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ARMOUR RESEARCH FOUNDATION OF ILLINOIS INSTITUTE OF TECHNOLOGY

ARF 3119-13
(Final Scientific Report)

SCAVENGING OF PARTICULATE MATTER
IN CONNECTION WITH NUCLEAR-POWERED SHIPS

J. Rosinski

United States Atomic Energy Commission
Washington, D. C.

Contract No. AT(11-1)-586

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IN CONNECTION WITH NUCLEAR-POWERED SHIPS

Report No. ARF 3119-13
(Final Scientific Report)

by

J. Rosinski

for

United States Atomic Energy Commission
Maritime Reactors Branch
Washington 25, D. C.

Attention: Mr. R. Longaker

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FOREWORD

This is Report No. ARF 3119-13 (Final Scientific Report) on ARF Project C 119, Contract No. AT (11-1)-586, entitled "Scavenging of Particulate Matter in Connection with Nuclear-Powered Ships." It covers the period from December 15, 1957, to June 30, 1960.

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Respectfully submitted,

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SCAVENGING OF PARTICULATE MATTER IN CONNECTION WITH NUCLEAR-POWERED SHIPS

ABSTRACT

This report is a summary of work carried out over a 2-1/2-year period on scavenging of radioactive particles which might be released by the reactor system of a nuclear-powered ship. Two types of dispersions were considered: aerosols and hydrosols.

Radioactive aerosols were scavenged by heterogeneous coagulation with solid and liquid aerosols produced within the radioactive aerosol cloud. Liquid or/highly hygroscopic particles, which can be classified as solid particles with liquid films on their surfaces, were found to be the most effective scavengers. The system composed of a fine water spray and hydrolysis products of silicon tetrafluoride was found to be suitable for field application. It is suggested that a scavenging system can be designed for operation inside the containment vessel or in connection with the ventilating system.

Scavenging of radioactive cations, anions, and colloids of corrosion and fission products was studied in substitute ocean water, natural ocean water, and natural harbor water. A scavenging system composed of potassium permanganate and ferrous salt successfully removed most of the radionuclides. Ferric hydroxide-manganese dioxide hydrate adsorbs and absorbs radioactive species, thus transferring them from a liquid into a solid phase. Addition of Floc lll to the system improved sedimentation. The potassium permanganate-ferrous sulfate-Floc lll system was found to be suitable for field application.

It is recommended that further research be conducted to increase the efficiency of the present system. It is also recommended that the possibility of preventing the formation of radioactive aerosols from fuel elements be investigated.

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SCAVENGING OF PARTICULATE MATTER IN CONNECTION WITH NUCLEAR-POWERED SHIPS

I. INTRODUCTION

The research performed on this program was directed toward studying two types of colloidal dispersions (aerosol and hydrosol) of radioactive fission and corrosion products. The program consisted of the following four phases:

I. A theoretical study of the diffusion and deposition of radioactive particulate matter formed in the free atmosphere due to release from a nuclear-powered ship.

II. A study of scavenging of radioactive particulate matter in the gaseous phase

III. A study of scavenging, flocculation, and settling of radioactive particulate matter in the liquid phase

IV. An estimation of the concentration of radioactive waste in the wake of the nuclear-powered ship.

Research was conducted on all four phases concurrently.

Progress and phase reports were issued regularly throughout the program. This final report summarizes the entire program. The work not described comprehensively in the other reports is discussed in some detail here.

During this last report period the fundamental mechanisms of scavenging were studied experimentally.

II. PHASE I - THEORETICAL STUDY OF DIFFUSION AND DEPOSITION OF RADIOACTIVE PARTICULATE IN THE FREE ATMOSPHERE

The first report on this program was a comprehensive report on Phase I. This report is available from the Technical Information Service, Oak Ridge, Tennessee, under No. AECU-4138. The study was based on Sutton's diffusion equation with Chamberlain's correction for deposition. The results are presented in a series of seventy-six graphs. The possible behavior of the cloud formed by radioactive gases or finely divided particulate matter released from a nuclear-powered ship is given for wind velocities of 5, 10, and 15 mph and for velocities of deposition equal to 0, 1, 2.5, 10, and 20 cm/sec. The ranges of the Q/C and Q/R parameters were 10^7 - 10^{15} cc/sec and cm^2 , respectively. An equation for diffusion in sea currents was proposed.

III. PHASE II - STUDY OF SCAVENGING OF RADIOACTIVE PARTICULATE MATTER IN THE GASEOUS PHASE

The extent of radioactive contamination of areas located downwind of an emission source will be strongly dependent on the sizes of the radioactive particles dispersed. Larger particles will contaminate only the area adjacent to the source; smaller particles and vapors, on the other hand, will travel intermediate and far distances to areas downwind of the source.

For the hypothetical case of the release of radioactive particles from a nuclear-powered ship, there will nearly always be a strip of water between the emission source and land. Therefore it may be practical to minimize or possibly eliminate contamination of the shore and land by scavenging the radioactive particles with particles of such a size that the radioactive material released into the atmosphere would "rain out" on the surface of the water. While this would contaminate the coastal waters, this contamination might not be too serious because the sea current would rapidly disperse and transport the contaminated material.

The release of radioactive particles from the fuel elements of the nuclear reactor of the ship could also contaminate the reactor vessel, the ventilating system of the ship, and the ship itself. Although confinement of the particles in the reactor vessel appears to be very difficult, this may be possible. In any event, the scavenging system selected should work rapidly in order to confine the released radioactive material preferably within the containment vessel.

Because of the lack of fundamental scientific data on heterogeneous coagulation of normal and radioactive aerosols, the research was directed toward studying coagulation in multiple-component scavenging systems. The systems studied were those which can produce liquid or solid aerosols through

rapid chemical reactions and which can operate independently of the power supply of the ship.

A. Experimental Procedures

Gold aerosols were prepared by electrically exploding previously irradiated pure gold wires (99.98%) of 0.006 in. in diameter. A 52- μ f 10,000-v condenser bank (GE model) charged to 6000v was discharged through a 16-mg, 46-mm-long gold wire inside an 81.9-liter Lucite chamber (Fig. 1).

Electrostatic wall effects were minimized by applying a conductive coating (antistatic compound No. 79 concentrate, Merix Chemical Company, Chicago) to the inside of the chamber. After the antistatic fluid was dried, the wire was mounted between pure gold electrodes and the cover of the chamber was clamped in place against an O-ring seal. The air in the chamber was purged by passing it through a filter (American Optical Company, filter R-57). Prior to the explosion, the chamber was partially evacuated to 2-1/2 in. of mercury below atmospheric pressure to permit subsequent entry of scavenging gases from 125-ml bottles.

Immediately after the explosion, scavenging gases or filtered room air was admitted to the chamber. Approximately 2-3 min elapsed before the pressure reached 1 atm inside the chamber, after which the stopcocks from the gas bottles were closed.

