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I

HRE EXPERIMENTS ON INTERNAL
RECOMBINATION OF GAS WITH A
HOMOGENEOUS CATALYST

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HRE EXPERIMENTS ON INTERNAL RECOMBINATION
OF GAS WITH A HOMOGENEOUS CATALYST*

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Upon successful conclusion of the Homogeneous Reactor Experiment (HRE),
the reactor was dismantled in June 1954 to make room for the Homogeneous
Reactor Test (HRT).

OAK RIDGE NATIONAL LABORATORY
Operated By
CARBIDE AND CARBON CHEMICALS COMPANY

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ABSTRACT

The use of copper dissolved in the reactor fuel for the complete recombination of radiolytic gas has been successfully demonstrated in the HRE. Copper ion was added as copper sulfate on four occasions, increasing the copper concentration to 10, 25, 75, and 150 percent of the estimated concentration necessary for complete recombination in a static system at 250°C, at 1000 psig total pressure, and at a uniform power density of 20 Kw/liter. The investigation was conducted at temperatures from 185 to 260°C, at pressures from 765 to 1200 psig, and at power levels as high as 1600 Kw.

In the main, the copper behaved as expected from previous static bomb tests; the reactor data have been shown to be consistent with the laboratory data if it is postulated that a small but relatively stagnant region exists in the core with characteristics predicted from mixing experiments with a plastic model. The highest power level for which all the gas was internally recombined was 1350 Kw. In the course of all copper experiments, including 350 hours operation at the highest copper concentration, 0.06 molar, no deleterious effects due to the presence of copper were observed.

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1. INTRODUCTION

In an aqueous homogeneous reactor, the water is continually dissociated by the fission fragments into H_2 and O_2 . During the early operation of the HRE,⁽¹⁾ this gas was continually removed from the core and bled to the low pressure system where it was recombined both by burning and by contact with a catalyst bed. The water was returned to the reactor system to maintain a constant fuel concentration. For 1000 Kw operation, gas was formed at the rate of 10.3 cfm at STP, the rate being independent of temperature. This corresponds to a " G_{H_2} " value--the number of hydrogen molecules produced for each 100 e.v. energy absorbed in solution--of 1.4, which is in agreement with predictions based on in-pile ampoule tests.⁽²⁾

It had been reported that, in the presence of dissolved copper salts as homogeneous catalysts, hydrogen and oxygen when dissolved in aqueous solutions at elevated temperatures recombine smoothly to form water.^(3,4)

The dependence of the rate constant on various parameters had been studied in in-pile static bombs and in rocking bombs primarily out-of-pile where the gas is charged into the bomb from supply cylinders. The rate of the recombination reaction was found to be first order both in the concentration of dissolved copper and in the concentration of dissolved hydrogen. Since the concentration of dissolved hydrogen is proportional to the partial pressure of hydrogen--the constant of proportionality being related to the solubility at the temperature--the recombination rate is also proportional to the partial pressure of hydrogen. The partial pressure of gas in a closed

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aqueous system having a vapor phase is the difference between the total pressure and the steam pressure at the temperature. The rate of recombination for a given hydrogen and copper concentration increases with temperature; there is a doubling of the rate constant, for example, from 240 to 256°C, corresponding to an activation energy of 24.4 kilocalories per mole.

It is a relatively simple matter to compute for a static isothermal system at equilibrium the minimum concentration of copper ion which is required for complete recombination at a specified temperature, power density, and total pressure (to prevent the accumulation of radiolytic gas in the gas phase). If we consider the effects of increasing the temperature with the total pressure of gas and steam remaining constant, we find that the concentration of gas in solution goes through a maximum and decreases rapidly as the boiling point is approached since the increase in solubility constant is out-weighted by the decrease in gas pressure. Although the reaction rate constant increases with temperature, the effectiveness of the copper as a recombiner catalyst also goes through a maximum and decreases due to the rapid decline in the gas in solution. The higher the total pressure, the higher will be the temperature at which the maximum effectiveness of the copper occurs.

The conditions which are obtained in a circulating homogeneous reactor are in general quite removed from those in a static test bomb. As the fuel solution circulates through the core, pump, heat exchanger, and other auxiliary equipment, the solution experiences changes in temperature,

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pressure, and power density. Reactors under consideration call for approximately a 40°C temperature increase from core inlet to outlet, a pressure drop of approximately 40 psi in the circulating loop, a residence time of 2 to 4 sec inside the core where the average power density is 50 to 100 Kw per liter, and a residence time of 3 sec outside where the power density is negligible. As an additional complication, a slug of solution during circulation may alternately experience conditions where the maximum concentration of dissolved gas from solubility considerations either exceeds or is less than that carried by the solution, with the result that equilibrium conditions may not prevail. A method has been worked out for computing the effect of residence in the external portion of the circulating system, assuming uniform pressure and equilibrium conditions;⁽⁵⁾ the results are the same as obtained by considering the reactor as a static system but with a volume 15 to 20 percent larger. This has the effect of decreasing the average specific power for a given total power, and therefore increasing the apparent effectiveness of the copper by 15 to 20 percent.

