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CORROSION OF URANIUM IN MOIST AIR

by

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METALLURGY AND CERAMICS

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METALLURGY AND CERAMICS

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Introduction

The corrosion of uranium in moist air is more rapid than had been thought previously. Earlier recommendations were based on tests of 300 hr duration. In tests which were conducted for over 1000 hr, moisture has less effect than in those tests made over shorter periods. This phenomenon is believed due to acceleration of the corrosion rate.

The parabolic law holds in the initial stages of corrosion. This law relates the thickness of oxide, y, to elapsed time of exposure, t, by the equation

$$y^2 = kt. \qquad (1)$$

After 100 to 500 hr, however, the rate no longer decelerates, but accelerates. The weight increase follows approximately the three halves power of t according to the equation

$$y = kt^{1.5}. \qquad (2)$$

The accelerated corrosion rate is thought to occur as a result of oxide fracture.

Experimental Details

Rolled sheets of uranium, 0.020 in. thick, were cut into specimens 0.5 in. by 0.75 in. and polished manually through 3/0 paper. The specimens were then immersed in 35 per cent nitric acid to remove any oxide film and to passivate the metal. They were then placed in platinum boats and these were placed in desiccators. Humidity control was obtained by placing selected saturated salt solutions in the desiccator. The desiccators were placed in thermo-

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statically-controlled ovens. For each daily weighing, the desiccators were cooled to room temperature, the platinum boats containing the specimens were weighed on an Ainsworth, type FDJ, microbalance, and the boats and contents were returned to the ovens.

Humidity Conditions

The driest condition used was afforded by air in contact with P_2O_5 at the test temperature. Laboratory air heated to 57 and 75°C contained less than 3 per cent relative humidity. The saturated salt solutions which were used to obtain other humidity conditions are listed in Table I. The deviations between desired and actual humidities are due to experimental difficulties.

TABLE I

Saturated Salt Solutions and Resulting Humidities

Salt Used	Test Temp. (°C)	Relative Humidity (%) Desired	Relative Humidity (%) Actual
Lithium Chloride	38	10	14.1
Lithium Chloride	57	10	10.9
Lithium Chloride	75	10	10.8
Lithium Nitrate	38	30	30.1
Magnesium Chloride	38	30	99.1
Magnesium Chloride	57	30	95.0
Zinc Ammonium Sulfate	75	30	87.0

Results

Figures 1 through 3 show weight increase per unit area, due to the oxygen pickup, of each specimen as a function of elapsed