The radioactivity of the gold aerosol was viewed through a 3/4-in.-wide window located 6 in. from the bottom of the chamber. A gamma scintillation probe (model 812, Atomic Institute Company) was used to follow changes in the activity. The activity was automatically recorded with a modified Packard Tri-Carb scintillation spectrometer. As the aerosol coagulated and settled to the bottom of the chamber, the activity diminished until all of the aerosol had

FIG. 1. THE SCAVENGING TEST APPARATUS

settled out of sight of the window. A second probe measured the background activity.

In experiments conducted with water-saturated air, the air was bubbled through a water bath before filtration. The bottom of the chamber was wetted with 40 cc of water, and partial evacuation of the chamber was limited to 1-1/2 to 2 in. of mercury below atmospheric pressure in order to preclude condensation. A water fog invariably formed whenever expansion to 2-1/2 in. below atmospheric pressure was attempted.

After the explosion and subsequent introduction of scavenging gas, the system was thermally isolated to minimize possible thermal effects. After 5 min the system became relatively quiescent, as frequently indicated by the development of a supernatant layer above the aerosol.

Gold wires of 16.0 ± 0.4 mg were irradiated to a level of 1 mc for all experiments, except for a 16-mc wire used in one experiment. A measured half-life of 64 hr indicated that the gold was quite pure and that nearly all the activity was due to disintegration of gold-198, which has a half-life of 64.6 hr.

In the experiments conducted without a scavenger the particle concentration was followed by withdrawing samples periodically at a rate of 20 cc/min through an oscillating thermal precipitator (Strong-Ficklen) modified for gastight operation. Dark-field photomicrographs of the deposits were made, and coagulation constants were determined from the concentration. Coagulation constants were also determined for nonradioactive gold aerosols.

B. Results of Scavenging Tests

Table 1 lists the experimental conditions and results. It can be seen from the table and from Fig. 2, 3, and 4 that radioactivity decreased as

Table 1
SCAVENGING OF RADIOACTIVE GOLD AEROSOLS

Radio-activity, %	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ
90	53	0.708	0.38	33	1.136	2.45	4.00	9.38	7.20	23	1.63	2.95	36	1.042	1.90	7.00	5.36	5.40
80	70	0.536	0.32	42	0.893	2.20	6.00	6.25	5.80	26	1.44	2.75	41	0.915	1.78	8.60	4.36	4.80
70	85	0.441	0.28	47	0.799	2.02	7.00	5.36	5.40	28	1.34	2.65	46	0.824	1.68	10.19	3.68	4.40
60	102	0.368	0.25	51	0.736	1.95	7.18	5.22	5.30	32	1.19	2.50	49	0.758	1.60	11.98	3.13	4.10
50	124	0.302	0.22	55	0.680	1.87	7.54	4.97	5.20	35	1.07	2.35	54	0.695	1.53	13.99	2.68	3.75
40	147	0.255	0.20	59	0.636	1.80	8.30	4.52	4.90	41	0.915	2.20	60	0.625	1.45	16.03	2.34	3.50
30	177	0.212	0.17	64	0.587	1.72	10.50	3.57	4.40	48	0.782	2.00	67	0.560	1.35	19.23	1.95	3.20
20	217	0.173	0.15	72	0.518	1.63	15.50	2.42	3.60	60	0.623	1.80	81	0.463	1.23	24.51	1.53	2.70
10	404	0.132	0.12	97	0.387	1.40	30.99	1.21	2.52	85	0.441	1.50	130	0.297	0.96	37.13	1.01	2.30
Expt. A			Expt. B			Expt. C and D			Expt. E			Expt. F			Expt. G			
Aerosol:	1 mc			1 mc			1 mc			1 mc			1 mc			1 mc		
R.h.:	55%			31%			90-100%			40%			32%			90-100%		
Temp.:	76°F			79°F			G, 73°F; D, 64°F			75°F			80°F			67°F		
Density:	~19.3 g/cc			~1.0 g/cc			~1.0 g/cc			~1.0 g/cc			~1.5 g/cc			~1.0 g/cc		
Scavenger:	None			0.153 ethylene oxide, 0.153 boron tri-chloride			0.153 silicon tetrafluoride			0.153 silicon tetrafluoride, 0.153 ammonia			0.153 ammonia, 0.153 hydrogen chloride			0.044 silicon tetrafluoride		
(vol/vol %)																		

Radio-activity, %	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ	t, min	V, cm/min	d _{sc} , μ
90	8.99	4.17	4.70	27	1.390	0.60	21	1.78	0.64	30	1.25	0.52	3.50	10.72	7.70	3.50	10.72	7.70
80	11.26	3.33	4.20	45	0.834	0.41	34	1.102	0.48	39	0.962	0.45	4.99	7.51	6.40	4.99	7.51	6.40
70	12.98	2.89	3.90	65	0.577	0.33	43	0.872	0.42	51	0.736	0.38	5.70	6.58	6.00	6.20	6.05	5.70
60	13.99	2.68	3.75	87	0.431	0.28	49	0.758	0.39	63	0.591	0.33	6.20	6.05	5.70	7.20	5.21	5.30
50	16.03	2.34	3.50	107	0.350	0.24	56	0.670	0.36	75	0.497	0.30	6.50	5.77	5.60	8.50	4.43	4.90
40	18.75	2.00	3.20	127	0.295	0.22	62	0.605	0.34	92	0.408	0.27	6.70	5.60	5.50	10.50	3.57	4.40
30	25.00	1.50	2.80	155	0.242	0.19	74	0.507	0.30	113	0.333	0.24	7.50	5.00	5.20	12.21	3.07	4.00
20	37.13	1.01	2.30	196	0.191	0.16	92	0.406	0.27	135	0.278	0.21	8.99	4.17	4.70	14.48	2.59	3.70
10	53	0.708	1.90	210	0.139	0.13	120	0.313	0.22	178	0.211	0.17	13.49	2.78	3.85	24.51	1.53	2.80
Expt. H			Expt. I			Expt. J			Expt. K			Expt. L			Expt. M			
Aerosol:	1 mc			16 mc			1 mc			1 mc			1 mc			1 mc		
R.h.:	60-100%			24%			90-100%			90-100%			90-100%			90-100%		
Temp.:	81°F			69°F			77°F			81°F			78°F			82°F		
Density:	~1.0 g/cc			~19.3 g/cc			~19.3 g/cc			~19.3 g/cc			~1.0 g/cc			~1.0 g/cc		
Scavenger:	0.153 ammonia, excess formic acid vapor			None			Fine water spray			Coarse water spray			Fine water spray, 0.044 silicon tetrafluoride			Coarse water spray, 0.044 silicon tetrafluoride		
(vol/vol %)																		

t = time after explosion. V = settling velocity. d_{sc} = Stokes-Cunningham diameter of aerosol particles.