In a homogeneous reactor, the Cu^{++} concentration for a given copper loading, is proportional to the concentration of U^{235} , and therefore increases with the operating temperature in the same manner as the critical fuel concentration.

The copper experiments were undertaken in the HRE primarily to show that the results of laboratory experiments on gas recombination in static bombs could be used to predict rates of recombination in a reactor. It

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was also desired to demonstrate in a reactor operating at full power density the overall feasibility of internal recombination of the gases which are formed from the radiolytic dissociation of water.

Although on the basis of laboratory and static in-pile tests no difficulty was anticipated with respect to the compatibility of copper and the reactor system--the stability of copper in solution, stability of the fuel, and effects on corrosion--the appearance of exotic effects within the reactor environment could not be completely ruled out in advance.

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2. EXPERIMENTAL PROCEDURE

2.1 High Pressure System

A schematic flow diagram for the HRE is shown in Figure 1. The high pressure fuel system consists essentially of an 18 inch diameter spherical core, a tube and shell type heat exchanger, and a centrifugal type pump. The volumes and residence times for a pumping rate of 120 gpm are given in Table I.

TABLE I
High Pressure Components of HRE

<u>Equipment</u>	<u>Volume for Fuel, liters</u>	<u>Residence Time, sec</u>
Core	50	6.6
Piping from Core to Heat Exchanger	4	0.53
Heat Exchanger	5.5	0.73
Pump and Return Piping to Core	6.1	0.80
Pressurizer	6.4	Negligible

The pressure is controlled by means of a steam pressurizer which is a vertical pipe above the core and is heated with steam. There is a pressure drop of 60 psi in the circulating high pressure system at 120 gpm; and at 1000 Kw, corresponding to an average power density of 20 Kw per liter in the core, the temperature rise across the core is 30°C. With the solution outlet at the north pole of the core, the inlet is located at 45° north

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latitude and so designed as to impart a tangential flow component. The gases which are produced are centrifuged toward a central vortex and withdrawn at the north pole.

2.2 Low Pressure System

The low pressure system operates near atmospheric pressure and consists of the fuel storage tanks and the equipment for handling the reactor gases. In the tanks, which have a capacity of 285 liters, there are normally present 20 to 40 liters of fuel solution which are continually recirculated to the high pressure system at a rate of 1 gpm. The quantity of water in the fuel solution and therefore the concentration of uranium can be varied by changing the hold-up of condensate in the weigh tanks. The concentration of the copper is therefore always proportional to the concentration of uranium and increases with the operating temperature as shown in Figure 2.

2.3 Gas Handling

The gases which are centrifuged toward the central vortex in the core are let-down to the low pressure system along with excess fuel solution. Steam which is generated in an evaporator appendage to the storage tanks at a rate of 0.5 Kg per minute dilutes the gases in the dump tanks. The gases then flow to a condenser where the steam is removed and before entering the flame recombiner where the hydrogen and oxygen are burned, the gases are again diluted with steam from a steamer pot (not shown) for the purpose of maintaining a sufficient velocity at the burner nozzle for low gas flows.

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Cooling water flows through the jacket of the flame recombiner; the flow rate and the temperature rise being measureable for the purpose of determining the rate of heat removal. If necessary to avoid hot spots in the bed, steam from a second steam pot (not shown) can again be injected into the gas stream upstream of the catalytic recombiner which follows the flame recombiner. The catalytic recombiner, which is steam jacketed to keep the catalyst dry, is followed by a second condenser where a heat balance on the cooling water can also be made. Residual gases are discharged through a cold trap to the charcoal absorbing bed, and thence to the stack. The recombined water from the flame recombiner and second condenser are continually returned to the fuel storage tanks. On the basis of a survey of temperatures in the catalyst bed, it has been established that all the dissociation gases from the water in the reactor are recombined.

2.4 Measurement of Gas Production

The rate of evolution of gas from the radiolytic dissociation of water in the reactor is measured by the rate of recombination in the off-gas system. This in turn is measured by the rate of removal of the heat of recombination. A correction is made for the heat contributed by the various extraneous heat sources such as the steamer pots. This can be readily calculated and is also checked by measuring the heat balance when no gas is produced in the reactor. The correction, 3.7 Kw, is nine percent of the heat removed from recombining the gas when the reactor operates at 1000 Kw.

