MASTER

4/3/59

EXTERNAL TRANSMITTAL AUTHORIZED

OAK RIDGE NATIONAL LABORATORY

Operated by

UNION CARBIDE NUCLEAR COMPANY

Division of Union Carbide Corporation

Post Office Box X

Oak Ridge, Tennessee

ORNL
CENTRAL FILES NUMBER

59-2-98

DATE: February 27, 1959

COPY NO. 18

SUBJECT: Summary of Runs D-77 through D-93. Rate of Oxidation of Chromium(III) in Dilute Uranyl Sulfate Solution in the Presence of Ruthenium.

TO: J. C. Griess

FROM: E. S. Snavelly, R. S. Greeley and S. R. Buxton

SUMMARY

The rate of oxidation of chromium(III) to chromium(VI), catalyzed by ruthenium, was determined at various temperatures and oxygen concentrations. The rate at 300°C was too rapid for measurement by aliquot sampling. In the temperature range of 225°C to 275°C oxidation was rapid and the rate increased with oxygen concentration. A linear dependence of initial oxidation rate on the reciprocal of chromium(VI) concentration suggested that a rate-controlling step in the reaction mechanism may be desorption of chromium(VI) from the ruthenium catalyst. The activation energy calculated for the reaction is 19 kcal/mole.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report. The information is not to be abstracted, reprinted or otherwise given public dissemination without the approval of the ORNL patent branch, Legal and Information Control Department.

RELEASE APPROVED
BY PATENT BRANCH1-11-61
DATE SIGNATURE

4-1

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Runs D-77 through D-93

Catalysis of the Oxidation of Cr(III) to Cr(VI) by Ruthenium

Conditions:

<u>Run</u>	<u>Solution</u>	<u>Gas</u>	<u>Temp. (°C)</u>	<u>Time (hrs)</u>
D-77(a)	0.025 m H ₂ SO ₄ , 100 ppm Ru	1000 ppm O ₂	250	115
(b)	0.05 m H ₂ SO ₄	1500 ppm O ₂	250	70
D-78	0.05 m H ₂ SO ₄ , 500 ppm Cr(III)*	1000 ppm O ₂	250	178
D-79	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III), 25 ppm Ru	500 ppm O ₂	200	118
D-80	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III), 25 ppm Ru	500 ppm O ₂	250	68
D-81	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III), 25 ppm Ru	1000 ppm O ₂	200	79
D-82	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III),* 25 ppm Ru*	1000 ppm O ₂	150	157
D-83	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III),* 25 ppm Ru*	1000 ppm O ₂	300	36
D-84	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.03 m CuSO ₄ ,	500 ppm O ₂	280	187
D-85	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III),* 25 ppm Ru*	1500 ppm O ₂	250	145
D-86	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III),* 25 ppm Ru*	300 ppm O ₂	275	94
D-87	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III),* 25 ppm Ru*	1400 ppm O ₂	250	130
D-88	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.01 m CuSO ₄ , 500 ppm Cr(III),* 25 ppm Ru*	270 ppm O ₂	225	145
D-89	0.7 m H ₂ SO ₄ , 0.66 m CuSO ₄	100 psi He	85	4
D-90	0.7 m H ₂ SO ₄ , 0.66 m CuSO ₄	100 psi He	85	4
D-91	0.75 m H ₂ SO ₄	100 psi H ₂	85	4
D-92	0.025 m H ₂ SO ₄	600 ppm O ₂	250	9
D-93	0.04 m UO ₂ SO ₄ , 0.025 m H ₂ SO ₄ , 0.03 m CuSO ₄ , 500 ppm Cr(III)*	1000 ppm O ₂	250	68

* Added to loop after operating temperature attained.

DISCUSSION

It has been shown that the addition of small amounts of ruthenium nitroso sulfate to high-temperature, dilute uranyl sulfate solutions containing oxygen inhibits the corrosion attack of stainless steel exposed in the solutions.^(1,2,3) The inhibition was apparently due to the presence of chromium(VI) produced by the ruthenium-catalyzed oxidation of chromium(III) leached from the corrosion products. The experiments reported here were performed to determine the mechanism by which ruthenium catalyzes the oxidation of chromium(III) to chromium(VI) in oxygenated uranyl sulfate solutions.