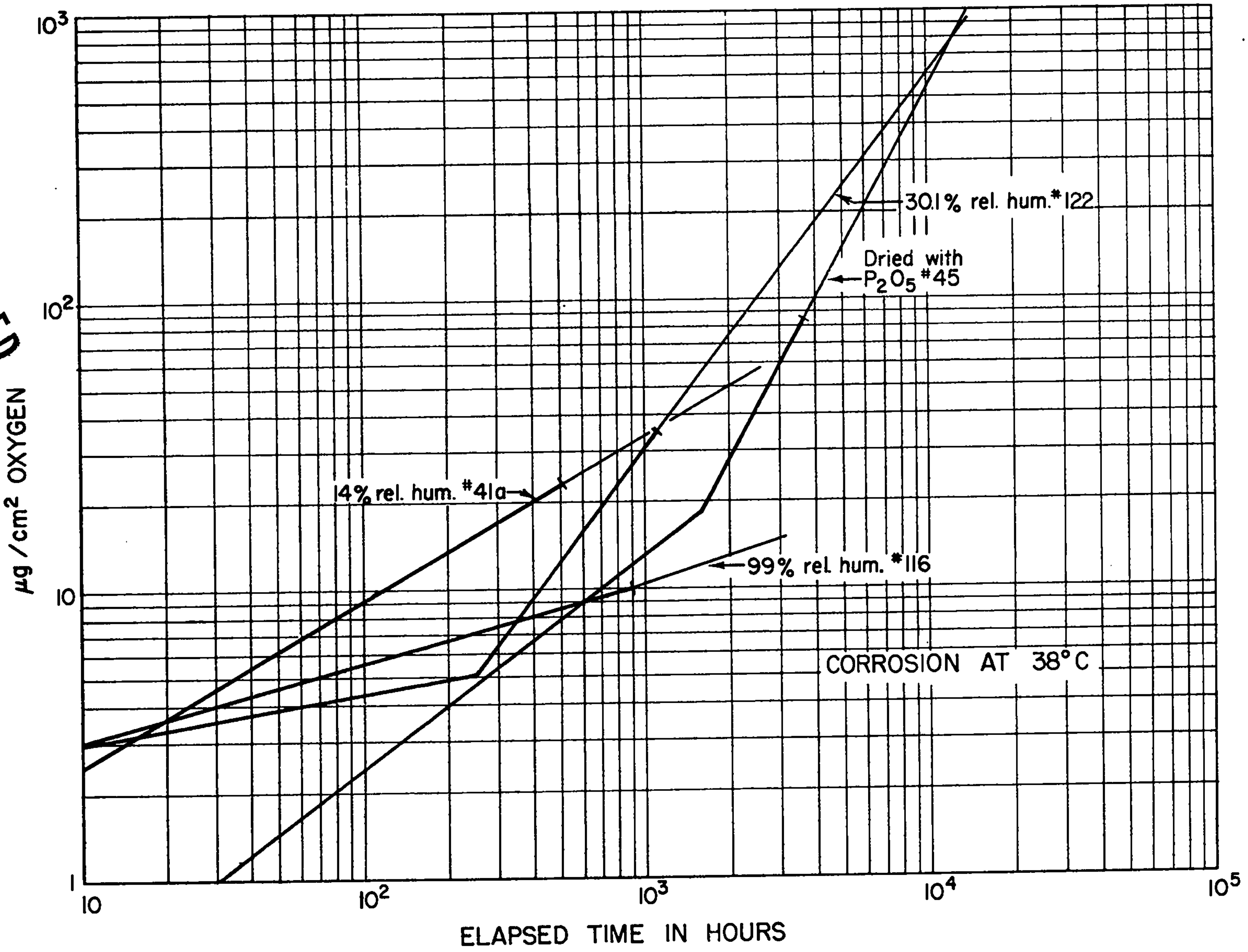

Fig. 1. Weight increase per unit area of uranium as a function of elapsed time at 38°C.

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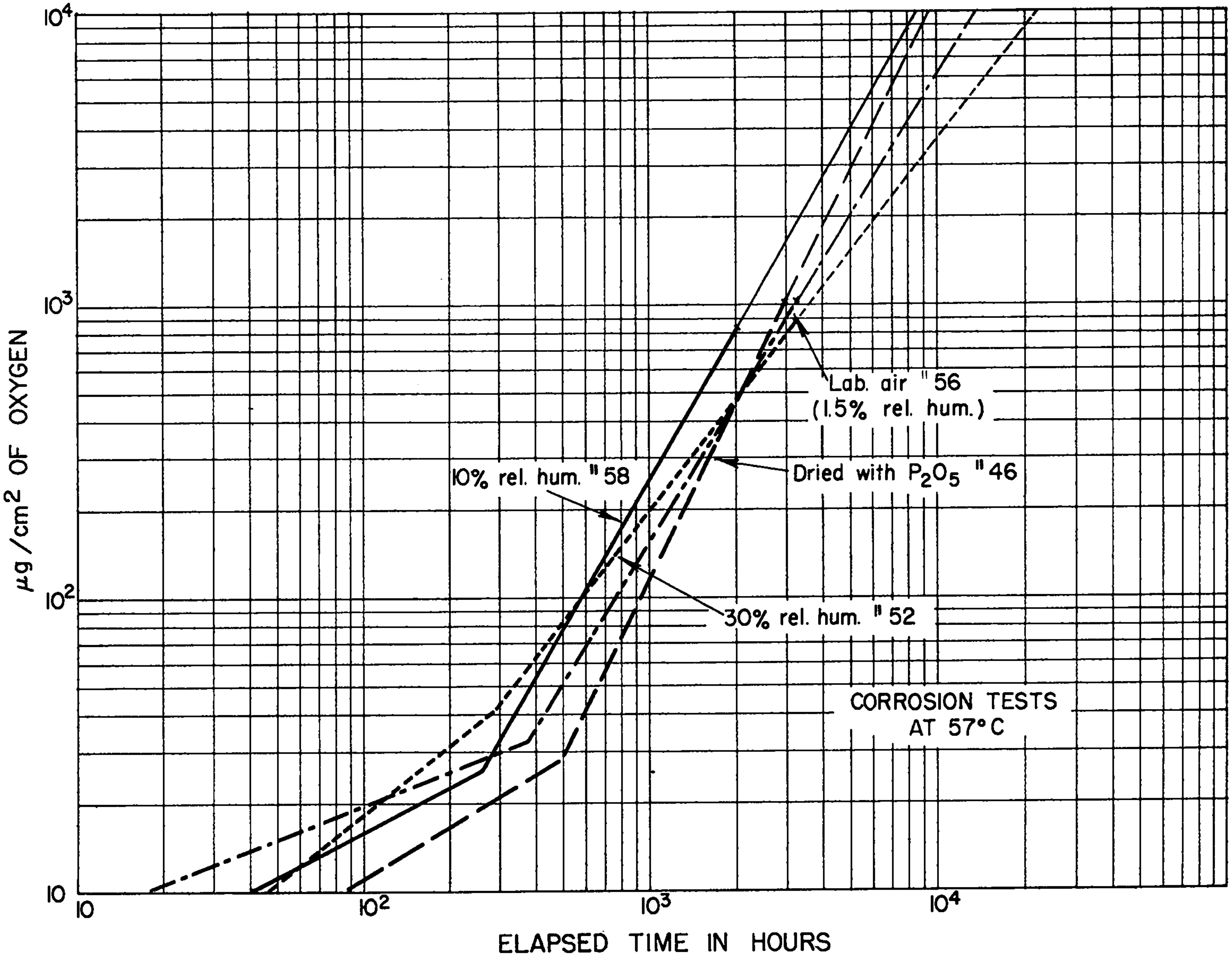

