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INVESTIGATION OF CATALYTIC RECOMBINATION OF RADIOLYTIC OXYGEN AND HYDROGEN

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Quarterly Report

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OF RADIOLYTIC OXYGEN AND HYDROGEN

October - December 1964

Prepared by:

C. Thomas Sawyer

F. M. Stern

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2	THE EFFECT OF EXTENDED OPERATION ON CATALYST EFFICIENCY

I. SUMMARY

The long-term endurance testing of catalysts has now been in progress for five months. During this time, Catalysts "D", "E", and "F" were tested in a parallel flow arrangement that was described in an earlier report* and the above sample of Catalyst "E", a new sample of the same catalyst, and Catalysts "C" and "G" were tested in a series flow arrangement. A flow diagram of this arrangement is shown by Figure 1. This endurance testing is continuing.

Catalyst "E" was tested in the parallel flow arrangement for 73-1/2 days without detectable loss of activity. Catalysts "D" and "F" were replaced after 38-1/2 days due to poisoning by sodium chloride collection. New samples were tested for 35 days with reduced chloride injection and showed no significant loss of activity.

Since Catalyst "E" was found to be less susceptible to salt poisoning, its endurance was further tested by placing it in series with new samples of Catalysts "E", "C", and "G". Individual efficiency checks after 14 and 30 days of operation showed that the old sample of Catalyst "E" had a loss in efficiency of $2\% \pm 0.5\%$. No such loss was observed in the other catalysts.

Previous corrosion tests had indicated that a recombiner can be used to inhibit or reduce chloride stress corrosion. During this reporting period, an effort was made to determine the effect of recombiners on intergranular corrosion.

* Investigation of Catalytic Recombination of Radiolytic Oxygen and Hydrogen, Quarterly Progress Report No. 4, July-September 1964, USAEC Report CEND-508, Combustion Engineering, Inc., October 10, 1964

This effort was not conclusive since there was no evidence of any intergranular corrosion for specimens located either upstream or downstream of the recombiner bed. This test was performed on the same type of specimens used in previous tests with the exception that these specimens were sensitized at a temperature of 1200°F for periods ranging from 2 to 6 hours. During this series of tests, the steam at the specimen locations was maintained at 800°F. Two weeks of testing with 2 ppm chlorides injected produced no evidence of intergranular corrosion.

Fourteen days of operation at 800°F, 835 psig, and 775 lb/hr without any injected chlorides produced no intergranular cracks or attack. A power plant failure which caused a loss of steam in the test loop exposed these specimens to unknown moisture and high oxygen and hydrogen concentrations. This caused some transgranular cracks in several specimens and therefore these specimens were discarded and new ones prepared in the same manner. Sixteen days of exposure of these specimens to the same conditions as above produced no intergranular corrosion. The effort to obtain intergranular corrosion is continuing.

II. ENDURANCE TESTING OF CATALYSTS

The endurance testing of catalysts is accomplished by taking 835-900 psig power plant steam, superheating it to the desired temperature, adding metered hydrogen and oxygen, passing the steam over the catalysts and monitoring the effluent for the remaining free oxygen. Catalysts "D", "E", and "F" were long-term tested in a parallel flow arrangement that was described in an earlier report.* The above sample of Catalyst "E", a new sample of Catalyst "E", Catalyst "C", and Catalyst "G" are being endurance tested in a series arrangement. A flow diagram of this arrangement is shown by Fig. 1.

For the parallel arrangement tests, 60 lb/hr of steam was passed through each of the catalysts. Several conditions existed in the catalyst beds during these tests. First, 900 psig steam, superheated 10-20°F, was used with and without 2 ppm chlorides. The chlorides were injected into the steam for corrosion tests. The second condition consisted of 860 psig steam at 825°F with 1.8 ppm chlorides. During all operations, hydrogen and oxygen were metered into the test loop to provide an oxygen concentration of 24-26 ppm with 10% excess hydrogen at the bed inlet. The effluent oxygen concentration for all tests using the parallel arrangement of the catalysts is shown by Fig. 2.