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2.5 Experimental Procedure

After the inventory of reactor fuel solution was established as 185 Kg of water and 3.75 Kg of U^{235} , the first of four additions of copper sulfate was made. For a given quantity of copper, the concentration in solution as mentioned earlier is proportional to the concentration of U^{235} . These concentrations vary with the reactor operating temperature; for example, from 200 to 260°C, the critical U^{235} concentration in gm/Kg H_2O increases from 33.5 to 44.0 or 31 percent. It has proved more reliable to infer the U^{235} concentration and therefore the copper concentration from the critical temperature of the core than from fuel samples or from considerations of inventory. The quantity of copper added on each occasion was that estimated to give approximately 10, 25, 75, and 150 percent recombination for a static system at 250°C, 1000 psig total pressure, and a power density of 20 Kw/liter. The quantities and concentrations are listed in Table II.

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TABLE II

Copper Additions to HRE

Date	CuSO ₄ Added gms	Cumulative CuSO ₄ in Reactor, gms	Copper Concentration at 250°C molar	Molar Ratio Cu to U ²³⁵	Percent of gas Estimated to be Recombined at 250°C, 1000 psig, 20 Kw/l, static system
12-5-53	74.6	74.6	0.00417	0.0293	9.5
12-6-53	111.4	186.5	0.0104	0.0732	23.7
12-18-53	373.0	559.5	0.0313	0.220	71
1-5-54	555.1	1114.6	0.0624	0.438	142

At each copper concentration, the reactor was operated over a range of power levels at various temperatures and pressures. The net gas production was measured and by comparison with the gas production at the same power level in the absence of copper, the effectiveness of the copper as a catalyst for internal recombination could be inferred.

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3. RESULTS AND DISCUSSIONS

3.1 Recombination Data

The data obtained on the net gas yield from the reactor at various power levels for the four copper concentrations are plotted in Figures 3, 4, 5, 6, 7, 8, and 9. The line which represents the gas production in the reactor in the absence of copper is shown in the figures. Also shown is a dotted line which represents the calculated performance with the same copper concentration in a static reactor at 250°C, 1000 psig, uniform power density, and without circulation. In general, it is possible to draw a straight line through all points taken at the same pressure and outlet temperature from the core. This line is roughly parallel to that for no copper, and its intercept at zero external gas recombination represents the highest reactor power for which all the dissociation gas is internally recombined, and is therefore a measure of the effectiveness of the copper. These intercepts have been compiled in Table III.

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TABLE III
Effectiveness of Copper from Intercepts

Molar Conc. of Cu ⁺⁺ at Temp.	Molar Ratio [Cu] / [U ²³⁵]	Fuel Temp. °C	Fuel Pressure psig	Maximum Reactor Power where all gas is recombined, Kw
0.0045	0.0293	260	1000	85
.0042	.0293	250	1000	120
.0040	.0293	240	1000	160
.0038	.0293	227	1000	90
.0034	.0293	190	1000	70
.0112	.0732	260	1000	240
.0104	.0732	250	1000	320
.0104	.0732	250	810	170
.0099	.0732	240	1000	240
.0093	.0732	224	1000	110
.0336	.220	260	1000	530
.0313	.220	250	1000	615
.0298	.220	240	1000	600
.0292	.220	235	1000	530
.0265	.220	210	1000	200
.0243	.220	182	1000	50
.0298	.220	240	945	440
.0290	.220	232	920	380
.058	.438	235	1200	1350
.058	.438	235	1100	1100
.058	.438	235	1060	940
.058	.438	235	1010	890
.058	.438	235	905	710
.058	.438	235	760	410
.067	.438	260	1010	690
.061	.438	245	1010	820
.056	.438	228	1010	830
.067	.438	260	1110	980
.067	.438	260	1200	1280

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3.2 Core Mixing and Temperature Distribution

Before attempting to correlate the reactor data with the predictions based on static experiments in the laboratory, it is necessary to examine the temperature distribution in the HRE core. The flow and temperature patterns inside the core are somewhat ambiguous because it has not been feasible to study the mixing during high power operation when gas bubbles and volume heat generation become important factors. Early mixing experiments at room temperature with a plastic model of the HRE core⁽⁶⁾ indicated that the main body was perfectly mixed except for a relatively stagnant region of 7.5 liter volume, shaped like a doughnut, 16 cm inside diameter and 22 cm outside diameter, with the vertical axis going through the poles. The residence time and temperature rise for the liquid in this region were estimated as approximately twice that for the main body of the 50 liter core.

