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INVESTIGATION OF CATALYTIC RECOMBINATION
OF RADIOLYTIC OXYGEN AND HYDROGEN

FINAL REPORT

March 1, 1965

Prepared for

The United States Atomic Energy Commission
and
The European Atomic Energy Community (Euratom)

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OF RADIOLYTIC OXYGEN AND HYDROGEN

Prepared by:

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Contract No. AT-(40-1)-3151

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I. INTRODUCTION

The presence of radiolytic oxygen in steam produced in a boiling water reactor represents a major deterrent to the superheating of this steam in either a nuclear or a conventional fossil-fired superheater. The possibility that radiolytic oxygen would aggravate corrosion problems to some degree has always been recognized. However, not until certain nuclear superheater experiments¹ resulted in failure of stainless steel cladding due to chloride stress corrosion was the extreme gravity of the situation fully appreciated. It now appears that boiling nuclear superheat reactors will require special cladding materials, a very low chloride content in the boiler water, thorough drying of steam prior to entry into the superheater, or reduction of the oxygen content of the steam to a level comparable to that existing in conventional fossil-fired superheaters.

The origin of radiolytic oxygen and hydrogen is from dissociation of water molecules. Decomposition of water into hydrogen and oxygen is due to high-energy radiation as the coolant flows through the reactor core or resides as moderator in the high flux region. While the detailed process of this breakdown is not completely understood, it is known that several conditions affect both the dissociation and recombination rates and, hence, the net rate of free gas production. These conditions include water chemistry, type and intensity of the radiation, operating pressures and temperatures, power levels and possibly core materials. Plots of radiolytic oxygen production in three different boiling reactors operating at four different pressures and temperatures are shown by Fig. 1.² Direct-cycle boiling reactors operating in the 600 to 1,000 psig range, with high-purity water coolant and moderator, normally

produce steam which contains 15-30 ppm (parts per million by weight) of oxygen and a stoichiometric amount of hydrogen. Only a fraction of one ppm of oxygen is produced in the superheating elements because of the short residence time of the steam in the high-flux region.

There are several reasons for the removal of water decomposition gases from boiling and especially boiling-superheating reactor systems. The removal of these gases will reduce corrosion rates in general and alleviate stress and intergranular corrosion problems in particular. It is generally agreed, and operating experience in conventional steam power plants dictates, that the oxygen content of steam should be maintained in the ppb (parts per billion by weight) range. In addition, internal recombination of decomposition gases would result in a considerable reduction in plant capital cost since the reactor off-gas systems could be reduced in size and complexity. Not only is the amount of radioactive off-gases reduced, but also the hazard of an explosive concentration of hydrogen and oxygen in the off-gas system is eliminated.

The experiments described herein were aimed at demonstrating the feasibility of catalytic recombination of radiolytic hydrogen and oxygen, and also at demonstrating that they can be used for extended periods without replacement. Enough data were obtained on each catalyst to allow the reactor designer to incorporate a recombiner in his design. Simultaneous corrosion tests were conducted to illustrate the benefits of the use of an internal recombiner in a reactor system.

Approval to conduct these tests under joint U.S.-EURATOM sponsorship was given on October 22, 1963. The test loop operation was initiated on November 12, 1963 in a test loop situated in and using steam obtained from the Bayboro Plant

of the Florida Power Corporation, St. Petersburg, Florida. The tests were completed in February, 1965.

II. SUMMARY

The main purpose of the program was to experimentally investigate the feasibility of reducing the radiolytic hydrogen and oxygen content of boiling water reactor steam by catalytic recombination. Initially, the efficiencies of commercial catalysts for the recombination of hydrogen and oxygen were determined under various temperatures, catalyst bed volumes, and steam flows with 25-30 ppm of oxygen in the bed inlet steam and a slightly above stoichiometric hydrogen concentration. Later, the long-term integrity of the catalysts and effects of such recombination on the reduction of corrosion were investigated.

The test program was divided into two phases. Phase I included determining the feasibility of the recombination of radiolytic gases and obtaining experimental data on the efficiency of commercially available catalysts under various conditions. Phase II, which was to be initiated only if Phase I was reasonably successful, was to determine the long-term endurance of a catalytic recombiner for use in a reactor system and also the benefits gained toward prevention of corrosion of reactor components when such recombiners are used.

A schematic flow diagram of the test loop for the Phase I tests is shown by Fig. 2. In general, the same testing procedure was used to obtain efficiency data for all catalysts. The desired amount of catalyst was placed in the catalyst vessel, the desired steam flow and temperature were obtained, metered hydrogen and oxygen were added to give a bed inlet concentration of 24-26 ppm oxygen and 5% excess hydrogen, and the catalyst effluent was monitored for the remaining free oxygen.

Nine commercially available catalysts were obtained and tested. These catalysts fall into what may be described as either the platinized metal group or the platinized alumina group. When possible, data were taken for all combinations of three steam temperatures, three steam flow rates, and two or three bed depths for each catalyst. Temperatures ranged between 500 and 900°F, mass velocities between 5000 and 18,000 lb/hr-ft², and bed depths between zero and 24 in. The resultant collection of data enabled the development of performance equations for most of these catalysts. Such equations not only allow reasonably accurate quantitative estimates of the promotional properties for each respective catalyst but also assist in an understanding of factors which affect these properties. It has been found that for all catalysts except the block type, labeled Catalyst "G", the reduction in gas concentration (O) versus bed depth (X) can be defined by the relationship:

$$-\frac{dO}{dX} = (A_r T^a W^b P^c) (O_x)$$

where:

A_r , a , b , and c = constants for a given catalyst

O_x = concentration of either hydrogen or oxygen at bed depth "X"

T = absolute temperature

W = steam flow rate for a given bed face area

P = absolute pressure of system.

For a given catalyst and a specific set of conditions, the term $(A_r T^a W^b P^c)$ is a constant and the relationship:

$$-\frac{dO}{dX} = A O_x$$

is satisfactorily descriptive. Each equation shows that the local reaction rate is proportional to the local gas concentrations. The first equation allows for the inclusion of specific flow rates, temperatures, and pressures. The value of the exponent for a certain condition provides some insight as to the limiting step(s) in the H_2-O_2 reaction when a given catalyst is considered. For example, the controlling mechanism for Catalyst "C" is believed to be the oxygen diffusion to the catalyst surface. The magnitude of exponent "a" has been found to range between + 1.5 and + 6.8; that of "b" between - 0.40 and - 0.87; and that of "c" approximately equal to that of "b" except opposite in sign.

All test data taken during Phase I indicate that:

1. Either of the catalysts described herein could be used to reduce radiolytic oxygen and hydrogen concentrations in reactor steam by large factors, however Catalyst "C" would be the most effective for an internal reactor application because of its physical characteristics.
2. Only a small amount of catalytic activity exists under wet steam conditions. However, no specific amount of steam superheat is required to obtain significant activity, only dryness.
3. The efficiency of each catalyst increases with increased temperatures.
4. The efficiency of each catalyst decreases with increased steam velocities.
5. Pressure variations between 415 and 1000 psia affect the reaction rate only indirectly because of changes in the steam velocity at a given flow rate.
6. There is no theoretical limit to the possible gas concentration reductions. A reduction to the parts per billion range is certainly feasible.

The test loop which had been used for Phase I work was altered for use in the Phase II program. Generally, the loop was altered such that sodium chloride solutions could be added to the steam upstream of the hydrogen and oxygen injection points. Also, provisions were made for exposing corrosion specimens immediately upstream and downstream of the catalyst bed. A schematic flow diagram of the loop used for Phase II tests is shown in Fig. 81. One platinized alumina catalyst was tested semicontinuously (bimonthly shutdown for efficiency checks) for seven months. Three platinized alumina and the mesh-type, platinized stainless steel ribbon catalysts were tested semicontinuously for various periods up to three and one-half months. These tests showed that large amounts of sodium chloride (and possibly other solids) in the 2-4 ppm range would poison the catalysts within a week by collecting on the surface. It was found that for two of the alumina catalysts there was some permanent poisoning, while for one, removal of the chloride deposits completely restored its activity. The permanent poisoning was believed to be due to the greater porosity of the surface of the poisoned catalysts. There was no loss or only minor loss of catalytic efficiency during the long-term endurance testing. Based on these results, it is believed that recombiners can be used in high-purity reactor steam for at least one year before the catalyst must be replaced.

Simultaneously with the endurance tests, corrosion tests were conducted to demonstrate the benefits of the use of a recombiner. The use of a recombiner has been shown to have these beneficial results:

1. Greatly reduces the rate of general corrosion
2. Greatly reduces the speed, severity, and amount of chloride stress corrosion

3. Possibly inhibits intergranular corrosion (See page 75).

It is concluded that not only is it feasible to use a catalytic recombiner to essentially eliminate the radiolytic hydrogen and oxygen in a reactor for extended periods, but that the use of a recombiner will be very beneficial in reducing the corrosion and failures of components. Indeed, the use of a recombiner may allow a return to the use of stainless steel as fuel cladding for superheaters instead of the expensive high nickel alloys. However, more data are needed before such a conclusion can be drawn. Enough data were obtained for six catalysts to allow reactor designers to incorporate a recombiner in their systems. While the platinized alumina catalysts were generally more efficient, it is believed that the platinized metal type and the block type will be best suited for most internal reactor applications because of their physical characteristics.

III. CATALYTIC EFFICIENCY TESTS

A. Description of Experimental Equipment and Procedures

A flow diagram and schematic drawing of the test loop is shown in Fig. 2. Referring to Fig. 2, the loop allowed the taking of wet and/or superheated steam from a power plant system; reducing the moisture content (if any) by mechanical means; accomplishing further drying by electric heaters; adding the metered hydrogen and oxygen to the steam at separate points; adding the desired amount of superheat to the gases and steam by using either a steam-heated preheater or additional electrical cartridge heaters; passing the steam and gases over the catalyst; condensing the catalyst bed effluent; and monitoring the condensate for free oxygen. Mixtures of superheated and wet steam could be used to obtain intermediate amounts of superheat in steam entering the loop. The catalyst bed could be bypassed when desired.

Generally, all piping and vessel materials were low alloy, 1-1/4 Cr, 1/2 Mo steel. The catalyst reactor was made from a 3 in. Schedule 80 pipe. Its over-all length was 42 in. and it would accommodate bed depths as large as 28 in. The catalyst was supported by a 1/4 in. x 1/4 in. ring which was welded to the inner vessel wall, a perforated plate which rests on this ring, and several layers of fine screen. As data from initial tests with 5 to 10⁰F of superheat indicated that condensation and rundown were occurring in the upper part of the reactor because of the large heat loss through the 3 in. flanges, a 750-watt ring heater was installed on the outside of the cover flange. Use of this external heater alleviated problems associated with moisture from this intermittent source.

The two gases were taken from commercial cylinders and metered into the steam loop from systems whose pressures were greater than the loop pressure, which was between 750 and 900 psia. The gas meters used were made by the Hastings-Raydist Corporation and are the lowest flow capacity meters for high-pressure gases presently known. The primary element consists of heated capillary tubes whose inlet and outlet temperatures are monitored with very small thermocouples. The thermocouple output is monitored, referenced, amplified, and indicated on a meter. A zero to 5.0 mv signal is produced for recording the gas flow rates. These meters are believed to be extremely accurate and reliable.

Problems were experienced concerning injection of the gases into the loop at uniform rates and in preventing gas leakage from the injection systems at the 1000-1100 psi operating pressure. Use of extreme care during construction was necessary to avoid gas losses. Losses were not tolerated because small losses would produce large errors in the experimental results. Also, careful checks were made of the calibration of the flowmeters to assure that the gas flow rates were accurately known. The results of one such calibration check are shown in Figs. 3 and 4.

Preliminary tests indicated that the gas injection rates were not uniform with time. This problem was reduced to tolerable limits by changing the last few feet of tubing before the loop injection points from 1/4 in. OD stainless steel tubing to 1/16-in. OD capillary tubing and throttling the gases just before they entered the capillary tubing. The possibility of a leakage problem was essentially eliminated by moving the hydrogen and oxygen transducers closer to the injection points. Also, by having the

transducers closer to the injection points, a non-uniform injection rate could be detected.

A Beckman Model-778 dissolved oxygen analyzer was used for determination of the oxygen content of the loop effluent. This analyzer has ranges of 0-2.5, 0-10.0, and 0-40.0 ppm, and a signal output of 0-50 mv for continuous recording of effluent concentrations. When catalyst bed outlet concentrations below 0.1 ppm were attained, the concentration was determined by taking grab samples and then using an ASTM-approved laboratory procedure (ASTM Designation D-888-49T Method B) for the oxygen analysis. This method was also used as a check on the oxygen analyzer.

