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DESIGN CONSIDERATIONS OF REACTOR CONTAINMENT
SPRAY SYSTEMS - PART I

T. H. Row
L. F. Parsly
H. E. Zittel

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REACTOR DIVISION
ANALYTICAL CHEMISTRY DIVISION

DESIGN CONSIDERATIONS OF REACTOR CONTAINMENT
SPRAY SYSTEMS - PART I

T. H. Row L. F. Parsly H. E. Zittel

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OAK RIDGE NATIONAL LABORATORY
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DESIGN CONSIDERATIONS OF REACTOR CONTAINMENT SPRAY SYSTEMS -- PART I

T. H. Row

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ABSTRACT

Pressurized water reactors currently being designed include a containment building spray system for pressure reduction following a design basis accident. An additional function proposed for these spray systems is the removal of fission products, particularly iodine, released to the containment building during such an accident. This report considers a number of design considerations associated with this fission product removal in light of the information developed in the Spray and Absorption Technology Program. Questions relating to the removal process and the radiation and thermal stability of the solutions are examined.

I. INTRODUCTION

A. History of the Spray Technology Program

In early 1967 the nuclear industry proposed that the pressure reduction sprays installed in pressurized water reactors (PWR) also be used as a means for significantly and rapidly reducing the fission product concentration in a containment building following a design basis accident (DBA).¹ Since the use of sprays for this purpose had wide applicability in the nuclear industry, a program was established at ORNL to investigate spray systems.²

The work at ORNL includes a search for solutions reactive to iodine in both elemental and organic form, experimental verification of the removal efficiency of these solutions, studies on the corrosive nature of proposed solutions, and an investigation of the thermal and radiation stability of the solutions. In addition to ORNL investigations, the program is responsible for coordinating information from industrial research and other Commission-sponsored work.

¹Preliminary Safety Analysis Report, Nuclear Plant -- Diablo Canyon Site -- Pacific Gas and Electric Company, U.S. Atomic Energy Commission Regulatory Docket No. 50-275, January 1967.

²T. H. Row, *Spray and Pool Absorption Technology Program*, ORNL-4360 (to be issued).

The work completed in the first 18 months of the program has indicated that sprays can be used effectively to remove elemental iodine from an environment typical of that expected under DBA conditions.³⁻³¹ Engineering-scale tests have demonstrated removal half-lives of less than 1 min, accompanied by decon-

³L. F. Parsly, Jr., *Removal of Elemental Iodine from Steam-Air Atmosphere by Reactive Sprays*, ORNL-TM-1911 (October 1967).

⁴L. F. Parsly, Jr., *Gas Absorption Theory Applied to Containment Sprays*, ORNL-TM-2002 (January 1968).

⁵R. A. Norelli and E. P. Tripp III, *Review of Methods for Measurement of Drop Size Distribution in Sprays and Recommendations for the Spray and Absorption Technology Program*, ORNL-MIT-29 (Oct. 13, 1967).

⁶L. F. Parsly, Jr., and J. K. Franzreb, *Removal of Iodine Vapor from Air and Steam-Air Atmospheres in the Nuclear Safety Pilot Plant by Use of Sprays*, ORNL-4253 (June 1968).

⁷B. A. Soldano and W. T. Ward, "Uptake of Methyl Iodide from Wind Tunnel Gases by a Suspended Drop of Water," *Trans. Am. Nucl. Soc.* 10, 720 (November 1967).

⁸B. A. Soldano and W. T. Ward, *A Wind Tunnel Study of the Mass Transport of CH₃I into a Drop of Water*, presented at the American Chemical Society April 1968 Meeting, San Francisco, Calif.

⁹C. S. Patterson and W. T. Humphries, "Distribution of Iodine Between Air and Aqueous Solutions," *Trans. Am. Nucl. Soc.* 11(1), 374 (1968).

¹⁰B. A. Soldano and W. T. Ward, "Uptake of Methyl Iodide from Wind Tunnel Gases by a Suspended Drop of Water, Part II," *Trans. Am. Nucl. Soc.* 11(1), 374 (1968).

¹¹L. F. Parsly and J. K. Franzreb, "Studies of the Removal of Iodine Vapor from Containment Building Atmospheres at the Nuclear Safety Pilot Plant," *Trans. Am. Nucl. Soc.* 11(1), 372 (1968).

¹²H. E. Zittel and T. H. Row, "Radiation and Thermal Stability of Sprays," *Trans. Am. Nucl. Soc.* 11(1), 375 (1968).

¹³T. H. Row, "Reactor Containment Spray Technology Program," IAEA Symposium on Operating and Developmental Experience in the Treatment of Airborne Radioactive Wastes, SM-110/26, New York City, Aug. 26-30, 1968.

¹⁴G. E. Creek et al., *The Dissolution and Hydrolysis of Methyl Iodide in Misting Spray Solutions*, ORNL-2053 (January 1968).

¹⁵G. J. Rogers, *Program for Containment Systems Experiment*, HW-83607 (September 1964).

¹⁶L. C. Schwendiman et al., *The Washout of Methyl Iodide by Hydrazine Sprays*, Progress Report, BNWL-530 (Dec. 1, 1967).

¹⁷*Nuclear Safety Quarterly Report November-December 1967, January 1968 for Nuclear Safety Branch of USAEC Division of Reactor Development and Technology*, BNWL-816 (September 1968).

¹⁸B. J. Newby, *Applicability of Conventional Protective Coatings to Reactor Containment Buildings*, IN-1169 (June 1968).

¹⁹B. J. Newby, *Applicability of Chemically Removable Coatings to Reactor Containment Buildings*, IN-1170 (August 1968).

²⁰R. V. Homsy and C. A. Glatron, *Review of Literature on Catalytic Recombination of Hydrogen-Oxygen*, ORNL-MIT-55 (May 3, 1968).

²¹T. H. Row, "Spray and Pool Suppression Technology Program," pp. 22-25 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for March-April 1967*, ORNL-TM-1864 (May 5, 1967).

²²T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 19-25 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for May-June 1967*, ORNL-TM-1913 (July 10, 1967).

²³T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 28-35 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for July-August 1967*, ORNL-TM-1986 (Sept. 21, 1967).

²⁴T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 21-42 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for September-October 1967*, ORNL-TM-2057 (Nov. 27, 1967).

²⁵T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 20-37 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for November-December 1967*, ORNL-TM-2095 (Feb. 5, 1968).

²⁶W. B. Cottrell, *Nucl. Safety Program Ann. Progr. Rept. Dec. 31, 1967*, ORNL-4228, pp. 191-239 (April 1968).

²⁷T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 47-71 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for January-February 1968*, ORNL-TM-2164 (Mar. 26, 1968).

²⁸T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 55-85 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for March-April 1968*, ORNL-TM-2230 (May 30, 1968).

²⁹T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 47-95 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for May-June 1968*, ORNL-TM-2283 (July 30, 1968).

³⁰T. H. Row et al., "Spray and Pool Suppression Technology Program," pp. 49-92 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for July-August 1968*, ORNL-TM-2368 (Nov. 1968).

³¹T. H. Row et al., "Spray and Pool Suppression Technology Program," sect. 3 in *ORNL Nuclear Safety Research and Development Program Bimonthly Report for September-October 1968*, ORNL-TM-2425 (to be issued).

tamination factors of better than 20,000. The solutions proposed have acceptable radiation and thermal stability for the job requirements. Radiolytic hydrogen generation from the solutions will require individual plant design considerations.

B. Plant Design Description

Fundamental to the understanding of the spray system is an awareness of the actual design of these systems in proposed PWR's. The Diablo Canyon plant is an example of a typical spray-protected system¹ and was chosen as a reference design for this report. This plant will be designed and constructed by the Pacific Gas and Electric Company with Westinghouse Electric Corporation supplying the nuclear steam supply system and equipment.

The plant is a four-loop design with a total heat output of 3250 Mw (thermal). The containment building is a reinforced concrete vertical cylinder with a flat base and hemispherical dome. The concrete vessel has a welded steel liner with a minimum thickness of $\frac{1}{4}$ in. The side walls are approximately 142 ft high, and the inside diameter of the structure is 140 ft. The free gas volume contained in the building is 2.6×10^6 ft³.

The containment spray system is designed for heat and iodine removal (Fig. 1). In the event of a loss-of-coolant accident, the spray system will be automatically actuated by a combination of high containment pressure and possibly other system signals. These will cause the two containment spray pumps located in an auxiliary building to start and take suction directly from the refueling water storage tank.