Catalyst "E" was endurance tested in the parallel arrangement 73-1/2 days without detectable loss of activity. Catalysts "D" and "F" were replaced after 38-1/2 days due to poisoning by sodium chloride collection. New samples were

* Investigation of Catalytic Recombination of Radiolytic Oxygen and Hydrogen, Quarterly Progress Report No. 4, July-September 1964, USAEC Report CEND-508, Combustion Engineering, Inc., October 10, 1964

II. ENDURANCE TESTING OF CATALYSTS

The endurance testing of catalysts is accomplished by taking 835-900 psig power plant steam, superheating it to the desired temperature, adding metered

tested for 35 days without significant loss of activity. It is noted that Catalyst "E" is less susceptible to poisoning due to the accumulation of sodium chloride and other solids.

Previous tests* have shown that operation of the catalysts with injection of appreciable quantities of sodium chloride leads to poisoning of the catalysts. In order not to confuse the endurance testing presently in progress, which is the major objective of the program, the injection of chlorides was discontinued at the end of October. To remove the chlorides which had been deposited in the various parts of the loop during previous tests, the loop was flushed for 2-1/2 days with approximately 500 lb/hr of wet steam. This flushing removed appreciable quantities of chlorides, but the effluent chloride content remained at 0.6 ppm at a flow rate of 775 lb/hr.

Endurance testing of the catalysts was continued by placing a sample of Catalyst "E" which had been tested previously for 73-1/2 days, a new sample of Catalyst "E", a new sample of Catalyst "C", and a new sample of Catalyst "G" in a series in the 2.91-inch I.D. catalyst vessel. The detail arrangement and a schematic flow diagram are shown by Fig. 1. Superheated steam at 800°F and 835 psig was passed through the catalysts at a rate of 775 lb/hr. The bed inlet oxygen concentration was 24 to 26 ppm and the hydrogen concentration was in slight excess of the stoichiometric ratio. After two weeks of operation in this manner, an explosion occurred in the Florida Power Corporation's Bayboro Plant which caused a loop shutdown for a week and a half.

* Investigation of Catalytic Recombination of Radiolytic Oxygen and Hydrogen, Quaterly Progress Report No. 4, July-September 1964, USAEC Report CEND-508, Combustion Engineering, Inc., October 10, 1964

Before operation was resumed, the individual efficiencies of the catalysts were checked. The efficiencies after 14 days of operation with the catalysts in series are given in Table I. The loop was operated under the same conditions for an additional 16 days. A second check of the individual efficiencies was made after a total of 30 days of series operation, and the results are given in Table II.

Table I EFFICIENCY CHECK OF CATALYSTS

<u>Catalyst sample</u>	<u>Time tested (days)</u>	<u>Bed effluent (ppm O₂)</u>		<u>Efficiency*</u> <u>(%)</u>	<u>Loss of efficiency</u> <u>(%)</u>
		<u>Meter</u>	<u>Titration</u>		
Control E	0	2.3	1.7	93.2	--
E #1 position**	88	2.4	2.25	91.0	2
E #2 position	14	2.15	1.47	94.0	0
Control C	0	0.34	0.25	99.0	--
C #3 position	14	0.5	0.31	98.8	0
Control G	(none tested)				
G #4 position	14	0.8	0.55	97.8	0

* Based on Titration

** Upstream or top position of catalyst in bed

Table II EFFICIENCY CHECK OF CATALYSTS

<u>Catalyst sample</u>	<u>Time tested (days)</u>	<u>Bed effluent (ppm O₂) Meter</u>	<u>Efficiency* (%)</u>	<u>Loss of efficiency (%)</u>	
Control E	0	1.7	1.3	94.8	--
E #1 position**	104	2.4	1.95	92.0	2
E #2 position	30	1.7	1.33	94.7	0
Control C	0	0.4	0.2	99.2	--
C #3 position	30	0.85	0.41	98.5	0
Control G	(none tested)				
G #4 position	30	0.95	0.58	97.6	0

* Based on Titration

** Upstream or top position of catalyst in bed

III. CORROSION TESTS

A. With Sodium Chloride Injections

Because the use of the catalytic recombiner was successful in inhibiting chloride stress corrosion, tests were conducted to investigate the effect of oxygen on intergranular corrosion. For these tests, stressed and sensitized Type 304 stainless-steel specimens were exposed to 800°F, 860 psig steam. Two weeks of testing produced no intergranular cracks or attack in specimens located either upstream or downstream of the catalyst bed.

