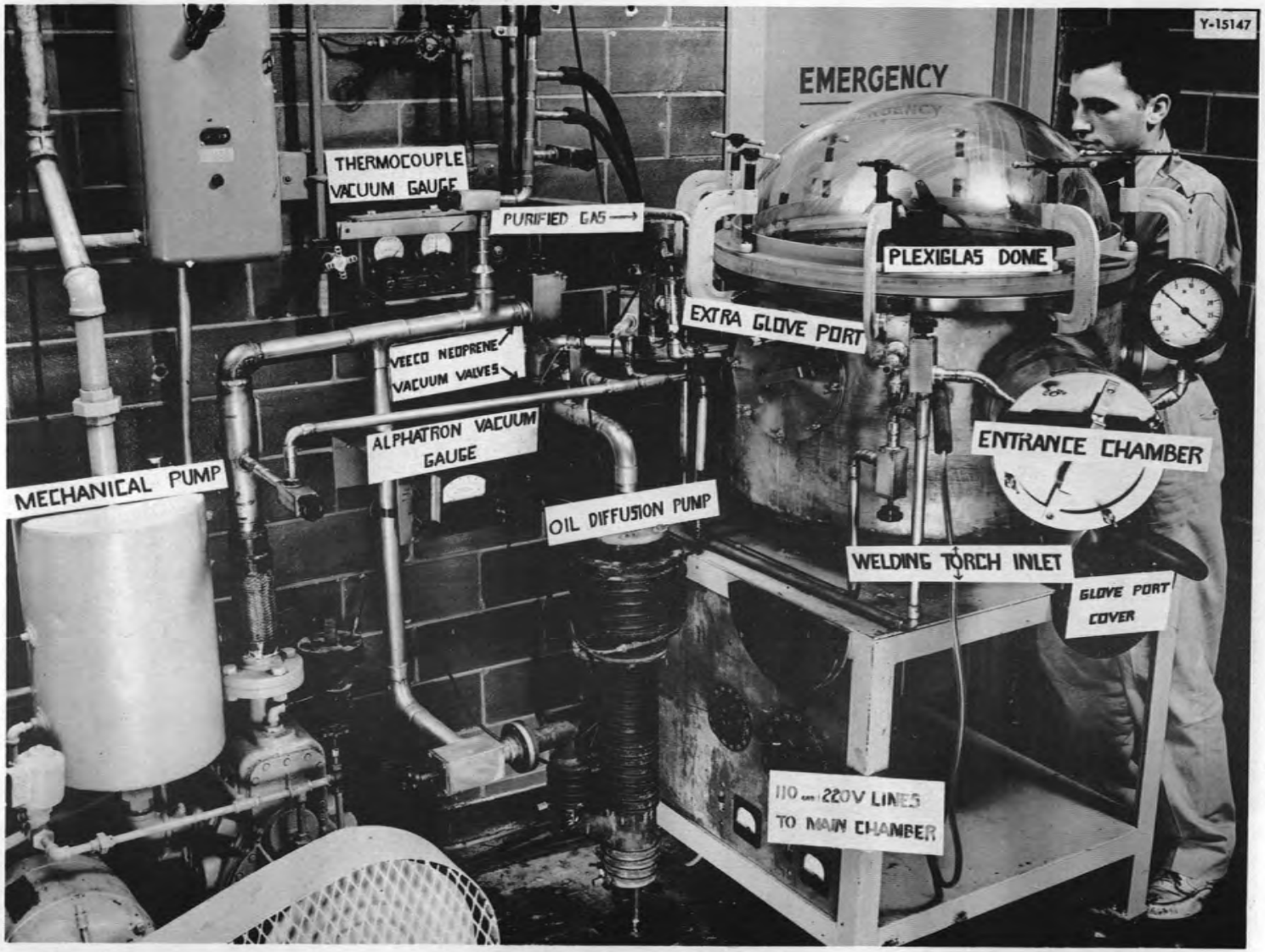

Fig. 4. Vacuum–Inert-Atmosphere Dry Box in Which Rubidium Metal was Melted and Transferred to Various Containers.

chamber was evacuated, vaporizing the residual liquid from the surface of the rubidium. After this operation, the rubidium was moved into the main chamber of the dry box where the rubidium metal was transferred to a pyrex distillation vessel (see section: "Loading of Distillation Apparatus").