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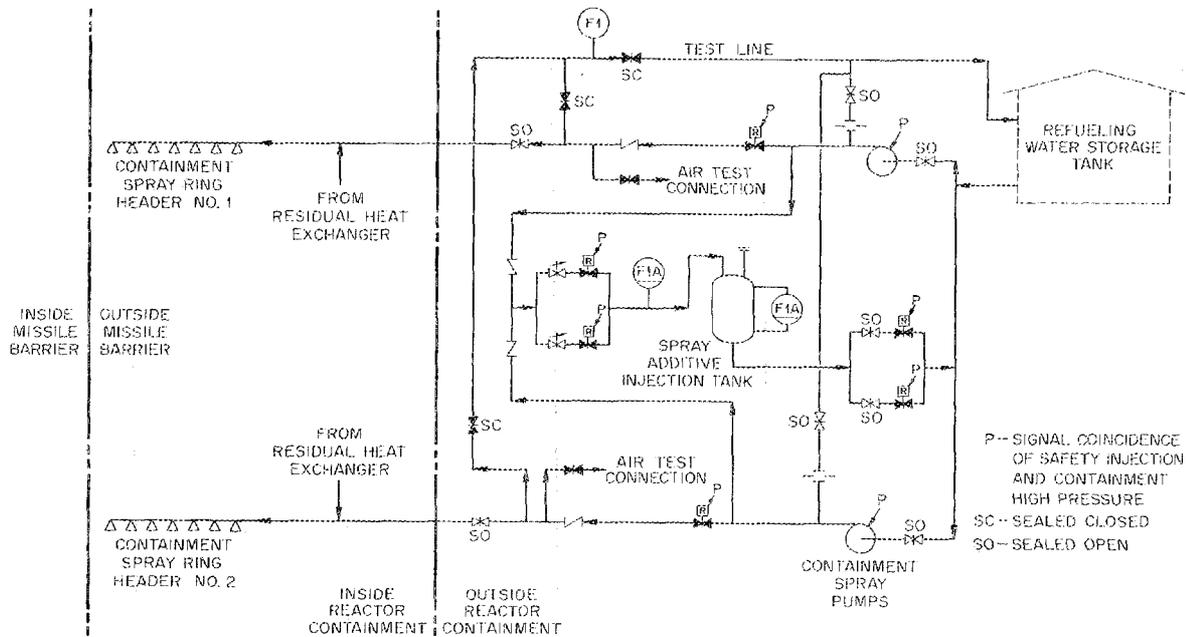


Fig. 1. Containment Spray System.¹

The safety injection system (emergency core cooling system) also takes suction from the refueling water storage. The spray solution chemical is added to the boric acid refueling water in the spray system and discharged into the spray headers, located in the dome of the containment building, at the design flow rate of 2600 gpm per pump.

Two solutions are being considered by industry for the iodine removal spray systems. Both solutions are based on the use of refueling water storage as the primary solution; this water contains approximately 3000 ppm boron. One solution proposed contains 0.17 M NaOH as the additive, while the second solution contains 0.17 M NaOH and 1 wt % $\text{Na}_2\text{S}_2\text{O}_3$. The 0.17 M NaOH, 3000 ppm boron solution was chosen for the Diablo Canyon reactor.

The spray nozzles are located on two ring headers attached to the steel containment liner in the upper part of the containment building. The spray nozzles are arranged to provide maximum coverage of the free gas volume and wall washdown and have an average spray drop fall of 140 ft. The spray headers are protected from missiles by concrete shielding.

The spray system and safety injection will exhaust the 350,000 gal of refueling water in approximately $\frac{1}{2}$ hr under design operating conditions. Pumps then begin drawing from the containment building sumps, which by now have accumulated enough spray solution for recirculation to the spray headers and to the reactor vessel for shutdown cooling of the reactor.

Several points need to be made about the spray system operation. The solution injected through the spray headers during the initial $\frac{1}{2}$ hr when refueling water storage is used is fresh solution. It has not encountered either high temperature, fission product radiation, or fission product contaminants before entering the vessel. The solution has the maximum theoretical iodine sequestering ability when sprayed during this period.

Operation of the safeguards equipment after the $\frac{1}{2}$ -hr switch to a recirculation mode will continue for some time. Spray cooling of the containment building interior may be terminated in the first 24 hr following the accident, but shutdown cooling of the reactor core will be required for months. This means that the spray solution will be circulated through the reactor core for an extended time period and must therefore demonstrate acceptable thermal and radiation stability.

C. Public Hearing Decisions

The AEC procedure for licensing of a nuclear plant provides for a public hearing conducted by an AEC-appointed Atomic Safety and Licensing Board (ASLB) in the locality where the proposed plant is sited. These hearings normally involve fairly detailed question and answer sessions which cover many aspects of plant design and operational philosophy. Three recent hearings have devoted significant time to the discussion of the spray systems proposed for the plants. The three hearings involved the Crystal River Unit 3 Nuclear Generating Plant of Florida Power Corporation (Docket No. 50-302),³²⁻³⁴ the Salem

³²In the Matter of Florida Power Corporation (Crystal River Unit 3 Nuclear Generating Plant), AEC Docket No. 50-302, Memorandum and Order dated September 24, 1968.

³³In the Matter of Florida Power Corporation (Crystal River Unit 3 Nuclear Generating Plant), AEC Docket No. 50-302, Exceptions and Brief dated October 14, 1968.

³⁴Exception by the applicant in the Matter of Florida Power Corporation Crystal River Unit 3, Atomic Clearing House, vol. 14, No. 43, pp. 8-19, October 21, 1968.

Nuclear Generating Station Units 1 and 2 of Public Service Electric and Gas Company (Docket Nos. 50-272 and 50-311),³⁵ and Zion Station Units 1 and 2 of Commonwealth Edison Company (Docket Nos. 50-295 and 50-304).^{36,37}

The ASLB hearing for the Zion 1 and 2 plants provided discussion of the spray system with a number of pertinent questions raised, typically:

1. Do we have any evidence to show that water alone is sufficient to take out the contaminant?
2. What has been the experience on each of the chemical additives?
3. What is the degree of corrosion by NaOH-type spray solutions?
4. Are there aspects of NaOH which give concern, for example, hydrogen formation?
5. Why has no one run drop size measurements on NaOH solutions?

These ASLB hearings have provided both industry and the ORNL program with useful review of the considerations necessary for proper spray system design.

D. Report Objectives

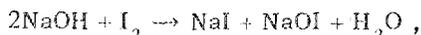
The purpose of this report is to discuss some of the pertinent PWR design considerations necessary for appropriate plant design. The emphasis in this report is on I₂ removal by sprays; additional documents will follow addressed to questions such as corrosion, aerosol removal, and methyl iodide removal by spray and pool suppression systems.

II. SPRAY SYSTEM DESIGN CONSIDERATIONS

As discussed in the Introduction, a number of questions regarding spray systems have been raised in the course of AEC review of proposed plants. Some of these will require additional experimental work, but many can be answered on the basis of information available either in existing Spray Program literature or in the open literature. This section presents discussions of a number of these spray system design considerations.

A. Reagent Requirements for a Design Basis Accident

1. Quantity Needed for Iodine Removal. — The iodine inventory of a uranium-fueled reactor core at 20,000 Mwd/metric ton burnup is 1.21 gram-atoms (156 g) per metric ton of uranium or approximately 121 gram-atoms for the core of a 1000 Mw (electrical) reactor. Reaction of NaOH with iodine,



³⁵In the Matter of Public Service Electric and Gas Company (Salem Nuclear Generating Station Units 1 and 2), AEC Docket Nos. 50-272 and 50-311, Memorandum Order dated September 24, 1968.

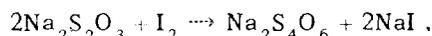
³⁶Personal communication, L. F. Parsly to T. H. Row, Sept. 27, 1968.

³⁷In the Matter of Commonwealth Edison (Zion Station Units 1 and 2), AEC Docket Nos. 50-295 and 50-304, Order dated October 17, 1968.

requires 1 g-mole of NaOH per gram-atom of iodine. Other reactions are possible, but the iodine equivalence is the same.

Using Diablo Canyon design values gives a 2.6×10^6 -ft³ free volume in the containment and a liquid volume 1.8% of the free gas volume; the available liquid is 4.7×10^4 ft³ (350,000 gal or 1.32×10^6 liters). The NaOH at 0.17 mole/liter is 2.24×10^5 g-moles. Thus the solution contains over 1800 times as much NaOH as is required to react with all of the iodine in the core.

In the case of the thiosulfate solution, a number of reactions are possible. In neutral or acid solution, the usual reaction involves oxidation of the sulfur to tetrathionate:



In basic solution, the sulfur can be oxidized to sulfate:



If we assume the second reaction goes until the NaOH is consumed and the first thereafter, we find that a liter of solution can react with 0.091 g-mole or 0.182 gram-atom of iodine. Thus 1.13×10^6 liters can react with 2.06×10^5 gram-atoms of iodine, or there is about 1700 times the amount required. Although the iodine equivalence is only slightly higher than for base alone, there is the advantage that all of the iodine is reduced to iodide.

2. Effect of Other Fission Products on Reagent Consumption. -- To illustrate the effect of *all of the fission products in the core* on the reaction capabilities of the spray solution, we have constructed Tables 1 and 2. Here we have assembled fission product inventory data computed by members of the ORNL Chemical Technology Division,³⁸ volatility data reported by Bedford and Jackson,³⁹ and the best judgment of members of the ORNL Nuclear Safety Program Staff⁴⁰ as to reactions which would consume sodium hydroxide, and we have calculated the sodium hydroxide equivalence of the mix. In the case of the alkali metals (rubidium and cesium) and the alkaline earth metals (strontium and barium) we credited rather than debited the NaOH balance. We assumed that those fission products which had vapor pressures of 0.1 atm or more at 2500°K would be released completely and that those with lower vapor pressures would not be released at all. In Table 1, we assumed that oxidizing conditions existed at the point of release and in Table 2 that conditions were reducing. Our calculations show that in the oxidizing case, 56.67 moles of sodium hydroxide are required per metric ton of uranium or 5667 in our reference core. For the reference case, the available sodium hydroxide is 34 times the requirement. In the reducing atmosphere case, there is negative sodium hydroxide equivalence. We conclude there should be no concern respecting the availability of sufficient reagent to remove the iodine. The excesses provided are overwhelming and ensure that individual drops are not depleted of reactive capacity during their residence time in the building.

³⁸E. D. Arnold, personal communication.

³⁹R. D. Bedford and D. D. Jackson, *Volatilities of the Fission Product and Uranium Oxides*, UCRL-12314.

⁴⁰G. M. Watson and G. W. Parker, personal communication.