Since previous work involved uranyl sulfate solutions, Run D-77 was made to determine if ruthenium would be an effective catalyst in the absence of uranyl ion. The loop was charged with 0.025 *m* H₂SO₄ containing about 100 ppm ruthenium, as the nitroso sulfate salt, and sufficient oxygen to yield a concentration of 1000 ppm at 250°C. When the loop temperature reached 250°C (about 3.5 hr) about 90% of the ruthenium had precipitated, presumably by disproportionation to the metal and dioxide. Within 40 hr the chromium concentration increased to 113 ppm indicating effective catalysis by the ruthenium. After a thorough rinsing, the loop was charged with fresh 0.025 *m* H₂SO₄ containing no added ruthenium and operated at 250° and 1000 ppm O₂. The chromium concentration again increased to a concentration of 140 ppm after 87 hr. Dissolution of the precipitated ruthenium occurred to some extent as a concentration of about 8 ppm was persistent throughout the run. Two additional runs with 0.05 *m* H₂SO₄, one 70-hr and the other 180-hr long (D-78) were made at 250°C without adding more ruthenium, and in both cases chromium(VI) concentration

increased. In the second run, D-78, the chromium(VI) concentration was nearly constant at 160 ppm after 100 hr indicating that chromium(III) was no longer being leached from oxide scale in the loop and the amount contributed by corrosion was negligible, or that the ruthenium was no longer effective in catalyzing the oxidation. To determine whether the former was true, sufficient concentrated chromic sulfate to give a concentration of 200 ppm chromium(III) in solution was pumped into the loop while in operation. The chromium(VI) concentration immediately increased and reached a value of 320 ppm within 80 hr which corresponds to oxidation of about 80% of the chromium(III) added.

To elucidate the mechanism of the catalytic activity of ruthenium, the reaction rate of the chromium(III) oxidation was studied at various temperatures and oxygen concentrations. The first of these runs was D-79 in which the loop was operated with a solution containing 0.04 m UO_2SO_4 , 0.025 m H_2SO_4 , 0.01 m $CuSO_4$, 500 ppm Cr(III) and 25 ppm ruthenium as $RuCl_3$. The ruthenium precipitated as previously mentioned. Within 8 hr of reaching the 200° operating temperature most of the added chromium(III) had also precipitated and subsequent analyses showed less than 100 ppm circulating throughout the run. Significant oxidation of the chromium(III) took place; however, the rate was slower than that at 250° as shown in Fig. 1.

Run D-80 was an observation of the reaction rate at 250° using a solution of the same composition as in the previous run. The concentration of chromium(VI) reached 780 ppm indicating that some of the precipitated chromium(III) retained in the loop from D-79 was involved in the oxidation.

The rate of oxidation at 300° was too rapid for measurement as shown by run D-81. All of the added chromium(III) had been oxidized by the time the loop reached 300°.

Fig.1. Cr(VI) Concentration vs Time .

The rate of oxidation at 150° was studied in Run D-82. As shown in Fig. 1 the rate was very slow and only 10% of the added chromium(III) was oxidized. After 70 hr of operation, 100 ppm cobalt and 25 ppm platinum were added to the loop; however, these additives had no significant effect on the oxidation.

Procedure was altered somewhat in run D-83. Solution containing all components except $\text{Cr}_2(\text{SO}_4)_3$ and RuCl_3 was added to the loop and circulated for 24 hr at the desired temperature. Sufficient chromic sulfate and catalyst were then pumped into the loop at operating temperatures and frequent sampling followed immediately. This procedure eliminated error due to oxidation of chromium(III) during the time required for the loop to reach experimental temperature. Using this procedure observation of the oxidation rate at 300° was repeated in Run D-93; however, within 15 min after adding the chromium(III) solution the chromium(VI) concentration was nearly at its maximum and a rate was not obtained.