One half of the specimens was sheared from a 0.028-in. thick sheet of Type 304 stainless steel and sanded slightly. The other half was sawed from a 0.063-in. thick sheet of Type 304 stainless steel and similarly sanded slightly. The thin specimens were sensitized by heating for 6 hours at 1200°F and air cooling. The thick specimens were heat treated for 2 hours at 1200°F and air cooled. The as-received and heat-treated samples were examined under the microscope after etching in a 10% oxalic solution and in a 10% nitric plus 4% hydrofluoric solution to confirm carbide precipitation at the grain boundaries. Considerable twinning was present in the thin specimens. The carbon content of the thin specimens is not known, while that of the thick specimens was 0.06%.

The 1/4-in. wide and 4-in. long specimens were formed into U-bends such that their ends were 3/8-in. apart. Five thin and five thick specimens were placed in upstream and downstream positions from the catalyst bed and exposed

to 180 lb/hr of 800°F steam at 860 psig. The upstream specimens were exposed to steam containing 1.8-2.0 ppm chlorides, 24-26 ppm oxygen, and an excess of hydrogen. The chlorides were injected into the loop in the form of an aqueous solution of sodium chloride. The downstream specimens were exposed to 0.4-0.6 ppm chlorides and 10-130 ppb (parts per billion) oxygen. The catalyst bed collected approximately two-thirds of the chlorides.

Examination of both sets of specimens at the end of one and two weeks of testing showed no intergranular cracking or corrosion. The specimens were examined under a stereomicroscope and one specimen from each set was examined metallurgically. The upstream specimens were much darker in appearance and covered with a salt deposit.

B. Without Sodium Chloride Injections

Since the results of the long-term endurance testing of the catalysts were confused by the injections of sodium chloride, they were stopped at the beginning of the long-term testing of Catalysts "C" and "G". The effort was continued to determine the effect of a recombiner on intergranular corrosion with similar conditions of temperature and pressure, but with only residual chlorides.

In the upstream corrosion position, there were three thick (0.063 in.) sawed specimens and three thin (0.028 in.) sheared specimens that had been exposed in the above test and were coated with the NaCl. Four new specimens were sawed from a Type 304 stainless-steel sheet, 0.063 in. thick and sensitized by heating at 1200°F for two hours. Downstream there were six

specimens that had been used in the above two-week test, but downstream of the catalyst bed. Four new specimens, prepared as the four above, were also placed downstream of the catalyst bed.

An examination after two weeks of operation showed that there was no intergranular corrosion or attack, but the rate of general corrosion upstream was greater. Metallurgical examination of three, four-week exposure specimens from each position determined that there were no cracks on the upstream ones but several transgranular cracks on two of the downstream specimens were noted. This is believed to be due to the unusual nature of the power plant failure shutdown. It should be noted that the specimens were exposed for one day to unknown moisture and to very high hydrogen and oxygen concentrations. There is no known explanation as to why no cracks were found upstream.

The above specimens were discarded because of the exposure to moisture and high oxygen and hydrogen concentrations. New specimens were prepared from Type 304 stainless steel. Five thick and five thin specimens were placed in each position. These specimens were sensitized by heating at 1200°F for two hours. Exposure to 800°F, 840 psig steam at a flow of 775 lb/hr for 16 days produced no cracks upstream (25 ppm oxygen) or downstream (5 ppb oxygen). An analysis of the effluent steam is given by Table III. The effort to obtain intergranular corrosion data is continuing.

Table III ANALYSIS OF LOOP EFFLUENT

Silica	ppb SiO_2	100
Iron	ppb Fe	27
M. O. Alkalinity	ppm CaCO_3	4.5
Total Hardness	ppm CaCO_3	0.0
Sulfates	ppm CaCO_3	0.52
Chlorides	ppm CaCO_3	0.21
Nitrates	ppm CaCO_3	Trace
Hydrogen Sulfide	ppm H_2S	0.0
Chlorine	ppm Cl_2	0.0
Morpholine	ppm $\text{C}_4\text{H}_9\text{NO}$	0.35
Total Solids	ppm	1.20

IV. FUTURE TESTS

The long-term endurance testing of Catalysts "C", "E", and "G" is continuing. Also, the effort to obtain intergranular corrosion data is continuing. The loop is operating with 775 lb/hr of 800°F, 840 psig steam with periodic checks of the individual efficiencies of the catalysts.

Fig. 1 Flow Diagram for Endurance Testing with the Catalysts in a Series Arrangement

Fig. 2 The Effect of Extended Operation on Catalyst Efficiency