Additional information on mixing the HRE core is available from operating the reactor at high power. It has been observed that within the error of measurement, the core outlet temperature remains constant as the power is rapidly increased from essentially zero to 1000 Kw. This would imply that there is near perfect mixing in the core as opposed to pure slug flow. The latter would have required the outlet temperature to increase by 15°C, which is one-half the temperature rise across the core, since the average nuclear temperature which depends only on the fuel concentration must remain constant. From considerations of criticality and

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conservation of energy, it can be shown that the presence of a hot region perfectly mixed and of the size and residence time indicated by the tests with the plastic sphere would cause, as the power is raised to 1000 Kw, a decrease in outlet temperature of only 2°C which is comparable to the error in observing the temperature for this type of test.

Another phenomenon at high power sheds additional light on the core temperature distribution. It has been noted that the fuel concentration in the core becomes enhanced due to the removal of radiolytic gases and associated steam.⁽⁷⁾ Although the mass rate of removal of the radiolytic gases is proportional only to the reactor power, the removal of steam depends also on the temperature. In order to account quantitatively for the enhancement in concentration as reflected by the rise in core outlet temperature, it has been necessary to postulate that the temperature of the steam-gas mixture leaving the core is approximately 20°C higher than the core outlet for the circulating fuel. This hypothesis is also supported by data from heat balances on the let-down heat exchanger where the mixture of gas and solution returned to the low pressure system is cooled by the upcoming stream. A hotter region surrounding the vortex is implied; however, the thickness of this region need only be sufficient to saturate the radiolytic gas passing through to the vortex. The volume of the region must be greater than 0.5 liter to satisfy the power requirements for saturating the gas with steam. In summary, the main body of the HRE core is in a state of perfect mixing with the temperature approximately the same as

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the outlet temperature. In addition, there is probably a region at the center with perhaps 15 percent of the core volume for which the residence time and temperature rise at one megawatt operation are approximately twice that of the main body.

3.3 Effect of Temperature

It is evident from Figures 3, 4, 5, and 9 and Table III that, at a total pressure of 1000 psig and for a given copper loading in the reactor, the most effective temperature for internal recombination is between 240°C and 250°C. This is more easily seen in Figure 10 where the theoretical curves for recombination at 1000 psig in an isothermal core but with circulation in the external system (calculated as shown in reference 5) are also plotted for comparison with the observations on the HRE. For reasons given earlier, the theoretical curves also have a maximum but at a temperature of 268°C. However, the experimental data in general indicate a maximum effectiveness at lower temperatures; the higher the copper content, the lower the temperature at which the maximum occurs. It should be pointed out that the intercepts which measure the effectiveness occur at higher power levels for the higher copper concentrations. What seems a plausible qualitative explanation for the shifting of the maximum to lower core outlet temperatures is the presence in the core of a region which is at a considerably higher temperature than the main body. Thus, the effectiveness of the copper in this hotter region would follow the actual temperature there and not the core outlet temperature which is measured. Furthermore,

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for a given outlet temperature, the temperature of the stagnant region is expected to rise with power level. The effect of a two-temperature region core on recombination will be discussed more fully in connection with the following discussion of the effect of pressure.

In Figure 11, the recombination rate constant calculated from the HRE data for 25 and 75 percent nominal copper content, is compared at various core outlet temperatures with that obtained by static bomb investigators. The only correction applied to the reactor data was for the recombination in the external high pressure loop. The agreement is in general very encouraging, ignoring the decrease at high temperatures which probably reflects the effect of the hot region in the core. This effect seems more pronounced for the data taken with 75 percent copper, probably for the reason that the temperature increase in the stagnant region is greater at the higher power levels associated with the higher copper content.

3.4 Effect of Pressure

With the highest copper concentration in the fuel, 0.06 molar nominal, an investigation was made of the effect of the total reactor pressure on the effectiveness of the copper for gas recombination. Although it would have been desirable to conduct this study at a number of temperatures, it was only possible because of equipment limitations to achieve a sizeable range of pressures at one temperature only, 235°C. The extrapolated reactor power for gas first to appear, which is a measure of the

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effectiveness of the copper, is plotted in Figure 12 against total reactor pressure. Also shown is a theoretical curve which was calculated on the basis of a completely isothermal core with recombination also occurring in the external high pressure system. In general, the experimental data agree well with the curve with indications that at the higher pressures, the copper was somewhat less effective than predicted by this model.