Table 1. Oxidizing Conditions

Fission Product Element	Gram-Atoms per Metric Ton of Uranium	Compound	Vapor Pressure (atm at 2500°K); 1 atm O ₂ Pressure	NaOH Equivalent per Metric Ton of Uranium for Volatile Compounds
Se	0.0905	Se	5	0.18
Br	0.0837	Br ₂	>100	0.08
Kr	2.90	Kr	>100	
Rb	2.84	Rb	5	-2.84
Sr	7.45	SrO	10 ⁻³	
Y	3.75	Y ₂ O ₃	10 ⁻⁷	
Zr	26.3	ZrO ₂	2 × 10 ⁻⁷	
Nb	0.5	Nb ₂ O ₅	10 ⁻⁵	
Mo	21.9	MoO ₂	7	43.8
Tc	5.6	Tc	6	5.6
Ru	14.1	RuO ₂	>100	28.2
Rh	2.98	Rh ₂ O	2 × 10 ⁻³	
Pd	4.48	Pd	20	
Ag	0.44	Ag	2	
Cd	0.17	Cd	>100	
Sn	0.21	SnO ₂	8	0.42
Sb	0.06	Sb	10	0.06
Te	2.38	Te	>100	4.76
I	1.21	I	>100	1.21
Xe	25.6	Xe	>100	
Cs	13.0	Cs	1	-13.0
Ba	5.9	BaO	10 ⁻¹	-11.8
La	5.5	La ₂ O ₃	5 × 10 ⁻⁵	
Ce	13.6	CeO ₂	5 × 10 ⁻⁷	
Pr	5.1	Pr ₂ O ₃	2 × 10 ⁻⁶	
Nd	16.5	Nd ₂ O ₃	2 × 10 ⁻⁵	
Pm	1.6	Pm ₂ O ₃	5 × 10 ⁻⁵	
Sm	2.8	Sm ₂ O ₃	10 ⁻⁷	
Eu	1.7			
U		UO ₂	2 × 10 ⁻¹	56.67

Table 2. Reducing Conditions

Fission Product Element	Gram-Atoms per Metric Ton of Uranium	Compound	Vapor Pressure (atm at 2500°K); 10^{-10} atm O_2	NaOH Equivalent per Metric Ton of Uranium for Volatile Compounds
Se	0.0905	Se	>100	0.18
Br	0.0837	Br ₂	>100	0.08
Kr	2.90	Kr	>100	
Rb	2.84	Rb	>100	-2.84
Sr	7.45	SrO	10^{-1}	-14.9
Y	3.75	Y ₂ O ₃	5×10^{-5}	
Zr	26.3	ZrO ₂	2×10^{-6}	
Nb	0.5	Nb	10^{-5}	
Mo	21.9	Mo	7×10^{-7}	
Tc	5.6	Tc	8×10^{-7}	
Ru	14.1	Ru	3×10^{-6}	
Rh	2.98	Rh	10^{-4}	
Pd	4.48	Pd	8×10^{-2}	
Ag	0.44	Ag	1.0	
Cd	0.17	Cd	>100	
Sn	0.21	Sn	10^{-1}	0.42
Sb	0.06	Sb	8	0.06
Te	2.38	Te	>100	4.76
I	1.21	I	>100	1.21
Xe	25.6	Xe	>100	
Cs	13.0	Cs	>100	-13.0
Ba	5.9	Ba	20	-11.8
La	5.5	La ₂ O ₃	10^{-2}	
Ce	13.6	Ce ₂ O ₃	8×10^{-4}	
Pr	5.1	Pr ₂ O ₃	7×10^{-4}	
Nd	16.5	Nd ₂ O ₃	3×10^{-3}	
Pm	1.6	Pm ₂ O ₃	5×10^{-3}	
Sm	2.8	Sm ₂ O ₃	10^{-4}	
Eu	3.2			
Gd	1.7			
U			10^{-4}	-35.83

B. The Question of Gas and Liquid Film Resistance

The process of transferring a contaminant from an atmosphere to a scrubbing liquid is conceived to comprise some or all of the following steps:

1. transfer by diffusion through a boundary layer to the liquid surface,
2. maintenance of equilibrium at the gas-liquid interface,
3. transfer by diffusion in the liquid away from the interface into the body of liquid,
4. removal by reaction in the liquid.

The transfer rate can be limited by step 1 or by steps 3 and 4 or by a combination of these. Step 2 is assumed instantaneous under all circumstances. Because of the different chemical characteristics of the base-borate and base-borate-thiosulfate solutions we must consider the question of gas and liquid film resistance separately for each.

1. Base-Borate-Thiosulfate Spray Solution. — In the absorption of iodine by sodium thiosulfate solution, a near-instantaneous reaction between iodine and sodium thiosulfate occurs. Astarita⁴¹ shows that for an instantaneous reaction, the reaction occurs at the liquid surface, and the mass transfer rate is controlled by transfer through the gas to the interface provided the following criterion is met:

$$k_c C_G \leq k_L^0 \left(\frac{D_R}{D_L} \right)^m \frac{C_{R0}}{q}, \quad (1)$$

where

k_c is the gas-phase mass transfer coefficient, cm/sec,

C_G is the concentration in the bulk gas, g-moles/cm³,

k_L^0 is the mass transfer coefficient without chemical reaction, cm/sec,

D_R is the diffusivity of a solution reagent, cm²/sec,

D_L is the diffusivity of transferring constituent in solution, cm²/sec,

C_{R0} is the reagent concentration in bulk solution, g-moles/cm³,

q is the moles of reagent used per mole of transferring constituent,

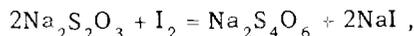
m is an exponent having a value between 0.5 and 1.0, depending on the model under consideration.

As an illustration of what this indicates, take the case of absorption of iodine by standard sodium thiosulfate solution (0.063 M Na₂S₂O₃) at 120°C in a reactor containment building with 120 ft fall height. Assume drops with 1000-μ surface mean diameter and uniform size (we choose the surface mean diameter because it has the least sensitivity to size distribution and also, if the drops are nonuniform, spray performance will actually improve). The drop fall time is approximately 10 sec.⁴² For 1000-μ drops at 120°C, k_c is 8.2 (ref. 3). As a first approximation, D_R and D_L may be assumed equal, and therefore the value of m assumed does not matter. If we assume the drops are stagnant, the proper value of m is 1.0.

⁴¹G. Astarita, "Regimes of Mass Transfer with Chemical Reaction," *Ind. Eng. Chem.* **58**, 18–26 (1966).

⁴²L. F. Parsly, unpublished spray performance calculations.

From the reaction



q is equal to 2. Other reactions between sodium thiosulfate and iodine are possible in basic solution. However, none of these will consume more thiosulfate per mole of iodine. Skelland and Wellek⁴³ present an equation from which k_L can be evaluated:

$$k_L = -\frac{6}{dt_c} \ln(1 - E_m) \quad (2)$$

where

d = drop diameter, cm,

t_c = drop lifetime, sec,

E_m = fractional saturation.

Values of $1 - E_m$ are tabulated and plotted by Geddes⁴⁴ as a function of dimensionless time ($4\pi^2 D_L t_c / d^2$). The value⁴² of D_L at 120°C is 6.6×10^{-5} cm²/sec. Thus $4\pi^2 D_L t_c / d^2 = 2.6$, and from the Geddes plot, $1 - E_m = 0.043$ and $\ln(1 - E_m) = -3.147$. Thus from Eq. (2)

$$k_L = -\left(\frac{0.1}{6 \times 10}\right)(-3.147) = 5.25 \times 10^{-3} ,$$

and from Eq. (1)

$$C_G \leq \frac{5.25 \times 10^{-3} \times 6.3 \times 10^{-2}}{8.2} = 3.8 \times 10^{-5} \text{ g-mole of } \text{I}_2 \text{ per liter ;}$$

$$C_G \leq 3.85 \times 10^{-5} \text{ g-mole/liter} \times 10^3 \text{ liters/m}^3 \times 2.58 \times 10^2 \text{ g/g-mole} = 9.9 \text{ g/m}^3 .$$

This calculation says that the gas-film-controlled model for I_2 absorption by 0.063 M $\text{Na}_2\text{S}_2\text{O}_3$ solution is valid whenever the concentration of I_2 does not exceed 9.9 g/m³. Since the maximum concentration in the containment vessel in the reference case is 0.21 g/m³, it applies for the concentrations of concern in our reference design.

2. Base-Borate Spray Solution. — In the case of the other solution proposed for iodine removal (0.17 M NaOH + 0.28 M H_3BO_3) the analysis is more complicated. Iodine undergoes a variety of hydrolysis reactions in water solution:⁴⁵



⁴³A. H. P. Skelland and R. M. Wellek, "Resistance to Mass Transfer Inside Droplets," *A.I.Ch.E. J.* **10**, 491-94 (1964).

⁴⁴R. L. Geddes, "Local Efficiencies of Bubble Plate Fractionators," *Trans. Am. Inst. Chem. Engrs.* **42**, 79 (1946).

⁴⁵A. E. J. Eggleton, *A Theoretical Examination of Iodine-Water Partition Coefficients*, AERE-R-4887 (1967).



The above list is typical but does not list all of the possibilities. These same reactions also exist with the base-borate-thiosulfate system.

Eggleton assumed HIO is not volatile in his calculations, although he recognizes that it probably is volatile and cautions that this may have to be considered if the partition coefficient neglecting HOI volatility exceeds 10^4 . Cartan⁴⁶ and co-workers at Idaho Nuclear Corporation have recently suggested that a previously unidentified volatile iodine species is probably HOI and that its formation is favored by high temperatures and by pH above 8. Calculations made at ORNL⁴⁷ using Eggleton's system of equations confirm that at 10^{-4} mole/liter I_2 equivalent, pH of 9.0, and 100°C , 45% of the dissolved iodine would be in the form of HOI.