Rubidium metal packed under petroleum ether or hexane is very hazardous to handle because of the low flash points of the liquids and the rapidity with which rubidium reacts on contact with air. However, the metal packed under hexane, which has a higher flash point than petroleum ether, was handled with greater ease and resulted in less contamination of the rubidium metal (Tables 1 *a* and 1 *b*).[4] Irrespective of whether glass or metal shipping containers are used, it is most desirable that the metal be stored in an inert atmosphere rather than in a protective liquid.

LOADING OF DISTILLATION APPARATUS

The as-received rubidium metal was covered on the outer surfaces by a thick black coating, which chemical analysis showed to be a mixture of alkali-metal carbonates and organic material. The complete chemical analysis is given in Table 1 *c*[4] of this report. It was known that a clean separation of the alkali-metals could not be effected by simple distillation because there is not a sufficiently large difference in the boiling points. But a distillation of the material was performed to remove oxygen and organic materials from the metal. The alkali-metal carbonates may be separated in an ion-exchange column if pure rubidium is desired. The rubidium carbonates may then be converted into rubidium fluoride, and this salt reduced to the metal by a calcium reduction process. However, the separation was quite involved and was considered to be unnecessary since it was concluded that these alkali impurities would have no appreciable effect upon the corrosive properties of the rubidium.

For the distillation of rubidium, a container as shown in Fig. 5 was found to be the most convenient type of vessel. Rubidium is quite easily melted by placing it in a pyrex beaker on a small hot plate inside the dry box (Fig. 4). The molten metal was transferred from the beaker to the container for distillation by means of the 200-ml syringe shown in Fig. 6. A funnel was placed in the side arm of the distillation container in order to keep the walls clean; this is quite important because the container must later be sealed to the vacuum-distillation apparatus.

TABLE 1. ANALYSIS OF AS-RECEIVED MATERIAL[4]

Element	Weight (%)	
a. Rubidium Packed Under Petroleum Ether – Duplicate Samples		
Calcium	0.360	0.240
Cesium	5.900	6.100
Lithium	None detected	None detected
Oxygen	Lost	0.500
Potassium	0.650	0.560
Sodium	0.043	0.037
b. Rubidium Packed Under Hexane – Duplicate Samples		
Cesium	2.700	2.700
Lithium	0.005	0.007
Oxygen	0.135	Lost
Potassium	0.060	0.390
Sodium	0.017	0.032
c. Sample* Taken from Black Residue of Both of the Above Shipments		
Rubidium	49.90	
Cesium	7.57	
Potassium	1.23	
Sodium	0.27	
Organic material	18.00	

*It was assumed that this material was composed of a mixture of alkali-metal carbonates and organic material. This assumption was based on the fact that the total of the approximate analyses for the alkali metals calculated as carbonates plus the organic material is 97%. Additional evidence was that the material liberated carbon dioxide when acidified, and, also, did not deliquesce when exposed to air. The hydroxide salts are known to be extremely deliquescent. Free alkali metal was present in some particles since these particles caught fire when the outer surface was removed in air. A more quantitative analysis of the composition was not practical because of the pronounced heterogeneity of the material.

DISTILLATION OF RUBIDIUM

The rubidium was distilled by means of the apparatus shown in Fig. 7. A vacuum of approximately 1×10^{-4} mm mercury was maintained

[4]The relative standard error in the analysis amounted to 5% for the alkali metals and 10% for the oxygen.

