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LAWRENCE LIVERMORE LABORATORY
University of California/Livermore, California

CORRELATION OF LONG STORAGE BEHAVIOR OF THORIUM-EPOXY COMPOSITES
WITH LABORATORY DATA ON THE CORROSION OF THORIUM

C. Colmenares, D. R. McKenzie, and J. Dickie

May 19, 1975

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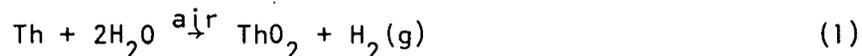
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CORRELATION OF LONG STORAGE BEHAVIOR OF THORIUM-EPOXY COMPOSITES
WITH LABORATORY DATA ON THE CORROSION OF THORIUM

C. Colmenares, D. R. McKenzie, and J. Dickie
Lawrence Livermore Laboratory
Livermore, California

(Presented at the 15th meeting of JOWOG-12, June 18-21, 1974,
held at AWRE, Aldermaston, England)

Large thorium and Mulberry parts were adhesively bonded to polystyrene foam by means of an epoxy. Thorium surfaces were present in two forms: machined or untreated and passivated in an HNO_3 - HF solution. Since the epoxy and the polystyrene foam are the main sources of water in the package described, we will expect thorium metal to oxidize in humid air according to the following reaction:



The contribution of oxygen to the oxidation process is very small compared to that of water vapor and it may be neglected for calculational purposes.

Experimental units were stored at temperatures ranging from 32° to 71°C for times greater than six months in order to test the integrity of the metal to foam bond.

Results

Two types of measurements were made in the evaluation of test units. Gases were extracted from the unit, measured and analyzed. The hydrogen present was taken as a measure of the extent of oxidation by water vapor as shown in equation (1). In addition, the units were disassembled and the thorium and Mulberry surfaces

examined for separation of the adhesive from the metal surface and for oxidation of the two metals. In cases where separation had occurred between the thorium surface and the adhesive due to oxidation, oxide thickness measurements were performed. Units stored at 71.1°C showed severe corrosion of the machined thorium and moderate corrosion of the passivated thorium. The Mulberry parts had a slight blue color. In both units there was separation between the thorium and the adhesive, which actually lifted a film of ThO_2 from the metal. Other two units which were stored at 48.9° and 60°C respectively, showed a light oxidation of the thorium both machined and passivated. Good adhesion was observed between the thorium and the adhesive.

Columns 3, 4, and 5 in Table I show the hydrogen generation of the test units and also the rate of generation in cc (STP)/week. Assuming that the hydrogen is produced by reaction 1, then from the kinetic data on the oxidation of thorium and the water vapor pressure dependence of the rate constant, we can calculate the water vapor pressure required to produce the measured quantities of hydrogen at the three storage temperatures. From experimental data on lapped, machined, and passivated coupons of thorium we know that:

$$\text{Corrosion rate of machined surfaces (mg/hr-cm}^2\text{)} = 1.4 \text{ Rate (lapped)} \quad (2)$$

$$\text{Corrosion rate of etched surfaces (mg/hr-cm}^2\text{)} = 0.08 \text{ Rate (lapped)} \quad (3)$$

From the stoichiometry of equation (1) we calculate that

$$1 \text{ mg of } \text{O}_2 \equiv 1.4 \text{ cc (STP) H}_2 \quad (4)$$

and that the volume of H_2 generated is:

$$\text{cc (STP)} = 1.4 \times \text{Rate (mg/hr-cm}^2\text{)} \times \text{time} \times \text{surface area (cm}^2\text{)} \quad (5)$$

For a unit at a known temperature, T_{exp} , and an unknown water vapor pressure, $P(\text{H}_2\text{O})_{\text{exp}}$, a total volume of H_2 , V_{exp} , in cc (STP) was collected. Then we may write:

$$V_{\text{exp}} = \Sigma (V_{\text{machined Th}} + V_{\text{passivated Th}} + V_{\text{Mulberry}})_{T_{\text{exp}}, P_{\text{H}_2\text{O}}} \quad (6)$$