FIG. 2. SCAVENGING OF RADIOACTIVE GOLD AEROSOLS

FIG. 3. SCAVENGING OF RADIOACTIVE GOLD AEROSOLS

1-mc Gold Aerosol
after 3 Min

16-mc Gold Aerosol
after 3 Min

1-mc Gold Aerosol
after 5 Hr

16-mc Gold Aerosol
after 5 Hr

FIG. 4. PHOTOMICROGRAPHS OF GOLD AEROSOLS
(Magnification 480x)

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a function of the time after explosion. The least effective scavengers were the "dry" nonhygroscopic chemical smokes, e.g., ammonium chloride and boron trichloride-ethylene oxide (expt. F and B, respectively). A more effective scavenger was ammonia with excess silicon tetrafluoride (expt. E); some hygroscopic aerosol particles were present.

The aerosol was most effectively scavenged when hygroscopic agents were used under conditions of high humidity (expt. C, D, G, H, L, and M). Particle growth, accretion, and settling occurred rapidly as a result of the large volume of water vapor available compared with the volume of the nonaqueous gaseous reactants. Expt. G was slightly less effective than C and D because of the smaller amount of silicon tetrafluoride used -- 0.044% by volume, or only 29% of that used in C and D.

In view of the violently corrosive nature of hydrolyzed silicon tetrafluoride, an attempt was made to substitute hygroscopic ammonium formate as the scavenging agent (expt. H). However, ammonium formate was only about half as effective as silicon tetrafluoride at the same volume concentration. Part of this difference may be due to the fact that the purged air was unavoidably dried when it was passed through the 88% formic acid solution. Therefore, at the time of the explosion the humidity was probably low despite the presence of water on the bottom of the chamber.

To determine the effect of a higher level of radiation upon aerosol formation and coagulation (expt. I), a 16-mc gold wire was exploded and allowed to settle in the absence of a scavenging agent. This aerosol settled faster than the less active 1-mc aerosol (A in Fig. 3). This difference in the sedimentation rates cannot in itself be considered significant. However, the difference in color of the 16-mc aerosol indicates a definite departure from

previous tests with less radioactive aerosols. Whereas tests with nonradioactive and 1-mc aerosols invariably resulted in a purple aerosol which coagulated and settled as a pale purple deposit, tests with the 16-mc aerosol produced a purple cloud which gradually changed gray and settled as a gray deposit.

Photomicrographs of the deposits suggest a reason for the color change. The particles formed in the first few minutes after explosion appear to be similar in both the nonradioactive and the 16-mc aerosols. However, coagulation of the nonradioactive aerosol resulted in chain agglomerates, whereas coagulation of the 16-mc aerosol resulted in essentially spherical agglomerates with no tendency toward chain formation (Fig. 4). In the chains the individual particles scatter light much as if they were not agglomerated. Therefore little color change can be seen except that the intense purple color fades to a dull hue upon coagulation. The spherical agglomerates produce an aerosol with a wide size distribution upon coagulation so that high-order Tyndall spectra cannot be observed. The high radioactivity of the 16-mc aerosol probably minimized formation or maintenance of electrically charged particles, since chaining is ordinarily attributed to the presence of magnetic, polar, or electrical attraction. The high temperature of the ionizing discharge as the gold wire explodes undoubtedly results in a highly charged aerosol which has a strong tendency toward chaining unless the charge is dissipated.

Values for 10 through 90% radioactivity were interpolated from the sedimentation data, and Stokes-Cunningham diameters for the aerosol particles were calculated and plotted on logarithmic probability paper (Fig. 5). The calculated diameter is somewhat artificial since particle accretion and growth occurred during sedimentation; therefore the calculated diameter is smaller

FIG. 5. STOKES-CUNNINGHAM DIAMETERS OF AEROSOL PARTICLES

than the true diameter. The particles were assumed to be spherical since the shape factor of the slow-settling chain agglomerates is unknown. Deviation from linearity was greatest when the greatest change in particle size occurred during sedimentation. In expt. A and I, the median particle size was 0.23 micron. In expt. C and D, a median size of 5.2 microns was developed through the condensation of water vapor on hydrolyzed silicon tetrafluoride.

The pronounced influence of water vapor in enhancing the scavenging effectiveness of silicon tetrafluoride led to tests with water sprays to improve the scavenging rate and to produce particles separable by standard equipment, e.g., the cyclone separator. A Bete PB-3 spray nozzle was used to evaluate the scavenging effectiveness of a fine water spray. When operated at 58 psig, drops ranging in size from 6 to 110 microns were produced. In expt. J (Fig. 5) the nozzle was operated for a 30-sec period 6 min after the explosion, and 76 cc of fine water spray resulted. In 56 min 50% of the radioactivity was scavenged. In comparison, 122 min was required to reduce the activity to 50% without the water spray.

When the fine water spray was used for 30 sec 3 min after the explosion in combination with 0.044% by volume of silicon tetrafluoride (expt. L, Fig. 6), only 7 min was needed to scavenge 50% of the radioactivity. When 0.044% silicon tetrafluoride was used to scavenge radioactive particles from saturated air (expt. G, Fig. 2), a 50% reduction in activity required 14 min. Even when 0.153% silicon tetrafluoride was used with saturated air at room temperature (expt. C and D, Fig. 2), the scavenging effectiveness did not match that of expt. L, in which a much smaller amount of silicon tetrafluoride was used. This indicates that the amount of moisture available in saturated air at room temperature is not sufficient to grow the larger drops which can be obtained by using a fine water spray.

FIG. 6. SCAVENGING OF RADIOACTIVE GOLD AEROSOLS WITH WATER SPRAYS

A Bete PT-20 spray nozzle operated at 20 psig produced water drops ranging in size from 40 to 860 microns (expt. K and M, Fig. 1). In 30 sec of operation 6 min after explosion, 87 cc of spray was produced. This coarse spray was less effective than the smaller volume of fine spray, as 76 min was needed to reduce radioactivity by 50% (expt. K). When the coarse water spray was used for 20 sec 3 min after the explosion in combination with 0.044% silicon tetrafluoride (expt. M), 8 min was needed to settle 50% of the radioactive aerosol. The rapid settling of the coarse water drops apparently reduced the effectiveness of the spray as a source of water vapor. This supports the observation that the growth of the water vapor drops is a time-dependent variable and therefore an optimum size distribution of water spray exists.

Experiments were performed in which liquid carbon dioxide was sprayed into the Lucite chamber. Expansion of the carbon dioxide formed a dry-ice snow cloud, which vaporized almost instantly after its formation downstream of the expansion nozzle. Since the pressure in the chamber built up rapidly, it was not considered advisable to conduct a test on a radioactive aerosol with the existing facilities. Removal of airborne particles by the liquid carbon dioxide spray is not considered effective or practicable.

