UNCLASSIFIED

EXTERNAL TRANSMITTAL AUTHORIZED

OAK RIDGE NATIONAL LABORATORY

Operated By

UNION CARBIDE NUCLEAR COMPANY

UCC

POST OFFICE BOX 9
OAK RIDGE, TENNESSEE 37831 ORNL
CENTRAL FILES NUMBER

56-11-54

DATE: November 13, 1956

COPY NO. 33

SUBJECT: Radiation Stability of Aqueous Fuel Systems. Material
for Revised Reactor Handbook.

TO: C. H. Secoy

FROM: C. J. Hochanadel

1. HRP Director's Office	29. R. N. Lyon
Room 259, 9204-1	30. J. P. McBride
2. G. M. Adamson	31. H. F. McDuffie
3. S. E. Beall	32. R. A. McNees
4. E. G. Bohlmann	33. E. C. Miller
5. F. R. Bruce	34. E. O. Nurni
6. W. D. Burch	35. L. F. Parsly
7. R. D. Cheverton	36. R. C. Robertson
8. E. L. Compere	37. A. M. Rom
9. J. S. Culver	38. W. L. Ross
10. W. K. Eister	39. H. C. Savage
11. D. E. Ferguson	40. C. L. Segaser
12. C. H. Gabbard	41-65. C. H. Secoy
13. W. R. Gall	66. I. Spievak
14. J. C. Griess	67. R. W. Stoughton
15. P. H. Harley	68. J. A. Swartout
16. P. M. Haubenreich	69. E. H. Taylor
17. J. W. Hill	70. D. G. Thomas
18. C. J. Hochanadel	71. T. H. Thomas
19. G. H. Jenks	72. D. S. Toomb
20. S. I. Kaplan	73. W. E. Unger
21. P. R. Kasten	74. R. Van Winkle
22. A. S. Kitzes	75. C. E. Winters
23. R. B. Korsmeyer	76. F. C. Zapp
24. K. A. Kraus	77. ORNL Document Reference
25. J. A. Lane	Library, Y-12
26. R. E. Leuze	78. Central Research Library
27. R. B. Lindauer	79-80. Reed Library
28. M. I. Lundin	81. ORNL-RC
	82-83. Lab. Records

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

UNCLASSIFIED

DISCLAIMER

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

DISCLAIMER

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

AQUEOUS FUEL SYSTEMSIV. Radiation Stability:A. Introduction.

Any aqueous reactor fuel solution will be subjected to intense fluxes of high energy radiations. The action of these radiations both on the water and on the solute is of considerable importance in reactor design and operation. Energy will be dissipated in a fuel solution by the stopping of fast charged particles. These include mainly the fission recoil particles, the recoil particles such as protons produced by elastic neutron scattering, and the fast electrons resulting from the absorption of gamma rays and from the decay of radioactive fission products. The extent to which each contributes to the total energy absorbed in the fuel solution depends upon the design of the reactor and the composition of the solution. The water is decomposed by all types of high energy radiations to give hydrogen, hydrogen peroxide and oxygen.¹ If the decomposition products are confined in solution, a radiation-induced back reaction will occur, and eventually steady state concentrations (pressure) of products will be attained. The rate of decomposition, the rate of the back reaction, and hence the steady state concentrations are sensitive to the conditions of the system, such as the nature of the radiation, the type of concentration of solutes present, and the temperature.

The solutes may also be acted upon both by direct absorption of the energy of the radiations (or by transfer of energy from the solvent) and also by reactions with the intermediate reactive species produced by the

decomposition of the water.