The procedure used during testing of the catalysts was as follows:

1. The catalyst reactor was filled to the desired depth with a specific catalyst.
2. A preset steam flow rate through the loop was obtained using the catalyst bed bypass.
3. The desired degree of steam superheat was obtained by use of electric heaters, the steam-heated preheater, or by mixing saturated and superheated steam.
4. Oxygen was injected at a rate calculated to give an oxygen concentration of 24-26 ppm in steam being passed through the loop. The loop effluent was monitored to ascertain that the expected concentration was being obtained.
5. A stoichiometric amount plus 5% excess hydrogen was injected.
6. Time was allowed for a state of equilibrium to be reached, then the gas-laden steam was passed through the catalyst bed.

7. The dissolved oxygen concentration in the loop effluent was monitored for approximately one hour.
8. Occasionally the hydrogen injection was stopped or the catalyst bed bypassed as a check on the experimental procedure.
9. Miscellaneous condition changes such as steam flow rate, degree of superheat, hydrogen input, etc., were investigated.

In general, all combinations of three steam flows and three temperatures for two or three bed depths were investigated for each catalyst. Temperatures ranged between 500 and 900°F, mass velocities between 5000 and 18,000 lb/hr-ft², and bed depths between zero and 24 in.

Due to the extremely small quantities of hydrogen and oxygen being recombined, only highly active catalysts could be used. Twenty-one potential suppliers, both domestic and foreign, were contacted and asked to submit what in their opinion was their best catalyst for this application. Due to the lack of data for this application there may be catalysts available which are better than the ones tested; however, a complete survey of the catalyst suppliers was made. Six of these companies submitted nine catalysts for testing. The catalytic material for most catalysts was platinum supported by either aluminum oxide or stainless steel ribbon. The catalysts were arbitrarily labeled as "A", "B", etc. for reporting purposes. A list of catalyst suppliers and other contributors to the program is given in the Appendix.

B. Tests Performed on Catalysts "A" and "B"

Catalysts "A" and "B" were not tested extensively because initial test data indicated that smaller diameter particles of the former and larger

diameter particles of the latter were needed. Catalyst "A" had a spherical form with diameters ranging between $3/32$ and $9/32$ in. Test data showed that large volumes of this catalyst would be required to give a substantial reduction in the hydrogen and oxygen content of the steam. For example, with 380°F of superheat and a steam flow rate of 500 lb/hr, a 24-in. deep bed of Catalyst "A" had a combination efficiency of 98%. The catalytic activity of this catalyst was not sufficient for this application and further testing was terminated. However, smaller diameter particles of this catalyst were obtained for later tests. The testing of bed depths of 12, 6, and 3 in. of Catalyst "B" produced no quantitative data because greater than 99.5% of the gases were removed by each bed depth. Therefore, particle diameters larger than the $1/16$ in. diameter of this catalyst were obtained for later tests.

C. Tests Performed on Catalyst "C"

1. Description of Catalyst "C"

The material labeled Catalyst "C" consisted of platinized stainless steel ribbon which had been formed into compact "mats." While the chemical composition and geometry of the support ribbon could be varied almost at will, properties of the material used in these tests were selected to give a large surface area-to-bed volume ratio, yet not be fine to the point that breakage and loss would occur. Using these criteria, a ribbon size of $0.005(t)$ by $0.063(w)$ in. was used in all of the tests described below. The exact lengths of the ribbon sections are not known, but they were at least as long as several inches, if not several feet. This ribbon was compacted into 2.91-in. diameter by about 1.5 in. deep mats which were contained in this cylindrical form by screen end covers and

interlaced small wire. This mat geometry was selected solely for test convenience. One or more mats were added to or removed from the test vessel to increase or decrease the bed depth as testing progressed. The density of the mats used was about 85 gm for a 2.91 in. diameter by 1.56 in. deep section. This resulted in about 1.90 ft² of apparent surface area per mat or about 320 ft² of surface per cubic foot of bed. A photograph of two such mats is shown in Figure 5. One spacer ring, which fits the vessel wall very closely and prevents bypassing of steam between the less dense outer edge of the mats and the vessel wall, is shown also.

The general physical properties of Catalyst "C" appeared to be completely acceptable for the intended application. There were no fines, the ribbon and mats were pliable, and no evidence of physical, chemical, or catalytic deterioration was noted. Where space limitations are severe, other catalysts with higher specific surface areas or greater catalytic activities may offer an advantage; however, reasonable bed sizes of this all-metal material were found to produce adequate reaction rates.

2. Discussion of Tests on Catalyst "C"

In general, the same testing procedure was used for Catalyst "C" as for "A" and "B". Each test was initiated by placing the desired amount of catalyst in the 2.91 in. ID, 28 in. deep catalyst reactor. Gas-laden steam was then passed through the catalyst bed bypass. The metered hydrogen and oxygen were added to the incoming steam at separate points upstream from the bed. The temperature or moisture content of the incoming steam was adjusted by using a moisture separator and electric heaters. Additional heat was added to this steam occasionally by a steam-heated preheater and by

additional electric heaters before the gas-laden steam was passed over the catalyst bed. The bed effluent was condensed and then monitored by using a dissolved oxygen analyzer. Mixtures of superheated and wet steam were used to obtain intermediate amounts of superheat in steam entering the test loop. A catalyst bed bypass was used during startups and while calibration checks were made on the oxygen analyzer.

Bed depths of Catalyst "C" between 3-1/4 and 12-3/4 in. were investigated while using steam flow rates between 270 and 900 lb/hr. The steam temperature and pressure ranges were 500 to 900°F and 400 to 850 psig. Gas inlet concentrations were approximately 25 ppm oxygen and usually a stoichiometric amount of hydrogen. The effects of using hydrogen input rates which were either greater or smaller than the stoichiometric ratio were observed. Also, the gas inputs were doubled occasionally and the effect noted. Several wet steam tests were made to determine the effect of moisture on catalytic activity.

There was some scatter in the first data taken for Catalyst "C" because of small loop pressure changes and a gas pocket at the oxygen injection point. The oxygen injection system was changed after the initial tests and this scatter was essentially eliminated. While small pressure and oxygen input changes still occurred when the power plant (steam source) accepted a different load, the data scatter was small after each change and the results were much more consistent than before. For this reason, the consistency of data reported in graphical form varies considerably, depending upon whether the data were produced before or after the system modification.

A typical graph of data obtained after the oxygen injection system change is shown in Fig. 6. With 500 lb/hr of steam flowing through the catalyst bed bypass, the addition of 70 ml/min (STP) of oxygen increased the condensate oxygen content to 25 ppm within 4 or 5 minutes. The injection of 140 ml/min (STP) of hydrogen resulted in an apparent decrease in the oxygen concentration of the condensate.* Later, at a time of about 50 minutes, the gas-laden steam was passed over a 12-3/4 in. deep bed of Catalyst "C" and the oxygen content of the steam was reduced to an average value of 0.2 ppm. The steam contained 60°F of superheat at this time.

Using the same conditions, the effect of varying the hydrogen flow was investigated. From time 85 minutes to 95 minutes, 20% excess hydrogen was added. This reduced the effluent oxygen concentration from an average value of 0.2 ppm to a constant value of 0.17 ppm. Reducing the hydrogen flow rate to a value which was 7% below the stoichiometric amount caused the oxygen concentration in the effluent to increase to one ppm. On the basis of these data, later data were taken while adding 5% excess hydrogen to ensure that enough hydrogen was available to overcome the remaining small fluctuations in the oxygen input rates.

The loop pressure was then reduced from about 800 psig to 400-413 psig to determine the effect of pressure on catalytic activity. The first data taken thereafter indicated an increasing effluent concentration versus time because of decreasing temperatures and because identical

* This false decrease is produced by hydrogen in excess of the soluble amount; hydrogen bubbling out of solution sweeps some of the oxygen out also. This does not occur at concentrations of only a few ppm.

ratios of gas and steam flows could not be obtained instantaneously at the new pressure. With a steam flow of 500 lb/hr, 25 ppm oxygen input, 5% excess hydrogen, and a steam temperature of 540°F, the effluent oxygen concentration was 0.73 ppm when the recombiner was operated at a pressure of 400 psig. Under almost identical conditions, except for a pressure of 800 psig, the effluent oxygen concentration had been 0.2 ppm. This increase in effluent concentration with decreasing pressures was an expected result as the steam density had been reduced by about 50%, which in turn had increased the steam velocity through the catalyst bed by 100%. To affirm these data, the mass flow rate of steam was reduced to approximately one-half the earlier value to obtain a velocity similar to the value used at 500 lb/hr and 800 psig. It can be seen that this velocity reduction produced an effluent oxygen concentration of 0.18 ppm, as compared to 0.17-0.2 ppm at 800 psig. The hydrogen input was then stopped to check the calibration of the oxygen analyzer before a reduction of the steam temperature was made. It was noted later that the effluent oxygen concentration increased rapidly after the bed inlet temperature reached the saturation value. Even though the test was terminated shortly thereafter, a significant loss in catalytic activity because of the presence of moisture was apparent.

The data shown in Fig. 7 indicate that use of a bed depth of 7-3/4 in. of Catalyst "C" resulted in a reaction between 35 and 40% of the gases in steam containing 1-2% moisture. However, it appeared that sporadic wetting of the catalyst caused the effluent oxygen concentration to occasionally rise momentarily to the input value of 25 ppm. The catalyst bed was bypassed, and later the hydrogen input stopped to confirm this degree of

reaction completion. Addition of one degree of superheat to the steam increased the degree of completion to approximately 80%;* with 50°F of superheat, the bed outlet oxygen concentration was 1 ppm for a 25 ppm input and 2.1 ppm for a 50 ppm input.

Figure 8 is a graphical illustration of the effects produced by varying steam flow rates at constant temperatures while using a 7-3/4 in. deep bed of Catalyst "C", an inlet oxygen concentration of 24 to 26 ppm oxygen, and 5% excess hydrogen. Three steam flow rates at three different temperatures were investigated during this one test. At a temperature of 550°F, a 25 ppm oxygen input was reduced by the catalyst to 1.9 ppm when the steam flow rate was 800 lb/hr, 1.2 ppm with a flow of 500 lb/hr, and 0.4 ppm with a flow of 280 lb/hr. Increasing the steam temperature to 666°F resulted in a 1.2 ppm effluent oxygen concentration with a steam flow rate of 820 lb/hr, compared to 1.9 ppm for 800 lb/hr at 550°F. At a steam temperature of 665 to 670°F, the catalyst reduced the oxygen content to 0.65 ppm when a steam flow of 518 lb/hr was used and 0.21 ppm for a flow of 285 lb/hr. Using a steam temperature of 855°F, the oxygen effluent concentration was 0.6 ppm at 761 lb/hr, 0.32 ppm at 486 lb/hr, and 0.14 ppm at 290 lb/hr.

Figures 9 and 10 illustrate some of the first data taken for Catalyst "C" and show the effect of using a 6-3/8 in. bed depth. Referring to Fig. 9, the passage of 405 lb/hr of steam superheated 375°F through the bed with input concentrations of 29 to 30 ppm oxygen and a stoichiometric

* This efficiency would have increased further with time as the catalyst was dried.

amount of hydrogen resulted in an effluent oxygen content of 0.4 ppm. Increasing the steam flow, but maintaining the same gas input rates, increased the effluent oxygen concentration to 0.6 ppm, with an input of 17.5 ppm. The bed outlet concentration was 1 ppm with a 700 lb/hr steam flow rate and a steam temperature of 890°F, compared to 0.4 ppm with a 405 lb/hr steam flow rate and a temperature of 895°F. Reducing the temperature to 836°F increased the effluent oxygen content to 1.3 ppm.

The effect of temperature changes on the efficiency of a 6-3/8 in. deep bed of Catalyst "C" is illustrated by Fig. 10. The bed outlet concentration increased from 0.5 ppm to 2 ppm as the temperature decreased from about 870°F to 515°F. As cooling progressed and moisture appeared in the steam, the activity of the catalyst declined sharply.

Figure 11 is a graphical illustration of the effectiveness of a 3-1/4 in. deep bed of Catalyst "C" for reducing the oxygen content of steam under various conditions. The initial effluent concentration peak was due to an unusually large oxygen input rate. At time equal 56 minutes, the oxygen flow was reduced to give an input concentration of 25 to 26 ppm. Later, passage of the 885°F steam through the catalyst bed at a rate of 398 lb/hr reduced the effluent oxygen concentration from 25-26 ppm to 2.8 ppm. Increasing the steam flow to 776 lb/hr while maintaining the same gas inlet concentrations resulted in a bed outlet oxygen concentration of 4.6 ppm. Decreasing the steam temperature from 885°F to 555°F increased the effluent oxygen content from 4.6 ppm to 10 ppm. Decreasing the steam flow from 776 lb/hr to 500 lb/hr, at a constant temperature of 555°F, reduced the effluent oxygen content to approximately 6 ppm. Figure 12, which is a continuation of the above graph, demonstrates the effect of reducing the temperature

from 555°F to a saturation temperature of 517°F on the catalytic activity. At the time these data were taken, it was believed that a minute amount of moisture in the steam would stop all catalytic activity. This had been found to be at least essentially true for the two catalysts tested earlier. Data taken at a later date showed that a reaction does occur even under wet steam conditions (see Fig. 7). The latter part of the effluent oxygen concentration versus time curve in this figure is therefore misleading because the bed was bypassed just before test termination.