By the use of experimental thorium corrosion data at 100 torr water vapor pressure*, we can calculate values of $R(\text{lapped})$ for 32.2°, 48.9°, 60°, and 71.1°. Applying equations (2), (3), (4), and (5), we obtain the total volume of hydrogen, V_{calc} , produced by oxidation according to equation (1) at the given temperatures and 100 torr H_2O (g). We also know that in the initial corrosion state of thorium, the rate is proportional to $(P_{\text{H}_2\text{O}})^{1/4}$. Consequently we may write:

$$\frac{(V_{\text{exp}})_{T_{\text{exp}}, P_{\text{H}_2\text{O}}}}{(V_{\text{calc}})_{T_{\text{exp}}, 100 \text{ torr H}_2\text{O}}} = \left(\frac{P_{\text{H}_2\text{O}}}{100} \right)^{1/4} \quad (7)$$

where, $V_{\text{calc}} = \Sigma (V_{\text{machined Th}} + V_{\text{passivated Th}} + V_{\text{Mulberry}})_{T_{\text{exp}}, 100 \text{ torr H}_2}$

The volume of hydrogen produced by the oxidation of Mulberry, V_{Mulberry} , was calculated by assuming that the oxide formed on the surfaces of the metal at 71.1°C was 1000 Å thick (slightly blue interference color). An activation energy of approximately 20 kcal/mol was used to calculate the hydrogen generated at other temperatures. The calculated water vapor pressure in the five units examined is shown in column 6 of Table I. Columns 7, 8, and 9 show the contribution of each component to the hydrogen generated in each unit at the experimental temperature and calculated water vapor pressure. The contribution of the machined thorium is the largest, and we have calculated the rate of hydrogen generation of the untreated

*See "Oxidation of Thorium in Oxygen, Humid Air, and Humid Nitrogen," by D. R. McKenzie and C. Colmenares, also presented at this JOWOG-12 meeting.

thorium per week, R_N as shown in column 10 of Table 1. Finally values of $R_O/P^{1/4*}$ and $R_N/P^{1/4}$ were calculated and are shown in the last two columns of Table 1. These values, as well as R_O are plotted versus $1/T$ in Figures 2 and 3. The overall hydrogen generation rate R_O , and the machined thorium generation rate R_N , do not fit a good straight line when plotted versus $1/T$ as expected for an Arrhenius plot. The calculated values of $R_O/P^{1/4}$ and $R_N/P^{1/4}$ do fall in a straight line when plotted versus $1/T$ (Figures 1 and 2). This is particularly significant in the case of $R_O/P^{1/4}$ because R_O is a directly measured quantity, and the calculated pressure correction is not that important since the dependence on pressure is a weak function (0.25 power). Furthermore, if a line were to be fitted by the least-square method through direct experimental points at the test temperatures, the slope obtained is practically the same as for the coupon experimental data (Figure 3), namely a slope corresponding to an activation energy of about 25 kcal/mol. The activation energy for the corrosion of thorium in humid air has been found to be 22.25 ± 0.51 kcal/mol (95% confidence level)** in the initial linear stage, which is in excellent agreement with the values of 22.08 ± 0.40 and 21.74 ± 0.31 kcal/mol found from plots of $R_N/P^{1/4}$ and $R_O/P^{1/4}$ versus $1/T$. The important question at this stage is whether the adhesive is capable of generating partial pressures of water between 71.4 and 95.8 torr at 71.7°C. If this range of pressures is not attainable at 71.1°C, then we must suspect that some impurity in the adhesive may be accelerating the oxidation process.

Even though, HCl and Cl₂ were found to outgass from the adhesive at temperatures above 60°C, direct determinations of the partial pressure of water above the adhesive indicated that between 60° and 70°C, the water in the solid was completely released; therefore, the pressure exerted by the released vapor was controlled by

* R_O = overall corrosion rate.

R_N = corrosion rate of untreated thorium.

** See reference on page 3.

the void volume and temperature of the system. Under this condition, the water vapor pressures of 95.8 and 71.4 torr could very well have been attained during the experiment at 71.1°C. The excellent agreement between coupon and large scale data, once the pressure effect was taken into account, adds credence to the postulate that high water vapor pressures were attained at 71.1°C. Hence, we must conclude that the presence of small amounts of HCl and Cl₂ did not significantly contribute to the oxidation of thorium in these experiments.