B. Kinetics of Water Decomposition.

1. Primary Chemical Reaction: Decomposition

The fast charged particles give up energy to the electronic systems of the molecules of the medium thereby producing various excited and ionized states. In liquid water, the ionized and excited molecules are rapidly transformed into the free radicals H and OH. These are formed in relatively high concentrations along the tracks of the fission recoils or other charged particles. As a result, many of the radicals combine before they can diffuse apart, thereby producing the stable molecules H_2O , H_2 and H_2O_2 . The primary chemical species are therefore considered to be H, OH, H_2 and H_2O_2 , and the yields per 100 electron volts of energy absorbed are expressed as $G(H)$, $G(OH)$, $G(H_2)$, and $G(H_2O_2)$. The primary chemical reaction can be written:

Some minor subtleties emerging from recent studies of the radiolysis of aqueous solutions are: (a) although stoichiometry demands that $G(H) + 2G(H_2) = G(OH) + 2G(H_2O_2)$, the yields of H and OH and also the yields of H_2 and H_2O_2 are not necessarily equal to each other;² (b) the yields of H_2 and H_2O_2 are lowered by solutes which scavenge the precursors in the particle tracks;³ (c) HO_2 may be another "primary" chemical species produced in small yield in the particle tracks.⁴

The yields of the primary chemical species depend markedly on the type of radiation, or more specifically, on the energy transferred to the solution per unit length along the track of the charged particle. The linear energy transfer (LET) parameter varies from 5×10^4 kev, micron⁻¹ of path for

fission recoils to 0.2 kev, micron⁻¹ for fast electrons. The yields $G(H_2)$ and $G(H_2O_2)$ are largest for radiations such as fission recoils with large LET, while the yields $G(H)$ and $G(OH)$ are largest for radiations such as fast electrons with small LET. This is illustrated in Figure 1 where the yields⁵ $G(H_2)$ and $G(H)$ are plotted as a function of LET.

2. Secondary Reactions: The Back Reaction and Effects on Dissolved Materials.

The free radicals which escape combination and diffuse into the bulk of the solution may react with solutes present, including the H_2 and H_2O_2 . In water with no added solutes, the principal reactions of the free radicals are believed to be:

Reactions 2 and 3 provide a chain mechanism for the back reaction of H_2 and H_2O_2 to reform water,⁶ thereby leading to steady state concentrations of decomposition products. The steady state concentration will depend on the relative yields of molecular products and free radicals in reaction 1. For gamma rays which produce the free radicals in high yield and the molecular decomposition products in low yield, the steady state in pure water is essentially zero. For fission recoils which produce essentially no free radicals to promote the back reaction, the steady state concentration

(pressure) is very high (several thousand psi). Reactions 4 and 5 provide a mechanism for decomposing H_2O_2 to O_2 , and reactions 3, 5, 6 and 7 provide a mechanism for combining H_2 and O_2 to form water at higher temperatures.⁷

Dissolved materials may be oxidized or reduced. In general, H atoms usually reduce the solute and OH radicals oxidize it back. Assuming equal numbers of H and OH, the net result depends on the action of the H_2O_2 . The peroxide may act in either way (depending on the redox potentials) but usually oxidation is favored. In the presence of O_2 , the H atom may be converted to HO_2 which usually acts as an oxidizing agent.

C. Uranium Solutions.

1. Decomposition.

In Table 1 are listed the hydrogen yields from the decomposition of solutions of various uranyl salts.⁸ The yield depends on the type of radiation and on the solute concentration, but is independent of temperature. Figure 2 shows how the yield of hydrogen produced by fission recoil decomposition, and by gamma ray decomposition, decreases with increasing uranium concentration. This decrease may result from scavenging of H atoms in the particle tracks by the uranyl ions. Decomposition by fission recoil particles produces mostly H_2 , (and an equivalent amount of H_2O_2 plus O_2); the yields $G(H)$ and $G(OH)$ are very small, probably in the range 0 to 0.1 per 100 ev.