C. Effect of Pressure and Temperature on Coagulation and Sedimentation

Since elevated temperatures and pressures are possible in a nuclear accident, a knowledge of the effect of these variables on the coagulation and scavenging of radioactive aerosols is desired. The coagulation factor of a homogeneous aerosol derived from the Smoluchowski theory¹ and using Cunningham's correction is:

$$k = \frac{4}{3} \frac{R T}{\eta N} \left(1 + A \frac{\ell}{r} \right) \quad (1)$$

¹Z. Physik. Chem. 29, 128, 1918.

where

A is a constant for any particular set of conditions

N is Avogadro's number

r is the radius of the particle

R is the gas constant

T is the absolute temperature

ℓ is the mean free path of the gas molecules

η is the viscosity of the gas.

Thus the coagulation is directly proportional to the absolute temperature if other factors remain constant. However, the viscosity of a gas increases with rising temperature. For practical purposes the effect of temperature on coagulation is relatively small, but on the whole K should be greater at a higher temperature.

An increase in pressure reduces the effect of the Cunningham factor $(1 + A \frac{\ell}{r})$ since ℓ varies inversely with the absolute pressure. Since the particles smaller than the mean free path of the gas ordinarily disappear in a fraction of a second due to accelerated coagulation, an increase in pressure will reduce the rate of coagulation of particles smaller than 1.0 micron at pressures above 1 atm. Therefore, coagulation of submicron aerosols should be slowed appreciably at elevated pressures. Millikan² experimentally determined that A is about 0.9 for typical smokes in air at ordinary pressures and temperatures. Since ℓ is 10^{-5} cm at these conditions, the product, $A\ell = 9 \times 10^{-6}$ cm, was used to calculate the coagulation constant for particles of different

²Phys. Rev. 22, 1, 1923.

sizes at 1 atm pressure. For k at 10 atm pressure, the product $AQ = 9 \times 10^{-7}$ cm was used. The uncorrected k was assumed to be 10^{-9} cm³/sec (Table 2).

Table 2
CALCULATED COAGULATION CONSTANT AT 1 AND 10 ATM FOR PARTICLES
OF VARIOUS SIZES

Particle Radius, microns	Coagulation Constant	
	1 atm	10 atm
0.01	10.0×10^{-9}	1.9×10^{-9}
0.02	5.5×10^{-9}	1.45×10^{-9}
0.05	2.8×10^{-9}	1.18×10^{-9}
0.1	1.9×10^{-9}	1.09×10^{-9}
0.2	1.45×10^{-9}	1.04×10^{-9}
0.4	1.22×10^{-9}	1.02×10^{-9}
1.0	1.09×10^{-9}	1.01×10^{-9}

Numerous complicating factors such as heterogeneity, agglomeration, particle charge, and radiation make a strict theoretical analysis difficult if not impossible. However, we can assume that coagulation is favored at high temperatures and low pressures. The increased coagulation rate at high temperatures may be advanced by agitation due to thermal convection. Therefore, the only conclusion that can be drawn is that the pressure of the containment vessel has little effect on coagulation of submicron particles.

D. Summary and Conclusions

The ultimate objective of this phase of the program was to develop a scavenging system capable of adsorbing radioactive aerosols under environmental conditions of the containment vessel and also if possible in the free atmosphere. The presence of water vapor in the containment vessel after the

water loop ruptures was one of the factors directing the study toward a scavenging system capable of reacting with water vapor. The present requirements are fulfilled by the silicon tetrafluoride system.

Since silicon tetrafluoride gas is highly toxic, its use should be approached with caution. Possibly it can be replaced by silicon tetrachloride (boiling point 58°C) without change in scavenging efficiency. The latter is less dangerous to handle. Another disadvantage of using silicon tetrafluoride is the possibility of shock shattering the compressed gas container. The system as developed at present should be used inside the containment vessel only. Further research should be performed to adapt the system for more extensive application.

The amount of silicon tetrafluoride which can be used in the containment vessel with a safety factor of 4 is approximately 0.2% by volume. This means that for 1000 m^3 of the containment vessel, approximately 10 kg of silicon tetrafluoride is required. Because silicon tetrafluoride is corrosive, 20 kg of sodium hydroxide or 15 kg of calcium hydroxide should be added to neutralize hydrofluoric acid. This can be easily incorporated in the spray which is used with this scavenging system.

Some large field experiments should be designed to determine the optimum methods of operation under simulated conditions.

The price of silicon tetrafluoride gas F.O.B. New Jersey is \$45 for 10 kg (three size 2 cylinders each containing 3.4 kg). The working surfaces of the valves, regulators, etc. should be coated with corrosion-resistant nickel, and the gaskets should be made of Teflon.

IV. PHASE III - STUDY OF SCAVENGING, FLOCCULATION, AND SETTLING OF RADIOACTIVE PARTICULATE MATTER IN THE LIQUID PHASE

A system was sought for scavenging radioactive fission and corrosion products of a nuclear reactor in ocean waters. The research was directed toward developing a system in the shortest possible time. The ultimate objective was to develop an economical system capable not only of adsorbing radioactive cations and anions but also of coagulation with radioactive colloids and particles.

The scavenging system dispersed in the contaminated area should be capable of adsorbing radioactive species in the shortest possible contact time. This adsorption is the first phase of the scavenging process. The system should also form large particles which settle rapidly or at a controllable rate. This is the second phase of the scavenging process. The dispersed radioactive products adsorbed on the scavenger are subject to diffusion and sedimentation in the ocean or harbor areas, where they will not be confined and their movement cannot be controlled.

The research program consisted of the following studies:

- A. Scavenging
 - B. Sedimentation
 - C. Dissolution of crystals
 - D. Disintegration of pellets
 - E. Field test program.
- A. Scavenging

The fission products accumulated in the fuel elements in the reactor of the nuclear-powered ship will consist mainly of the following radioisotopes: barium-140, cerium-144, cesium-137, lanthanum-140, niobium-95, promethium-147, praseodymium-143, ruthenium-103 and -106, samarium-151, strontium-89 and -90.

yttrium-91, and zirconium-95. The predominant corrosion products will be chromium-51, cobalt-60, iron-55 and -59, manganese-56, and tantalum-182. In addition to the isotopes listed, scavenging of hafnium-181 was also studied.

The scavenging systems studied were: potassium permanganate-ferrous sulfate; potassium permanganate-potassium oxalatoferrate(II); potassium permanganate-barium chloride-ferrous sulfate; potassium chromate-ferrous sulfate; potassium chromate-barium chloride-ferrous sulfate; sodium aluminate; tribasic potassium phosphate; sodium pyrophosphate-barium chloride; barium, calcium, magnesium, strontium, and zinc carbonate; and processed sodium-substituted bark. The most effective scavengers were the permanganate-ferrous salt systems.

The scavenging studied are discussed comprehensively in Summary Report No. 6, Scientific Report No. 10, and in our paper entitle "Scavenging Radionuclides in Substitute Ocean Water," published in Industrial and Engineering Chemistry, volume 52, page 429, 1960. Further studies with modified permanganate-ferrous salt systems are described below.