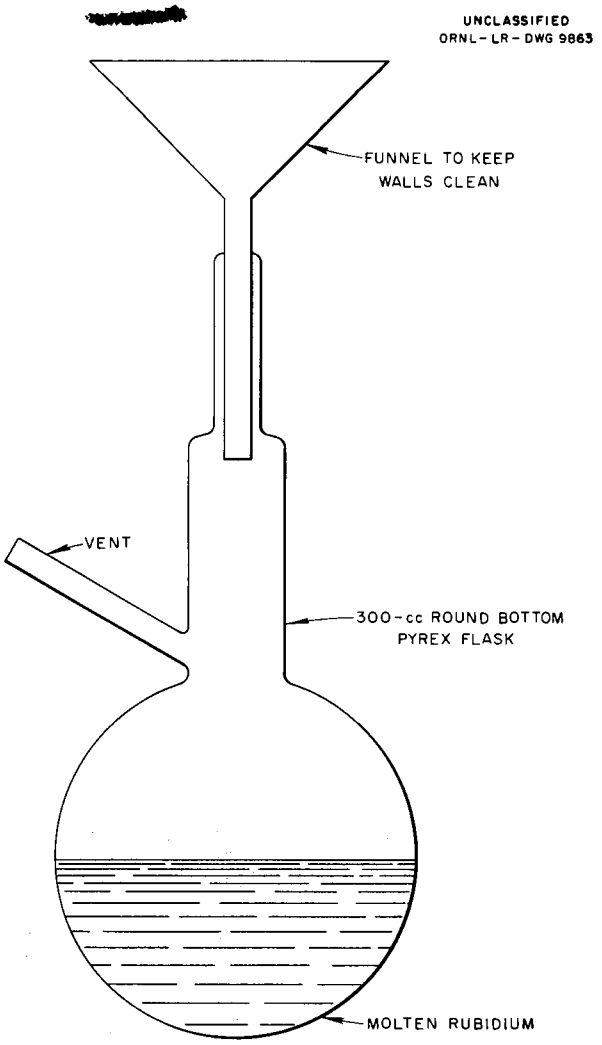

Fig. 5. Distillation Container.

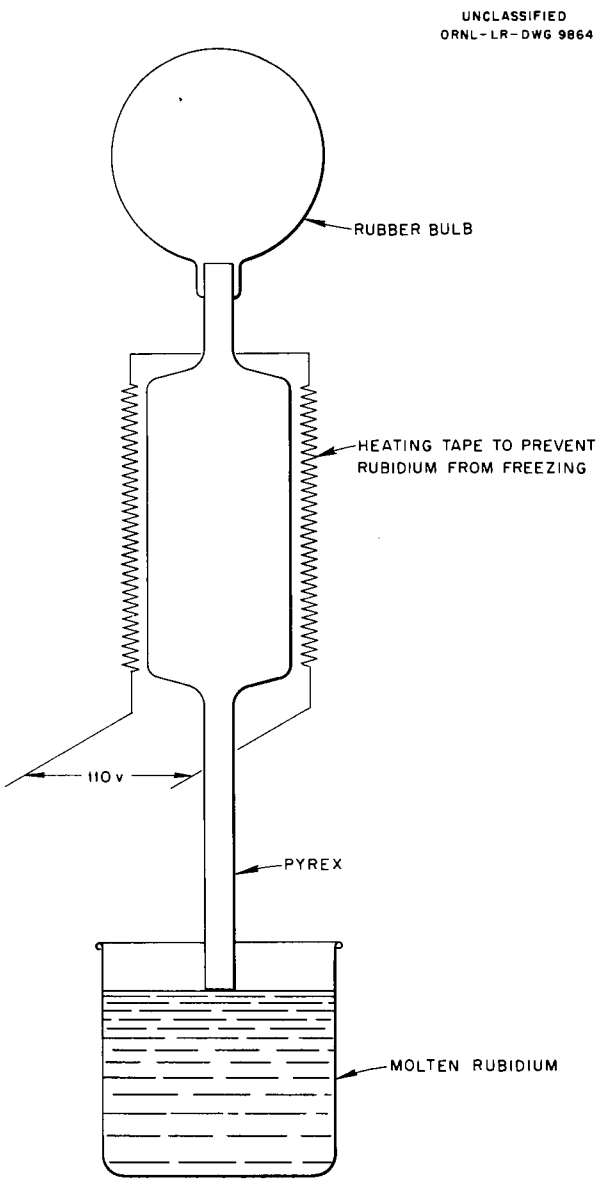

Fig. 6. Transfer Syringe.

throughout the distillation with the use of a Duo-Seal Mechanical Pump and a VMF 20-A Diffusion Pump. The impure rubidium was heated, by means of a Glas-Col heating mantle, to approximately 360°C, at which temperature the metal vapor rose to the neck of the vessel. The vapor was driven up the tube and around the bend of the pyrex vapor line by a heating tape which was maintained at 375°C. The lower part of the vapor line was insulated only to prevent the metal from freezing before it reached the receiver (a modified 100-ml round-bottom pyrex flask, which is quite convenient for storing the purified rubidium until it is needed).

Figure 8*a* shows the container of impure rubidium after it was sealed to the vacuum-distillation system. Figure 8*b* shows the container of impure rubidium ready for distillation. The composition of the distilled rubidium at various times during the distillation process is given in Table 2.