In an aqueous homogeneous reactor fuel solution, the water is decomposed by fission recoils, proton recoils, and fast electrons. The rate of formation of hydrogen, in moles per liter per minute, can be expressed by the equation:

TABLE I

The Effect of Enrichment, Concentration, Type of Anion and pH on The Initial Yields for H_2 Production In Reactor Irradiate Uranium Solutions

Solute	Concentration (Molality)	Enrichment (U^{235} Molality)	Fission Recoil (Total Energy)	pH	$G(H_2)$ (Molecules/ 100 e.v.)
UO_2SO_4	0.0017	$>90\% U^{235}$	$>.65$		1.61
	0.017	$>90\% U^{235}$	$>.91$	3.26	1.66
	0.08	0.007	.89	2.90	1.48
	0.16	0.0012	.61		0.95
	0.17	$>90\% U^{235}$	$>.94$	2.42	1.53
	0.44	0.16	.98	2.00	1.35
	0.44	0.16	.98	0.10*	1.20
	0.47	0.16	.98		1.35
	0.88	0.00027	.27		0.69
	0.88	0.16	.98	1.61	1.11
	0.90	$>90\% U^{235}$	$>.95$		1.11
	1.01	0.007	.89		0.98
	1.42	0.00041	.36		0.62
	1.80	0.007	.89		0.80
	2.04	0.16	.98	1.32	0.77
	2.08	0.013	.93		0.73
	2.28	0.0006	.46		0.56
	3.65	0.14	.98		0.56
	4.17	0.16	.98	1.03	0.49
UO_2F_2	0.018	$>90\% U^{235}$	$>.91$	4.25	1.63
	0.16	$>90\% U^{235}$	$>.94$	3.32	1.58
	0.50	0.16	.98	2.98	1.36
	1.19	0.16	.98	2.64	1.11
	1.68	0.16	.98	1.35*	0.84
	1.81	0.17	.98	2.41	0.95
$UO_2(NO_3)_2$	0.018	$>90\% U^{235}$	$>.91$		1.63
	0.18	$>90\% U^{235}$	$>.94$	2.05	1.5
	1.46	0.010	.91	1.03	0.6
	1.98	0.15	.97	0.60	0.55
$U(SO_4)_2$	0.18	$>90\% U^{235}$	$>.94$	1.95	1.45
	0.38	0.15	.98	0.1	1.25
	1.62	0.14	.98	0.1	0.75

*The pH was adjusted by adding acid.

$$\frac{d(H_2)}{dt} = 0.00622 \left[G_{fr} \times W_{fr} + G_p \times W_p + G_e \times W_e \right] \quad (8)$$

where G is the hydrogen yield in molecules per 100 electron volts absorbed; and W is the power density in kilowatts per liter. The subscripts f.r., p, and e refer to the values for fission recoil particles; protons produced by neutron scattering, and electrons produced by gamma-ray absorption and by radioactive decay of fission products. For an operating homogeneous reactor, most of the hydrogen gas produced in solution results from decomposition of the water by the fission recoil particles, and therefore the last two terms in equation 8 may be neglected. This is shown in Table II. The

TABLE II

Relative Amounts of H_2 Produced by the Decomposition of the Water
By the Various Radiations in an Aqueous Homogeneous Reactor

	Mev	Maximum $G(H_2)^*$	Fraction of Total H_2 Produced
Kinetic energy of fission recoils	168	1.8	0.96 minimum
Kinetic energy of prompt neutrons	5 ± 0.5	1.0	0.02 maximum
Prompt gamma-rays	4.6 ± 0.5	0.45	0.02 maximum
Radioactive decay	13 ± 2		

*Assuming no lowering of the yield by the solute. (See Figure 2).

fraction 0.96 represents a minimum value since part of the energy of the prompt neutrons, gamma rays, and radioactive decay escapes from the solution.

The rate of H_2 formation can therefore be closely approximated by the equation:

$$\frac{d(H_2)}{dt} = 0.00622 G_{fr} \times W_{fr} \quad (9)$$

The value of G_{fr} for a given solute concentration can be obtained from Figure 2 and the value for W_{fr} can be calculated from the neutron flux, the concentration of fissionable atoms, the fission cross section, and the kinetic energy of the fission recoils.

Along with the hydrogen, an equivalent amount of oxidant (either peroxide or O_2) will be formed.

2. Recombination

a. Radiation Induced Recombination.