Figures 13 and 14 illustrate tests run with a 7-3/4 in. bed depth of Catalyst "C" before the oxygen injection system modification. Referring to Fig. 13, wet steam was passed through the catalyst bed bypass and oxygen was injected to produce a 25 ppm input concentration. A stoichiometric amount of hydrogen was injected also. Passage of the gas-laden wet steam through the bed had no detectable effect, partly because of the scatter in the data due to oxygen input rate variations. Later, it can be seen that the addition of only a few degrees of superheat reduced the bed outlet oxygen concentration to approximately 2 ppm. Increasing the steam flow rate caused the bed effluent oxygen content to increase to approximately 6 ppm when 13°F of superheat was being added upstream of the bed. Returning to wet steam conditions caused an immediate rapid increase in the effluent oxygen concentration.

Figure 14 demonstrates the effectiveness of Catalyst "C" for reducing the oxygen content in steam for several different conditions and also the effect of stopping the hydrogen input. The average effluent oxygen

concentration was 1.2 ppm from time 50 to 120 minutes, 0.8 ppm from 121 to 180 minutes, 0.2 ppm from 200 to 229 minutes, and 0.4 ppm from 265 to 290 minutes. This figure should be compared with Fig. 8 for evaluation of the oxygen injection system modification.

Figure 15 demonstrates the extremely small pressure drops that occurred as the steam transversed the catalyst bed. Due to the difficulty of reading these small pressure drops on a 0 to 10 psi differential pressure gauge, the data are only accurate to within ± 0.05 psig.

3. Discussion of Test Results for Catalyst "C"

The physical characteristics as well as the catalytic activity of Catalyst "C" indicate that it could be used for most reactor applications. The above data have proven that with only a few degrees of superheat, a stoichiometric amount of hydrogen, and reasonable bed depths, the radiolytic oxygen content of steam can be reduced to almost any desired value. The major advantage of using Catalyst "C" over pellets or spheres is its ease of containment. Also, there is no danger of initial fines or the appearance of fines by cracking. Too, the pressure drop across the bed is almost negligible compared with that associated with the pellet-type catalysts. The only question concerns its susceptibility to poisoning or loss of activity after extended periods of operation. These problems were investigated during Phase II of this program.

The data obtained strongly support the applicability of the relationship:

$$C_x = C_0 e^{-AX}$$

where:

C_x = bed effluent gas concentration, any units

C_o = bed inlet gas concentration, any units

A = activity coefficient for a specific set of conditions,
i.e., for a given catalyst, steam temperature, steam
pressure, and steam flow rate

X = catalyst bed depth, any related unit.

Agreement with this relationship was obtained while varying the bed depths, the inlet gas concentrations, and using several different catalytic materials. The plots of such relationships and supporting data points for Catalyst "C" at several temperatures and flow rates are shown in Figs. 16 through 18. It is believed that this relationship will hold for gas concentrations between zero and a few per cent. More data were taken but are not shown on the referenced figures as only a small amount fell within the narrow steam temperature and flow rate ranges. It was found that increasing the bed inlet gas concentrations resulted in closely proportionate increases in bed outlet concentrations, all other conditions being held constant and stoichiometric ratios of gases being injected. It was also found that if the hydrogen input rate was sufficiently greater than the oxygen input rate (2-3%), such that oxygen input variations never resulted in an excess of oxygen being present in the bed inlet steam, the bed efficiency was not affected by an input of large excesses of hydrogen.

The reliability of the relationship described above was checked for much higher gas concentrations by plotting data obtained several years ago at ORNL.³ Raw data were simply lifted from the referenced report and plotted. The resultant plots are shown in Fig. 19. These data support the

relationship described above in that either straight-line or "drooping" plots were obtained. The droop, or increased reaction rate, was expected because the steam temperature increased as it was passed through those beds as energy released by the H_2-O_2 reaction was absorbed. If the 2 in. bed depth effluent concentration (0.3%) for the 1000 psia data is increased by the temperature relationship discussed below, assuming an effective average bed temperature of $700^{\circ}F$, a constant temperature effluent concentration of 0.5% is obtained. This "adjusted" value provides a straight-line plot for these data. No such value could be obtained experimentally, of course, as a temperature increase will unavoidably occur when gas concentrations in the per cent range are passed over catalyst beds. When concentrations in the 25 ppm (O_2) range are used, a temperature increase of only about $0.2^{\circ}F$ is seen. Therefore, during the tests performed, no detectable temperature change occurred as the bed was traversed. Examples of recombination at two different temperatures are shown for this high-concentration data. The line with the greatest slope (for C') is representative of operation at a constant temperature of 675 to $725^{\circ}F$. The other is representative of operation at 550 to $600^{\circ}F$. It has, therefore, been concluded based on the presently available information that the ratio of bed outlet and inlet gas concentrations will be constant for a given set of conditions, irrespective of the inlet concentration. This is, of course, based on the use of stoichiometric gas ratios and gas concentrations between zero and about 3 per cent.

Very early during the test program it became apparent that greater recombiner efficiencies were obtained at higher steam temperatures and that lower efficiencies were obtained when higher steam velocities were used. The large amount of data taken for Catalyst "C" enabled an analysis of such effects.

As discussed above, it was found that recombination versus bed depth, for a specific set of conditions, follows the relationship:

$$C_x = C_o e^{-AX}.$$

This general relationship was also found to hold for all other catalysts except Catalyst "G". It was also found that the coefficient "A" could be divided into terms which show the effects of temperature, pressure, and steam velocity changes. In the range of pressures used in these tests, the effect of pressure changes was apparently solely one of the affecting steam velocities. A satisfactory representation of the test data can be obtained throughout the ranges of conditions used by rewriting "A" as

$$A = A_r T^a W^b P^c,$$

where:

A_r = coefficient at an intermediate set of reference conditions

T^a = the absolute steam temperature raised to some experimentally determined power (a)

W^b = the steam flow rate raised to some experimentally determined power (b)

P^c = the steam pressure raised to the same exponent as "W", except opposite in sign.

In order to show the direct effects which result from variations in conditions, the coefficient "A" was produced as

$$A = A_r T/T_r^a (W/W_r) (P_r/P)^b,$$

where the ratios of actual temperatures, flow rates, and pressures to reference temperatures, flow rates, and pressures were raised to experimentally determined powers. It was found that "a" is positive and greater than 1.0 while "b" is negative and smaller than 1.0.

In order to determine the values of "a" for Catalyst "C", values of "A" ($A = 1/X \ln C_0/C_X$) for constant flow rates were plotted on log-log graph paper versus absolute temperatures. The value of "b" was likewise determined by plotting values of "A" for constant temperatures versus steam flow rates. Plots of the latter and former are shown in Figs. 20 and 21, respectively. It can be seen from Fig. 20 that the slopes of plots for the three different temperatures agree satisfactorily; thereby indicating that the use of a single value of "b" is permissible. When the plots in Fig. 21 were examined, it was found that each constant flow rate curve was not a straight line. However, if two of each three data points for a specific steam flow rate are adjusted by the flow change effect shown in Fig. 20 to account for velocity changes which result from temperature changes, relatively straight lines are produced. It was then possible to satisfactorily describe the performance of Catalyst "C" by the relationship

$$C_X = C_0 \exp. - (0.475) \left[T/1130 \right]^{1.50} \left[(W/500) (800/P) \right]^{-0.40} (X).$$

However, it should be understood that this equation only applies to the catalyst tested, very low gas concentrations, temperatures between 500 and 900°F, steam flow rates between 300 and 900 lb/hr (per 0.0461 ft² of bed face area), and pressures between 400 and 1000 psia.

D. Tests Performed on Catalyst "D"

1. Description of Catalyst "D"

The fourth material tested, labeled Catalyst "D", consisted of 0.5% platinum on alumina pellets. The cylindrical, extruded pellets had a uniform diameter of 5/32 in. and lengths which varied from 1/8 to 7/16 in.

The loading density was 51 lb/ft³ and the approximate surface area was listed as 165 m²/gm. The maximum volatile matter content was 2.5%. A photograph of this catalyst is shown in Fig. 22.

The initial passage of steam through a 12 in. deep bed of Catalyst "D" resulted in the release of fines which appeared temporarily as a milky substance in the bed effluent. However, once the new fines were removed, the loss apparently stopped. No detectable damage resulted from this loss. A later examination of the bed contents showed that a few fines had been produced by cracking during testing. Also, testing caused the color of the catalyst to change from a dark gray to a light gray. However, five days of testing indicated no loss of activity due to poisoning or erosion. The overall physical and chemical properties of Catalyst "D" were deemed satisfactory for combining hydrogen and oxygen under the conditions investigated.

2. Discussion of Tests on Catalyst "D"

The general test procedure began by placing the desired bed depth of catalyst in the 2.91 in. ID, 28 in. deep reactor vessel. Metered hydrogen and oxygen were added at separate points to saturated or superheated power plant steam in the test loop upstream from the bed. This steam had been conditioned by a mechanical moisture separator and electric heaters. Additional heat was added occasionally by a steam-heated preheater and by additional electric heaters before the gas-laden steam was passed over the catalyst bed. The bed effluent was condensed and then monitored by using a dissolved oxygen analyzer. Occasionally, grab-samples of the condensate were taken and analyzed in the laboratory. Mixtures of superheated and wet steam were used to obtain intermediate amounts of superheat in steam entering the

the test loop. A catalyst bed bypass was used during startups and to assist in a calibration check on the oxygen analyzer.

Bed depths of 3 and 6-1/4 in. were tested with steam temperatures of 555, 665, and 860°F at each bed depth and with steam flow rates of approximately 280, 500, and 800 lb/hr at each temperature. One test was made while using a 6-1/4 in. bed depth to determine the effect of wet steam on catalytic activity. During each test, oxygen was added to attain a concentration of 25 ppm in the inlet steam. Five per cent excess hydrogen was added to ensure that enough hydrogen was present to overcome small fluctuations in the oxygen input rates.

The data obtained for a 6-1/4 in. deep bed of Catalyst "D" are shown in Fig. 23. Referring to this figure, with 800 lb/hr of steam flowing through the catalyst bed bypass initially, the addition of 114 ml/min (STP) of oxygen at time zero increased the effluent oxygen concentration to about 27 ppm within 5 minutes. The calculated concentration was 25 ppm and the 2 ppm error was presumably due to drift in the calibration of the oxygen analyzer. The addition of 240 ml/min (STP) of hydrogen produced a false indication of a decrease in the effluent oxygen content because the hydrogen solubility of the condensate was exceeded. This effect was discussed above in Section III.

C. Passage of the 555°F gas-laden steam through the catalyst bed reduced the oxygen content of the steam to 3.8 ppm within 10 minutes. The steam flow was then reduced to 500 lb/hr, the gas input flow rates adjusted to give 25 ppm oxygen and 5% excess hydrogen, and the steam temperature was maintained at 555°F. Use of these conditions resulted in an average effluent oxygen concentration of 1.2 ppm. Reducing the steam flow rate to 277 lb/hr while maintaining the gas concentrations and the steam temperature constant resulted in an oxygen concentration at the bed outlet of 0.18 ppm. At a temperature of 670°F, the bed effluent oxygen concentration was 0.32 ppm

at 815 lb/hr, 0.1 ppm at 500 lb/hr, and approximately 0.015 ppm at 286 lb/hr. With a 775 lb/hr steam flow rate at 860°F, Catalyst "D" reduced the oxygen concentration of the steam from 25 ppm to 0.1 ppm. Reducing the steam flow rate to 510 lb/hr but maintaining the steam temperature and inlet gas concentrations constant, resulted in an effluent concentration of approximately 0.005 ppm. The effect of temperature, i. e., increasing catalytic efficiency with increasing temperature, can be determined by comparing data at approximately equal steam flow rates.