It may be noted that the cesium content is quite high in the samples taken early in the distillation. Repeated distillation might, therefore, be useful in decreasing the cesium impurity; however, because the difference between the boiling points of cesium and rubidium is not sufficiently large, it would be

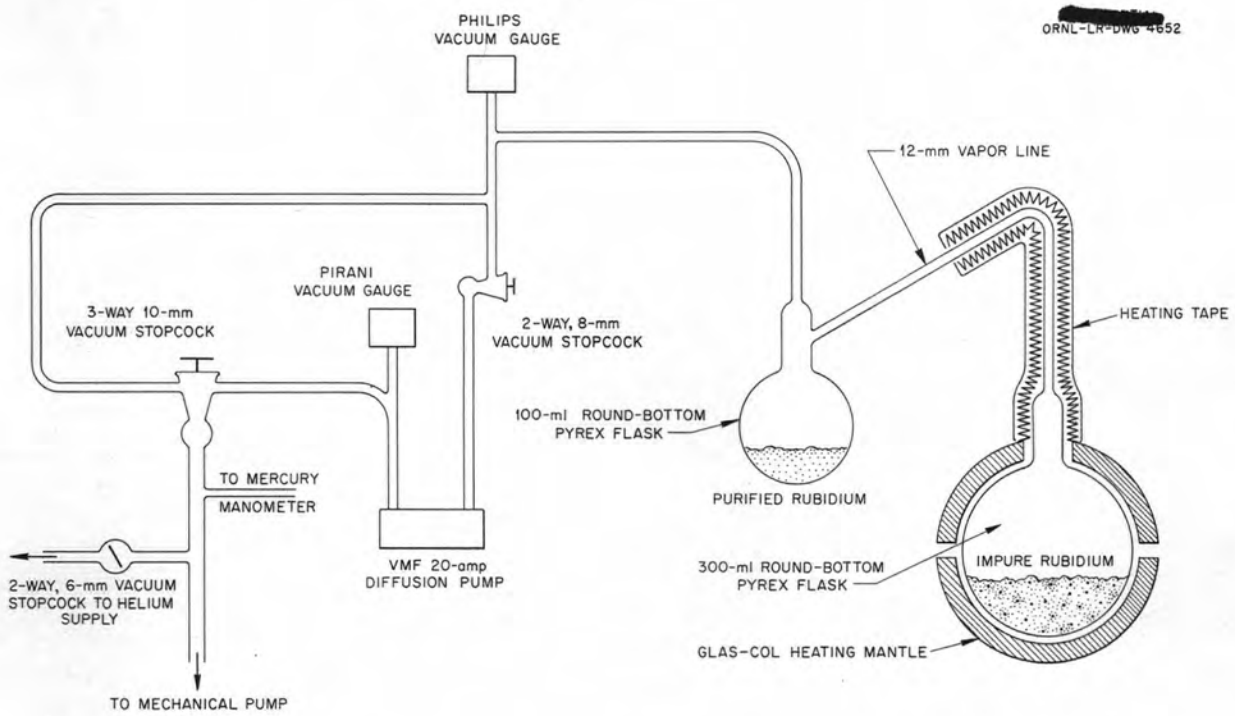

Fig. 7. Apparatus for Distilling Rubidium.