The data were also analyzed on the basis of a core model in which there is a relatively stagnant region where 15 percent of the power is generated. It is postulated that the fuel solution entering the core divides into two streams, one for the stagnant region and one for the main body of the core. Each region is assumed to be perfectly mixed and therefore at uniform but, in general, different temperature and gas concentration. For each region, the pressure required for total recombination is calculated, as shown in the Appendix, as a function of the power density. The curve giving the performance of the stagnant or hotter region at a constant core outlet temperature of 235°C is shown in Figure 12, while that for the main body is represented essentially by the curve already drawn for the isothermal core model. For pressures up to 840 psia, gas bubbles by this model are formed first in the stagnant region when the reactor power is increased, while at higher pressures, they appear first in the main body.

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It is now necessary to discuss more fully the significance of the intercepts which were obtained by extrapolating the experimental data by means of a straight line parallel to the line which gives the gas generation in the whole reactor in the absence of copper. The assumption is implicitly made that with copper the gas production is proportional to the power in the same way. This in general is not true since the gas production should, to a first approximation, be proportional to the fraction of the total power which is generated in the region where the gas phase is present provided the temperature and pressure remain constant. However, because of the experimental error, it has not been possible, where the dependence of gas production on power was followed over an appreciable range, to detect any significant deviation from the slope of the no-copper line. In those cases where, as the power is increased, gas is first produced in the main body in which 85 percent of the power is produced, the true intercept should be 15 percent of the way between the power for gas generation in the main body and the power for gas generation in the stagnant region. A theoretical curve composited in this manner is also shown in Figure 12.

In general, the experimental data appears to favor the two-temperature core model, although additional data at higher pressures, which were not obtainable, might have made this choice more definite. Also, additional data at lower pressures would have been helpful in verifying that the intercept on the pressure axis, for no recombination, is the

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steam pressure for 235°C. A limited amount of data were taken at 260°C outlet temperature at total pressures from 1000 to 1200 psig for the nominal copper concentration of 0.06 M. At the highest power level attained at each set of conditions, the reactor was on the verge of instability due to the fuel concentration effect in the core. The intercepts were obtained by the usual extrapolation, shown as the dashed lines in Figure 8. The analysis based on a two-temperature region core reveals that at all pressures gas bubbles are first generated in the hotter region as the power is raised.

Furthermore, as the power is increased from the point at which gas first emerges to the point at which the solution boils in the stagnant region, the gas production as shown by the solid curves in Figure 8 increases as rapidly as if the gas were generated throughout the reactor core. This arises from the fact that the gas generation in the stagnant region is supplemented by two other phenomena: first, a fraction of the solution which leaves the main body enters the hotter, stagnant region where the gas dissolved in the solution is stripped; second, as the boiling point is approached in the stagnant region, the recombination rate falls off rapidly. It so happens here that the linear extrapolation of the data in the usual manner yields intercepts which are identical to the threshold powers for gas production, which are calculated on the basis of the two-temperature core model. The effectiveness of the copper as measured by this threshold power is plotted in Figure 14 against the total pressure in the reactor.

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The data are in excellent agreement with the predictions based on the two-temperature core model while the calculations for an isothermal core predicted an effectiveness for the copper three to four times greater than observed. This experiment at 260°C outlet temperature from the core thus demonstrates in a very striking manner the necessity of taking into account the detailed temperature pattern in the core and also the validity of the assumptions concerning the stagnant region. These assumptions were based on the results from the mixing experiments performed with the plastic model of the HRE core.⁽⁶⁾

It also explains the incipient instability in the reactor at the highest power levels achieved at 260°C on the basis of incipient boiling in the stagnant region. This results in an inordinately large rate of steam removal from the core and a corresponding enhancement of the fuel concentration in the core.

Also shown, Figure 14, are some data on pressure dependence obtained with 0.0104 M concentration of Cu^{++} at relatively low power levels where the effect of the doughnut would not be too important. The agreement with the predictions based on an isothermal core model is reasonably good.

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4. CONCLUSIONS

The application of dissolved Cu^{++} as a catalyst in a homogeneous reactor has been demonstrated for the recombination of the hydrogen and oxygen which are formed from the radiolytic dissociation of water. At 1000 psig pressure and 235°C fuel outlet temperature from the core, essentially all the gas formed at 1350 Kw--which normally is equivalent to 13.9 cfm at STP--was recombined in solution with 0.058 M concentration of Cu^{++} . If an accurate picture is available of the flow, pressure and temperature patterns in the reactor, it would appear from the present results that one should predict the copper requirements for recombination on the basis of the published data obtained with laboratory systems.