Figure 24, which was developed during testing of a 3 in. deep bed of Catalyst "D", illustrates the effect of using three different steam temperatures and three steam flow rates at each temperature. Referring to this figure, the addition of oxygen increased the effluent concentration to the calculated 25 ppm value within three minutes. The addition of hydrogen again resulted in a false indication of a drop in the effluent oxygen content. Passage of 800 lb/hr of steam which had been superheated 40°F through the catalyst bed reduced the condensate oxygen content to 9.4 ppm. Maintaining the temperature constant at 555°F and decreasing the steam flow rate to 500 and 280 lb/hr reduced the oxygen concentrations at the bed outlet to 5.8 ppm and 2.7 ppm, respectively. The scatter in these data was due to small fluctuations in the gas input rates because of loop pressure changes of ± 10 psi. At a steam temperature of 665°F, use of the same bed depth (19.95 cubic in.) of Catalyst "D" reduced the effluent oxygen concentration to 3.4 ppm at 830 lb/hr, 1.5 ppm at 510 lb/hr, and 0.48 ppm at 285 lb/hr. When the steam temperature was increased to 860°F, the same catalyst bed reduced the effluent concentration to 1.1 ppm at 778 lb/hr, 0.4 ppm at 517 lb/hr, and approximately 0.002 ppm at 291 lb/hr.

Figure 25 illustrates the effect of wet steam on the efficiency of a 6-1/4 in. deep bed of Catalyst "D". The addition of oxygen at time zero quickly increased the oxygen concentration to the calculated value of 25 ppm. Addition of hydrogen decreased the oxygen content indication, as discussed earlier. Passage of 500 lb/hr of wet steam through the catalyst bed at time equal 35 minutes possibly combined 1.5 to 7.5 ppm of oxygen. The exact value is not known as dual gas concentrations in this high range could not be determined accurately. The hydrogen input was stopped and the bed bypassed to check this indication. The data taken during the period when only oxygen was being added indicated that the oxygen analyzer calibration was low. The calibration was corrected before superheating the steam. The drying heaters were turned on at time equal 95 minutes and within 10 minutes the steam temperature had increased to 555°F. Attainment of this temperature (35°F of superheat) increased the efficiency of the catalyst such that the effluent oxygen concentration was reduced from 18 ppm to 1.2 ppm within 10 minutes. It should be noted that the 1.2 ppm is the same result shown in Fig. 23 when a similar set of conditions were used. At time equal 165 minutes, all heaters were turned off. Three minutes later the steam temperature had reached its saturation value. The effluent oxygen concentration then increased rapidly, as did the steam moisture content. Bypassing the catalyst bed and stopping the hydrogen input indicated 3 or 4 ppm of oxygen combination had been accomplished under wet steam conditions. The difference between this and earlier data taken under wet steam conditions was probably due to a lower steam moisture content during the later test because of prior use of superheated steam.

Other data taken indicated that a 12 in. deep bed of Catalyst "D" reduced the oxygen content of 555°F steam from 25.0 to 0.2 ppm with a steam flow

rate of 800 lb/hr and to approximately 0.04 ppm with a flow rate of 500 lb/hr.

The pressure drop data for Catalyst "D" are shown in Fig. 26. These data are accurate to about $\pm 5\%$ and should be used only as an approximate indication of the pressure drop or for comparison with similar data for other catalysts.

3. Discussion of Test Results for Catalyst "D"

It was found that Catalyst "D" promoted the H_2-O_2 reaction with satisfactory efficiencies. In fact, per inch of bed depth, greater degrees of reaction completion were obtained than were possible when using Catalyst "C". This was expected as the alumina support materials provide very large surface area-to-mass ratios. This is true even when particle diameters in the 1/8 to 1/4 in. range are used.

It was found also that the performance of Catalyst "D" followed the relationship

$$C_x = C_o \exp. -A_r T^a W^b P^c X,$$

which was discussed above in Section III. C. The applicability of this form of an equation is illustrated by the curves in Figs. 27 through 29.

It can be seen from these plots of bed effluent oxygen concentration versus catalyst bed depth, on semi-log paper, that straight-line relationships result for a specific set of conditions. It can also be seen that the use of greater steam flow rates and steam temperatures increase and decrease the bed effluent concentrations for a given bed depth. This was the same effect but of a different magnitude, noted for Catalyst "C". The data for Catalyst "D" resulted in the relationship

$$C_x = C_o \exp. - 0.898 \left[T/1130 \right]^{3.4} \left[(W/500)(820/P) \right]^{-0.87} (X)$$

where the several terms are the same as those listed above in Section III.C. The curves and their respective slopes, which were used to obtain the values for temperature and flow term exponents, are shown in Figs. 30 and 31. While

this equation does not represent the experimental data as well as the respective equation does for Catalyst "C", its accuracy is believed to be acceptable. Slight errors exist in the data plots as well as the equation because of the pronounced effects of both temperature and flow rate changes and because of difficulties in accurately measuring and maintaining catalyst bed depths between 2 and 6 in. in a 28 in. deep vessel.

When the catalyst over-all activity coefficients were plotted versus steam flow rates and absolute temperatures, on log-log paper, it was found that relatively constant temperature and flow rate effect term exponents could be obtained, as had been done for Catalyst "C". However, these exponents, "a" and "b", were found to be greater in absolute magnitudes than the values for Catalyst "C". In addition, no velocity correction was necessary to obtain straight-line plots for the temperature effect curves. Each of these observations indicated that a difference in controlling mechanisms existed for these two catalysts. It appeared that oxygen diffusion was controlling for Catalyst "C"; the controlling mechanism for Catalyst "D" was not known. The magnitude of the reference activity coefficient, (A_r), for Catalyst "D" was also almost twice as great as that of Catalyst "C". This difference was probably due to differences in specific surface area values, as well as the respective rate controlling steps. Apparently, even though different controlling mechanisms existed, both mechanisms were related to the local concentration of reactants.

The test data for Catalyst "D" indicate that no gas concentration limit exists beyond which further catalytic reductions are impossible. On the other hand, because of the exponential relationship, neither will a value of zero ever be attained. Also, very pronounced temperature and flow rate effects were observed. It is apparent that where high steam

mass velocities and/or very low pressure and relatively low steam temperatures are used, much larger bed depths are necessary to obtain a given degree of recombination compared to a situation where the opposite conditions are available.

The effect of using wet steam was similar to that noted when Catalyst "C" was tested, i.e., a few per cent of the entering gases were reacted but the efficiency was probably too low for any practical application. However, the efficiency increases sharply and then follows the relationship given above if the steam is dry or superheated even slightly. Near-maximum catalytic activity was obtained almost immediately after passage of superheated steam through a cold wet bed. The exact rate of appearance of this activity is expected to be proportional to the amount of steam superheat. When 35° F of superheat were added to steam flowing through a wet bed, essentially maximum activity was reached within five minutes. This reaction rate was slower than that of Catalyst "C", which was an all-metal material, but is certainly acceptable.

E. Tests Performed on Catalyst "E"

1. Description of Catalyst "E"

The material labeled Catalyst "E" was basically composed of a combination of platinum group metals on an alumina-silica type, 1/4 in. spherical support. The support was very hard and brittle. It had a low chloride content and no initial fines. However, some fines were produced during testing because of cracking. A photograph taken of Catalyst "E" before testing is shown in Fig. 32.

2. Discussion of Tests on Catalyst "E"

Test procedures for Catalyst "E" were identical to those used for Catalysts "C" and "D". Bed depths of 2-1/2, 5, and 8 in. of Catalyst "E"

were tested at steam temperatures of 555, 665, and 855°F and with steam flow rates of 280, 500, and 800 lb/hr at each temperature. A test of the catalytic efficiency under wet steam conditions was made also, as was the effect of doubling the inlet gas concentrations or reducing them by one-half. The gas input rates were normally set to obtain a bed inlet oxygen concentration of 25 ppm, with 5% excess hydrogen being added to overcome any small fluctuation in the oxygen input rate.

Figure 33 illustrates the efficiency of an 8 in. deep bed of Catalyst "E" for reducing the 25 ppm of oxygen and 5% excess hydrogen in 555°F steam. Referring to Fig. 33, at time zero the addition of oxygen produced an effluent concentration of about 28 ppm, rather than the calculated 25 ppm, indicating a calibration error in the oxygen analyzer. The addition of hydrogen produced the usual indication of a reduction in the effluent oxygen concentration. Passage of the gas-laden, superheated steam through the catalyst bed reduced the oxygen content of the steam to 0.65 ppm when a steam flow rate of 800 lb/hr was used. Maintaining the steam temperature constant and decreasing the steam flow rate to 500 and then to 272 lb/hr resulted in bed outlet concentrations of 0.093 ppm and approximately 0.015 ppm, respectively.

The efficiency of a 5 in. deep bed of Catalyst "E" at three steam temperatures and three flow rates at each temperature is illustrated by Fig. 34. The addition of oxygen again caused the bed effluent concentration to rise to the calculated 25 ppm. Later, the addition of hydrogen suppressed the oxygen concentration indication. Passage of the 555°F steam through the catalyst bed at a flow rate of 800 lb/hr reduced the 25 ppm to 2 ppm. While maintaining the temperature and gas concentrations as before, the catalyst reduced the effluent oxygen concentration to 0.8 ppm

when a steam flow rate of 500 lb/hr was used and 0.2 ppm when a steam flow rate of 286 lb/hr was used. When a steam temperature of 667°F was attained, use of the same 5 in. deep bed (33.25 cubic in.) of catalyst reduced the oxygen content of the steam to 1 ppm at 815 lb/hr, 0.3 ppm at 512 lb/hr, and 0.09 ppm at 286 lb/hr. When the steam temperature was increased to 855°F, use of the 5 in. deep bed reduced the 25 ppm to 0.40 ppm at a steam flow rate of 765 lb/hr, 0.12 ppm at 514 lb/hr, and approximately 0.005 ppm at 276 lb/hr.

Figure 35 illustrates a similar test with a catalyst bed depth of 2-1/2 in. The conditions exemplified in Fig. 34 were repeated very closely, except the oxygen sensor was not pressurized after the effluent oxygen concentration had fallen below 10 ppm. At concentrations above 10 ppm, the sensor was pressurized in an attempt to keep all hydrogen and oxygen in solution. A laboratory analysis of steam samples was made at each condition and this value was recorded if it differed from the meter indication. For a steam temperature of 555°F, the 16.6 cubic in. (2-1/2 in. depth) of Catalyst "E" reduced the 25 ppm oxygen concentration to 5.6 ppm at a steam flow rate of 800 lb/hr, 3.3 ppm at 500 lb/hr, and 1.7 at 280 lb/hr. Increasing the steam temperature to 665°F increased the catalytic efficiency such that the effluent concentration was 3.6 ppm at 812 lb/hr, 2.1 ppm at 515 lb/hr, and 1.1 ppm at 286 lb/hr. When a steam temperature of 855°F was used, the same bed reduced the oxygen content of the steam to 3.0 ppm at 782 lb/hr, 1.6 ppm at 510 lb/hr, and 0.56 ppm at 282 lb/hr.

The effect of moisture on the efficiency of Catalyst "E" is shown in Fig. 36. It can be seen that passage of the steam through the catalyst bed at time equal 40 minutes had no significant effect on the effluent

oxygen concentration. However, the addition of superheat caused the concentration to decrease as the steam temperature increased. The 2-1/2 in. deep bed of Catalyst "E" reduced the 25 ppm of oxygen in 555⁰F steam at a flow rate of 500 lb/hr to 5.0 ppm. A comparison with earlier data will show that the use of the same bed depth under similar conditions resulted in an effluent oxygen concentration of 3.3 ppm. This later decrease in efficiency could possibly be due to less catalyst surface area as a new catalyst sample was used during the second test. The earlier data were taken with a sample which contained fines and therefore more surface area, smaller flow channels between the particles, and a greater packing density. Reducing the gas injection rates to produce an input oxygen concentration of 12.5 ppm and 5% excess hydrogen caused the effluent oxygen concentration to decrease from 5 ppm to 3 ppm, which was slightly higher than the expected 2.5 ppm. Adding 50 ppm oxygen and 5% excess hydrogen increased the concentration to only 8 ppm. However, bubbles appeared in the condensate and the oxygen sensor was later pressurized to 25 psig in an attempt to maintain these gases in solution. This pressurization increased the indicated oxygen concentration to approximately 11 ppm, which was 1.0 ppm higher than the expected result. The gas inlet concentrations were reduced to 25 ppm oxygen and 5% excess hydrogen and the heaters turned off at time equal 185 minutes. Within four minutes the steam had reached its saturation temperature. Thereafter, the effluent oxygen concentration increased rapidly, to 22 ppm. Bypassage of the bed produced data which indicated that 2-3 ppm of oxygen had been combined under wet steam conditions. However, it should be remembered that some drying of the steam could have been occurring because of prior use of superheated steam.

The pressure drop data for Catalyst "E" is given in Fig. 37. These data are accurate within $\pm 5\%$ and should be used only as an approximate indication of the pressure drop.