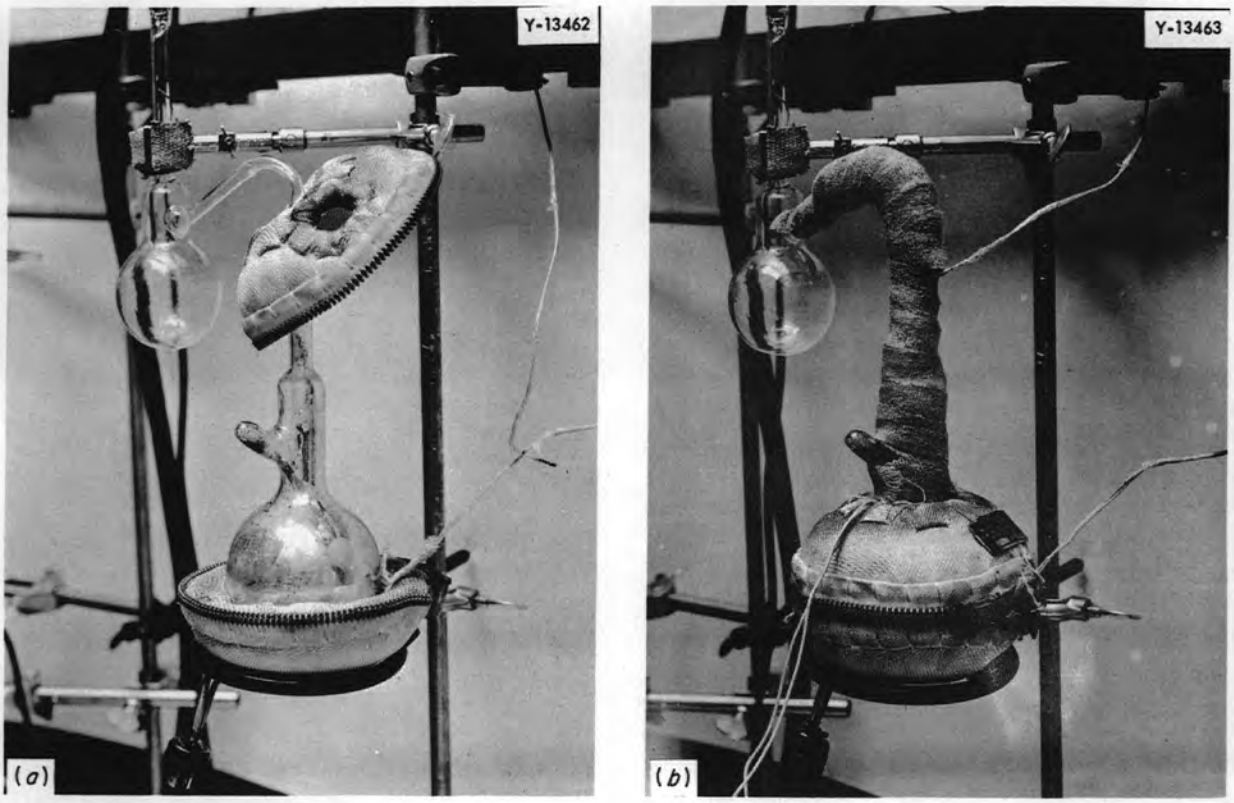

Fig. 8. Rubidium Distillation Vessel. (*a*) Impure rubidium sealed to distillation apparatus. (*b*) Impure rubidium ready for distillation.

TABLE 2. ANALYSIS OF DISTILLED RUBIDIUM

Element	Weight (%) at Various Intervals*				
	Start	30 min	60 min	120 min	End
Cesium	15.1	14.4	9.6	5.6	6.4
Lithium	0.0026	0.0032	0.0032	0.0020	<0.002
Oxygen	0.195	0.181	Lost	0.227	0.200
Potassium	0.038	0.045	0.071	0.081	0.21
Sodium	0.47	0.0069	0.0083	0.012	0.0034

*Previous samples taken from the beginning and end of distillation runs showed such fluctuations in chemical composition that a run was made in which samples of the distillate were taken at various intervals during the distillation. A vacuum manifold was constructed which contained five sampling tubes. The samples were taken at the various time intervals given above.

difficult to reduce the cesium content to a very low level.

FILTRATION OF RUBIDIUM

Since essentially none of the alkali-metal impurities were removed by distillation and since the oxygen content was only slightly reduced, an experiment was conducted to determine whether filtration would produce rubidium in as pure a condition as was obtained by distillation. The as-received material was transferred in the dry box to the apparatus for filtering that is shown in Fig. 9. The two openings to the flask were sealed temporarily with corks until the apparatus could be attached to the vacuum system and to the hydrogen source. The entire system was evacuated, and the rubidium was melted. After the material was completely degassed, purified hydrogen under pressure was used to force the molten rubidium (140°C) through the 50-μ glass filter into the bottom of the apparatus. The entire system was then evacuated, and the bulb of filtered rubidium was sealed from the rest of the system. A sample of the material for analysis was obtained by tilting the bulb on its side and allowing a small amount of the rubidium to flow into the 8-mm tube attached to the side of the bulb. The sample tube was removed from the bulb, and the remainder of the filtered material was stored in this bulb until needed.

The as-received rubidium contained a black cinder-like contaminant. The black contaminant comprised approximately 15% of the total as-received material, and the analysis of the contaminant is given in Table 1 *c*. Analysis of the