In the main, the results obtained over a sizeable range of temperatures, power levels, and pressures are consistent with the findings of the static system investigators. The quantitative interpretation of the data has been complicated by the flow and temperature distribution in the reactor core which is peculiar to the HRE. There is evidence--both from mixing experiments in a plastic model and from the manner in which the temperature increases with reactor power due to stripping of gas and steam in the vortex--that at the center of the core, there exists a relatively stagnant region which at 1000 Kw reactor power may be as much as 30°C hotter than the main body.

The data obtained from the HRE can be directly correlated to the results in static systems only to the extent that the reactor can be

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approximated by an isothermal system, a good approximation only at low power. At the higher power levels, this approximation apparently becomes poorer since the difference in temperature between the outlet and that of any stagnant region in the core becomes more and more appreciable. Thus, at the two lowest copper concentrations, 0.004 and 0.010 M, the power required for gas to appear is 300 Kw or less, and the agreement between the observed dependence on temperature and that predicted for a static system, Figure 11, is reasonably good. At higher copper concentrations, where the reactor power must be raised as high as 900 Kw for the appearance of gas, the data must be analyzed on the basis of a two-temperature region core model.

The comparison with earlier work on static systems can be summarized as follows:

1. Over the temperature range of 182° - 250°C , Figure 12, one-half of the recombination rates calculated from the HRE data at low power fall within the range of the data presented by the investigators of static systems. The slope also appears reasonably consistent with their reported activation energy of 24.4 kilocalories, although possibly somewhat lower.
2. The effectiveness of the copper, at conditions where the effect of the stagnant region is not important, is apparently proportional to the copper concentration, Figures 11 and 12.
3. The effect of the pressure or the concentration of hydrogen in solution on the recombination reaction is obscured in the in the reactor because of non-isothermal conditions in the core.

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The data at 235°C with 0.058 M, Cu^{++} , Figure 13, and at 250°C with 0.0104 M, Cu^{++} , Figure 14, clearly support the first power dependence of recombination rate on gas pressure. However, the data obtained at 260°C core outlet temperature with 0.067 M Cu^{++} , Figure 14, agrees very well with the static bomb information only when analyzed on the basis of the two-temperature region core with the characteristics of the stagnant region derived from the mixing experiments with the plastic model. Calculations for an isothermal core model predict an effectiveness for the copper three to four times greater than observed.

Because of the copper, it has been possible to extend the permissible power level of the HRE from 1000 to 1500 Kw. The removal from the core of the decomposition gases with associated steam increases the concentration of fuel in the core with respect to the low pressure system. Because the region about the vortex apparently runs 20 to 30 degrees hotter than the remainder of the core, the removal of steam and the concentration effect were enhanced to the point where an instability developed in the operation of the reactor. (8) By reducing the net gas production by means of the copper, the concentration effect in the core was also reduced permitting the operation of the reactor at high power levels.

Finally, no harmful effects from the copper were found in the operation of the reactor for 350 hours with 0.06 M Cu^{++} . There was no significant change in the corrosion rate as determined from the nickel

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concentration in the fuel solution, and there was no evidence of any chemical instability either with respect to the copper or the uranium.

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5. APPENDIX: RECOMBINATION IN A TWO-TEMPERATURE REGION HRE CORE MODEL

5.1 Calculation of Doughnut Temperatures

The behavior of flow in the HRE core under the influence of density differences had been investigated in the full scale plastic model by Spiewak and Bradfute.⁽⁶⁾ They report a characteristic stagnant region coaxial with the vortex with the following average dimensions:

Average radius 9.5 cm
Thickness 3 cm
Average height 41.6 cm
Volume 7.45 liters

Bradfute and Spiewak also give an expression by which the temperature in the stagnant region or "doughnut" can be estimated. The density in the doughnut is given by

$$a_1(\rho_1 - \rho) + \frac{a_2}{\rho_0}(\rho_0 - \rho)^2 - \frac{\phi x}{C_P \rho_0} = 0 \quad (1)$$

where

ρ = density in doughnut, gm/cm³
 ρ_1 = core inlet density, gm/cm³
 ρ_0 = core outlet density, gm/cm³
 ϕ = specific power in doughnut, cal/cm³-sec
 x = temperature coefficient of density, gm/cm³-°C
 C_P = specific heat, cal/gm-°C
 a_1 = experimentally determined mixing coefficient, sec⁻¹
 a_2 = experimentally determined mixing coefficient, sec⁻¹

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The specific heat and temperature coefficient of density are evaluated at the core outlet temperature which is usually about halfway between inlet and doughnut temperature. The doughnut temperature can be found from the density by

$$T = T_0 + (\rho_0 - \rho) x$$

The mixing coefficients, a_1 and a_2 , were found to be directly proportional to the flow through the core.

$$a_1 = 0.0227 \text{ g/100 sec}^{-1}$$

$$a_2 = 1.65 \text{ g/100 sec}^{-1}$$

where g is the flow rate in gpm. For the HRE, the flow rate is 120 gpm and

$$a_1 = 0.02724 \text{ sec}^{-1}$$

$$a_2 = 1.98 \text{ sec}^{-1}$$

Spiewak and Bradfute also made a calculation of the power density in the doughnut compared to the average for the core. Taking into account the flux distribution and density differences, they found that at 1000 Kw the doughnut power density was only ten percent above the average for the core. In calculating temperatures for this report, the power density in the doughnut was assumed to equal the core average.