3. Discussion of Test Results for Catalyst "E"

The data for Catalyst "E" were processed exactly as was done for Catalyst "D". Plots of bed effluent oxygen concentrations versus bed depths are shown in Figs. 38 through 40. Plots on log-log paper of over-all activity coefficients versus steam flow rates and absolute temperatures are shown in Figs. 41 and 42, respectively. It was found that from these plots that the relationship

$$-\frac{dO}{dX} = AO_x$$

could be applied to Catalyst "E" also. The effects of temperature, steam flow rate, and pressure changes were slightly more pronounced than had been seen for Catalyst "C" but less pronounced than those of Catalyst "D". If these effects are expressed in a slightly oversimplified form, the relationship

$$C_x = C_o \exp. - (0.877) \left[T/1127 \right]^{1.6} \left[(W/512) (820/P) \right]^{-0.56} (X)$$

can be used to express the gas reductions possible through the use of Catalyst "E" as a function of steam temperature, steam flow rate, steam pressure, and catalyst bed depth.

Data taken for the wet steam test were compared to that taken earlier for other catalysts. It appeared that a reaction was occurring but at an efficiency which was much lower than when the steam was superheated slightly. Once again, it appeared that no specific amount of superheat was required for reasonable efficiencies but that the steam must be free of moisture

F. Tests Performed on Catalyst "F"

1. Description of Catalyst "F"

The sixth material tested, labeled Catalyst "F", consisted of 0.77% platinum on gamma alumina pellets. The extruded cylinders had a uniform diameter of 1/16 in. and various lengths from 1/6 to 1/4 in. The chlorine content was 0.05% and the volatile matter content was 2.85%. The bulk density was 41 lb/ft³.

Exposure to 550°F steam at 800 psig changed the color of the catalyst from white to a light gray and there apparently was a slight increase in surface roughness. A noticeable decrease in activity occurred during the first two hours of testing but additional use produced no further change. Four days of testing caused a minor amount of cracking and produced a few fines. The catalyst performed satisfactorily under the conditions investigated.

2. Discussion of Tests on Catalyst "F"

The general test procedure was to install the desired amount of catalyst, add metered hydrogen and oxygen to power plant steam, adjust the conditions of the steam to the desired values, pass this steam through the catalyst bed, and monitor the effluent for dissolved oxygen. For Catalyst "F", bed depths of 3 and 1-1/2 in. were tested with steam temperatures of 555, 665, and 865°F and steam flow rates of approximately 800, 500, and 280 lb/hr at each temperature. The effect of wet steam on the activity of a 3 in. deep bed of Catalyst "F" was investigated also. Some preliminary tests were made using a 6 in. deep bed.

The first test was made with a steam flow rate of 500 lb/hr at 550°F, using a 6 in. deep bed in the 2.91 in. ID catalyst vessel. The catalyst reduced the 24-26 ppm oxygen input, with 5% excess hydrogen, to 0.05 ppm as the bed approached the 555°F temperature of the steam. For two hours the efficiency of the catalyst steadily decreased and the effluent oxygen concentration increased from 0.05 to 0.95 ppm. During this time the color of the catalyst changed from white to a light gray and there was an increase in the surface roughness. This change was possible due to loss of volatile components. Additional tests with the same catalyst sample produced no further change or loss in activity. The data taken after the catalyst became stabilized are presented in Figs. 43 through 45.

Figure 43 illustrates the efficiency of a 3 in. deep bed of Catalyst "F" for combining hydrogen and oxygen under reactor-like conditions. Referring to this figure, at time zero the addition of 70 ml/min (STP) oxygen resulted in an effluent oxygen concentration equal to the calculated 25 ppm input. After adding 5% excess hydrogen [147 ml/min (STP)] and pressurizing the oxygen sensor to 25 psig, the oxygen analyzer continued to indicate approximately 25 ppm. The oxygen sensor was pressurized to reduce the rate of hydrogen evolution from the condensate and the resultant loss of some oxygen at these high gas concentrations. Passage of 500 lb/hr of gas-laden steam at a temperature of 555°F through the catalyst bed reduced the effluent oxygen concentration to 3.5 ppm within 10 minutes. The steam temperature and input gas concentrations were maintained constant and the steam flow changed to 280 and 800 lb/hr, resulting in effluent oxygen contents of 0.8 and 7 ppm, respectively. The steam temperature was then

increased to 660°F by mixing a small amount of superheated steam with the saturated steam and by adding more heat with the electrical heaters and the steam heated preheater. These conditions resulted in effluent oxygen concentrations of 1.8 ppm at a steam flow rate of 825 lb/hr, 0.4 ppm at 520 lb/hr, and 0.08 ppm at 290 lb/hr.

Fig. 44 is the same type of test but illustrates the effectiveness of a 1-1/2 in. deep bed at three steam temperatures and three flow rates at each temperature. The following effluent oxygen concentrations were obtained with a 25 ppm oxygen input:

1. With a steam temperature of 555°F; 14 ppm at 800 lb/hr, 8 ppm at 500 lb/hr, and 4.6 ppm at 280 lb/hr.
2. With 665°F steam; 4.5 ppm at 800 lb/hr, 2.2 ppm at 525 lb/hr, and 0.7 ppm at 286 lb/hr.
3. With 865°F steam; 0.8 ppm at 785 lb/hr, 0.12 ppm at 500 lb/hr, and approximately 0.005 ppm at 275 lb/hr.

The effect of temperature on catalytic efficiency can readily be seen by comparing data taken at similar steam flow rates.

The effect of wet steam on the efficiency of Catalyst "F" is shown in Fig. 45. From this figure it can be seen that the addition of oxygen at time zero increased the monitored effluent concentration to the calculated 25 ppm within two minutes. The later addition of hydrogen caused a false indication of a drop in the effluent oxygen concentration. Passage of the wet, gas-laden steam through the 3 in. deep catalyst bed resulted in about 8% combination of the oxygen. This reaction was checked by bypassing the bed. At time equal 65 minutes, superheat was added to the

steam by using electrical heaters and the steam heated preheater. The appearance of superheat increased the efficiency to 96% within 10 minutes. Turning off the electrical heaters and the preheater caused an immediate increase in the effluent oxygen concentration when the steam temperature reached the saturation value. The effluent oxygen content increased rapidly with increasing moisture until the moisture content of the steam became constant. At time equal 109 minutes, an effluent oxygen concentration peak appeared. This peak was probably due to a slug of water passing over the catalyst. Bypassing the bed and then passing the flow through the catalyst bed again demonstrated that 16% of the oxygen was being recombined. This increase in efficiency over the first value was probably due to the drying effect of the hot pipe walls.

The pressure drop data for Catalyst "F" are shown in Fig. 46. These data are accurate to within $\pm 5\%$.

3. Discussion of Test Results for Catalyst "F"

It was found that Catalyst "F" promoted the reaction

very efficiently, even where bed depths of only a few inches were used. During the initial test, when increasing bed effluent oxygen concentrations were noted, it was feared that the catalytic agent was being eroded away. However, the change was apparently only due to the loss of loose fines which existed on the new material.

Insofar as the effect of wet steam operation is concerned, it appears that this catalyst behaved as had all materials tested earlier, i.e., a small amount of moisture essentially eliminated all activity.

Evidence which supports the applicability of the relationship

$$C_x = C_o \exp. - A_r T^a W^b P^c X$$

is shown in Figs. 47 through 49. While there is some indication that the slope of such plots decreases with increasing bed depths, this effect is believed to result from the difficulties in correlating data for such small bed depths and dissolved gas concentrations. Plots of over-all activity coefficients versus steam flow rates and absolute temperatures on log-log paper are shown in Figs. 50 and 51. Approximations of the effects of steam flow rate and temperature changes were obtained from these plots. The relationship

$$C_x = C_o \exp. - 1.46 \left[T/1123 \right]^{6.78} \left[(W/512)(820/P) \right]^{-0.83} (X)$$

was developed and found to interpret, with reasonable accuracy, the data exemplified in Figs. 47 through 49. However, as discussed earlier, this oversimplified equation is not believed to be exactly representative of the test data or unmistakably definitive as to the limiting step. It is presented solely to illustrate approximations of such factors.

G. Tests Performed on Catalyst "G"

1. Description of Catalyst "G"

Catalyst "G" was quite different physically from any of the other catalysts which were tested. The support material was of monoblock construction,* with longitudinal internal channels. The catalytic agent was composed of platinum-group elements. The support was made from a high surface area refractory material. It appeared that the block-like construction had been achieved by fusing thin layers of the refractory material, with flow channels being formed by alternating layers of flat and corrugated sheets. This construction produced channels which were somewhat triangular in shape.

* Two 3 in. deep blocks were used in the tests to allow depth variations.

A photograph of Catalyst "G" is shown in Fig. 52. Three chipped spots on the top of the block are visible in this photograph. This damage occurred during handling after testing.

The unique physical features of Catalyst "G" may be found to offer considerable convenience for certain nuclear applications.

2. Discussion of Tests and Test Data

The general test procedure was the same as had been used for the other catalysts. The desired amount of catalyst was placed in the catalyst vessel, the desired steam flow and temperature were obtained, metered hydrogen and oxygen were added to give a bed inlet concentration of 25 ppm oxygen and 5% excess hydrogen, and the effluent was monitored for its dissolved oxygen content. A 3 in. deep catalyst bed was tested with 557°F steam at steam flow rates of 280, 500, 800 and 1000 lb/hr. In addition, at a steam flow rate of 500 lb/hr, steam temperatures of 670 and 860°F were used with this same bed depth. At a bed depth of 6 in., the effect of wet steam on the activity of Catalyst "G" was observed, as was the effect of three temperatures (557, 665, and 800°F) and three flow rates (280, 500, and 800 lb/hr) at each temperature. The results of these tests are shown in Figs. 53-55.

Catalyst "G" was found to be relatively insensitive to steam flow rate and temperature changes. There was no detectable increase in catalytic efficiency when the flow was changed from 800 to 500 lb/hr and only a small increase in efficiency when the flow was changed from 500 to 280 lb/hr. There was a slight increase in efficiency with increasing temperatures. For example, the effluent oxygen concentration dropped from 1.6 to 1.1 ppm as the temperature was changed from 557 to 800°F. From Fig. 53 it can be seen that the addition of 30% excess hydrogen had no effect on the effluent

oxygen concentration and that doubling the gas inputs essentially doubled the oxygen content of the effluent. It is not known what caused the two peaks shown on Fig. 54, at times 150 minutes and 175 minutes.

Figure 55 is of particular interest because it shows that 54% combination was achieved under wet steam conditions during this test. This was the greatest efficiency observed under wet steam conditions. The reason for the high efficiency was probably the unique geometry of Catalyst "G" which produced straight line flow and possibly less wetting by moisture in the steam. The addition of 26° F of superheat caused the effluent oxygen concentration to decrease to 1.5 ppm within four minutes. It should be noted that this is the same value as obtained with similar conditions during the test shown in Fig. 54. Turning off the heat sources caused the steam temperature to decrease to the saturation value within three minutes. The oxygen content increased rapidly thereafter, to about 12 ppm. Stopping the hydrogen input and bypassing the bed confirmed the 54% combination, while using steam which contained about 1% moisture.

Referring to Fig. 56, a 6 in. deep bed of Catalyst "G" was tested again at a steam temperature of 550-560° F, with various steam flow rates and with one-half the flow area of the catalyst restricted. This test was made to determine the effect of flow rate changes as the transition from laminar to turbulent flow was accomplished. It was not possible to achieve turbulent flow within the catalyst channels without a reduction in the bed face area as loop steam flow rates were limited to about 1000 lb/hr because of condenser capacity. It can be seen from this figure that flow rate changes had little effect on the over-all catalyst efficiency coefficient until flow rates above 500 lb/hr* were achieved. However, it can be seen that there was a greater decrease in efficiency with increasing flow rates

* These values should be doubled for comparison with other tests to account for the use of only one-half the bed area.

above 500 lb/hr.* A rough calculation showed that the transition from laminar to turbulent flow began to occur at approximately 400 lb/hr.*

The pressure drop data for Catalyst "G" are shown in Fig. 57. The accuracy of these data is about $\pm 10\%$.

3. Discussion of Test Results for Catalyst "G"

Catalyst "G" satisfactorily combined hydrogen and oxygen under the test conditions. Its efficiency and pressure losses are similar to those of Catalyst "C". Figures 58 through 60 show that the effluent oxygen concentration was an exponential function of the bed depth as given by the relationship:

$$C_x = C_o e^{-AX}, \text{ where:}$$

C_x = oxygen concentration at bed depth "X"

C_o = bed inlet oxygen concentration;

A = experimentally determined coefficient, for
a specific set of conditions;

X = bed depth.

For the other catalysts tested, it was possible to represent the coefficient "A" by the relationship

$$A = A_r T^a W^b P^c, \text{ where:}$$

A_r = coefficient at an intermediate set of reference conditions;

T^a = the absolute steam temperature raised to some experimentally
determined power (a);

W^b = the steam flow rate raised to some experimentally determined
power (b);

* These values should be doubled for comparison with other tests to account for the use of only one-half the bed area.