Run D-84 was made at 280°C ; however, no ruthenium or chromic sulfate was added to the loop. Several thermocouples were tested by exposing them to the solution circulated in this run. These thermocouples were similar to those exposed in HRT in run 17 and their corrosion resistance was satisfactory. Further testing of the thermocouples was carried out in conjunction with other loop runs, so specific data are not reported here. Chromium(VI) concentration reached a maximum of 476 ppm in 144 hr indicating that appreciable quantities of Cr_2O_3 had been retained by the loop from previous runs.

Runs D-85 through D-88 were determinations of the rate of oxidation of chromium(III) at various temperatures from 225° to 280° . In each case the procedure was to add chromic sulfate and ruthenium chloride after the loop reached operating temperature. Figure 2 shows results of these runs as

Fig. 2. Ruthenium Catalyzed Oxidation of Cr(III) to Cr(VI) in $0.04m$ UO_2SO_4 + $0.025m$ H_2SO_4 + $0.03m$ $CuSO_4$.

4-7

chromium(VI) concentration vs time. The chromium(VI) concentration is plotted as $Cr_t - C_0$ where Cr_t is the concentration at a given time and C_0 is the concentration present when chromic sulfate was added to the loop. These results clearly show the dependence of the rate of oxidation on temperature and oxygen concentration. A plot of $d Cr(VI)/d t$ vs $1/Cr(VI)$ yields straight lines for the various runs as shown in Fig. 3. This result indicates that desorption of chromium(VI) from the catalytic site is a rate-determining step of the reaction mechanism. If the slopes of the curves in Fig. 3 are divided by the oxygen concentration to the $3/2$ power and the resulting reaction rate constants (k) plotted as $\log k$ vs reciprocal of the absolute temperature, a straight-line relationship is obtained as shown in Fig. 4. The activation energy calculated from this slope is 19 kcal. per mole.

The limiting slope for plots of Cr(VI) concentration vs time should be proportional to the corrosion rate in an out-of-pile system. When all added chromium(III) has been oxidized, the only source is chromium(III) formed by dissolution of the steel itself plus that formed by reduction of chromium(VI) by ferrous ions.⁽⁴⁾ This system can be represented by a diagram as shown in Fig. 5. Assuming that reaction (2) is fast and corrosion is slow, then reaction (3) is negligible and the final rate of increase of Cr(VI) is simply equal to the rate of contribution of Cr(III) to the solution by corrosion. A comparison of the final slope of two runs in Fig. 2 and the slopes calculated from corrosion data based on nickel analyses are given in Table I. Since the slopes calculated from nickel concentrations are smaller than the observed slopes for increase in chromium(VI) it is assumed that chromium was still being leached from the oxide scale on the loop walls.

Fig.3. Rate of Chromium (VI) Production vs. Reciprocal of Chromium (VI) Concentration.

Fig. 4. Reaction Rate Constant vs. Reciprocal Absolute Temperatures for the Ruthenium Catalyzed Oxidation of Chromium (III).

Figure 5

Table I

<u>Conditions</u>	<u>d Cr(VI)/dt (ppm/hr)</u>	
	<u>Observed</u>	<u>Calculated from Ni</u>
250°, 1500 ppm O ₂	3.2	1.7
275°, 270 ppm O ₂	1.0	0.6

Runs D-89 and D-90 employed a chromous sulfate descaling solution for cleaning the loop. This method of scale removal has been described previously. (5)

In run D-91 a descaling method involving sulfuric acid with hydrogen pressurization was tried. Results of many experiments have shown that the high-temperature corrosion of stainless steel results in the formation of a refractory scale consisting of a mixture of Fe₂O₃ and Cr₂O₃. The nickel formed by corrosion remains in solution and analysis for this ion can provide a means of determining the rate of attack. The purpose of the sulfuric

acid-hydrogen treatment was to reduce the Fe(III) in the oxide scale and thereby form soluble Fe(II) salts according to the following reaction:

Hot sulfuric acid under reducing conditions is very aggressive toward stainless steel, however, and it was desirable to operate Run D-91 for a sufficient period of time so that a large quantity of scale might be dissolved; yet, the steel itself would remain unharmed. Circulation of 0.75 m H_2SO_4 for four hours at 85°C resulted in removal of a large amount of Fe_2O_3 from the loop based on analyses of the solution for iron. It was difficult to estimate the total quantity of scale removed by this method as a considerable amount was removed in the form of finely divided solids. There was, however, 2.64 g/l iron and 0.05 g/l nickel dissolved in the acid when the loop was drained. Since the ratio of iron to nickel in stainless steel is about 7:1, less than 13% of the dissolved iron was produced by corrosion.