On the other hand, when reaction (6) attains equilibrium, the formation of HIO is greatly suppressed. For example, for 25°C , pH 9, and 10^{-4} mole/liter total iodine, the concentration of HIO is calculated to be 9.4×10^{-5} mole/liter without reaction (6) and 2.9×10^{-10} mole/liter if reaction (6) goes to equilibrium. Eggleton⁴⁵ indicated reaction (6) at 25°C will have caused 10% of the change in partition coefficient in ten years at pH 5, 11 hr at pH 7, and 4 sec at pH 9. Data reported by Cartan *et al.*⁴⁶ for I_2 dissolved in H_2O at 90°C indicate 50% of the HOI destroyed in 1 hr and 90% in 16 hr. The pH was not reported but should have been less than 7. Thus there is a reasonable basis for speculating that reaction (6) might well be instantaneous at 90°C and pH of 9. It should be possible to arrive at a conservative limiting value by taking the lower limit given by Cartan *et al.*⁴⁶ for the partition coefficient for HOI between water and air and assuming that the iodate reaction (6) does not occur at all. We suspect that such a value would be conservative by several orders of magnitude.

For instance, at 100°C and 5×10^{-5} mole/liter of I_2 in the spray solution, which are typical of design basis accident conditions, the limit value of the partition coefficient including HOI volatility would be 200; excluding HOI volatility, it is 27,000. If the iodate reaction is considered, it is probably even higher. The results of the NSPP experiments using base-borate spray solution indicate that the lower limit value is not valid.²⁶ If it were, we would expect to observe very small overall decontamination

⁴⁶F. O. Cartan *et al.*, Evidence for the Existence of Hypoiodous Acid as a Volatile Iodine Species Produced in Water-Air Mixtures, presented at 10th USAEC Air Cleaning Conference, New York City, Aug. 28, 1968.

⁴⁷L. F. Parsly, unpublished calculations.

factors. It has been shown⁴ that the limiting decontamination factor for a containment system is given by $D_F = 1 + (Q_L/Q_G)H$.

For the NSPP, the liquid to gas volume ratio (Q_L/Q_G) is approximately 0.009. If H is 200, then the limiting D_F is $1 + (0.009)(200) = 2.8$. We have observed decontamination factors in excess of 1000, which requires that H be of the order of 10^5 , which confirms Eggleton.⁴⁵

C. The Effect of Spray Drop Saturation on Removal Efficiency

The question of whether spray drops will become saturated during their transit through a containment atmosphere is sometimes asked. The maximum mass transfer rate is achieved for 100% gas-film resistance. It is given by:

$$dw/dt = k_c \pi d^2 C_G,$$

and the total transferred up to time t , assuming a constant transfer rate, is

$$w = k_c \pi d^2 C_G t.$$

The amount of reagent used up is given by

$$w = \frac{\pi}{6} d^3 \frac{(C_{R0} - C_{Rt})}{q}.$$

In order to get a lower limit for saturation time, assume transfer occurs at the gas-film-controlled rate until the inventory of reagent in the drop is used up. Then

$$k_c \pi d^2 C_G t_{\text{sat}} = \frac{\pi d^3}{6} \frac{C_{R0}}{q},$$

$$t_{\text{sat}} = \frac{1}{k_c} \frac{d}{6} \frac{C_{R0}}{q C_G}.$$

Using the reference case values:

$$t_{\text{sat}} = \frac{1}{8.2} \times \frac{0.1}{6} \times \frac{0.17}{2 \times 1.08 \times 10^{-6}} = 1.6 \times 10^2 \text{ sec}.$$

This is much longer than the 10-sec residence time and indicates that (1) saturation will not occur and (2) the approximate approach taken in the calculation was justified. This calculation applies when spraying starts. As spraying continues, C_G rapidly becomes smaller and t_{sat} therefore becomes larger. Since we have shown above that there is about a 1600-fold reagent excess in the solution, C_R remains practically constant.

It is necessary to point out that other factors may influence the availability of the 1600-fold reagent excess. The presence of other fission products as well as construction materials, such as aluminum, which react with the reagent must be considered. However, the value of 1600 is also conservatively based on the unrealistic case of total iodine release for reaction with the spray solution.

D. The Effect of Spray Drop Size

1. Small (1 to 2 μ) Drops. — It is a well-known fact that the liquid drops produced by spray nozzles are not all the same size, but rather cover a range of sizes. Actually there are two size groups — the primary group of relatively large drops ($> 100 \mu$ diam) and a group of “fines” of 1 to 2 μ diameter. The fines are produced in the process of breaking the liquid sheet or jet into drops. They represent a negligible fraction of the liquid mass and surface and therefore are generally not considered. Because of their relatively small diameter, they constitute a relatively persistent aerosol and, unless collected by filters or by the walls of the leakage path, must be considered as a part of the source term for leakage. However, it is relatively easy to show that the liquid holdup represented by the “fines” is an unimportant fraction of the available inventory.

For instance, in our reference case we are delivering 2600 gpm to a 2,600,000-ft³ building. Converting to centimeter-gram-second units this is a liquid flow of 1.64×10^5 cm³/sec to a volume of 7.36×10^{10} cm³. Suppose the number mean diameter of the spray drops is 700 μ ; then the volume of an average drop is 1.8×10^{-4} cm³, and the spray is introducing 9.1×10^8 drops per second into the building. Further suppose that ten fine drops are created for each primary spray drop (two to three is the normal expectation). We are introducing 9.1×10^9 fine drops per second into a volume of 7.36×10^{10} cm³, or we have a source term of 0.124 drop cm⁻³ sec⁻¹.

Now assume that the only mechanism for removing the drops is agglomeration due to Brownian movement. According to Green and Lane,⁴⁸ the coagulation constant should be approximately 5×10^{-10} cm³/sec,

$$-\frac{dn}{dt} = 5 \times 10^{-10} n^2 .$$

At equilibrium, the removal rate should equal the source term. Substituting and solving for n :

$$n = 1.57 \times 10^4 \text{ fine drops/cm}^3 .$$

If one assumes these drops have a diameter of 2 μ , their volume is calculated as follows:

$$V = \frac{\pi}{6} (2 \times 10^{-4})^3 = 4.2 \times 10^{-12} \text{ cm}^3 .$$

The liquid fines holdup per cubic centimeter of containment volume is then

$$V_L = 4.2 \times 10^{-12} \times 1.57 \times 10^4 = 6.6 \times 10^{-8} \text{ cm}^3 .$$

As stated above, the total volume of liquids in the containment building is 1.8% of the free gas volume. If all of the fission products are in the liquid and it is uniformly mixed, the solution aerosol contains

$$\frac{6.6 \times 10^{-8} \times 10^2}{1.8 \times 10^{-2}} = 3.7 \times 10^{-4} \%$$

of the fission product inventory.

⁴⁸H. L. Green and W. R. Lane, *Particulate Clouds, Dusts, Smokes, and Mists*, Spon, London, 2d ed., 1964.

This calculation is based on conservative assumptions throughout and clearly shows that the source term from the spray aerosol is of negligible importance.

2. Drop Size Distributions. — Turning back to the primary spray, a number of size distribution functions have been proposed by various workers. One which appears to give a fairly good fit to most spray data is the log-normal distribution. This states that the logarithm of the property on which the distribution is based is normally distributed. For a log-normal distribution, two parameters, the mean and the geometric standard deviation, are required to describe the distribution. If the size distribution is log-normal a plot of the cumulative value of the property vs diameter on log-probability graph paper gives a straight line. The standard deviation may be defined as the ratio of the 84.13% size to 50% size or as the logarithm of that ratio. We prefer the first definition.

The mean diameter of a spray may be defined on the basis of several different properties:

1. number mean, based on the number of drops as a function of diameter,
2. surface mean, based on the surface of drops as a function of diameter,
3. Sauter (surface-per-unit-volume) mean, based on the surface per unit volume of the drops as a function of diameter,
4. volume (or mass) mean, based on the volume or mass of drops per unit of diameter.

Of these, the number mean or the mass mean is normally obtained directly by size measuring techniques. If the distribution is log-normal, the standard deviation for all means is the same for any given spray. Further, the means are related to each other as simple functions of the standard deviation.

We have developed a computer program to deal with the performance of a spray having a log-normal drop size distribution by dividing the spray into a large number of size groups, each of which we presume can be characterized by a uniform diameter for all members of the group. Using this program we have run a sensitivity analysis of the effect of standard deviation for the same spray when defined by its number, surface, Sauter, and mass mean diameters. The standard deviation for the spray is taken as 1.5. The results are presented in Table 3.

Table 3. Effect of Standard Deviation on Calculated Half-Life for Gas-Film-Controlled Absorption of Iodine from an Air-Steam Atmosphere at 120°C, Using a Flow of 13.2 gpm in the Nuclear Safety Pilot Plant

Standard Deviation	Calculated Half-Life			
	Number ^a	Surface ^b	Sauter ^c	Mass ^d
1.0	27.2	57.5	68.1	80.6
1.5	53.9	53.8	53.8	53.8
1.8	117.5	50.7	40.8	32.8
2.0	211.5	48.4	33.1	22.5

^aMean diameter, 733 μ .

^bMean diameter, 1018 μ .

^cMean diameter, 1105 μ .

^dMean diameter, 1200 μ .

Table 3 shows that the half-life increases with standard deviation if the spray is described by the number mean but decreases with increasing standard deviation if any of the other three means is used. The surface mean is the least sensitive to standard deviation.

This means that performance calculations made using any mean diameter except the number mean and assuming all drops are mean size should give conservative results.

E. Scale-Up from Nuclear Safety Pilot Plant and Containment Systems Experiment to Large Pressurized Water Reactors

Significant in the application of spray experiments to the accident analysis of large PWR's is the scale-up from smaller containment research facilities. We believe that this can be reasonably accomplished through the use of conservative models in existence. In addition to the design considerations discussed in other sections of this report there are two areas that need to be considered in this scale-up:

1. the effect of the liquid which reaches the vessel wall and runs down it,
2. the effect of drop coalescence.