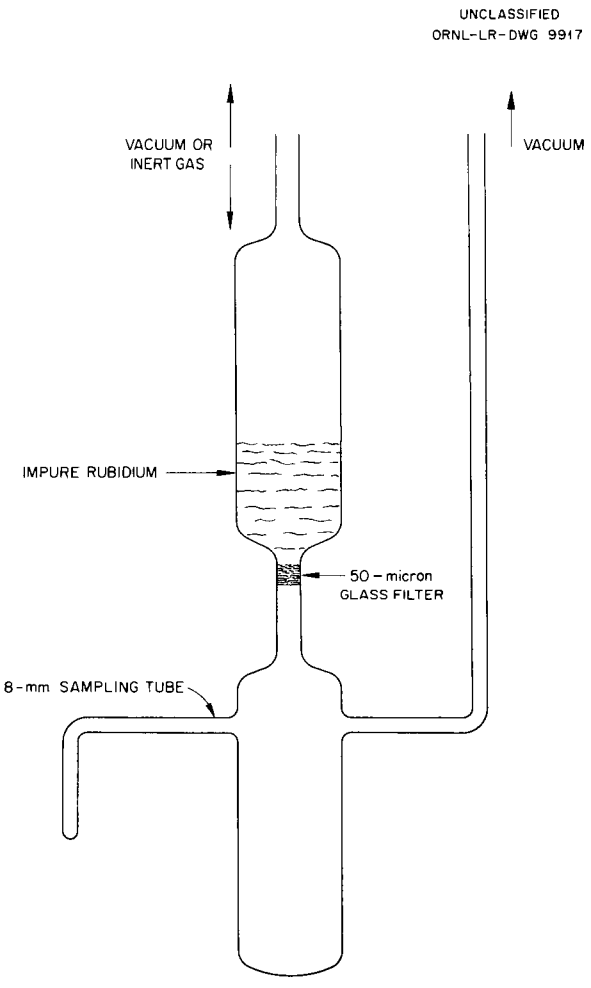

Fig. 9. Pyrex Apparatus for Filtering Rubidium.

as-received rubidium metal, exclusive of the black material, is shown in Table 1 *a*.

The analysis of the filtered rubidium (Table 3) shows that the alkali impurities in the filtered rubidium are essentially the same as those of the distilled material. The oxygen content is slightly less in the filtered material. However, the metal was slightly contaminated by rubidium hydride which formed on its surface when hydrogen was used to force the rubidium through the filter. A purified inert-gas atmosphere was found to be more satisfactory than hydrogen.

TABLE 3. ANALYSIS OF FILTERED RUBIDIUM

Element	Weight (%)
Cesium	4.700
Potassium	0.190
Oxygen	0.150
Sodium	0.015
Hydrogen	0.010
Lithium	0.006

Of the two purification procedures, filtration was found to be as effective in reducing the oxygen and carbonate impurities as was distillation. Filtration is recommended since it is a much simpler process.

LOADING OF CORROSION-TESTING SYSTEMS

Corrosion-testing systems may be filled with relative ease in the dry box. Following distillation or filtration, the purified rubidium was placed in the dry box. The rubidium was heated with a Glas-Col heating mantle and was then poured into the metal testing system by simply breaking the side arm of the container. After the rubidium had been transferred, the system was sealed by welding and was then removed from the dry box ready for testing.

RUBIDIUM-CORROSION TESTS

Static Tests. – Static tests of rubidium at 1500 and 1650°F in Inconel containers showed an attack of 1 to 2 mils in 100 hr. The attack on the surface of the container was in the form of both intergranular penetration and small subsurface voids. Inconel was chosen for preliminary tests because of its high-temperature strength and its good corrosion resistance to attack by molten sodium.

Dynamic Tests. – Since the above tests indicated that the corrosion of Inconel by rubidium was no serious problem under static isothermal conditions, a dynamic test was conducted. A loop (Fig. 10) containing 8 cc of boiling vacuum-distilled rubidium was run for 312 hr with a hot-zone temperature of 1520°F and a cold-zone temperature of 160°F. The maximum attack in the loop was intergranular and had penetrated to a depth of one mil, and it occurred in the hot leg just below the liquid level (see Fig. 11; note the grain about to separate from the wall). A weld area (Fig. 12) in the boiler section of the loop showed no attack.

STRIPPING OF RUBIDIUM FROM CONTAINERS

Only a slight amount of experience has been acquired in the stripping of vessels which contain rubidium, and this is still a problem. Very smal