Fig. 2. Weight increase per unit area of uranium as a function of elapsed time at 57°C.

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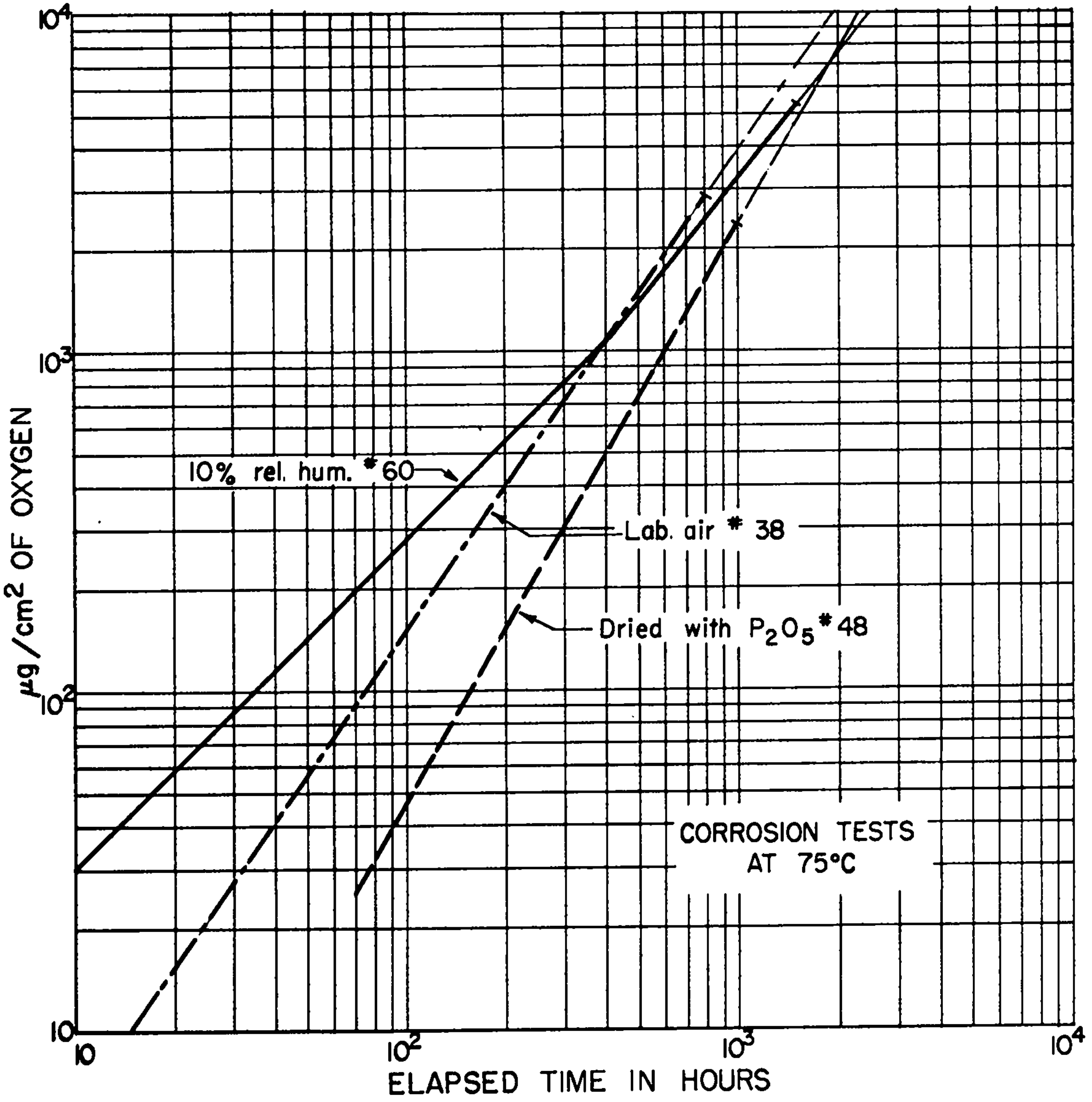