1. Wall Film Effect. — For most of the setups in the NSPP, a significant fraction of the liquid hits the vessel wall and runs down it. The surface area of the film running down the walls turns out to be several times that of the spray drops falling through the vessel atmosphere. Thus, even assuming the mass transfer coefficient from vessel atmosphere to wall film is substantially lower than that from vessel atmosphere to drops, a significant part of the absorption is probably done by the wall film.

It seems evident that the wall film effect is much more important in recent runs where we have used three Spraying Systems Company 7G3 nozzles spaced uniformly on a 36-in.-diam circle than in earlier runs which used one Sprayco type 1713 nozzle on the vessel center line. The spray pattern of the former nozzles has a larger included angle than that from the latter. In addition, the minimum distance to the wall is 18 in. less. This is confirmed by our experience that we had trouble getting wall runoff samples when we were using the 1713 nozzle, as well as by trajectory calculations which indicated that very little of the spray from the 1713 should reach the wall.

We frequently have observed better performance of the spray in our experiments than predicted by our analytical model. It is certainly possible that the wall film accounts for the difference.

As the vessel size increases, the wall film effect should become less. We would expect much less effect in the CSE than in the NSPP, and even less in the large PWR. At the present time we have not developed an analytical model which predicts the rate of absorption into wall films.

The theoretical models used to predict spray experiments in the NSPP and CSE have, with minor exceptions, predicted conservative answers. We feel that the same theory should be applicable to large PWR's and suggest that predictions be based on spray performance models rather than on experimental data.

2. Drop Coalescence. — In a system containing an array of spray nozzles, the possibility of drops colliding and coalescing is present. On the other hand, even though the reference design spray is the equivalent of a very severe rainstorm (2600 gpm to a 140-ft-diam building amounts to a rainfall of 16

in./hr), the drop density is not terribly high. Mason⁴⁹ gives an equation which can serve as a basis of a model for removal of drops by coalescence. This is:

$$dm/dt = E_1 E_2 \pi R^2 w (V - v),$$

where

dm/dt = rate of increase of mass of larger drop,

E_1 = collision efficiency, that is, the probability that if the equations of motion say that two drops will collide they will do so,

E_2 = capture efficiency, that is, the probability that if there is a collision, capture will occur,

R = radius of the large drop,

w = concentration of liquid as smaller drops, g/cm³,

V = terminal velocity of large drop,

v = terminal velocity of small drop.

We assume that all drops are falling at their terminal velocities, that drops of all sizes are uniformly distributed throughout the containment building, and that the properties of the large drop are not changed as a result of the capture. It is rather simple to modify the equation so that what we calculate is the rate of removal of the smaller drops by the larger. Using a 61-group model, we use the above equation to calculate the rate at which drops of a given size are being removed by all larger sizes. This is done for all of the drop sizes. At this point in the program, the calculation indicates several of the smaller sizes are being removed faster than they are introduced by the spray nozzles. We handle this by arbitrarily reducing the population of each size until the calculation says no size is being removed faster than it is being supplied. Thus we arrive at a new size distribution corrected for coalescence effects. Our calculations indicate that a column 1 cm² × 3658 cm (120 ft) high contains only 255 drops, or the drops are about 14 cm (6 in.) apart on the average. Calculations based on this coalescence model show that at the spraying rates proposed for containment buildings currently being designed, the removal constant is reduced 10 to 20% as a result of drop coalescence.

F. Radiolytic H₂ Generation

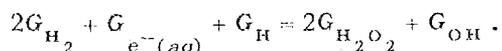
1. **Theory.** — For the last several decades the radiolytic decomposition of water and aqueous solutions has been thoroughly investigated. An excellent summary of the fundamental theory of the processes involved is given by Allen.⁵⁰

The radiolytic degradation of dilute aqueous solutions is an extremely complex process. In the simplest sense it may be said that the initial products of the radiolytic degradation are those resulting from water decomposition, that is, the hydrated electron e⁻(aq), the OH radical, and H⁺(aq). These are formed heterogeneously in the initial spur (path) along which the energy is being absorbed. As they form they may (1) react with each other or (2) diffuse to the body of the solution where they may continue to

⁴⁹B. J. Mason, *The Physics of Clouds*, p. 110, Oxford, 1957.

⁵⁰A. O. Allen, *The Radiation Chemistry of Water and Aqueous Solution*, Van Nostrand, 1961.

react with each other or with a reactive solute. The consequence of the interaction among themselves results in the formation of the so-called molecular products H_2 and H_2O_2 , O_2 (plus the re-formation of H_2O). The extent to which these entities are formed is normally expressed as a G value, that is, the number of molecules or radicals of each such species formed per 100 ev of energy absorbed. The primary yield is normally expressed as a subscript and the net or actual yield as a parenthetical notation. For example, $G_{H_2O_2}$ is the hydrogen peroxide formed directly from the water by radiation while $G(H_2O_2)$ is the actual amount measured by some physical or chemical means. In a sense the subscript G value may be considered as that occurring within the spur or close to it while the parenthetical G value is that resulting after diffusion away from the spur and subsequent reaction with the solute or other radiolytic species. The primary radiolytic products are of necessity in balance just as is any other chemical reaction, that is, for every oxidation there must be an equal reduction. The material balance normally used is the following:



The commonly accepted G values for the direct yield are the following:

$$G_{H_2} = 0.44, \quad G_{e^-(aq)} + G_H = 2.9, \quad G_{H_2O_2} = 0.70, \quad G_{OH} = 2.34.$$

It should be emphasized here that the values shown are those for pure H_2O under gamma radiation.⁵⁰ These values may be modified by the presence of an active solute; for example, the presence of a reducing agent may decrease the H_2O_2 yield while at the same time apparently increasing the OH yields. Qualitatively this would mean that solute molecules in the spur might react with a radical before it has an opportunity to react with another radical to form a molecular product. There has been some tendency to consider the above G values as limiting in all aqueous solutions, that is, to consider that the $G(X)$ values can be no higher than the $G_{(x)}$ value. This is, of course, fallacious since the $G(X)$ value may be much larger than $G_{(x)}$ because of secondary reactions taking place between the various entities and the solute. Allen⁵⁰ gives higher $G(H_2)$ values for other systems. The G values above obtain only for pure water; for the spray solutions under study the $G(H_2)$ should not differ greatly from the theoretical value.

Once formed, the primary radiolytic species diffuse to the body of the solution where they may undergo a variety of chemical reactions homogeneously. Those listed below are considered to show the principal modes of interaction taking place:





The interactions shown lead to the re-formation of H_2O and to steady-state concentrations of the molecular species. Jenks⁵¹ has derived a series of simultaneous equations involving the direct radiolysis yields, reaction rates, and equilibrium concentrations by which it should be theoretically possible to closely estimate the equilibrium gas concentrations in an aqueous system. These equations are similar to those derived earlier by Allen⁵⁰ and give a relationship between excess oxidant concentration and steady-state concentrations of H_2 , H_2O_2 , and O_2 . Both treatments use a material balance involving the parameter α , which represents the excess of oxidant. The material balance is

$$[\text{H}_2] + \alpha = [\text{H}_2\text{O}_2] - 2[\text{O}_2].$$

It should be noted that this material balance is different from that shown previously, in that this involves only the molecular species while the previous material balance equation involved only the direct primary radiolytic species. Therefore it is evident that, as pointed out earlier, the two quantities $G(X)$ and $G_{(X)}$ should be clearly distinguished. While the G_{H_2} yield for pure H_2O has been fairly well established, the $G(\text{H}_2)$ value is subject to a variety of parameters. Under the treatment of both Allen⁵⁰ and Jenks⁵¹ the G_{H_2} value determines the equilibrium concentration of H_2 in a closed system, whereas the $G(\text{H}_2)$ value determines the rate of approach to equilibrium.

The two mathematical treatments discussed above have certain limiting factors which may have great import in the case at hand. These are briefly:

1. Few data are available for the G values at high pH levels.
2. The effect of gas/liquid ratios on the equilibrium concentrations is not known.
3. No data are available on the exact effect of the presence of $\text{Na}_2\text{S}_2\text{O}_3$.

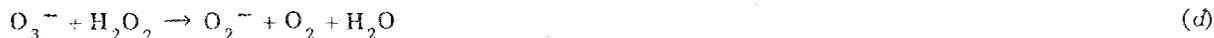
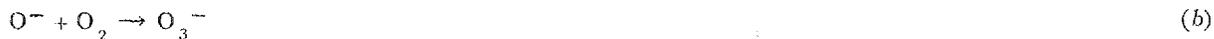
In amplification of each of the above in the order listed:

1. Recent works^{52,53} have indicated that, in basic solutions, other reactions than those given previously may have a great effect. Examples of these are:

⁵¹G. H. Jenks, *Effects of Reactor Operation on HFIR Coolant*, ORNL-3848 (October 1965).

⁵²W. A. Armstrong, "The Radiolysis of Alkaline Aqueous Solutions Containing Hydrogen and Oxygen," *Can. J. Chem.* **44**, 737 (1966).

⁵³G. E. Adams, J. W. Boag, and B. D. Michael, "Spectroscopic Studies of Reactions of the OH Radical in Aqueous Solution," *Trans. Faraday Soc.* **61**, 492 (1965).



The rate constants of these reactions are of such an order that the mathematical treatment of Jenks may not hold for the basic borate and basic $\text{Na}_2\text{S}_2\text{O}_3$ borate spray systems contemplated.

2. The high gas/liquid ratio may have the effect of constantly replenishing the O_2 consumed in solution by H_2O_2 formation. Therefore equilibrium, as illustrated by the molecular balance, may be attained at a higher gas concentration since the α may have a higher effective value.
3. The effect of the presence of $\text{Na}_2\text{S}_2\text{O}_3$ on the radiolytic H_2 generation has not been pinpointed, although data generated at this Laboratory would indicate that it has an enhancing effect. If we assume that the $\text{S}_2\text{O}_3^{2-}$ ion is oxidized simply to $\text{S}_4\text{O}_6^{2-}$, then an equivalent amount of H^+ would be reduced to H_2 . This would be additive in some amount to the radiolytic H_2 produced from the water radiolysis.