TABLE I. Experimental and Calculated Results

UNIT NO.	TEST TEMP °C	STORAGE TIME WEEKS	H ₂ cc(STP) EXP. MEASURED	OVERALL RATE H ₂ cc(STP) PER WEEK R ₀	CALC. WATER VAPOR PRESSURE TORR	CONTRIB. OF PASSIVATED THORIUM H ₂ cc(STP)	CONTRIB. OF MULBERRY H ₂ cc(STP)	CONTRIB. OF UNTREATED THORIUM H ₂ cc(STP)	UNTREATED THORIUM NET RATE H ₂ cc(STP) PER WEEK R _{II}	$\frac{R_0}{p0.225}$	$\frac{R_N}{p0.225}$
021	71.1	26.00	850	32.7	95.8	133.0	3.5	713.5	27.4	11.72	9.82
025	71.1	28.71	822	28.64	71.4	137.6	4.0	680.4	23.7	10.96	9.07
024	60.0	28.71	122.5	4.27	1.27	20.8	1.0	100.7	3.51	4.05	3.33
023	48.9	28.71	34.58	1.20	0.735	6.42	0.25	27.91	0.972	1.29	0.99
026	32.2	70.43	22.22	0.315	7.74	4.78	0.02	17.42	0.247	0.20	0.156

OVERALL RATE H₂ CC(STP) PER WEEK/((TORR H₂O)^{0.228})