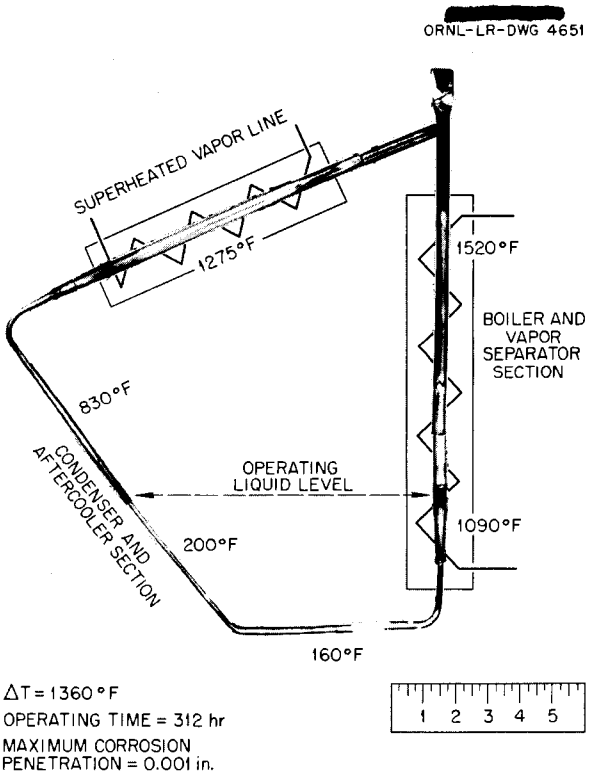

Fig. 10. Sectioned Inconel Loop After Exposure to Boiling or Vaporized Rubidium for 100 hr.

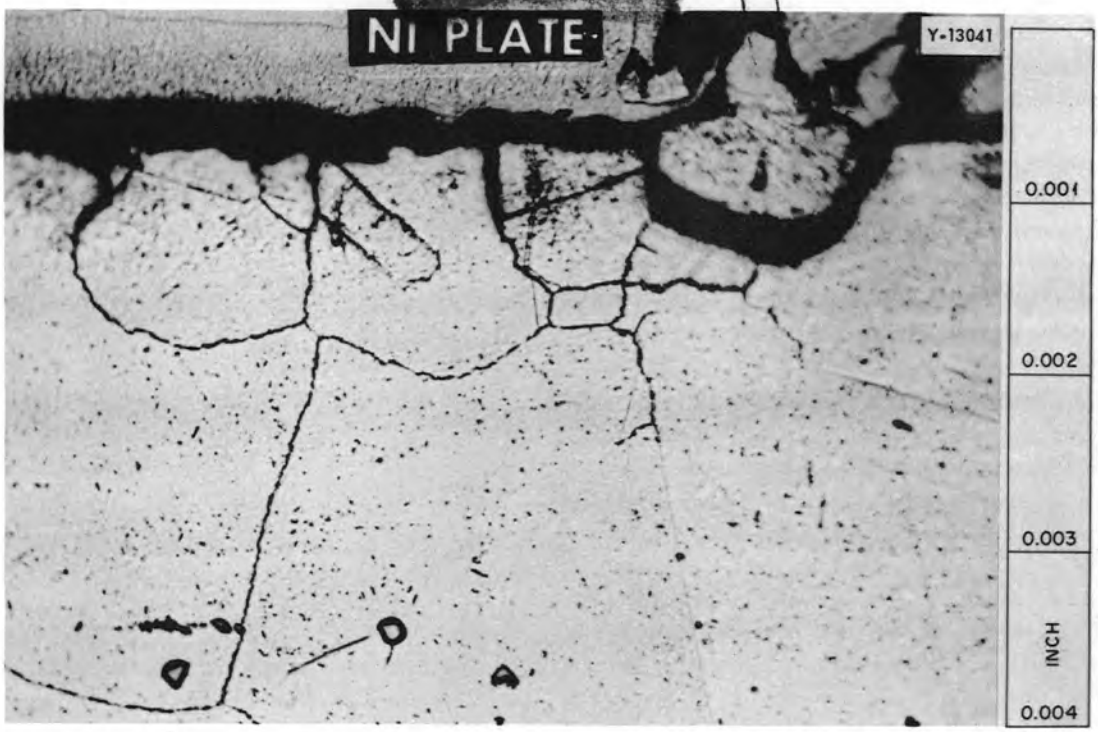

Fig. 11. Wall of Hot Leg of Inconel–Boiling-Rubidium Loop Just Below Bath Level. Specimen was nickel-plated after the test in order to protect the edge during metallographic polishing. Etched with aqua regia. 1000X. Reduced 10%. [redacted]