2. The Evaluation of $G(\text{H}_2)$. — As pointed out above, the radiolytic generation of H_2 involves two factors, namely, G_{H_2} and $G(\text{H}_2)$. In pure water or in water containing a solute which is not reactive, $G(\text{H}_2)$ will approach G_{H_2} as a limit. The presence of some oxidizing agent such as O_2 may cause $G(\text{H}_2)$ to be less than G_{H_2} , that is, less than 0.44. In the irradiation of water containing O_2 it has been found that $G(\text{H}_2) \approx 0.2$.⁵⁴ Conversely, when the H_2 is swept out of the system as rapidly as it is formed, $G(\text{H}_2) \approx G_{\text{H}_2}$. It should be understood that here, even at equilibrium conditions, $G_{\text{H}_2} = \sim 0.44$ while $G(\text{H}_2) = 0$. In other words the molecular H_2 is recombining as quickly as it is formed.

Utilizing both the Jenks and the Allen approach it may be estimated that the equilibrium concentration of radiolytic H_2 from an air-saturated solution should be ~ 3 vol % (at 25°C). This is strictly true only for a pure air-saturated H_2O system.

Studies carried out on the proposed sprays ($\text{NaOH} \cdot \text{H}_3\text{BO}_3 \cdot \text{Na}_2\text{S}_2\text{O}_3$ and $\text{NaOH} \cdot \text{H}_3\text{BO}_3$) do not result in any such low equilibrium H_2 overpressure.²⁸ All data reported were obtained from capsule irradiation of the solutions. In Fig. 2 are shown the results obtained from a study carried out to ascertain the radiolytic gas overpressure as a function of dose. Neither of the two proposed sprays shows a true equilibrium state at over 3 atm gaseous overpressure. The curvature exhibited at the higher overpressure does indicate that equilibrium conditions are being approached. It should be stated here that the relative pressures of the two proposed spray solutions should not be taken as any indication of relative amounts of radiolytic H_2 being generated. The gas/liquid ratio used in this test was only approximate since the purpose was to determine the pressures which could be built up by the radiolytic gases at the approximate dose expected. By comparison both the H_2O and the H_3BO_3 solution exhibit equilibrium overpressures of ~ 0.3 atm.

The above test does not give any indication of the composition of the radiolytic gas, although previous data indicated it to be largely H_2 . Therefore another test was carried out under more exacting conditions whereby the amount of radiolytic H_2 was measured under conditions similar to the preceding test.

⁵⁴J. A. Ghormley and C. H. Hochanadel, *J. Am. Chem. Soc.* **76**, 335 (1954).

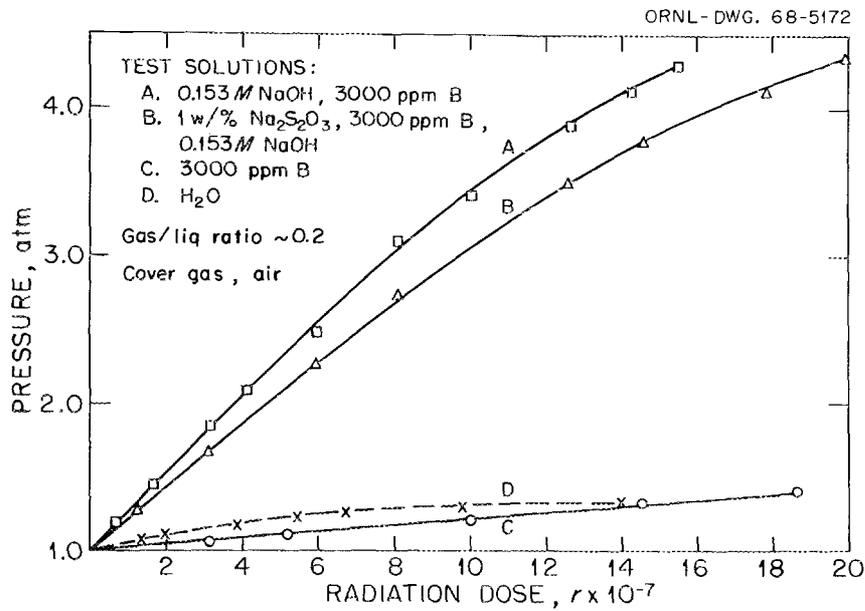


Fig. 2. Pressure vs Dose.

Table 4. Radiolytic Hydrogen Generation as a Function of Gas/Liquid Ratio and Total Dose

Gas/Liquid Ratio	Dose (r)	Solution 1 ^a			Solution 2 ^b		
		H ₂ (cc/ml)	P _{H₂} (atm)	G(H ₂)	H ₂ (cc/ml)	P _{H₂} (atm)	G(H ₂)
25/1	1 × 10 ⁸	0.70		0.31	0.63		0.29
5/1	1 × 10 ⁸	0.90		0.40	0.89		0.39
1/1	1 × 10 ⁸	1.00	1.0	0.43	0.90	0.9	0.39
0.2/1	1 × 10 ⁸	0.74	3.7	0.32	0.54	2.7	0.24

^a1 wt % Na₂S₂O₃, 3000 ppm boron, 0.15 *N* NaOH.

^b3000 ppm boron, 0.15 *N* NaOH.

The data shown in Table 4 indicate strongly that a great percentage of the overpressure noted was indeed due to radiolytic H₂. The data also point up some difference in the gas generation per unit dose of the two spray solutions. The basic borate solution does not build up radiolytic H₂ quite so quickly nor to so high an overpressure [G(H₂)] (per unit dose) as does the basic thiosulfate solution. As has been reported,²⁶ the gas/liquid ratio does have an effect on the rate of H₂ generation, increasing as the ratio decreases. This is undoubtedly due to the O₂ interaction with H₂ to re-form H₂O, that is, more O₂ available less net H₂ formed. At very low gas/liquid ratios this effect is apparently reversed (at high doses) due to the very high H₂ buildup approaching an equilibrium concentration. The data also illustrate the fallacy of using G(H₂) as an exact measurement for the rate of H₂ buildup. It is clear that it should be used only to specify the net H₂ found under specific conditions.

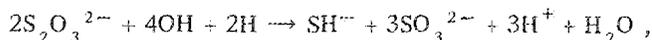
In conclusion the following points can be made:

1. The equilibrium concentration of radiolytic H_2 from both basic borate and basic borated thiosulfate solutions is significantly higher than predicted by the Jenks equations. The Jenks equations were derived for an essentially pure water-air system, while the solutions under question do not fit this category.
2. In the basic borate solution the equilibrium concentration of radiolytic H_2 would seem to be lower than in the case of the basic borated thiosulfate solution. The difference is very probably of no great import in view of the large H_2 overpressures (vol %) involved at the equilibrium state. In both cases the H_2 overpressure at equilibrium would probably be greater than ~ 3 atm.
3. At a dose of 2×10^8 r and a gas/liquid ratio of 25, sufficient radiolytic H_2 is generated to be of concern. The expected gaseous H_2 concentration under these conditions would not be less than ~ 6 vol %.
4. All the tests carried out to date have been carried out with "clean" solutions. In the actual case the pickup of impurities from the reactor environs could tend to cause the radiolysis results to be worse than reported.

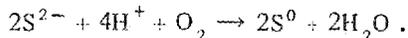
G. Radiolytic Solids Generation

Of the two spray solutions under consideration, the basic borated thiosulfate is the one of major concern insofar as radiolytic solids generation is concerned. Neither the NaOH nor the H_3BO_3 present can be considered to be a source of such solids except as they may react with an external ion. This is considered highly unlikely since the formation of insoluble compounds of either Na^+ or BO_3^{3-} is difficult. It is, of course, true that the reaction of the base (NaOH) with metals such as aluminum to form insoluble hydroxides is possible, but the use of this metal is very probably ruled out on the basis of corrosion and/or H_2 generation. Therefore the thiosulfate is the sole remaining major source of solids generation.

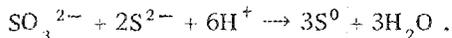
If we consider that even in basic medium the $S_2O_3^{2-}$ probably undergoes radiolytic reaction of the type



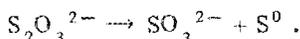
we have a possible source of colloidal sulfur. It is known that the sulfide ion may react with O_2 to give S^0 . A possible reaction mode is the following:



It has also been observed that, when a solution of SO_3^{2-} and S^{2-} is made acidic, elemental sulfur results:



The thiosulfate itself will, of course, decompose under acid conditions:



However, it should be pointed out that it is stated that thiosulfate can readily be obtained by boiling sulfur with solutions of sulfite,⁵⁵ so that under the conditions of the postulated accident the reaction to decompose $S_2O_3^{2-}$ to SO_3^{2-} and S^0 should be minimal.

⁵⁵F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Interscience, 1966.

Table 5. Effect of pH on Radiolytic Sulfur Formation

Test solution: 1 wt % $\text{Na}_2\text{S}_2\text{O}_3$, 3000 ppm boron, 1.0 N NaOH to give desired pH

Solution pH ^a	Sulfur Appearance Dose ^b (r)
	$\times 10^7$
4.9	1
6.0	2
8.0	6
9.0	15
9.6	30

^apH as measured before radiation.^bDose required to bring about visible sulfur formation.