The radionuclides were purchased from Oak Ridge National Laboratory in the form of chlorides in hydrochloric acid solution, except for zirconium-95-niobium-95, which was an oxalate complex in oxalic acid solution. The radionuclides were scavenged in tall, 1000-ml beakers without spouts, equipped with magnetic stirrers. A solution of radionuclide was added to 500 ml of the substitute ocean water (ASTM D1141-52) and the pH was adjusted 8.2 with sodium hydroxide. The ocean water was obtained from Wrightsville Beach, North Carolina, through the courtesy of the Nalco Chemical Company, Chicago. An additional 250 ml of ocean water with adjusted pH was added, the solution stirred, and samples withdrawn. The concentration was determined by a suitable emission counter (gamma or beta), depending on the radionuclide. Then a scavenging agent with a

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predetermined quantity of sodium hydroxide to maintain constant pH was added to the solution and the suspension was stirred for 1 min. Samples were withdrawn after settling times of 2.5, 5, and 24 hr, specific radioactivity was determined, and the percentage of radioactive material removed was calculated.

The change in radionuclide concentration was determined as the number of counts per minute per milliliter with the following instruments: a gamma, well-type, sodium iodide, thallium-activated crystal, Baird-Atomic scintillation detector, model 810A, and a beta, well-type, crystal, Baird-Atomic scintillation detector, model 810A, both connected to two Tri-Carb liquid scintillation spectrometer, glow-tube scalers, model 314, with a printout system. Proportional beta counting equipment consisted of a Packard Instrument Company Flo-window counter, model 210, with a model 220 proportional counting amplifier, a Baird-Atomic regulated high-voltage power supply, model 319, and a model 131A glow-tube scaler. The length of counting was varied according to the concentration and type of radiation to maintain accuracy in the net counting rate at the 95% confidence level. Only changes in gross gamma and beta radioactivity were determined. The counting equipment was of a standard type.

The oxalatoferrate(II) salts were prepared as follows. Potassium hydroxide was neutralized with oxalic acid. An excess of oxalic acid was added to maintain a slightly acidic solution. Potassium oxalate and oxalic acid can also be used. The solution was heated and ferrous oxalate was added until no more ferrous oxalate dissolved. A yellow-reddish solution was obtained, which was filtered in an inert atmosphere while hot. On cooling in the absence of oxygen, golden yellow crystals were obtained. Oxalatoferrate(III) salts form green crystals which are stable in air. In solutions exposed to light, the tri-valent iron oxidizes the oxalic acid, thus reducing itself to the bivalent state and forming a mixture of iron II and III complexes.

The efficiency of removal of various radionuclides from substitute ocean water is given in Tables 3 and 4. Three parameters were investigated: concentration of the scavenging agent, pH range of the dispersion, and settling time. The scavenging systems used were potassium permanganate-ferrous sulfate (Table 3) and potassium permanganate-potassium oxalatoferrate(II) (Table 4). The concentration is given for potassium permanganate only. The reducing agents were added at concentrations which reduced the permanganate; no excess was used.

The potassium permanganate-potassium oxalatoferrate(II) system removed strontium more effectively than the other systems tested. The presence of the oxalate anion enhanced scavenging by forming insoluble strontium oxalate. The system has potential for field application. Possibly other multicomponent systems can be designed. For example, additives such as orthosilicates and phosphates can be incorporated in the system to enhance removal of specific radionuclides.

The possibility of replacing the pellets or crystals of the potassium permanganate-ferrous salt system by a slurry was considered. A slurry could be easily stored aboard the ship and the delivery system would be much simpler. In addition to these advantages, different additives could be incorporated in a slurry. It is well known that both the permanganate and the ferrous salt are not stable in solution. Sodium hydroxide, sodium orthosilicate, sodium orthophosphate, and bentonite were tried unsuccessfully in attempts to form a stable slurry. Some suspensions lasted up to 3 weeks. More work of a fundamental nature is needed to resolve the possibility of slurry formation with permanganates.

Table 3

REMOVAL OF RADIOACTIVITY
BY THE POTASSIUM PERMANGANATE-FERROUS SULFATE SYSTEM

Radio-nuclide	Order of Addition	KMnO ₄ ppm	pH		Removal, %		
			Initial	Final	2.5 hr.	5 hr	22-24 hr
Cr ⁵¹	KMnO ₄ FeSO ₄	10	8.3	7.6	13.74	10.01	9.31
		50	8.3	8.0	41.94	43.80	40.10
		100	8.3	8.8	30.60	30.45	25.46
		10	7.3	7.0	49.48	54.55	57.07
		10	10.0	9.7	89.73	92.63	92.03
		10	8.4	8.3	61.43	62.24	63.39
		50	8.4	8.2	99.05	99.29	99.38
		100	8.4	8.0	31.08	31.93	26.79
		100	8.3	8.5	96.31	97.15	97.11
	FeSO ₄ KMnO ₄	10	7.0	7.0	96.85	94.21	98.90
		10	10.0	9.7	93.54	97.78	96.39
		10	8.3	8.0	90.64	90.81	88.56
		50	8.3	8.1	96.34	97.20	97.74
		100	8.3	8.8	98.55	98.92	98.61
		10	7.0	7.1	88.49	87.09	87.72
		10	10.0	9.7	93.99	96.10	95.63
Fe ^{55,59}	KMnO ₄ FeSO ₄	10	7.0	7.2	85.0	89.2	94.2
			8.4	7.8	94.2	98.5	98.4
			10.0	9.8	98.7	99.4	99.5
	FeSO ₄ KMnO ₄	50	8.4	7.1	93.7	95.3	97.6
		100	8.4	6.9	94.8	95.7	98.3
Co ⁶⁰	KMnO ₄ FeSO ₄	10	7.0	6.9	0.1	1.3	
			8.2	8.1	22.7	26.2	34.9
			10.0	9.8	99.8	99.8	99.9
	FeSO ₄ KMnO ₄	50	8.2	8.2	60.0	60.7	63.8
		100	8.2	8.2	81.6	82.6	83.4
Hf ¹⁸¹	KMnO ₄ FeSO ₄	10	7.0	6.5	94.9	95.2	95.5
			8.2	7.5	97.2	97.5	97.7
			10.0	9.6	96.7	99.5	97.2
	FeSO ₄ KMnO ₄	50	8.2	7.3	98.8	99.3	98.7
		100	8.2	8.2	98.7	99.4	98.8
Ta ¹⁸²	KMnO ₄ FeSO ₄	10	7.0	6.9	88.5	90.9	97.0
			8.3	8.2	91.1	96.9	97.6
			10.0	9.7	97.4	98.2	98.4
	FeSO ₄ KMnO ₄	50	8.3	8.0	97.9	99.3	99.1
		100	8.3	8.3	99.1	99.7	99.8