The inlet temperature is less than the outlet by an amount which depends upon the power. For the HRE, the difference has been found to be 0.030°C/Kw .

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Other constants which were used in evaluating the doughnut temperatures are given in the following table. Densities are for water at 75 atmospheres and are taken from Dorsey, Properties of Ordinary Water Substance. Specific heats are from ORNL CF 52-1-124.

T, °C	ρ , gm/cm ³	α , gm/cm ³ °C	C _p , cal/gm °C
220	0.8449	0.001275	1.102
230	0.8318	0.001345	1.120
235	0.8251	0.001380	1.129
240	0.8180	0.001425	1.139
250	0.8033	0.001510	1.162
260	0.7878	0.001615	1.188

The differences in doughnut temperature and core outlet temperature which were calculated using the above information are shown in Figure 16. This particular curve is for a 250°C outlet; curves for other temperatures are only slightly different because of small differences in specific heat and temperature coefficient of density.

5.2 Calculation of Total Pressure

The following model is assumed for the purpose of calculating the relationship between total pressure and the reactor power at which gas first appears. As the fluid enters the core, it is assumed to be divided into two streams; one through the doughnut and the other through the main body of the core. Each region is assumed to be perfectly mixed, at uniform temperature, pressure, power density, and hydrogen concentration. The following procedure is then used:

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- a. For a specified power density and outlet temperature, the temperatures in the two regions are estimated. For all practical purposes, the temperature of the main body can be taken equal to the outlet temperature. The temperature of the doughnut can be calculated as shown in the previous section. Also, the power density in the two regions can be taken as equal.
- b. The copper concentration in the main body is obtained from the copper and uranium inventories and the critical uranium concentration from the outlet temperature. The ratio of the copper concentration in the doughnut region to that in the main body is given by the ratio of the liquid densities.
- c. The residence time in the doughnut is calculated from the temperature rise, power density, specific heat, and density of the solution. From the residence time and assumed volume can be obtained the flow rate through this region.
- d. The required concentration of H_2 for recombination is then calculated for each region.
- e. From solubility data, the required partial pressure of H_2 is calculated; the pressure due to $2H_2$ and O_2 is 50 percent greater.
- f. The total pressure in the region is then the sum of the gas pressure and the steam pressure.

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Denote by the subscript 1 all properties pertaining to the main body and by 2 the properties in the hot region or doughnut.

p^t = total pressure of gas and steam, psia

p^s = steam pressure, psia

p^{H_2} = H_2 partial pressure, psi

y = concentration of H_2 in solution, moles/liter

x = concentration of Cu^{++} in solution, moles/liter

α = solubility of H_2 , psi/mole/liter

T = temperature in core, $^{\circ}C$

P = power density, Kw/liter

f = fraction of flow through region 1

t = residence time in core, sec

$1 - \beta$ = fractional reduction in H_2 concentration in external loop due to recombination, ~ 0.08

A = rate of formation of H_2 by dissociation of water, $= 1.47 \times 10^{-4}$ moles H_2 /Kw

The specific rate constant for Cu^{++} ions, k , is a function of temperature, and the data from McDuffie et al ⁽⁷⁾ were used to obtain

$$k = 7.16 \times 10^9 \exp (-12,200/T_{abs})$$

At equilibrium, the rate of production of H_2 in each region is equal to the rate it is being removed. The removal is due both to recombination and to transport in and out of the region.