It is to be noted that all of the above reactions require an acid solution to be of any consequence. Work carried out at the Laboratory²⁶ in capsules has shown that radiolysis of an acid borated thiosulfate solution does result in significant amounts of colloidal sulfur. However, the basic borated thiosulfate solutions studied demonstrate little or no radiolytic sulfur formation. Table 5 gives the results of a study carried out to determine the effect of pH on the minimal dose required to bring about visible sulfur formation.³⁰ As can be seen, the required dose is a function of pH, and at the more basic pH values an extremely high dose is required before any visible sulfur appears. The data would indicate that, if the spray solution is kept basic, radiolytic sulfur should be no problem. The only other source of solids is the precipitation of metal ions as the sulfide. It is known that many metals form insoluble sulfides. However, it might again be stated that such metals in the main would necessarily be excluded from the reactor environs because of corrosion problems. Significant work on the effect that construction materials will have on the solution stability is now under way.

H. Loss of Reactivity from Radiolytic and Thermal Degradation

The loss of reactivity of the proposed sprays may be considered as deriving from two main sources, that is, radiolytic and thermal degradation of the spray. Insofar as thermal degradation is concerned it would seem that the basic borated spray should be unaffected. It is stated⁵⁵ that the alkali hydroxides can be sublimed unchanged at 350 to 400°C. Therefore, since this is true, it would seem unlikely that NaOH would be thermally degraded. The thiosulfate solutions (acid and basic), however, are known to undergo some degree of degradation, both autoxidation and reduction and air oxidation, at higher temperatures. The extent to which this might occur in the spray situation has been studied and reported.²⁸ Figure 3 is reproduced from that report. It shows very definitely that acidic thiosulfate is far less thermally stable than basic thiosulfate. The data reported indicate that basic thiosulfate does thermally degrade to some extent but that the degradation tends toward an equilibrium state at some fairly low percent

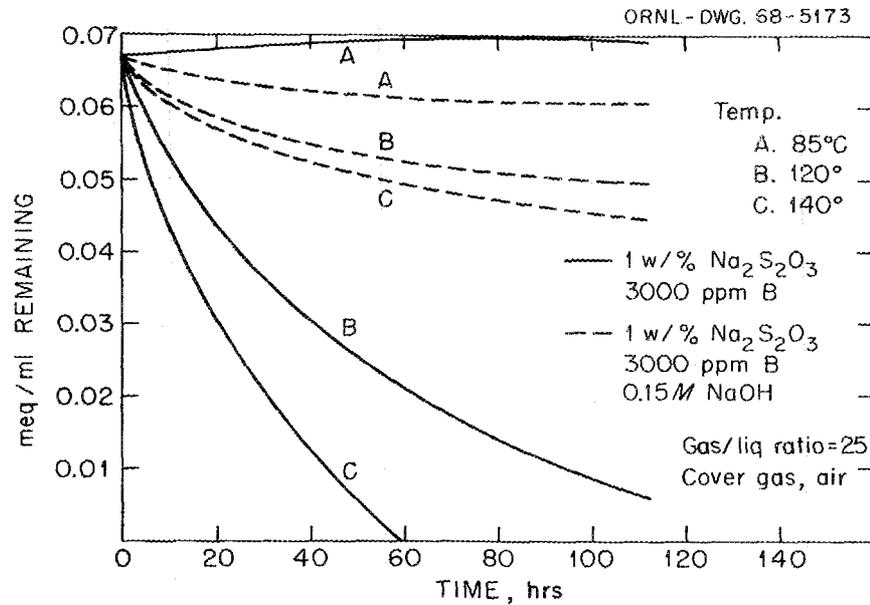


Fig. 3. $\text{Na}_2\text{S}_2\text{O}_3$ Stability vs Temperature.

of degradation. The results of this study show that the basic borated thiosulfate spray should be sufficiently thermally stable to achieve its objective.

The radiolytic degradation of the acidic and basic thiosulfate solutions has been previously reported.²⁶ In Fig. 4 are given the results of that report. The data indicate that the basic thiosulfate is more radiation resistant than the acidic thiosulfate. For a dose of 10^8 r, essentially all of the acid thiosulfate is destroyed, while less than half of the basic thiosulfate undergoes radiolytic degradation. Since it is considered that the basic thiosulfate will be present in at least a tenfold excess of what will be required to react with the I_2 , it is evident that the basic thiosulfate will be radiolytically stable enough to carry out its function.

The radiolytic degradation of the basic borate spray should be minimal. Neither NaOH nor H_3BO_3 is considered to be active toward the radiolytic products of water.

The combined effects of radiation and temperature on the basic borated thiosulfate spray solution have been reported.³⁰ The data are reproduced in Fig. 5. As can be seen, the thermal and radiolytic effects seem to be essentially additive. The data points obtained from extrapolation of the separate thermal and radiolytic degradation studies, referred to previously, fall fairly close to actual experimental data.

It can be concluded from the data presented that both the basic borate and the basic borated thiosulfate spray would seem to be thermally and radiolytically stable enough for usage in the accident case.

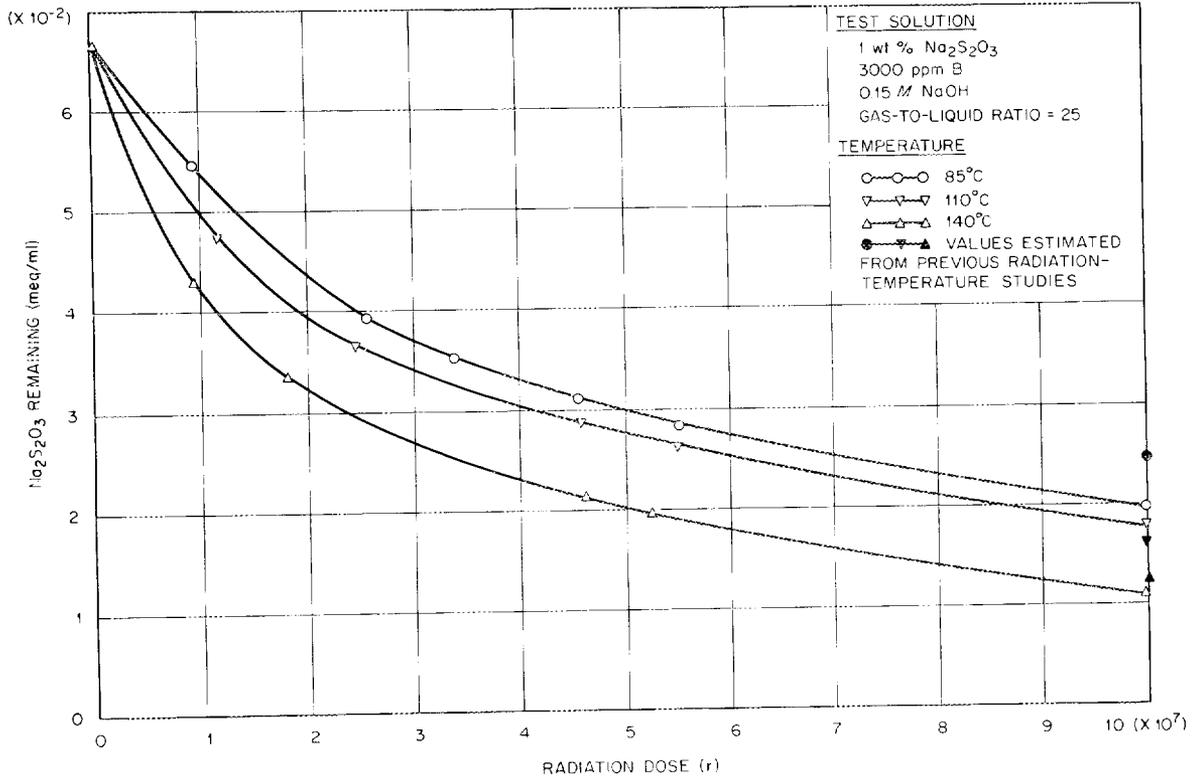


Fig. 4. Effect of Temperature and Radiation on $\text{Na}_2\text{S}_2\text{O}_3$.

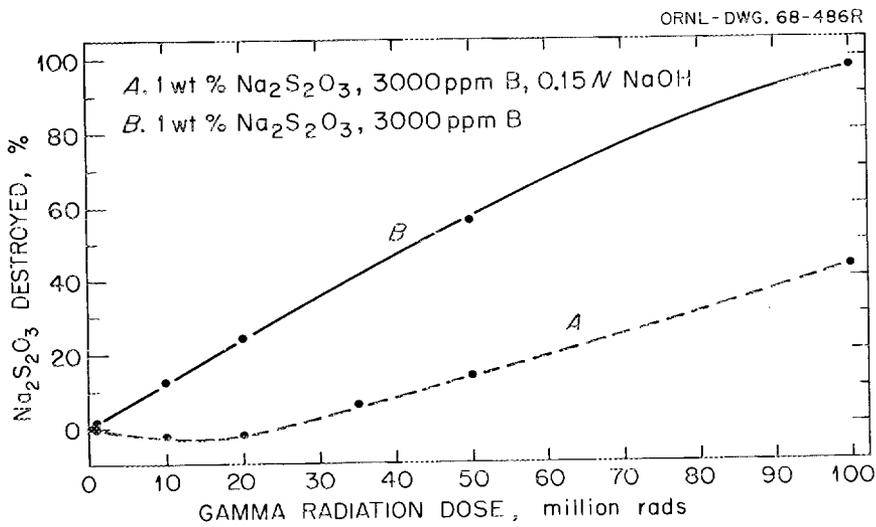


Fig. 5. Effect of Gamma Radiation on Solutions of Sodium Thiosulfate.

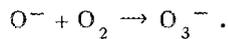
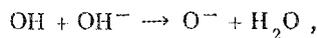
I. Radiolytic pH Change

The major pH changes (due to the radiolytic effects) noted thus far have occurred in the acidic borated thiosulfate solution.²⁶ However, even the basic borated thiosulfate solution does become more acid on radiolysis. If the reaction given previously for the reaction of $S_2O_3^{2-}$ with the radiolysis products of water,



is valid, then it is apparent that the radiolytic decomposition of $S_2O_3^{2-}$ will result in an increase in acid concentration.