Table 4

REMOVAL OF RADIOACTIVITY
BY THE POTASSIUM PERMANGANATE-OXALATOFERRATE(II) SYSTEM

Radio-nuclide	Order of Addition	KMnO ₄ , ppm	pH		Removal, %		
			Initial	Final	2.5 hr	5 hr	22-24 hr
Cr ⁵¹	KMnO ₄ K ₂ [Fe(C ₂ O ₄) ₂]	10	8.4	8.4	65.15	65.64	65.72
		50	8.4	8.4	96.34	97.57	99.34
		100	8.4	8.1	67.60	66.48	61.40
		100	8.3	8.2	78.97	78.58	72.22
		10	6.9	6.7	55.77	56.26	55.36
		10	10.0	9.5	94.95	94.00	91.17
	K ₂ [Fe(C ₂ O ₄) ₂] KMnO ₄	10	8.3	8.0	74.34	55.31	31.53
		50	8.3	8.0	85.76	78.73	66.49
		100	8.3	8.3	96.74	96.59	94.58
		10	6.9	6.8	93.16	90.13	79.94
		10	10.0	9.4	90.02	87.73	77.66
Co ⁶⁰	KMnO ₄ K ₂ [Fe(C ₂ O ₄) ₂]	10	8.2	7.2	32.23	30.06	33.98
		50	8.3	8.4	90.02	90.37	90.92
		100	8.2	8.0	86.49	86.29	87.16
		10	6.8	7.0	28.97	29.32	31.64
		10	10.0	9.7	99.23	99.66	99.54
Sr ⁸⁹	KMnO ₄ K ₂ [Fe(C ₂ O ₄) ₂]	10	8.2	7.6	4.23		10.31
		50	8.2	7.9	24.20		26.53
		100	8.2	7.9	47.17		51.44
		10	7.0	6.8	8.13		7.94
		10	9.8	9.4	6.84		6.56
	KMnO K ₂ [Fe(C ₂ O ₄) ₂] 1/2K ₂ C ₂ O ₄	10	8.0	7.8	2.97	5.34	
		50	8.0	8.8	38.25	33.97	86.51
		100	8.0	8.2	64.03	67.20	69.24
		10	6.9	6.9	7.95	12.49	13.06
		10	9.9	9.7	6.83	2.82	2.44
Zr ⁹⁵ Nb ⁹⁵	KMnO ₄ K ₂ [Fe(C ₂ O ₄) ₂]	10	8.5	7.4	89.62		96.67
		50	8.5	6.0	94.13		99.01
		100	8.5	5.9	89.49		95.11

Because of lack of data on solubilities, a preliminary study was undertaken. The solubility of potassium permanganate is low, 2.83 and 6.38 g/100 ml of water at 0 and 20°C, respectively. Sodium permanganate was considered for the preparation of slurries because of its high solubility in water. A literature search on the solubility and density of sodium permanganate gave either incomplete³ or indefinite values. Therefore solutions of sodium permanganate (Carus Chemical Company, LaSalle, Illinois) were prepared. Density was determined with a pycnometer, and concentration was determined by titration with sodium oxalate. Saturated solutions were aged in darkness for 1 day to attain equilibrium. All solutions were filtered through glass wool. The results are given in Table 5 and Fig. 7.

Table 5

DENSITY AND CONCENTRATION OF SODIUM PERMANGANATE-WATER SOLUTIONS
AT 26-28°C

Density, g/cc	Sodium Permanganate, % by weight	
	Technical Grade	Reagent Grade
1.027	4.49	
1.073	11.28	
1.121	17.27	14.38
1.244	32.52	
1.368	44.43	37.73
1.377		39.18
1.478	53.81	45.98
1.497		47.78
1.508		48.23
1.564		52.25
1.573		52.40
1.60	63.32	53.92
1.628		56.29
1.676		57.17
1.677		58.70
1.70	70.57	59.80
1.701		59.22
1.80	76.47	59.73

³White and Miller, J. Am. Chem. Soc. 75, 3282-3, 1953.

FIG. 7. DENSITY VERSUS CONCENTRATION OF SODIUM PERMANGANATE SOLUTIONS

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B. Sedimentation

As already stated, any scavenging system to be applicable for field application should adsorb the radioactive fission and corrosion products, whether ionic, colloidal, or finely divided, in the shortest possible time. In addition, the scavenging agent should form particles of such a size that they will be transported to the bottom of the ocean by sedimentation under turbulent conditions. This rapid separation from the dispersion will leave the water practically free from radioactivity. The highly radioactive solids will not settle in one place because the high turbulence and rapid currents usually present in oceans will disperse them. Therefore it is unlikely that the radioactive materials will adversely affect marine life.

Sedimentation of scavenging flocs formed in natural ocean water (NOW), natural harbor water (NHW), and substitute ocean water (SOW) was studied. A 150-cm-tall, 23-cm-diameter column was used, with two Baird-Atomic model 812 scintillation probes connected to two glow-tube scalers of the model 314 Packard Tri-Carb spectrometer and printout system. The positions of the probes were varied. Zirconium-95-niobium-95 was used as the tracer; it was adsorbed by scavenging flocs formed during a 1-min stirring period. The hydrosol was allowed to settle, and the sedimentation velocity profile or Stokes size distribution was calculated from results printed at preset times. The interpretation of the results was based on the assumption that the activity is proportional to the mass, which is true as long as precipitate is formed simultaneously in the whole volume of water.

The parameters investigated were: the scavenging system -- either potassium permanganate-ferrous sulfate or potassium permanganate-potassium oxalatoferate(II), flocculating additives, and settling velocity profile

versus depth. The experiments were performed with 50 ppm of potassium permanganate and corresponding amounts of ferrous sulfate or potassium oxalate-ferrate(II). This concentration was found to be optimum (Report No. 10). The scavenging precipitate at this concentration is polydispersed to such an extent that the sedimentation is of the desired autocatalytic character. Approximately 50 flocculating additives were screened through preliminary sedimentation trials in a 1-liter graduate, and three were selected for further study. The results of the experiments are presented in Table 6 and 7 and Fig. 8 and 9.

The removal of radioactivity was practically identical in the three types of water used, i.e., substitute ocean water, natural ocean water, and natural harbor water. The analysis of the first two waters is given in Table 8 and 9. The harbor water (New York) was not analyzed. It contained an inorganic salt content of roughly one-third, and organic matter was present in large quantities in the form of fine suspensions.

Sedimentation was similar in substitute and natural ocean water for scavenging agent without and with Floc 111 additive (Fig. 8). Sedimentation was retarded, however, in harbor water due to the presence of dispersed organic materials. Removal of approximately 95% radioactivity by sedimentation to a depth of 1 m was achieved in natural ocean water in 4 min and natural harbor water in 11 min. The other flocculating agents were not as effective as Floc 111 (Fig. 9). Since sedimentation was improved considerably by the use of Floc 111, it should be incorporated in the present scavenging system.