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$$(1) \quad 0 = AP_1 - k_1 x_1 y_1 - (y_1 - y_0) \frac{1}{t_1}$$

$$(2) \quad 0 = AP_2 - k_2 x_2 y_2 + (y_0 - y_2) \frac{1}{t_2}$$

$$(3) \quad y_0 = \beta \left[f y_1 + (1 - f) y_2 \right]$$

After substituting for y_0 from (3), subtract (2) from (1);

$$(4) \quad 0 = y_1 \left\{ \beta f \frac{(t_2 - t_1)}{t_1 t_2} - \frac{1}{t_1} - k_1 x_1 \right\} + y_2 \left\{ \beta (1-f) \frac{(t_2 - t_1)}{t_2 t_1} + \frac{1}{t_2} + k_2 x_2 \right\}$$

or,

$$(4') \quad y_1 = M y_2, \quad \text{where}$$

$$M = \frac{k_2 x_2 + \frac{1}{t_2} + \beta (1-f) \frac{(t_2 - t_1)}{t_2 t_1}}{k_1 x_1 + \frac{1}{t_1} - \beta f \frac{(t_2 - t_1)}{t_2 t_1}}$$

We then have for incipient gas production

$$(1') \quad y_1 = AP_1 \frac{1}{k_1 x_1 + \frac{\beta}{t_1} \left(\frac{1}{\beta} - f - \frac{1-f}{M} \right)}$$

$$(2') \quad y_2 = AP_2 \frac{1}{k_2 x_2 + \frac{\beta}{t_2} \left(\frac{1}{\beta} - (1-f) - Mf \right)}$$

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Only one of the above equations can be used--the one for the region where gas is first produced--since complete recombination in both regions is postulated. The problem of calculating H_2 concentration for incipient gas production in the remaining region while gas is coming out of solution in the other is somewhat simplified since the H_2 concentration in the other region is that in a saturated solution. Thus, if it is required to determine the H_2 concentration for bubble production in region 2 while gas is being removed from region 1, we write

$$(5) \quad 0 = AP - \left\{ k_2 x_2 + \frac{1}{t_2} - \frac{\beta(1-f)}{t_2} \right\} y_2 + \frac{\beta_f}{t_2} y_1$$

$$\begin{aligned} (6) \quad y_1 &= \frac{p_1^{H_2}}{\alpha_1} = \frac{2}{3} \frac{(p^t - p_1^s)}{\alpha_1} \\ &= \frac{2}{3} \left[\frac{(3/2) p_2^{H_2} + p_2^s - p_1^s}{\alpha_1} \right] \\ &= \frac{\alpha_2}{\alpha_1} y_2 + \frac{2}{3} \frac{(p_2^s - p_1^s)}{\alpha_1} \end{aligned}$$

After substituting (6) into (5), we obtain

$$(7) \quad y_2 = \frac{AP + \frac{2}{3} \frac{\beta_f}{t_2} \frac{(p_2^s - p_1^s)}{\alpha_1}}{k_2 x_2 + \frac{1}{t_2} \left[1 - \beta_f \frac{\alpha_2}{\alpha_1} - \beta(1-f) \right]}$$

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Fig. 1. Homogeneous Reactor Experiment Schematic Flow Diagram

ORNL-LR-Dwg. 5002

Fig. 2. Variation of Copper Concentration with Core Temperature

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ORNL-LR-Dwg. 5003

Fig. 3. Internal Gas Recombination in HRE with 0.004M Cu^{++}

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ORNL-LR-Dwg. 5004

Fig. 4. Internal Gas Recombination in HRE with 0.01M Cu⁺⁺

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Fig. 5. Internal Gas Recombination in HRE with 0.03M Cu^{++}

ORNL-LR-Dwg. 5006

Fig. 6. Internal Gas Recombination in HRE with 0.03M Cu^{++}

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ORNL-LR-Dwg. 5007

Fig. 7. Gas Production in HRE with 0.06 M Cu^{++} at 235°C Core Outlet Temperature

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Fig. 8. Internal Gas Recombination in HRE with 0.06M Cu^{++} , Core Outlet Temperature, 260°C

ORNL-LR-Dwg. 5009

Fig. 9. Internal Gas Recombination in HRE with 0.06 M Cu^{++}
Total Pressure 1010 psig

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ORNL-LR-Dwg. 5010

Fig. 10. Internal Gas Recombination in HRE as a Function of Core Outlet Temperature. Total Pressure, 1000 psig

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ORNL-LR-Dwg. 5011

Fig. 11. Effect of Temperature on Recombination Rate Constant at Low Power (Data Interpreted on Basis of Isothermal Core with Recombination in External System)

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ORNL-LR-Dwg. 5012

Fig. 12. Gas Recombination in HRE 235°C Core Outlet Temperature, 0.058M Cu^{++}

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ORNL-LR-Dwg. 5013

Fig. 13. Effect of Total Pressure on Internal Gas Recombination, 260°C Fuel Outlet Temperature, 0.067 M Cu⁺⁺

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ORNL-LR-Dwg. 5014

Fig. 14. Pressure Dependence of Internal Gas Recombination in HRE 250°C, 0.0104M Cu^{++}

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ORNL-LR-Dwg. 5015

Fig. 15. Calculated Increase in "Doughnut" Temperature with Respect to Main Body

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