P^c = the steam pressure raised to the same exponent as "w"
except opposite in sign ($c = -b$).

It can be seen from Figures 61 and 62 that the coefficient "A" for Catalyst "G" cannot be represented by a simple equation. The efficiency of Catalyst "G" was only slightly sensitive to temperature changes, insensitive to flow changes between 500 and 800 lb/hr, slightly sensitive to flow changes below 500 lb/hr but very sensitive to changes above 1000 lb/hr. Calculations showed that this insensitivity at low flow rates was due to the existence of essentially laminar flow through the triangular channels of this catalyst.

Figure 63 illustrates the effect of greatly increased flow rates on the coefficient "A". Some of these data which were taken with one-half the flow area of the catalyst restricted were plotted at twice the actual test flow rate so that the velocities through the bed could be compared with earlier rates which were used with the full flow area. The transition from laminar to turbulent flow was calculated to be between 800 and 1000 lb/hr. From this figure it can be seen that the efficiency decreased slowly with increasing flow rates in the laminar-transition region but quite rapidly in the turbulent region. The slope of the curve in the turbulent region appeared to approach -0.90, as compared to -0.80 for Catalyst "F" and -0.87 for Catalyst "D".

Catalyst "G" appeared to be quite resistant to damage from the high pressure, high temperature steam conditions. The only noticeable change which occurred during the short-term tests was that of color, from black to a gray brown. However, as the support material can be broken, it would require a firm support if long-term operation were intended.

Comparing Catalyst "G" with other catalysts which were tested, it appears that features worth noting are its physical form, its lack of sensitivity to temperature changes, lack of sensitivity to flow rate changes in the low and intermediate mass velocity range, and its low pressure drop characteristics. While turbulent flow exists with almost all flow rates when pellet or ribbon materials are used, this is not true of Catalyst "G". As the channels in Catalyst "G" are longitudinal and tubular in form, turbulence does not occur in the fluid film on channel walls until quite high steam flow rates are attained.

H. Tests Performed on Catalyst "H"

Catalyst "H" was composed of 1/16 in. diameter spheres. It was identical to Catalyst "A" except for particle diameters. After preliminary tests indicated that there was no marked difference between the large size material tested earlier and the 1/16 in. diameter material, no detailed tests were conducted.

It was observed that a 6 in. deep bed of the smaller material reduced the 25.0 ppm oxygen concentration to 16 ppm when a steam flow rate of 820 lb/hr at 800 psig and 563°F were used. With a steam flow rate of 500 lb/hr at 866°F and 865 psig, the bed outlet concentration was reduced to 3.0 ppm. The two bed pressure loss values were 5.5 and 4.0 psi, respectively. These results may be compared with earlier data to obtain a geometry-effect factor for this catalyst.

I. Tests Performed on Catalyst "I"

1. Description of Catalyst "I"

The ninth material tested, labeled Catalyst "I", was a 3/16 in. diameter spherical catalyst composed of 0.5 platinum on an alumina

support material. It was the same as Catalyst "B" but larger in diameter. Figure 64 is a photograph of Catalyst "I". This catalyst was found to be satisfactory for the combination of hydrogen and oxygen under test conditions. There were some fines produced during testing due to cracking. However, no loss of activity occurred during three days of test operation.

2. Discussion of Tests and Test Data

The general test procedure was the same as had been used for the other catalysts. The desired amount of catalyst was placed in the catalyst vessel, the desired steam flow and temperature were obtained, metered hydrogen and oxygen were added to give a bed inlet concentration of 24-26 ppm oxygen and 5% excess hydrogen, and the effluent monitored for dissolved oxygen content. Catalyst bed depths of 3 and 6 in. were tested at steam temperatures of 560, 665, and 810°F, with steam flow rates of 280, 500, and 800 lb/hr at each temperature. Using a bed depth of 3 in., a test was made to determine the effect of wet steam on the efficiency of Catalyst "I". The results of these tests are shown in Figs. 65 through 67.

Figs. 65 and 66 illustrate the effect of flow rate and temperature changes on the efficiency of Catalyst "I". Referring to Fig. 65, the addition of 115 ml/min (STP) oxygen at time zero caused the effluent oxygen concentration to increase from zero to the calculated input value of 25 ppm. The addition of 240 ml/min (STP) hydrogen caused a false indication of the effluent oxygen concentration since some of the hydrogen and oxygen came out of solution at those concentrations. A 6 in. deep bed of Catalyst "I" reduced the effluent oxygen concentration to 2.0 ppm within 5 minutes at a steam flow rate of 800 lb/hr at 560°F. The effect

of steam flow variations on catalytic efficiency can be seen by comparing the oxygen concentration at a constant steam temperature. For example, the bed effluent oxygen content at a steam temperature of 560°F was 0.9 ppm when a steam flow of 500 lb/hr was used and 0.2 ppm when a flow of 280 lb/hr was used. The effect of temperature changes on catalytic efficiency can be seen by comparing the effluent oxygen concentration at constant steam flow rates. For example, at 500 lb/hr the oxygen content at the bed outlet was 0.9 ppm with a steam temperature of 560°F and 0.37 ppm with a steam temperature of 665°F. Figure 66 shows the effect of steam temperature and flow rate variations on the efficiency of a 3 in. deep bed of Catalyst "I".

Fig. 67 illustrates the effect of wet steam on the efficiency of Catalyst "I". From this figure it can be seen that no detectable reaction was occurring with wet steam passing through the bed. It should be pointed out, however, that as much as 10% combination could be occurring without detection because of the effect of gaseous hydrogen on the indication of effluent oxygen content at oxygen concentrations of 25 ppm. The addition of 31°F of superheat caused the bed outlet concentration to decrease to 3.2 ppm oxygen. Reducing the superheat to zero caused the effluent oxygen concentration to increase rapidly with increasing moisture content.

The pressure drop data for Catalyst "I" is given in Fig. 68. These data are accurate to within $\pm 5\%$.

3. Discussion of Test Results for Catalyst "I"

Catalyst "I" satisfactorily combined hydrogen and oxygen under the test conditions. There is no evidence of loss of activity due to

poisoning or erosion during three days of testing. However, some cracking did occur.

Figs. 69 through 71 show that the effluent oxygen concentration for Catalyst "I" is an exponential function of the bed depth. Figures 72 and 73 demonstrate that the relationship described in Section III.G above is applicable. The following equation has been found to satisfactorily represent the experimental results obtained for Catalyst "I".

$$C_x = C_o \exp. - 0.92 \left[\frac{T}{1125} \right]^{4.5} \left[\left(\frac{W}{510} \right) \left(\frac{835}{P} \right) \right]^{-0.64} (X)$$

J. Saturated Steam Tests Using Catalysts "C" and "D"

Because it was impossible to pass saturated, dry steam through the test loop for periods longer than a few seconds, it was decided to conduct two simple autoclave tests where steam which contained essentially no moisture or superheat could be obtained for extended intervals. This decision was based partially on the availability of an existing autoclave.

A schematic of the autoclave and associated equipment used in these tests is shown in Fig. 74. The equipment consisted primarily of a stainless steel pressure vessel which contained a heater for steam production and an electrolytic cell for production of H_2 and O_2 . Deionized water was fed into the vessel as gas-laden steam was withdrawn through a bed of catalyst.

In order to obtain moisture-free steam at the catalyst bed inlet, the bed was suspended inside the vessel, with a surrounding steam gap which served as an insulator and therefore prevented undue condensation on the catalytic materials. A low-power electric heater was placed on the auto-

clave cover to prevent condensation and dripping at this point. Power to this heater was adjusted to produce a maximum cover temperature which was less than 10°F above the water saturation temperature. The vessel was operated at 37-43 psig. A low pressure was used to obtain reasonable steam velocities through the catalyst bed. Boiler heater power, cell current, and the steam draw-off rate were set to obtain a steam flow velocity (based on the catalyst bed face area) of about 0.3 ft/sec and an oxygen concentration in the steam of 25-30 ppm.

It was determined during subsequent tests that the autoclave effluent contained the expected 25-30 ppm of O₂ if the catalyst bed was bypassed but only 1-2 ppm when the presumably saturated steam was passed through a 10 in. deep bed of either Catalyst "C" or "D".* These data indicate, as have other tests, that only dryness is required to allow catalytic activity, not any specific amount of superheat. One specific observation, made after each test completion, was that the lower few (2-3) inches of the catalyst bed was thoroughly wet. Apparently, water droplets carried from the water-steam interface, which was between 6 and 8 in. below the bed, caused this wetness. Therefore, the "effective" bed depths were much less than the 10 in. mentioned above, possibly as small as 6 in.

While the data from this experiment indicated that recombination can be accomplished under saturated but dry steam conditions, it should be remembered that a significant difference existed between these autoclave

*These two were selected as being representative of all-metal and alumina-type catalysts.

conditions and reactor operating conditions because of pressure differences. At pressures below about 400 psia, saturated steam tends to become superheated as pressure losses occur. At higher pressures, it tends to become wet. This effect could reduce the relative catalytic efficiency if pressures higher than 400 psia were used.

A similar test was conducted where the autoclave system was completely closed and the steam was superheated before it was passed over the catalyst bed. The purpose of this test was to demonstrate the effect of a catalyst on the oxygen concentration in a closed, natural circulation system. A schematic of the system is shown in Fig. 75. It should be noted that this test was qualitative and that all numbers are approximations or average values.

During this second test, the pressure varied between 30 and 40 psig and the saturation temperature between 275 and 287°F. The steam flow rate was approximately 8 lb/hr and was maintained constant insofar as was possible during the entire test. The steam was superheated 50-100°F by an electric heater before it was passed over the catalyst. The system was first operated for 3-1/2 hours with no catalyst in the loop. The electrolytic cell current was 204 ma and would have produced an oxygen concentration of approximately 16 ppm if a once-through system had been used. During this test, the oxygen content of the steam increased to 54 ppm after 3-1/2 hours of operation. The autoclave was then drained and refilled with demineralized water. With all conditions being held as close as was possible to the ones described above, a second 3-1/2 hour

test was run while passing the circulating steam through a 10 in. deep bed of Catalyst "C". This operation maintained an oxygen concentration of about 16 ppm in the steam dome and between 0.7 and 2 ppm in the return condensate. From these results it can be concluded that a recombiner of this type can be used to reduce oxygen concentrations in a closed but circulating steam system. However, the effect of selective buildup of one gas, because of non-stoichiometric gas production rates, should be studied before such use is attempted.

K. Tests Using Pure Nickel Ribbon

Because of the considerable success attained by use of commercial platinum-family catalysts in promoting the reaction

the question arose concerning the necessity of using such exotic and somewhat expensive materials. It was therefore decided to test a bed of nickel ribbon. A bed of 0.007 x 0.031 in. nickel ribbon was constructed and tested. Use of this bed, which was physically comparable to a 7.0 in. deep bed of Catalyst "C", did not produce any detectable reaction between the two gases. Such tests were then abandoned and it is not known if other pure materials, such as silver, may be of interest in this field.

L. Conclusions Based on Efficiency Tests

A rough comparison of all the catalysts tested is given by Table I. It can be seen from Table I that the activities of the catalysts with the

TABLE I. A COMPARISON OF CATALYSTS TESTED

Catalyst	Description	% O ₂ Combined*	Pressure Drop* Across Bed, psi	Temperature Exponent	Flow Rate Exponent	Remarks
A	3/32" to 9/32" spheres**	N.D.***	N.D.	N.D.	N.D.	Activity not sufficient for this application.
B	3/32" spheres**	≈ 100%	1.4	N.D.	N.D.	Particle size too small to obtain quantitative data.
C	Mesh-type platinum-coated S.S. ribbon	94%	0.06	1.5	-0.4	--
D	5/32" pellets,** 1/8" to 7/16" lengths	99.6%	1.2	3.4	-0.87	--
E	1/4" spheres**	99.6%	1.0	1.6	-0.56	--
F	1/16" pellets,** 1/6" to 1/4" lengths	99.9%	2.4	6.78	-0.80	--
G	Block-type with** small flow channels	95.6%	0.05	--	--	Relatively insensitive to temperature and velocity changes in range of tests.
H	1/16" spheres**	N.D.	N.D.	N.D.	N.D.	Activity not sufficient for this application.
I	3/16" spheres**	99.6%	0.75	4.5	-0.64	--

* Based on a 6-in. deep bed in a 2.9 in. dia. pipe with 500 lb/hr of 665°F steam

** Platinum on alumina support material.

*** Not determined.

cylindrical and spherical geometries are compatible and somewhat greater than the block-type and the mesh-type catalysts. Referring to Table I, the greater the absolute value of the temperature and flow rate exponents, the greater the sensitivity of the activity of the respective catalyst to changes in temperatures and flow rates. In general, the catalysts with cylindrical and spherical geometries were more sensitive to temperature and flow rate changes than the block-type and the mesh-type catalysts. Catalyst "F" was most sensitive to temperature changes and Catalyst "D" was most sensitive to flow rate changes. Catalysts "C" and "E" were relatively insensitive to temperature and flow rate changes. Catalyst "G" was found to be only slightly sensitive to temperature changes and insensitive to flow rate changes below $21,700 \text{ lb/hr-ft}^2$, but highly sensitive to flow rate changes above $21,700 \text{ lb/hr-ft}^2$. It should be noted that the pressure drop across a bed of Catalyst "C" or "G" is a factor of 20 to 40 less than that of the cylindrical and spherical geometries.