Table 6

SETTLING VELOCITY DISTRIBUTIONS OF POTASSIUM PERMANGANATE-FERROUS SALT SYSTEMS CONTAINING ADDITIVES

Settling Velocity, cm/min	Settling, % Depth, cm															
	20	100	20	100	20	100	20	100	20	100	20	100	20	100	20	100
0-2	4.3	0.5	8.0	1.7	1.0	0.4	2.0	1.4	0.9	0.2	3.0	0.2	0.9	1.2	1.0	1.4
2-4	29.7	2.5	42.0	2.7	1.0	0.8	6.2	0.4	0.4	0.1	0.5	0.1	3.1	1.8	1.0	1.6
4-6	44.0	73.0	33.0	29.6	5.5	1.0	18.8	1.7	0.6	0.1	0.5	0.1	16.0	1.0	1.8	0.1
6-8	9.0	23.0	6.5	56.0	14.5	1.1	28.0	5.5	0.7	0.1	1.0	0.4	27.0	1.2	5.0	1.2
8-10	3.5	1.0	1.5	10.0	18.0	2.9	14.5	27.0	0.9	0.2	1.0	0.4	21.0	2.8	8.2	2.0
10-12	1.5		0.2		14.0	17.8	6.5	28.0	1.0	0.2	2.0	0.4	10.0	10.0	9.0	3.2
12-14	1.0		0.2		10.0	56.0	3.0	3.0	1.1	0.1	2.0	0.2	6.0	32.0	7.5	6.5
14-16	0.5		0.2		8.0	10.0	2.0	2.0	1.4	0.1	2.0	0.4	3.0	13.0	6.5	13.0
16-18	0.1		0.1		5.0	6.5	2.0	1.0	2.0	0.1	2.0	0.7	1.5	7.0	5.0	19.0
18-20	0.2		0.1		3.0	3.5	1.0	1.0	2.0	0.2	2.0	0.9	1.5	4.0	5.0	24.0
20-22	0.1		0.1		3.0		1.0	0.5	2.0	0.4	2.0	1.0	0.5	3.0	4.0	6.0
22-24	0.1		0.1		2.0		1.0	0.4	3.0	2.4	2.0	1.2	0.5	2.0	4.0	3.0
24-26	0.2		0.1		1.5		0.5	0.1	3.0	3.0	2.0	2.0	0.5	3.0	3.0	2.0
26-28	0.1		0.2		1.0		0.5	0.4	3.0	5.0	2.0	3.0	0.5	5.0	3.0	1.0
28-30	0.1		0.2		1.0		0.5	0.6	6.0	6.0	2.0	4.0	0.5	3.0	2.0	1.0
30-35	0.1		0.2		1.0		1.0	1.0	8.0	22.0	6.0	21.0	0.5	5.0	6.0	1.0
35-40	0.1		0.3		1.0		0.5	1.0	10.0	32.0	8.0	22.0	0.5	2.0	6.0	2.0
40-45	1.0		1.0		3.0		1.0	1.0	10.0	22.0	14.0	16.0	1.0	2.0	7.0	4.0
45-50	2.0		1.0		3.0		1.0	2.0	11.0	15.8	14.0	11.0	1.0	1.0	6.5	2.0
50-60	2.1		2.0		3.0		5.0	3.0	33.0		31.0	10.0	2.0		6.5	3.5
<60	0.3		3.0		0.5		4.0	19.0				5.0	2.5		2.0	2.5
	Expt. I		Expt. II		Expt. III		Expt. IV		Expt. V		Expt. VI		Expt. VII		Expt. VIII	
Removal of Radioactivity:			99.1%		99.3%		99.3%		99.3%		99.3%		99.2%			
Type of Water:	SOW		NOW		SOW		SOW		SOW		NOW		NHW		SOW	
pH:	8.3-8.2		8.1-7.4		8.2-8.1		8.3-7.5		8.3-8.1		8.1-8.0		8.1-8.0		8.1-8.2	
Additive (10 ppm):	None		None		Aerofloc 550		BP 296 BT		Floc III		Floc III		Floc III		Floc III	
Ferrous Salt:	Sulfate		Sulfate		Sulfate		Sulfate		Sulfate		Sulfate		Sulfate		Oxalato-	
(with 50 ppm permanganate)															ferrate(II)	

Table 7

TIME FOR REMOVAL OF RADIOACTIVITY TO A DEPTH OF 1 M BY SCAVENGING
WITH POTASSIUM PERMANGANATE-FERROUS SALT SYSTEMS CONTAINING ADDITIVES

Time, min	Removal, %							
	I	II	III	IV	V	VI	VII	VIII
1.5				19.0		5.0		2.5
1.8				22.0		15.0		6.0
2.1				24.0	5.8	26.0	1.0	8.0
2.3				25.0	27.8	42.0	3.0	12.0
2.7				26.0	59.8	64.0	5.0	14.0
3.1				27.0	81.8	85.0	10.0	15.0
3.4				27.6	87.8	89.0	13.0	16.0
3.7				28.0	92.8	92.0	18.0	17.0
4.0				28.1	95.8	94.0	21.0	19.0
4.3				28.5	98.2	95.2	23.0	22.0
4.8				29.0	98.6	96.2	26.0	28.0
5.3			3.5	30.0		97.1	30.0	52.0
5.9			10.0	31.0		97.8	37.0	71.0
6.7			20.0	33.0		98.2	50.0	84.0
7.7			76.0	36.0		98.4	82.0	90.5
9.1			93.8	64.0		98.8	92.0	93.7
11.1	1.0	10.0	96.7	91.0		99.2	94.8	95.7
14.3	24.0	66.0	97.8	96.5		99.6	96.0	96.9
20.0	97.0	95.6	98.8	98.2			97.0	97.0
33.3	99.5	98.3	99.6	98.6			98.8	98.6
100.0								

Table 8

CHEMICAL COMPOSITION OF SUBSTITUTE OCEAN WATER

Chemical Compound	Concentration, g/m ³
NaCl	24,533.8
MgCl ₂ ·6H ₂ O	11,109.9
Na ₂ SO ₄	4,093.9
CaCl ₂	1,158.7
KCl	6.95
NaHCO ₃	2.01
KBr	1.01
SrCl ₂ ·6H ₂ O	0.43
H ₃ BO ₃	0.27
NaF	0.03
Ba(NO ₃) ₂	0.0994
Mn(NO ₃) ₂ ·6H ₂ O	0.0546
Cu(NO ₃) ₂ ·3H ₂ O	0.0396
Zn(NO ₃) ₂ ·6H ₂ O	0.0151
Pb(NO ₃) ₂	0.0066
AgNO ₃	0.0005

FIG. 8. TIME FOR REMOVAL OF RADIOACTIVITY TO A DEPTH OF 1 M BY SCAVENGING WITH POTASSIUM PERMANGANATE-FERROUS SULFATE SYSTEMS CONTAINING FLOC 111