For fission recoil particles the radiation induced back reaction of H_2 , O_2 and H_2O_2 is relatively slow. Also, the thermal recombination rate in the absence of added catalyst is relatively slow, and as a result, the steady state pressure of gases is very high; e.g. at $250^\circ C$. the pressure is of the order of thousands of psi.

b. Catalyzed Thermal Recombination.

Certain solutes, notably copper salts, have been shown to act as homogeneous catalysts⁹ in the thermal combination of hydrogen and oxygen in aqueous uranium solutions. This provides a convenient method for recombining the radiolytic hydrogen and oxygen gases.

The reaction rate is first order in hydrogen and in copper concentration, and independent of the oxygen concentration. The rate determining step is the reaction of hydrogen with the catalyst, and the activation energy

is about 24 kcal, mole⁻¹. For a particular uranium solution, the rate of hydrogen removal, in moles, liter⁻¹, min⁻¹, can be expressed by:

$$\frac{-d(H_2)}{dt} = k_{cu} (Cu) (H_2) \quad (10)$$

where k_{cu} is the catalytic constant in liter, mole⁻¹, min⁻¹, and concentrations are given as moles, liter⁻¹. Some selected values of k_{cu} are listed in Table III. Increasing the concentration of uranyl sulfate or of sulfuric

TABLE III

Selected Values of k_{cu} at Several Temperatures and
Uranium Concentrations. (Cu) = 10⁻³ M.

Uranium Concentration (m)	Temperature °C	k_{cu} (liter, mole ⁻¹ , min ⁻¹)
0.17	190	4.3
0.17	220	26.6
0.17	250	90.0
0.17	250	83.0*
0.01 to 0.1	250	133
0.01 to 0.1	275	380
0.01 to 0.1	295	850

*With 10⁻³ M Cu(ClO₄)₂ plus HClO₄ in concentrations ranging from 0.005 M to 0.05 M.

acid decreases the catalytic activity of the copper somewhat, possibly as a result of complexing. Also, the rate of reaction with D₂ is about .6 that with H₂.

The concentration (solubility)¹⁰ of H₂ is related to the partial pressure of hydrogen by the proportionality factor:

$$S = \frac{P_{H_2}}{(H_2)} \quad (11)$$

where P_{H_2} is given in psi, (H_2) in moles, l^{-1} , and S in psi, l , mole^{-1} .

Equation 10 can then be written:

$$\frac{-d(H_2)}{dt} = k_{cu} (Cu) \frac{P_{H_2}}{S} \quad (12)$$

At the steady state, the rates of formation and removal of hydrogen are equal, and from equation 9 and 12, the steady state pressure is given by:

$$P_{(H_2)ss} = \frac{0.00622 \times G_{fr} \times W_{fr} \times S}{(Cu) k_{cu}} \quad (13)$$

A typical calculation indicates that the concentration of (Cu) required to maintain a steady state partial pressure of H_2 of 1000 psi at a fission power density of 10 kw, l^{-1} , at a temperature of $250^\circ C$, and at a uranium concentration of 0.16 M, is 7×10^{-3} mole, l^{-1} .

3. Peroxide Decomposition:

The hydrogen peroxide produced by decomposition of the water can undergo several secondary reactions: (1) it can react with uranyl ion forming the slightly soluble peroxide $UO_4(aq.)$ according to the reaction:

The $UO_4(aq.)$ will precipitate if its solubility ($\approx 10^{-3}$ M) is exceeded; (2) it (or the UO_4) can decompose by a radiation induced reaction via the free radicals H and OH produced by decomposition of the water; (3) in a reactor operating at high temperatures the H_2O_2 will decompose thermally at an appreciable rate according to the over-all reaction

and the UO_4 will decompose thermally according to the reactions

Studies of the kinetics of the thermal decomposition of peroxide in uranyl sulfate solutions^{1,11} have shown the rate to be first order with respect to peroxide concentration in the range from 0.4 to 5×10^{-3} M, independent of uranium concentration in the range from 4.5×10^{-3} to 0.65 M, and independent of the acidity from pH 1.6 to 3.3. Traces of certain ions showed pronounced catalytic effects. The rate of decomposition could be expressed by the equation:

$$\frac{-d(\text{H}_2\text{O}_2)}{dt} = k (\text{H}_2\text{O}_2) + k_{\text{cat}} (\text{Cat}) (\text{H}_2\text{O}_2) \quad (18)$$

where (H_2O_2) represents total peroxide concentration ($\text{UO}_4 + \text{H}_2\text{O}_2$) in moles per liter at time t , k is the molar rate constant in the absence of catalyst, k_{cat} is the catalytic constant and (Cat) the concentration of catalyst in moles per liter.

Values of k for uranyl sulfate solutions (4.5×10^{-3} M to 0.65 M) with no added catalyst depended upon the adventitious impurities present, and were in the ranges as listed in Table IV. The indicated activation energy is 25.5 kcal, mole⁻¹. For pure water, the rate constant at 78° C. was 4.5×10^{-4} , min⁻¹.

Catalytic constants, k_{cat} , for various ions added are listed in Table V.

TABLE IVMolar Rate Constants for Peroxide Decomposition in UO_2SO_4 Solutions

Temperature	k
53° C	1.2×10^{-3} to $12 \times 10^{-3}, \text{min}^{-1}$
78° C	1.8×10^{-2} to $14 \times 10^{-2}, \text{min}^{-1}$
100° C	1.8×10^{-1} to $12 \times 10^{-1}, \text{min}^{-1}$

TABLE V

Catalytic Constants at 100° C for Peroxide Decomposition
By Various Ions Added to UO_2SO_4 Solution

Catalyst	$k_{\text{cat}}(1, \text{mole}^{-1}, \text{min}^{-1})$
Fe^{+2}	135,000
Ru^{+4}	121,000
Ag^{+1}	4,550
Ni^{+2}	2,640
Cu^{+2}	1,200

4. Steady State Peroxide Concentration.

The net rate of peroxide formation is the difference between the rate of production and the rate of decomposition. At the steady state the two rates are equal. The rate of formation of peroxide in an operating reactor in terms of moles per liter per minute can be expressed in terms of the yield, G , in molecules per 100 electron volts of fission recoil energy, and the average fission recoil power density of the reactor, W , in kilowatts per liter, by the equation:

$$\frac{d(H_2O_2)}{dt} = 0.00622 \times G \times W \quad (19)$$

The maximum value of G for the particular solution used is that given for the H_2 yield in Figure 2. During reactor operation the radiation induced decomposition of peroxide is negligible, and the rate of decomposition is essentially the thermal rate given by equation 18. At the steady state the peroxide concentration is given by:

$$(H_2O_2)_{ss} = \frac{0.00622 \times G \times W}{k + k_{cat} (Cat)} \quad (20)$$

The maximum allowable power density, W_{max} , before precipitation occurs is given by:

$$W_{max} = \frac{(H_2O_2)_{sol} [k + k_{cat} (Cat)]}{0.00622 \times G} \quad (21)$$

For example, in 0.17 M UO_2SO_4 solution at $100^\circ C$ with no added catalyst, the peroxide solubility is $\approx 4 \times 10^{-3}$ M, $k \approx 1, \text{ min}^{-1}$, and $G \approx 1.5$, then $W_{max} \approx 0.4 \text{ KW, l}^{-1}$.

Following reactor shut-down, peroxide formation and decomposition will result from the delayed neutrons and from the β^- and γ radiation of the fission products. The yield for peroxide formation will be essentially that for γ rays, $G = 0.46$. The yield for radiation induced decomposition⁷ may be as high as 4.5, but will depend in a complicated way on the amount of oxygen, hydrogen, and other solutes such as fission products, corrosion products, etc., present.