All test data taken during Phase I indicate that:

1. Either of the catalysts described herein could be used to reduce radiolytic oxygen and hydrogen concentrations in reactor steam by large factors.
2. The effluent oxygen concentration (C_x) versus the bed depth (X) of a given catalyst was found to be defined by the relationship:

$$C_x = C_o e^{-AX}, \text{ where:}$$

C_o = catalyst bed inlet oxygen concentration;

A = experimentally determined constant that is a

function of steam temperature, flow rate, and pressure.

(This equation is explained in greater detail in Section III. C above.)

3. The efficiency of each catalyst increases with increased temperatures.
4. The efficiency of most catalysts decreases with increased steam velocities.
5. Only a small amount of catalytic activity exists under wet steam conditions. However, no specific amount of steam superheat is required to obtain significant activity, only dryness.
6. Pressure variations between 400 and 1000 psia affect the reaction rate only indirectly, because of changes in the steam velocity at a given flow rate.
7. There is no theoretical limit to possible gas concentration reductions. A reduction to the parts per billion range is certainly feasible.
8. Only a stoichiometric gas ratio is required for maximum efficiency of the respective catalyst.
9. Starting with a cold, wet catalyst bed, the reaction will proceed to the maximum efficiency of the catalysts for the conditions used within 5 to 10 minutes if the steam is superheated 35°F. The metal-type catalyst is somewhat faster than the alumina catalysts.

Since all the catalysts reported can be used to reduce the radiolytic gas content of boiling water reactors, other properties will control the selection of a catalyst for a given application. This selection will be based on the physical characteristics of the catalyst, location of the recombiner, pressure drop, and activity per unit volume of catalyst. Because of its physical properties and low pressure drop, Catalysts "C" and "G" will probably be the best selections for most internal reactor applications while the more active alumina catalysts will be best suited to external applications where special containment can be used.

IV. INTERIM CORROSION TEST

While Phase II loop modifications were being made, some parts of the loop were available for limited use and tests were conducted to obtain some reference stress corrosion data. Steam which contained approximately 0.005 ppm O_2 , 0.025 ppm chlorides, and 2-3% moisture, at 900 psig and 533°F, was taken from the plant and used in these tests. A solution of NaCl and dissolved oxygen was pumped into the flowing steam such that the oxygen and chloride contents were increased to 0.17-0.25 and 1.8-2.2 ppm, respectively. The steam was then passed over a set of 10 stressed Type 304 stainless steel specimens. The oxygen content of this steam was then increased to 30-35 ppm and the steam passed over a second set of identical specimens. Both sets of specimens were fastened to racks and positioned in 1 in. Schedule 80 pipes. A 1000-watt electric heater was positioned between the two sets to add heat at a rate equal to the calculated pipe loss rate, therefore maintaining roughly the same steam moisture content at each set. A flow diagram for these tests is shown in Fig. 76. A sketch of a typical U-bend specimen is given in Fig. 77. When mounted for exposure, the specimens were stressed such that the ends of each U-bend were 3/8 in. apart.

After one week of exposure to the above conditions and a steam flow of 200 lb/hr, the specimens were removed and examined under a microscope. Several cracks were found in each of the downstream specimens but none in the upstream specimens. All specimens were then returned to the loop for two additional days. Examination with a microscope after this additional

exposure revealed that there were numerous cracks in each of the downstream specimens and possibly one or two cracks in one upstream specimen. Metallographic examination of two downstream specimens confirmed that each contained 30 to 40 cracks and showed that the cracks were transgranular.

Metallographic examination of three upstream specimens showed that there were two cracks in one specimen but none in the others. The cracks in the downstream set were generally 0.015 to 0.025 in. deep and had progressed inward from the specimen edge a similar amount. The cracks are shown in Fig. 78. It was believed that the rapidity of attack and the direction of crack propagation (from the edges) were due partly to the procedure used in sizing the specimens; they were sheared and then ground slightly.

This test was repeated in an attempt to learn whether or not factors other than the oxygen concentration difference contributed to the difference in the rate of cracking. Another set of specimens were prepared and exposed to conditions identical to those described above. One specimen in both the upstream and downstream positions was prepared by shearing and grinding slightly while the other eighteen specimens were fabricated by sawing and grinding slightly. Six days of exposure produced many chloride stress corrosion cracks in the downstream sheared specimen but none in the upstream sheared specimen. No cracks were found in any of the eighteen sawed specimens.

A third set (20) of specimens were prepared from the same sheet of Type 304 stainless steel. However, all of these specimens were formed by

sawing and grinding. The test described above was then repeated. The upstream specimens (10) were exposed to 900-psig, wet steam containing 0.17-0.25 ppm oxygen and 1.8-2.2 ppm chlorides. The ten downstream specimens were exposed to the same steam, but after the oxygen content had been increased to 28-32 ppm. The moisture content of the steam at each point was 2-3%.

Examination under a microscope after three and one-half days of exposure revealed that no cracks existed in either the upstream or the downstream corrosion specimens. The same specimens were returned to the loop and exposed for an additional period of five and three-fourths days. A subsequent microscopic and metallographic examination showed no cracks in either the upstream or downstream specimens.

Later, in an attempt to determine if greater specimen thickness would accelerate cracking, five of the above specimens and five new, thicker (0.062 in.) specimens were placed in each of the corrosion specimen positions. The thicker specimens were sawed and ground slightly and were used to achieve higher stresses. Exposure of these specimens for about two weeks produced no cracks. The exposure history for these tests is shown in Fig. 79.

Based on the corrosion data described above, it was concluded that the shearing process, used in preparing the first two sets of specimens, cold-worked the edges of the specimens thereby producing local edge conditions from which the cracks could easily originate. Greater exposure times are apparently required under the above conditions to produce cracks in the sawed specimens. It has been concluded that the higher

oxygen concentrations greatly increased the rate of cracking in the sheared specimens. However, it should be mentioned that the upstream specimens were mounted horizontally in a 1 in. pipe while the downstream specimens were mounted vertically; therefore, the behavior of the moisture could have been different.

Visual examination of the corrosion specimen holder indicated that the 28-32 ppm oxygen greatly increased the rate of general corrosion. A photograph of the specimen holder is shown in Fig. 80. Both parts shown, which served as ballast, were made from carbon steel. The downstream holder had corroded to a much greater extent than had the upstream holder. The latter was exposed to only 0.17-0.25 ppm oxygen while the former was exposed to 28-32 ppm oxygen concentrations. Both holders were used in each of the tests described above.

V. ENDURANCE TESTING OF CATALYSTS AND RELATED CORROSION TESTS

A. Description of Experimental Equipment and Procedures

The test loop used in Phase I was modified for Phase II tests. A section of 1 in. pipe was added downstream of the catalyst vessel for containment of stress corrosion specimens and a heat exchanger was placed between the catalyst vessel and this container location to increase the moisture content to the same value as was present at the upstream corrosion specimen position. Also, provisions were made for injecting chlorides in the form of solutions of sodium chloride into the loop upstream of the gas injection points. A simplified flow diagram of the steam used during Phase II is shown in Fig. 81. The stress corrosion specimens were located at points A and B, and the general surface corrosion coupons were located just above and below the catalyst bed inside the catalyst vessel.

The general test procedure for Phase II tests began by placing the desired amounts of the catalysts to be long-term tested in the catalyst vessel and by positioning the corrosion specimens in their respective positions. The desired steam flow and temperature were obtained for the endurance testing of the catalyst. Generally, high steam velocities were used and 10 to 20°F of superheat was maintained at the catalyst bed inlet. The hydrogen and then the oxygen were added so that the downstream corrosion specimens were never exposed to high oxygen concentrations. The gases were added at rates sufficient to give 24-26 ppm oxygen and 5% excess hydrogen. Sodium chloride solutions were injected into the loop at a rate that maintained the steam chloride content at approximately

2 ppm. The results of the interim corrosion showed that exposure times of only one week were required before the loop should be shut down for examination of the corrosion specimens.

B. Endurance Testing of Catalysts "D", "E", and "F"

1. Tests without Chloride Injection

Catalysts "D", "E", and "F" were tested semi-continuously for 25 days in a parallel flow arrangement. The catalyst holder used for this test is shown by the photograph in Fig. 82. This holder fits inside the 2.91 in. ID catalyst vessel. The catalyst chambers are 24 in. long and the ID of each tube is 1.18 in. The chamber plugs shown were used to plug two chambers so that the individual efficiency of each catalyst could be determined. The catalyst volumes were calculated to give 98-99% recombination initially. The resultant bed depths were 7.8 in. of Catalyst "D", 12.6 in. of Catalyst "E", and 8.4 in. of Catalyst "F". The steam flow through each catalyst bed was adjusted by orificing such that it was 60 lb/hr. The 900 psig steam was superheated 10-20°F before passage through the beds. The bed inlet oxygen concentration was 24-26 ppm, with an excess of hydrogen being added to ensure the presence of a stoichiometric amount irrespective of small fluctuations in either or both gas inputs.

The oxygen concentration in the effluent ranged from 0.15 to 0.4 ppm. A plot of the effluent oxygen concentration is shown in Fig. 83. As can be seen from Fig. 83, there was no significant loss in the activity of either of the catalysts.

2. Tests with Chloride Injection

After the catalyst operation had been observed for 25 days and without any significant change in the combined efficiencies, as-received Type 304, non-sensitized stainless steel corrosion specimens were placed in the loop in an effort to obtain chloride-related stress corrosion data and general corrosion data for low alloy piping materials. To obtain the former data, sodium chloride solutions were injected in the loop such that the steam chloride content was 3.0-3.7 ppm. The loop effluent oxygen and chloride concentrations for this test are shown in Fig. 84. It can be seen from this figure that a large fraction of the chlorides were being collected by the bed and that this collection gradually poisoned the catalysts. After six days of testing, the chlorides "broke through" and a concentration approximately equal to the calculated loop inlet value appeared in the effluent and the bed outlet oxygen concentration increased to 5.6 ppm. The test was terminated at that time. The respective corrosion data are discussed below in Section V. D.

An examination of the catalyst revealed that Catalysts "D" and "F" had retained approximately three times as much NaCl as had Catalyst "E". Washing the catalysts in distilled water and with wet steam rejuvenated the three to the extent that the combined effluent oxygen concentration was 1.3 ppm under the same conditions as when it averaged 0.3 ppm before the chloride injection was started. Replacing Catalyst "F" and then "D" with new materials proved that these two catalysts had been poisoned by the sodium chloride and that "D" was somewhat worse than "F". The effluent oxygen content with Catalyst "D" and "F" replaced with new catalysts was approximately 0.2 ppm, showing that Catalyst "E" had not lost any of its original activity.

Catalysts "D" and "F" were replaced and the endurance testing and related corrosion tests were continued for 35 days.

3. Conclusions

The effluent oxygen concentration and the various conditions for the entire parallel flow arrangement tests are given by Fig. 85. It should be noted that the last 13 days of operation were conducted with 300°F of superheat. This value of superheat was used in an effort to obtain intergranular corrosion data. Catalyst "E" was endurance tested in the parallel arrangement for 73-1/2 days without detectable loss of activity. Catalyst "D" and "F" were replaced after 38-1/2 days due to poisoning by sodium chloride collection. New samples were tested for 35 days without significant loss of activity. It is noted that Catalyst "E" was less susceptible to poisoning due to the accumulation of sodium chloride and other solids.

C. Endurance Testing of Catalysts "C", "E", and "G"

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, which was 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 series in the 2.91 in. ID catalyst vessel. The detail arrangement and a schematic flow diagram are shown in Fig. 86. 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. At intervals of approximately two weeks, the loop was shut down and checks were made of the individual efficiencies of each catalyst. The efficiency checks were made using steam at 500 lb/hr and at a steam temperature of 820-830°F. The bed inlet oxygen concentration was 24-26 ppm and 5% excess hydrogen was added. When available, a control sample was tested with each catalyst at each efficiency check. The results of these checks are given in Table II. This endurance test was operated semi-continuously for 4 months.