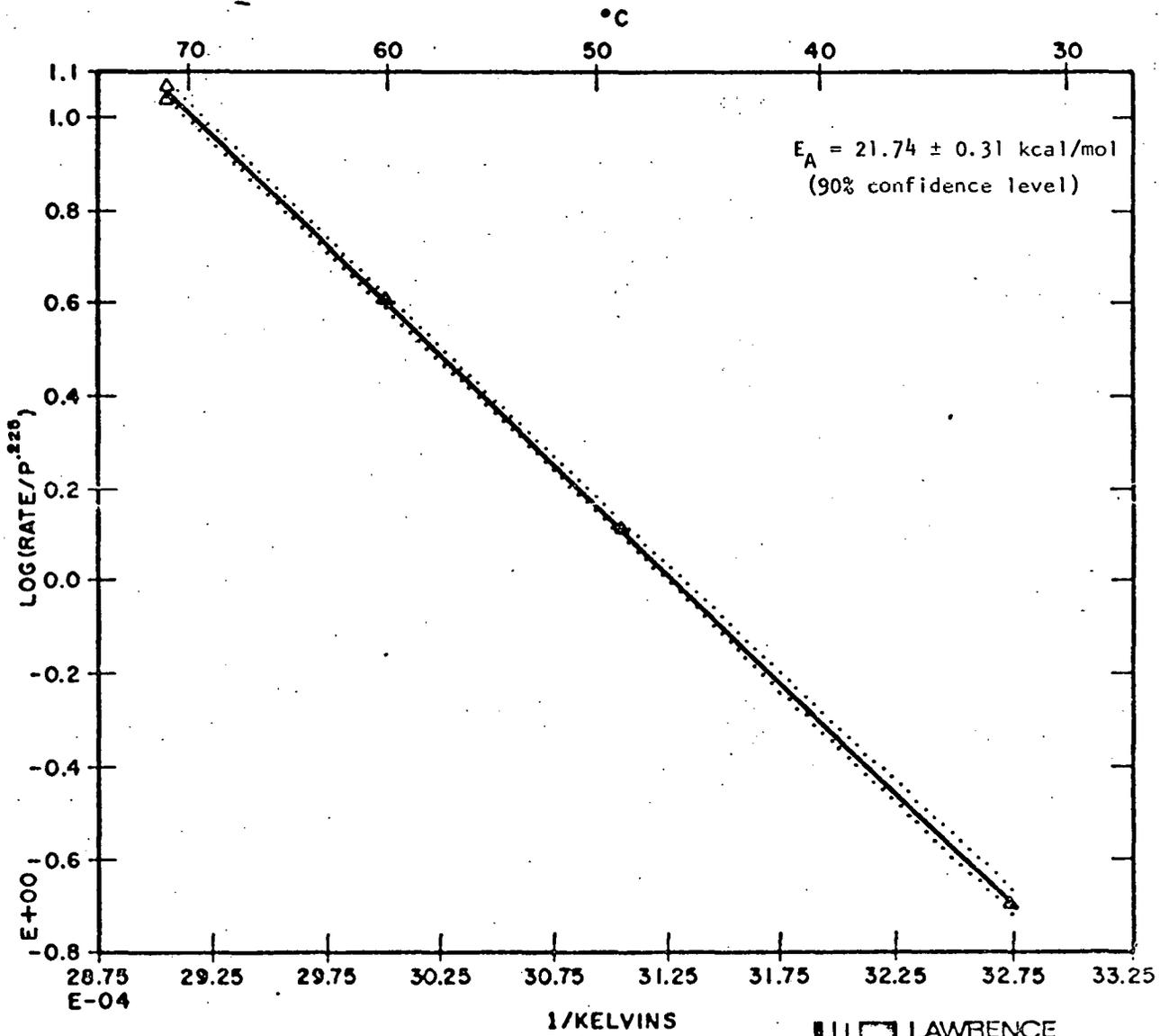


Figure 1



UNTREATED THORIUM NET RATE H₂ CC(STP)
PER WEEK/((TORR H₂O)^{0.225})