D. Thorium Solutions.

Thorium nitrate solution may possibly be used as a blanket in a breeder reactor. Under radiation the solution decomposes¹² to give H_2 , H_2O_2 and O_2 from decomposition of the water, and O_2 , N_2 , and oxides of nitrogen from decomposition of the nitrate. Yields of H_2 and N_2 for several types of radiation, and for several concentrations of thorium nitrate, are given in Table VI. The hydrogen yield decreases with increasing solute concentration, the same for uranium solutions. The nitrogen yield increases with increasing nitrate concentration. The N_2 is presumably formed by direct action of radiation on the nitrate. The N_2 yield is greater for radiations of greater LET. The N_2 yield is independent of temperature, and little or no radiation induced back reaction takes place.

Uranyl nitrate solution also decomposes to give N_2 in yield comparable to that for thorium nitrate solution.

TABLE VI

The Effects of Concentration and Type of Radiation on the Yields of
 H_2 and N_2 in the Decomposition of Thorium Nitrate Solutions

$\text{Th}(\text{NO}_3)_4$ (Molality)	$\text{G}(\text{H}_2)$		$\text{G}(\text{N}_2)$	
	Fission Recoils (a)	Fission Recoils (a)	ORNL Graphite Pile Radiation	Gamma Rays
0.26	1.11	0.002	0.003	0.04×10^{-3}
0.55	0.93	0.016	0.003	0.5×10^{-3}
1.5	0.51	0.047	0.005	1.5×10^{-3}
2.7	0.33	0.063	0.006	1.1×10^{-3}
7.2	$\sim 0.08^{(b)}$	0.16		

(a) 0.14 molal enriched UO_2SO_4 added in order to make the energy contributed by fission recoils $> 95\%$ of the total energy absorbed.

(b) Estimated by extrapolation.

REFERENCES

- (1) See e.g., Allen, A. G., J. Phys. Colloid Chem., 52, 479 (1948).
- (2) Dainton, F. S. and Sutton, H. C., Trans. Far. Soc., 49, 1011 (1953).
- (3) Sworski, T. J., J. A. C. S., 76, 4687 (1954).
- (4) Hart, E. J., Radiation Research, 2, 33 (1955).
- (5) Selected Values from Several Literature References.
- (6) Allen, A. O., Hochanadel, C. J., Ghormley, J. A. and Davis, T. W., J. Phys. Chem., 56, 575 (1952); Hochanadel, C. J., J. Phys. Chem., 56, 587 (1952).
- (7) Hochanadel, C. J., Proceedings of the International Conferences on the Peaceful Uses of Atomic Energy, 1, 521, United Nations, New York, 1956.
- (8) Boyle, J. W., Kieffer, W. F., Hochanadel, C. J., Sworski, T. J. and Ghormley, J. A., Nuclear Engineering and Science Congress, Preprint 222, American Institute of Chemical Engineers, New York (1955).
- (9) McDuffie, H. F., Compere, E. L. Stone, H. E., Woo, L. F., and Secoy, C. H., ORNL Report C.F. 54-1-122, (1954), Declassified 1956.
- (10) For solubilities of H_2 and O_2 in water and in UO_2SO_4 solutions at high temperatures see: Pray, H. A. H., Schweichert, C. E., and Minnich, B. H., Ind. Eng. Chem., 14, 1146 (1952), also: Stephan, E. F., Hatfield, N. S., Peoples, R. S. and Pray, H. A. H., BMI-1067 (1956).
- (11) Silverman, M. D., Watson, G. M. and McDuffie, H. F., Ind. Eng. Chem., 48, 1238 (1956).
- (12) Boyle, J. W. and Mahlman, H. A., Paper presented at the 2nd Annual Meeting of the American Nuclear Society, Chicago (1956).

FIGURE 1
YIELDS OF ATOMIC AND MOLECULAR HYDROGEN
FROM THE DECOMPOSITION OF WATER
BY VARIOUS IONIZING RADIATIONS

ORNL-LR-Dwg. -17095
UNCLASSIFIED

FIGURE 2
THE EFFECTS OF URANIUM CONCENTRATION AND TYPE OF RADIATION ON
THE INITIAL H_2 YIELD FROM IRRADIATED UO_2SO_4 SOLUTIONS