Fig. 3. Weight increase per unit area of uranium as a function of elapsed time at 75°C.

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time for test temperatures of 38, 57, and 75°C, respectively. The lines in the figures correspond to actual humidities. Extrapolation of lines beyond experimental data points is indicated by lighter lines. Specimen numbers are shown on the figures as they refer to specific runs.

Discussion

In the initial stages, the corrosion of uranium in moist air proceeds slowly and follows approximately a parabolic growth law,

$$y^2 = kt, \qquad (3)$$

where y is the oxide thickness (or weight increase per unit area), k is a rate constant, and t is the elapsed time. The parabolic law is a solution of Fick's law of diffusion, which is appropriate to flat specimens. The thicker the film, the slower is diffusion. Thus corrosion decelerates with increasing time. After several hundred hours the corrosion rate ceases to follow the parabolic law, acceleration is observed, and the oxide thickness becomes related to elapsed time by the equation

$$y = kt^2. \qquad (4)$$

Differentiation of this time squared law shows that the rate of attack increases linearly with time. This law has been observed under dry air conditions. A modified form of it, in which the exponent 2 is changed to 1.5, holds in moist air. Exponents of t which are greater than unity denote an accelerated corrosion rate, but the rate of increase is lower when the exponent is less than 2.

Both growth laws have been observed at 38, 70, 75, and 100°C and repeatedly observed at 57°C.

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The parabolic and time squared laws may both be represented by the general equation

$$y^n = k_n t. \tag{5}$$

The exponent n may be obtained from the slope of isothermal data plotted on a log log scale, since Equation 5 is equivalent to

$$\log y = \left(\frac{1}{n}\right) \log k_n + \left(\frac{1}{n}\right) \log t. \tag{6}$$

It is evident that the slope is $\frac{1}{n}$. Hence many of the data for this report are presented on log log plots.

In these tests no evidence has been observed of the formation of uranium hydride, nor has any pyrophoricity been noted. Absence of the hydride is probably due to the repeated contact of the specimen with fresh air: the specimens were frequently removed from the dessicators for weighing and thus the air in the desiccators was changed. Under conditions where the oxygen may be exhausted, as might be obtained in a closed container, the hydride and, possibly, lower oxides of uranium may form. Reaction of uranium with moisture in the absence of oxygen does produce pyrophoric corrosion product powders. Attack in distilled water or in moist helium are examples of such conditions.

Examination of Figs. 1, 2, and 3 confirm the statement that the early effect of moisture in increasing the corrosion rate is largely overcome after 3000 hr. Higher temperatures rapidly increase the amount of corrosion, shorten the parabolic growth law period, and lengthen the period of accelerated corrosion rate.

Figure 4 has been included to give a clearer picture of the accelerating rate of attack. The oxygen weight increase per unit

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area is plotted as a function of elapsed time for the corrosion of uranium in dry air at 57 and 75°C.