The next experiment, run D-92, was a repeat of D-77; however, no ruthenium was added. This was done to determine if the descaling method had been effective in removing precipitated ruthenium from the loop. The presence of ruthenium would presumably be shown by a build-up of chromium(VI) in solution during the run. After operation for 9 hr at 250° and 600 ppm O_2 , analysis of the solution indicated 15 ppm chromium(III) and no detectable chromium(VI); ruthenium concentration reached a value of 24 ppm although none had been added. Nickel concentration was 160 ppm after only 9 hr indicating a fairly high loop corrosion rate. It is likely that the small amount of chromium(VI) which could have been produced was reduced by ferrous ion and thus none was detected.

Early termination of run D-92 was caused by a massive leak through the pump intake line where the line passed through a cooling-water box. Metallographic examination of the failure disclosed a group of transgranular cracks around the leak and a probability that the leak was initiated as a stress-corrosion crack propagating from the outside. Cracking was also observed on areas of the pipe where leaking had not occurred; however, none of the cracks observed appeared to have initiated from the inside. This condition is to be expected where intermittent wetting of the pipe occurs and deposits from the water are allowed to accumulate. Analysis of the scale on the outside of the pipe showed 250 ppm chloride to be present. This is the first instance of failure observed in a straight section of pipe cooled in this fashion.

Run D-93 was made to determine the rate of chromium(III) oxidation at 250° in the absence of ruthenium; however, results indicate that some ruthenium remained and retained catalytic activity as shown in Fig. 2. The descaling operations had apparently altered the nature of the catalyst somewhat since a plot of $d\text{Cr(VI)}/dt$ vs $1/\text{Cr(VI)}$ had a much lower slope than was expected from previous runs.

These experiments show that small quantities of ruthenium effectively catalyze the oxidation of Cr(III). It is likely that this method can be used to maintain Cr(VI) concentrations at a corrosion-inhibiting level under conditions where Cr(VI) is constantly consumed. The rates of oxidation of chromium(III) to chromium(VI) depends on the temperature, oxygen concentration, and catalyst surface area. In-pile studies of the reaction are necessary before the value of ruthenium in reactor systems can be ascertained.

REFERENCES

1. J. C. Griess et al., Quar. Rep. of the Solution Corrosion Group for the Period Ending July 31, 1958, ORNL CF-58-7-132.
2. J. C. Griess et al., Quar. Rep. of the Solution Corrosion Group for the Period Ending October 31, 1958, ORNL CF-58-10-95.
3. R. S. Greeley, S. R. Buxton and J. C. Griess, Summary of Run D-76; Test with Ruthenium Nitroso Sulfate in Uranyl Sulfate Solution, ORNL CF-58-6-115.
4. Brasher, D. M. and Kingsbury, A. H. "The Study of the Passivity of Metals in Inhibitor Solutions Using Radioactive Tracers. I-Neutral Chromates", Trans. Faraday Soc., 54 1214 (1958)
5. J. C. Griess et al., HRP Dynamic Corrosion Studies: Summary of Run E-57: Descaling Loop E with Chromous Sulfate Solution. ORNL CF-56-2-134

DISTRIBUTION

1. HRP Director's Office
2. S. E. Beall
3. E. G. Bohlmann
4. S. E. Bolt
5. E. L. Compere
6. R. J. Davis
7. D. E. Ferguson
8. R. S. Greeley
9. J. C. Griess
10. G. H. Jenks
11. R. N. Lyon
12. H. F. McDuffie
13. H. C. Savage
14. M. D. Silverman
15. M. J. Skinner
16. E. S. Snavelly
17. R. E. Wacker
18. C. E. Winters
- 19-20. Central Research Library
- 21-22. Laboratory Records
23. ORNL RC
- 24-26. REED Library
27. Document Reference Section
28. J. L. English

DO NOT PHOTOSTAT