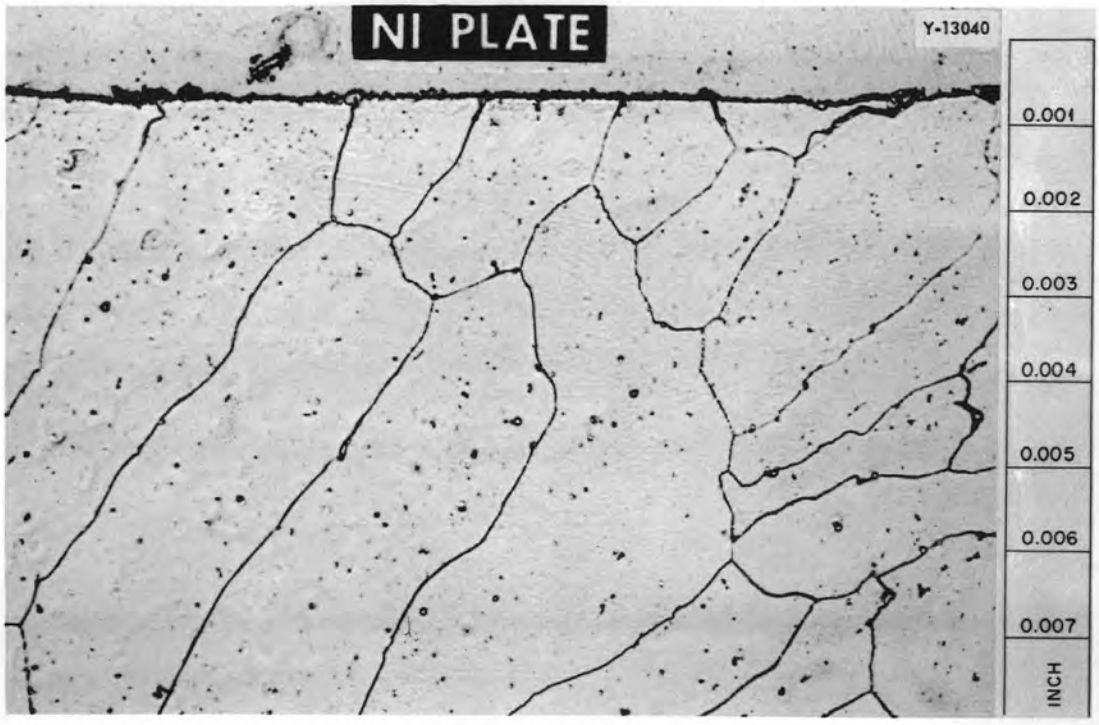

Fig. 12. Weld Area from Hot Leg of Inconel–Boiling-Rubidium Loop Just Below Bath Level. Specimen was nickel-plated after the test to protect the edge during metallographic polishing. Etched with aqua regia. 500X. Reduced 10%. [redacted]

amounts of the metal should be stripped in water rather than in inflammable liquids (alcohol, etc.). However, large quantities of rubidium if exposed to water will cause a violent explosion. Moreover, if the rubidium metal is not instantly and completely submerged it will ignite alcohol and the evolved hydrogen gas; therefore, without some modifications this method is not satisfactory for stripping.

Metallic rubidium has been successfully removed from containers by placing the metal under hexane and by adding small amounts of alcohol to the hexane in order that tne reaction between the rubidium and alcohol may be controlled. A flowing blanket of helium is maintained over the hexane in order to disperse the hydrogen evolved by the reaction (Fig. 13). Alcohol and rubidium combine to form rubidium ethylate (C_2H_5ORb), which is quite unstable and may be explosive in high concentrations. Therefore as a safety precaution, hydrochloric acid is added to the hexane-alcohol-ethylate solution to form rubidium chloride (RbCl), which is quite stable and safe to handle.

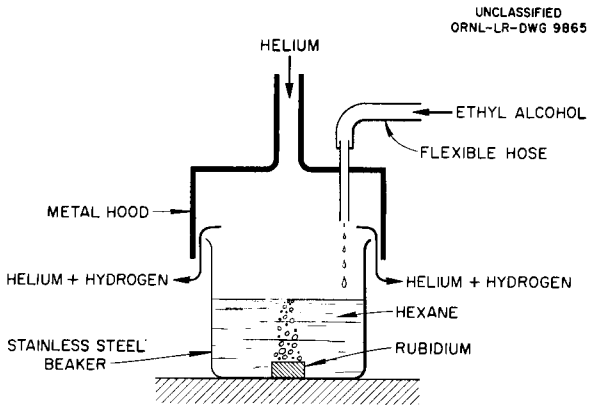

Fig. 13. Apparatus for Dissolution of Rubidium.

ACKNOWLEDGEMENTS

The authors wish to acknowledge their appreciation to J. V. Cathcart and M. J. Whitman for the assistance rendered during this work. J. C. White, Analytical Chemistry Division, Oak Ridge National Laboratory, performed the analytical work which is reported in this paper.

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S. I. Cohen and T. N. Jones of the Reactor Experimental Engineering Division obtained the data in Fig. 1, which show the influence of temperature on the density of rubidium; these data are discussed in their report entitled: *Measurement of the Density of Liquid Rubidium*, ORNL CF-54-8-10 (August 4, 1954).

[redacted]