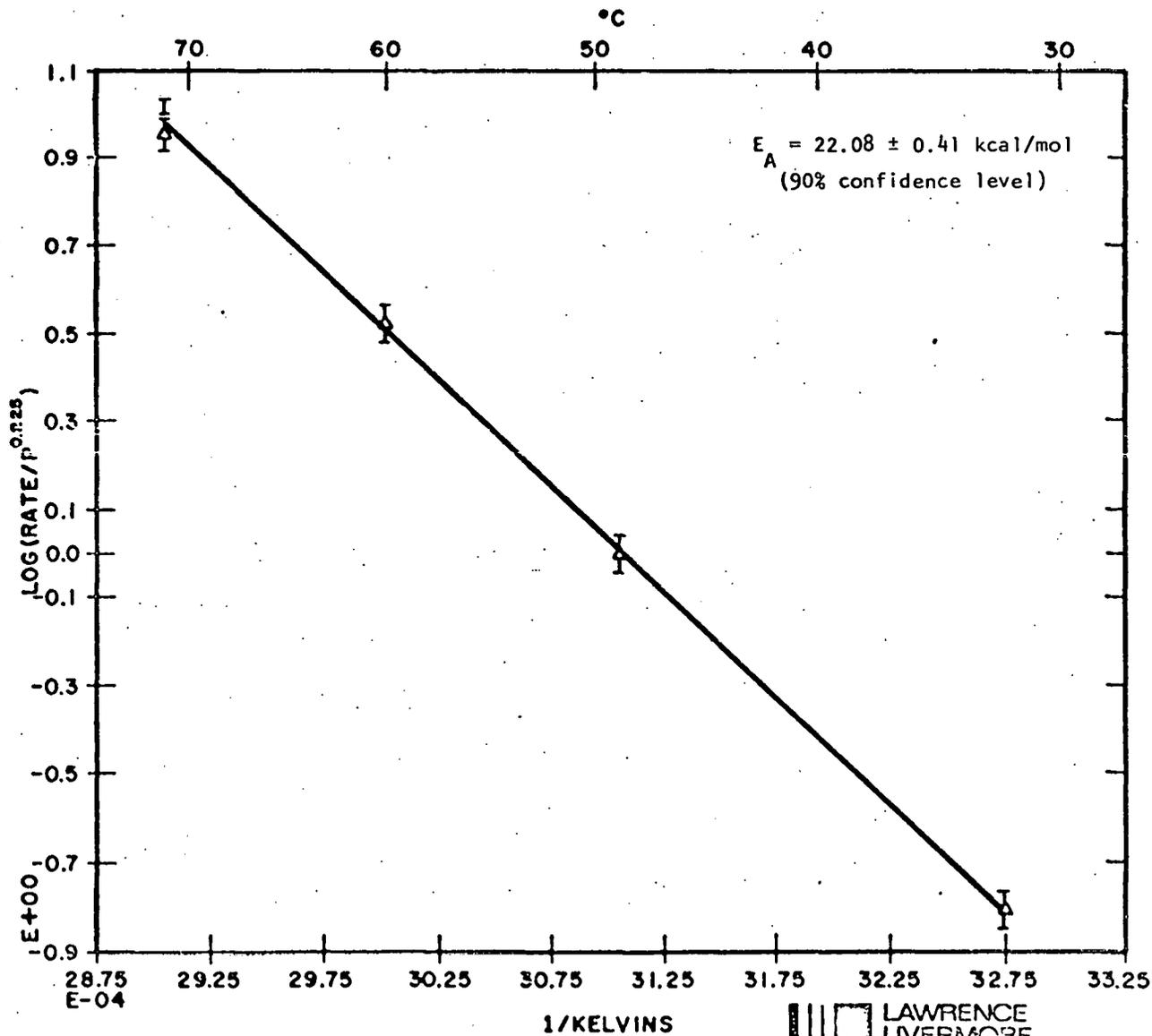


Figure 2



OVERALL RATE H₂ CC(STP) PER WEEK

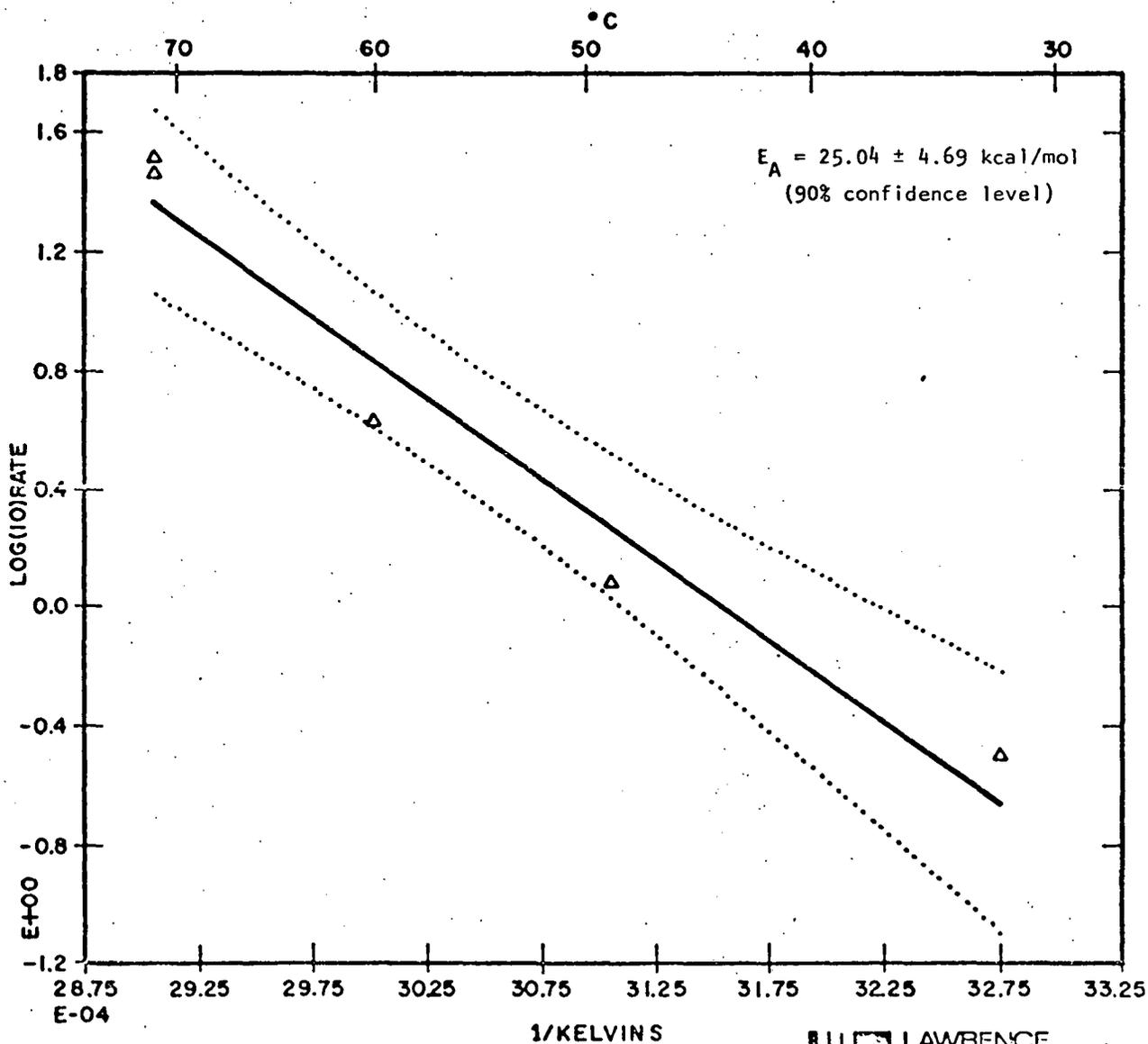


Figure 3



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