As can be seen from Table II., there was no significant loss of activity by the catalysts. The small loss by the sample of Catalyst "E" that was tested longest was probably due to a collection of solids while that of Catalyst "C" was probably due to a loss of platinum.

D. Recombiner-Related Corrosion Tests

1. Chloride Stress Corrosion and General Corrosion Tests

After Catalysts "D", "E", and "F" had been endurance tested for 25 days, corrosion specimens were placed upstream and downstream from the catalyst bed in an effort to demonstrate the value of a catalytic recombiner

* The high temperature was used because of a simultaneous intergranular corrosion test.

TABLE II. EFFICIENCY CHECKS OF CATALYSTS

<u>Catalyst Sample</u>	<u>Time Tested (days)</u>	<u>Bed Effluent (ppm O₂)</u>	<u>Efficiency (%)</u>	<u>Loss of Efficiency (%)</u>
Control E	0	1.3-1.4	94.5	-
E #1 position*	88	2.20	92.0	2.5 ± 0.5
E #1 position	104	1.95	92.0	2.5 ± 0.5
E #1 position	123	1.9	92.0	2.5 ± 0.5
E #1 position	132	1.95	92.0	2.5 ± 0.5
E #1 position	150	1.9	92.0	2.5 ± 0.5
E #2 position	14	1.40	94.8	0
E #2 position	30	1.33	94.8	0
E #2 position	49	1.3	94.8	0
E #2 position	58	1.3	94.8	0
E #2 position	76	1.3	94.8	0
Control C	0	0.2-0.25	99	-
C #3 position	14	0.3	98.8	0
C #3 position	30	0.4	98.5	0
C #3 position	49	0.4	98.5	0
C #3 position	58	0.4	98.5	0
C #3 position	76	0.6	97.6	1.0 ± 0.5
Control G	(none tested)			
G #4 position	14	0.55	97.8	0
G #4 position	30	0.58	97.6	0
G #4 position	49	0.6	97.6	0
G #4 position	58	0.6	97.6	0
G #4 position	76	0.6	97.6	0

* Upstream Position (See Fig. 86)

in reactor systems. During the earlier 25 days of testing, the oxygen content downstream from the catalyst bed averaged 0.3 ppm and the upstream oxygen concentration varied between 24 and 26 ppm. The steam flow rate was 180 lb/hr at approximately 885 psig. After the corrosion test was initiated, 2 ppm of chlorides (as NaCl) were added to the steam at a point upstream from the first set of corrosion specimens.

Two types of specimens were used to obtain corrosion data; stressed stainless steel specimens and general corrosion specimens. The stressed specimens were taken from a Type 304 stainless steel sheet and were 4 in. long and 1/4 in. wide. During testing, they were in the form of U-bends. Eleven of the stressed specimens were sheared from a 0.028 in. thick sheet and then ground slightly. Nine similar specimens were sawed from a 0.062 in. thick sheet and then ground slightly. The thick specimens had a prior corrosion test exposure history (see Section IV.). A tabulation of properties for the thick specimens is given in Table III. Both thicknesses were taken from as-received sheets.

The general corrosion coupons were 1/2 by 1-1/4 by 0.060 in. There were six Type 304, six T-11, and six T-22 coupons.

Five thin-sheared and five thick-sawed stainless steel specimens were placed upstream of the catalyst bed where the steam moisture content was approximately 2%. These upstream stress corrosion specimens were exposed to 24-26 ppm oxygen and approximately 3.6 ppm (avg.) chlorides. The downstream set of stress corrosion specimens included four thick-sawed and six thin-sheared specimens which were exposed to the same steam as the upstream specimens except that the oxygen content and, incidentally, the chloride

TABLE III. PROPERTIES OF THICK TYPE 304 STAINLESS STEEL SPECIMENS

Gauge	No. 16
Tensile strength	85,500 psi
Yield strength	45,800 psi
Elongation in 2 in.	55%
Hardness	RB 80

Chemical Composition

<u>C</u>	<u>Mn</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ni</u>	<u>Cr</u>
0.06	1.53	0.022	0.013	0.54	9.14	18.43

content, had been reduced by the catalyst bed. The exposure history for each set is given in Fig. 84.

It should be noted that the moisture content of the steam at each stress corrosion position was approximately 2%. Initially, the downstream oxygen content was approximately 10 ppm for 15 hours because of the passage of wet steam through the catalyst bed. After 10⁰F of superheat were obtained at the bed inlet, the effluent oxygen content remained below 0.5 ppm for 3 days. However, the chlorides were apparently collecting on the catalysts during this time and gradually reduced their efficiencies. During the sixth day of corrosion testing, the chlorides "broke through" and the downstream chloride content approached the calculated input value. The effluent (downstream) oxygen concentration thereafter increased to 5.6 ppm. The loop was shut down because of these occurrences, after 140 hours of corrosion test operation.

The general corrosion coupons were exposed to steam which had been superheated 10-15⁰F immediately upstream and downstream from the catalyst bed. There were three coupons of each type of alloy in each position. The upstream specimens were exposed to 24-26 ppm oxygen and 2 ppm chlorides. The downstream (effluent) oxygen and chloride concentrations are shown in Fig. 84.

Upon removal of the stress corrosion specimens from the loop, it was immediately apparent that each of the upstream specimens, five thick-sawed and five thin-sheared, had cracked and failed totally. The appearance of these specimens before removal from the rack is shown by Fig. 87 with a closeup view shown in Fig. 88.

The downstream specimens exhibited no cracks visible to the naked eye but examination with a binocular microscope and further metallurgical examinations disclosed five cracks in one sheared thin specimen, with one possible, but somewhat doubtful, crack in a thick specimen. No other cracks were found in this group.

Both upstream and downstream specimens were mounted and polished for metallographic examination. Of the downstream specimens, the thick specimen which contained a possible crack was thoroughly examined at 100X and then greater magnifications. No definite crack was found although it is possible that the evidence of an incipient crack may have been removed during preparation. All the cracks examined metallographically were found to be true transgranular stress corrosion cracks with the normal branched "streak-of-lightning" appearance. Figure 89 shows the appearance of representative failures.

It was obvious from this and previous work that preparation by shearing produced specimens of above normal sensitivity to chloride stress-corrosion failures. High localized stresses are evidently produced in the specimen edges and cracks are easily initiated in these areas. On the thick-sawed and polished specimens, the localized stress areas are removed and the resultant surface more nearly represents the condition of structural stainless steel when exposed to chloride stress corrosion-producing conditions. Therefore, it was determined that the downstream conditions were such as to produce cracks in only one high-sensitivity specimen out of five but no positive cracks in specimens of normal sensitivity.

As an additional observation, the occurrence of small mounds of black material about the cracked areas on the upstream specimens should be mentioned. These black materials which formed at the cracks are shown in Fig. 88. The material was only loosely attached to the surface, and, from its appearance, could have either been deposited from the gas stream at these locations but more probably resulted from oxidation of the local metal during crack formation. From its appearance and magnetic character, it was plausible to identify the particles as magnetic iron oxide (Fe_3O_4), or a material which contained a large percentage of this oxide. It is of primary interest that this phenomena was not found on the downstream specimens. The oxidation of stainless steel in oxygen containing NaCl has been described⁴ with the emphasis on the formation of chromates and chrome oxides. However, localized oxidation of the stainless steel at the failures points to an iron-rich oxide in the high-oxygen, upstream conditions although considerably more data would be required before such a mechanism could be formally supported.

In order to confirm the stress corrosion test results described above, the week-long test was repeated. The conditions during this test were essentially identical to the earlier conditions except (1) chloride input was reduced by approximately 50% to 2 ppm, (2) greater care was taken to prevent the appearance of wet steam on the catalyst, thereby preventing the early appearance of higher chloride and oxygen concentrations downstream; and (3) the test was terminated before the chlorides and oxygen "broke through" the bed. The test conditions are shown in Fig. 90.

An initial microscopic visual examination of the stress corrosion specimens indicated that the results of the second test were identical to or possibly more definitive than the first test data. Each of the upstream (high oxygen, high chloride) specimens had failed. No cracks were found in any of the downstream (low oxygen, low chloride) specimens.

As stated above, six T-11 (1-1/4 Cr, 1/2 Mo), six T-22 (2-1/4 Cr, 1 Mo), and six Type 304 stainless steel surface corrosion specimens were exposed to high oxygen (25-32 ppm) or low oxygen (0.2-1.0 ppm) concentration conditions. These 18 specimens, divided into two sets, were exposed to the slightly superheated steam which existed just upstream or downstream from the recombiner bed. It was apparent from the data obtained by an examination of these coupons that, for a time of approximately 400 hours, the low alloy materials corroded differently. The higher oxygen concentration conditions produced a rougher surface appearance and resulted in a weight gain which was almost 400% as great as the low oxygen (downstream) conditions. A photograph of representative coupons exposed to high and low oxygen concentration is shown in Fig. 91. An approximate weight gain plot is shown for each set in Fig. 92. There was only insignificant difference in weight gained by the two sets of stainless steel coupons.

2. Intergranular Corrosion Tests

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.

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.

After two weeks of operation, an explosion occurred in the power plant which caused a loss of steam to the test loop. This exposed both sets of specimens to high oxygen and hydrogen concentrations and unknown amounts of moisture. This caused transgranular cracking in both the upstream and downstream specimens. There was one intergranular crack on a thin upstream specimen and also some intergranular attack on the same specimen. No intergranular corrosion was found downstream. Photographs of the intergranular crack and attack are given in Fig. 93.

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. They were exposed to 800°F, 840 psig steam at a flow of 775 lb/hr. Metallurgical examination after 14, 30, 49, 58, and 76 days of operation showed that there were no cracks either upstream (25 ppm oxygen) or downstream (5 ppb oxygen).

E. Conclusions on Endurance Tests

The long-term operation caused no significant loss of catalytic activity. It is, therefore, concluded that the catalysts can be used in high purity reactor steam with a mass velocity of 20,000 lb/hr ft² for extended periods without excessive loss of activity. Unfortunately, the presently preferred catalyst (Catalyst "C", platinum on stainless steel ribbon) has only been tested for 75 days. It is believed, however, that this catalyst would last for one year or more under reactor operation conditions. The test conditions for the 75 days of operation were considerably more severe than those expected under reactor operating conditions as exhibited by the analysis of the loop effluent steam condensate given in Table IV.

Tests to determine the effect of the recombiner on the corrosion on stainless steel were conducted simultaneously with the endurance testing. These tests demonstrated that the use of an internal recombiner greatly reduces the general corrosion rate, and in addition, markedly reduces the severity and the rate of chloride stress corrosion. In fact, these tests indicate that the use of a recombiner in a reactor system may actually eliminate chloride stress corrosion in the superheater fuel elements. No conclusive results can be stated regarding the effect of the recombiner

TABLE IV. 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

on intergranular corrosion. Only one upstream and no downstream specimens exhibited such corrosion. This is insufficient statistical evidence to demonstrate the effect of a recombiner on an intergranular corrosion.

The still unresolved problems regarding the use of a recombiner in a reactor system are:

- (1) Will the catalyst be poisoned by constituents, commonly present in reactor steam which were not present during the test, such as iodine? This problem refers particularly to a recombiner between the boiler and superheater in a boiling superheat reactor, to a closed cycle boiling water reactor system, and to an open cycle boiling water reactor system where the recombiner is used upstream of the turbine. In an open cycle boiling water reactor where the recombiner is used in the offgas system downstream of the condenser, the severity of this problem would depend upon the poison concentrations present in the low pressure condenser.
- (2) Are there any problems likely to crop up with operation of the catalyst for periods longer than those of the test?
- (3) Are there any harmful effects on the catalyst due to radiation?

It is believed the answer to the above questions will be in the negative, and that a catalyst can be used in a reactor system for acceptably long periods. These questions can be answered more definitively either by further testing and/or the use of a catalytic recombiner in a reactor.

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4. W. R. Grace and Company
Davison Chemical Division
5. Oxy - Catalyst, Inc.
6. Houdry Process and Chemical Company
7. American Cyanamid Company

UNITS

$^{\circ}\text{F}$	degrees Fahrenheit
ft^2	feet squared
in.	inch or inches
lb/hr	pounds per hour
lb/hr-ft^2	pounds per hour per square foot
lb/ft^3	pounds per cubic foot
m^2/gm	square meters per gram
ma	milliamperes
min	minute
ml/min (STP)	millimeters per minute at standard temperature and pressure
mv	millivolt
ppb	parts per billion by weight
ppm	parts per million by weight
psi	pounds per square inch
psia	pounds per square inch absolute
psig	pounds per square inch gauge
$^{\circ}\text{R}$	degrees Rankine

ILLUSTRATIONS

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Fig. 2 Flow diagram and schematic of test loop.

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