There is no reason for believing that the basic borate solution will become more acid on irradiation except for the possible radiolytic reactions involving atmospheric O_2 :



The data previously reported²⁶ have indicated some small lowering of the pH upon radiolysis. There is, of course, always the possibility in the real case of some reaction between metal ions present and OH^- to form insoluble hydroxides. If this does occur, obviously the solution will become more acidic. In any case it should be stated that the pH of the spray solution must be monitored during the accident. If loss of basicity does occur, addition of more NaOH should present no major problem.

III. DISCUSSION AND CONCLUSIONS

While this document does not presume to answer all of the questions concerning spray systems, it is designed to answer many questions of significant importance to the acceptance of these systems as reliable engineered safeguards. The problems discussed apply mostly to the removal of I_2 by sprays. The conclusions are those of the research staff involved in the Spray and Pool Absorption Technology Program at ORNL and do not necessarily reflect the opinion of industry or the regulatory branch of the AEC.

A. Reagent Requirements for a Design Basis Accident

The reagent concentration, 0.17 mole/liter in the typical reference case, is adequate for the mitigation of the accident. The solution contains over 1800 times as much NaOH as is required to react with the total core inventory of iodine. Since other fission products will be released and come in contact with the spray solution, a determination of this effect was made. For the unrealistic total fission product release case assumed, the NaOH available is 34 times as much as needed.

In the case of the thiosulfate solution, 1700 times as much reagent exists as is required to react with the total core inventory of iodine.

B. The Question of Gas and Liquid Film Resistance

The assumption of a gas-film-controlled model for I_2 removal by the base-borate-thiosulfate solution is valid as long as the iodine concentration in the gas does not exceed 9.9 g/m^3 ; the reference case value is 0.21 g/m^3 . The case for the base-borate solution is yet to be demonstrated. The speed of reactions involved and the volatility of HOI may influence this.

C. The Effect of Spray Drop Saturation on Removal Efficiency

Assuming the maximum rate of transfer into the drop, we find that a typical drop residence time of 10 sec compares favorably with the 162 sec required to saturate the drop. Therefore drop saturation with resulting decrease in removal effectiveness should not be a problem.

D. The Effect of Spray Drop Size

The persistence of very small, 1- to $2\text{-}\mu$ -diam, drops in the containment atmosphere does not constitute a problem. Only 3.7×10^{-4} of the fission product inventory would be airborne as spray "fines" if the inventory was assumed uniformly mixed in the spray solution.

Spray distributions are of considerable interest. Calculations indicate that performance estimates based on any mean diameter except the number mean, with the additional assumption that all drops are mean size, should be conservative.

E. Scale-Up from Nuclear Safety Pilot Plant and Containment Systems Experiment to Large Pressurized Water Reactors

Plant design requires the ability to scale results up from smaller experimental facilities to large PWR-size systems. Two factors should be considered in this question: (1) wall effects in experimental facilities and (2) drop coalescence. The wall film effect will influence the data obtained in facilities, resulting in more rapid removal rates. It is suggested that as long as the theoretical models used to estimate spray performance give conservative predictions for NSPP and CSE, these models be used as a basis for system scale-up. Drop coalescence should not be a major problem; calculations indicate the removal constant is reduced 10 to 20% by this effect.

F. Radiolytic Effects

The question of solution radiolysis producing hydrogen, solids, pH change, and/or reduced iodine capacity is important. The following points should be made.

1. The mathematical treatment of the equations for pure water by Jenks may not hold for the base-borate or base-borate-thiosulfate spray solutions.
2. The equilibrium concentration of radiolytic H_2 from both base-borate and base-borate-thiosulfate solutions is significantly higher than predicted by the Jenks equations.⁵¹ The H_2 overpressure in both cases would probably be greater than $\sim 3 \text{ atm}$.

3. Slightly more H_2 generation may result from the base-borate-thiosulfate solution than the base-borate solution.
4. About 4 vol % gaseous H_2 is achieved at a dose of 2×10^8 r for a gas/liquid ratio of 25.
5. The presence of impurities may cause the radiolysis results in an actual "dirty" system to be worse than the "clean" solution tests conducted.
6. Radiolytic sulfur should not be a problem in the base-borate-thiosulfate if the pH is maintained ≥ 8.5 .
7. Thermal degradation of base-borate-thiosulfate tends toward an equilibrium state at some fairly low percent of degradation.
8. Acid-borate-thiosulfate solution is not acceptable as a spray solution because of excessive solids generation.
9. Test results of the combined effect of radiation and temperature on the base-borate-thiosulfate and base-borate solutions indicate acceptable stability under expected accident conditions.
10. The spray solution pH should be monitored during the course of an accident.

We present Fig. 6 as a graphical summary of a DBA and the relationship of the various accident parameters with the spray system. The containment building temperature and pressure are given from 10^{-1} to 10^6 sec. These curves do not apply to any one plant but are composite curves representing the worst conditions for all of the plant accidents for the majority of PWR's now in the various stages of licensing. The dose to the spray solution is taken from Rancho Seco docket information.^{5,6} This indicates that a dose of $\sim 10^8$ rads is accumulated by the spray solution in ~ 14 days. The value of 14 days is the result of a conservative evaluation of the radiation dose received by the solution. Detailed consideration of a particular plant could result in increasing the estimated time to accumulate 10^8 rads to 100 days. The

^{5,6}Sacramento Municipal Utility District to AEC, Docket 50-312, April 1968, available at AEC Public Document Room.

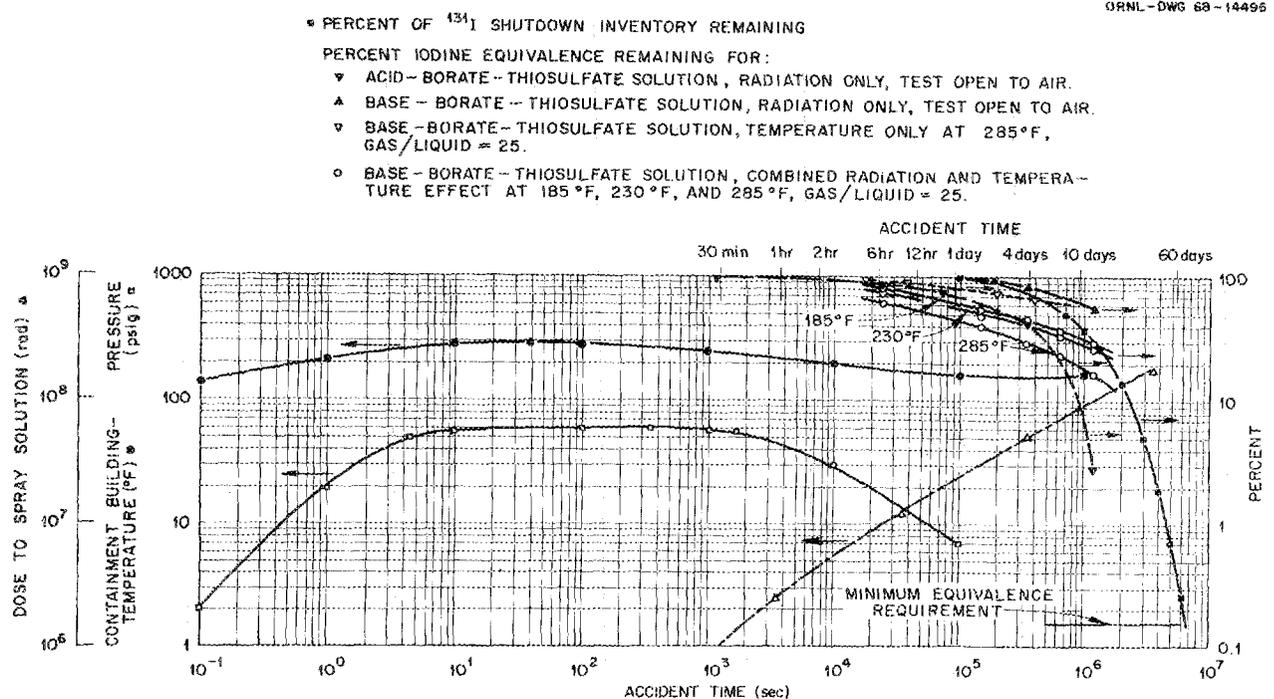


Fig. 6. Typical Design Basis Accident Parameters.

percent of ^{131}I shutdown inventory is also given to indicate the relationship of the decaying source term. As stated previously, *the base-borate system is stable under the accident conditions predicted.* The data on the thiosulfate system are presented to show the separate and combined effects of radiation and temperature on the iodine equivalence of the system. The data show the acid-borate-thiosulfate equivalence dropping sharply with less than 10% equivalence remaining in 10 days.²⁶ The major problem with this mixture of course is the excessive solids generation. The base-borate-thiosulfate system stability is presented for the separate effect of temperature²⁸ (285°F for the duration of the test) and radiation²⁶ and the combined effect at temperatures of 185, 230, and 285°F.³⁰ The information presented in Fig. 6 points out the base-borate-thiosulfate system iodine removal capability under DBA conditions. The predicted building temperature history indicates temperatures less than 200°F in 4 hr, leveling off at ~160°F for long-term considerations. This is a significantly less destructive situation than the test results shown, where the solutions were maintained at the temperatures of 185, 230, and 285°F for the duration of the test. Even under these severe conditions the solutions are not degraded to the point that they approach the calculated minimum equivalence value necessary for removal of all of the iodine, 0.147%.

At the present time it is not possible for the ORNL program to single out one solution as the best. Either the base-borate or the base-borate-thiosulfate solution can be used if appropriate design considerations are made based on the information generated in this and other privately sponsored research programs.

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