Figure 5 shows the relation between weight increase of oxygen in milligrams per square centimeter, and the thickness in millimeters of consumed uranium. The minimum thickness of oxide corresponding to any given weight increase of the specimen due to oxygen is also shown. Because the bulk density of the oxide is almost always less than the X-ray density, the thickness of the oxide is generally greater than shown in the figure.

Summary

The corrosion of uranium by dry and moist air has been studied at 38, 57, and 75°C. Although moisture increases the rate of initial attack, after 200 to 500 hr the effect is reduced and an accelerating corrosion rate overshadows the initial effects of moisture.

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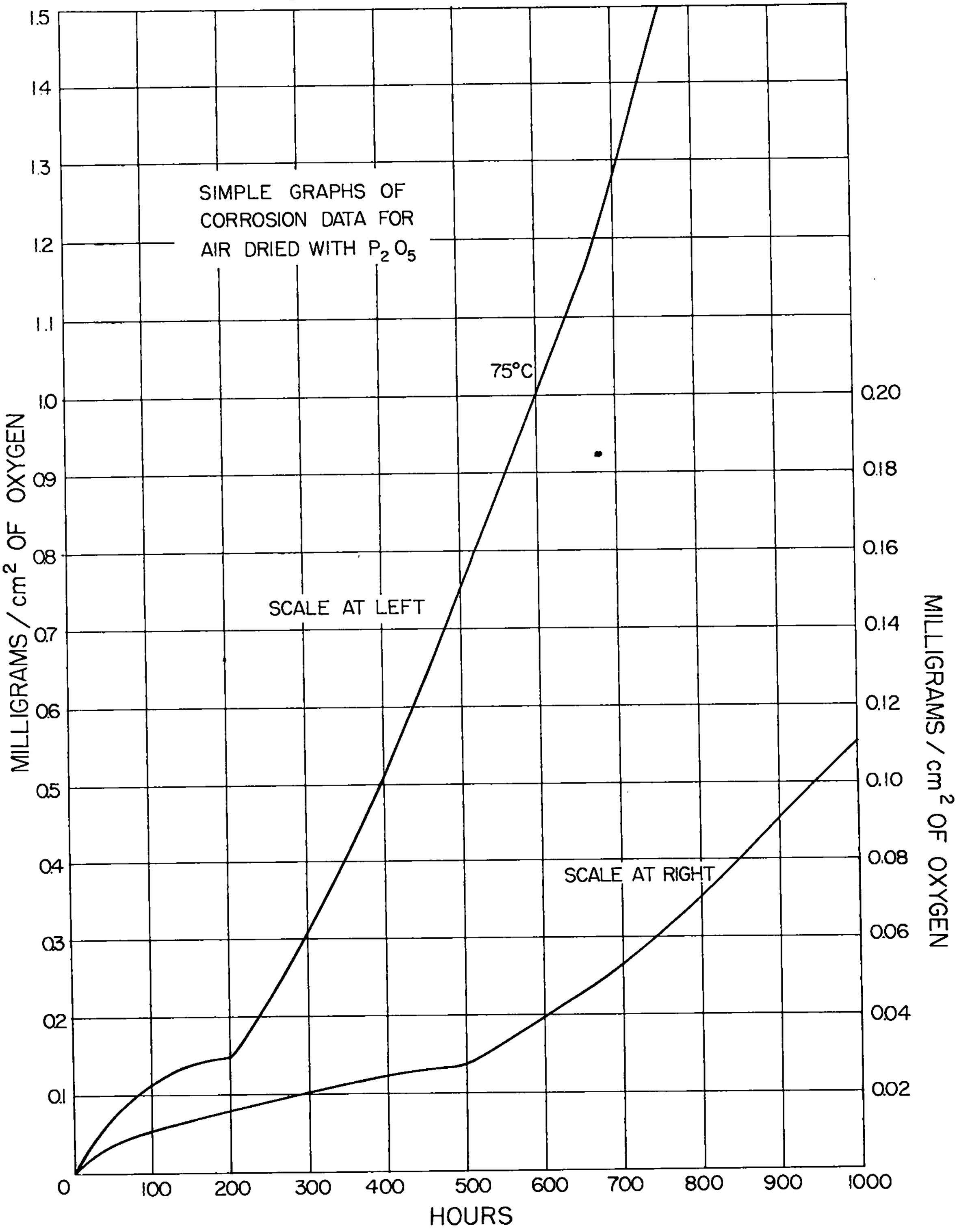

Fig. 4. Weight increase data for 57 and 75°C, plotted to emphasize acceleration.

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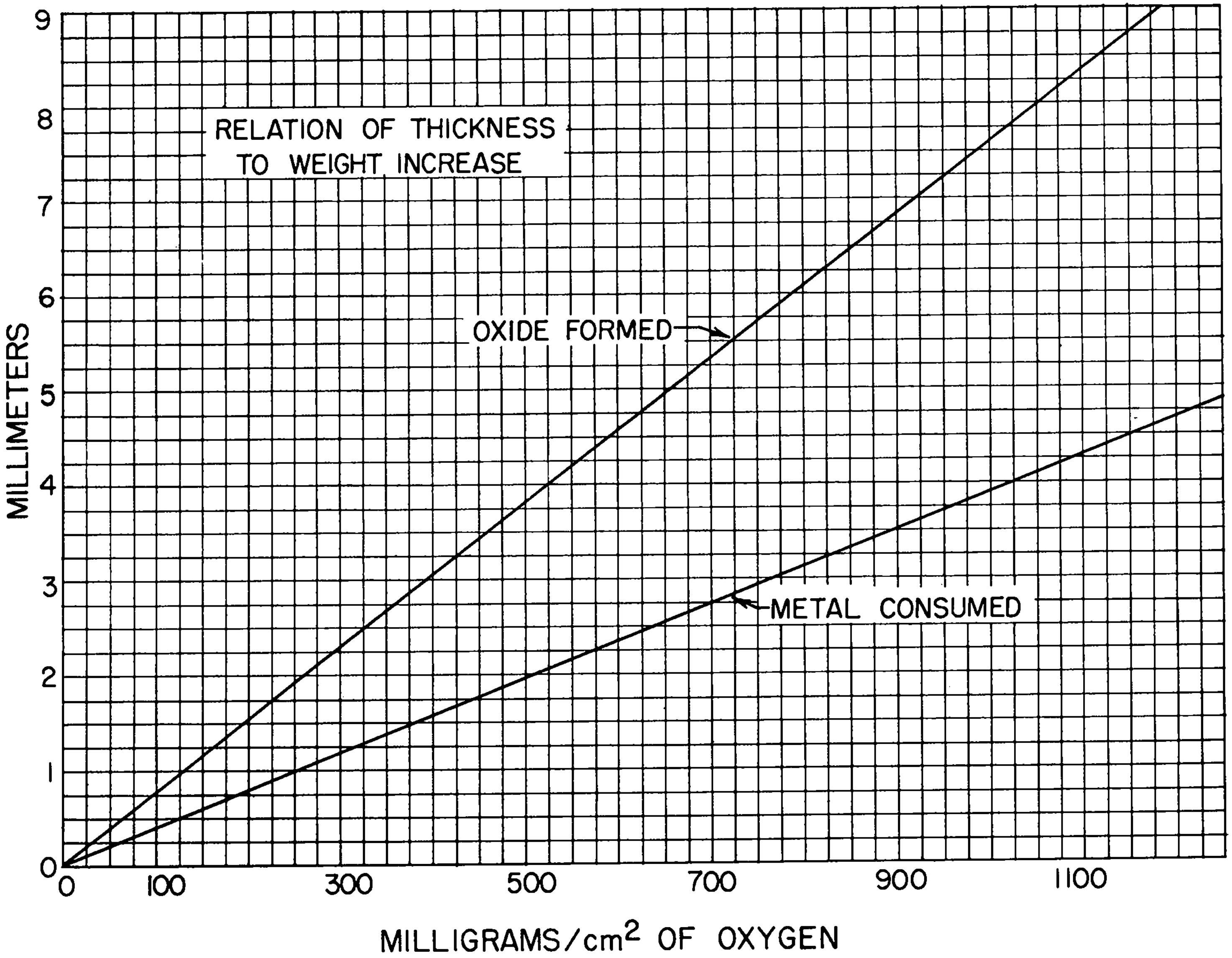

Fig. 5. Graph for converting weight increase to minimum oxide thickness.

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