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FIG. 9. TIME FOR REMOVAL OF RADIOACTIVITY TO A DEPTH OF 1 M BY SCAVENGING WITH POTASSIUM PERMANGANATE-FERROUS SALT SYSTEMS CONTAINING VARIOUS ADDITIVES

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Table 9

ANALYSIS OF NATURAL OCEAN WATER (pH 8.0)

Component	Concentration, g/m ³
Total dissolved solids	36,850
Suspended solids	10
Total hardness (as CaCO ₃)	7,800
Calcium hardness (as CaCO ₃)	1,500
Magnesium hardness (as CaCO ₃)	6,300
Phenolphthalein alkali (as CaCO ₃)	22
Total alkali (as CaCO ₃)	121
Chloride (as NaCl)	33,500
Sulfate (as Na ₂ SO ₄)	3,510
Silica (as SiO ₂)	1
Total iron (as Fe)	0.8

C. Dissolution of Crystals

This part of the program was directed to the possible use of chemical compounds in crystalline form for scavenging purposes. An important aspect of the problem of scavenging radioactive waste from ocean water by adding chemicals is the behavior of the chemicals themselves in the water. In order to determine the most effective means of adding scavenging chemicals, e.g., as crystals or pellets of various sizes, it is necessary to understand their behavior as they fall through the water.

Results are given in detail in Scientific Report No. 10 and can be summarized as follows. Previously known correlations between evaporation of droplets in air and dissolution of large spheres of solute in a stream of water were shown to agree with experimental data on rates of dissolution of small crystals of a number of substances falling through sea water. Convective dissolution due to differences in solution density was found to be unimportant for this experimental situation. This confirmation of the applicability of these correlations permits calculation of the dissolving rate of a sinking crystal of

any substance by knowing only its solubility, density, molecular diffusivity, and weight, provided that the substance does not form a precipitate in the solute.

D. Disintegration of Pellets

A scavenging system in the form of pellets was developed for field application. This work is discussed in Report No. 10. The description and results of the field application are described in Section IV-E below.

The cost of the materials used in the scavenging system is given in Table 10.

Table 10

COST OF MATERIALS USED IN THE PELLETED SCAVENGING SYSTEM

<u>Material</u>	<u>Supplier</u>	<u>Cost</u>
Potassium permanganate	Carus Chemical Co. LaSalle, Ill.	\$0.25/lb
Ferrous sulfate heptahydrate	American Cyanamid Co. 30 Rockefeller Plaza New York 20, N. Y.	\$33.00/ton
Ferrous sulfate monohydrate		Approx. \$80.00/ton
Floc 111	Hodag Chemical Corp. 7247 N. Central Park Chicago 45, Ill.	\$0.80/lb
Citric acid		\$0.30/lb
Sodium carbonate, anhydrous		\$0.04/lb
Kelacid	Kelco Co. 20 N. Wacker Drive Chicago 6, Ill.	\$1.80/lb
Keltose		\$1.00/lb
Organic binder		Approx. \$0.10/lb

The cost of one metric ton of the scavenging agent, including pelleting (\$100-200/ton), is given in Table 11.

Table 11
COST OF ONE METRIC TON OF THE PELLETED SCAVENGING SYSTEM

Material	Cost		
220 kg Potassium permanganate	\$130	\$130	\$130
640 kg Ferrous sulfate	115	115	115
20 kg Floc III	44	44	44
40 kg Citric acid	26	26	26
40 kg Sodium carbonate	2	2	2
35 kg Kelacid			140
35 kg Keltose		79	
35 kg Binder	8		
	<u>\$325</u>	<u>\$396</u>	<u>\$457</u>

The advantage of using Kelacid as a binder is that the pellets form a very fine floc. Under field conditions an organic binder may be satisfactory. The influence of Kelacid on sedimentation will be completely masked by the presence of the flocculating agent Floc III. Fabrication of pellets with standard equipment does not introduce any problems, although several companies contacted did not favor the manufacture of a limited quantity of scavenging agent.

E. Field Test Program

A limited number of field tests were performed in Lake Calumet and Lake Michigan. On September 24, 1959, a field test was conducted in Lake Calumet to determine whether a potassium permanganate-ferrous chloride system produces flocs under field conditions and, if possible, to measure the settling rate of the flocs.

The flocculent chemicals were prepared in solution form with distilled water. The permanganate solution contained approximately 30 g of potassium permanganate and 1.0 g of sodium hydroxide per liter of solution. The ferrous

chloride solution contained approximately 90 g/liter. The solutions were applied to the surface of the lake by spraying the two solutions simultaneously from two hand-operated pumps. Approximately 2 liters of each solution was sprayed over a circular area about 1.5 m in diameter. Surface samples were taken by dipping glass jars into the lake.

No noticeable flocs formed until 30 sec after the chemicals were pumped into the lake. This may be because of inadequate mixing of the chemicals on the lake surface. The covered area was not of a uniform color; some parts contained more permanganate than others. After 30 sec flocs appeared on the surface and were visible in the lake as well as in the deep sample. The flocs persisted on the surface for 2 min, after which it was impossible to find them. Several samples were taken below the surface in an attempt to find the flocs, but these attempts were only partially successful. Even in apparently calm water there were sufficient currents to disperse the flocculated area. The disappearance of the flocs was due to settling and dispersion. Which of the mechanisms was predominant was not conclusively determined.

Pellets of potassium permanganate and ferrous chloride were tested in Lake Michigan. The experiment was designed to study the interaction between the two types of pellets under actual field conditions and to determine the amount of precipitate formed. It was visualized that the test volume in the lake would be only about 2 m wide and about 10 m deep, so the amount of pellets dropped corresponded to 50 ppm of potassium permanganate and 154 ppm of ferrous chloride. The sodium salt of fluorescein was used to mark the experimental area, and 2 kg of sodium hydroxide pellets was added to counteract the change in pH caused by the chemical reaction. Different depths were sampled with a device consisting of a brass cylinder lowered

by a chain and two rubber balls attached to another chain to act as valves on both ends of the cylinder. The sampling volumes varied from 250 to 300 ml.

The experiment showed definite precipitation of iron oxide-manganese oxide hydrates near the surface of the water only at the spots where the reactants were mixed. Due to diffusion, turbulence, and currents, the test volume kept moving about and spreading. When the fluorescein dye, sodium hydroxide, potassium permanganate, and ferrous chloride were all placed in the water one after the other, they did not disintegrate in the same column but were scattered around. Small blotches of concentrated spots were formed while other areas remained fairly free from the chemicals. When the pellets were mixed together and dropped at the same time, there was still difficulty in following the concentrated part of the test volume.

To minimize some of these difficulties, experiments were performed in shallow water. Visual observation showed formation of large amounts of precipitate. Sampling below a depth of 1 m was again difficult because of currents shifting the experimental volume. Free permanganate or ferrous ions were practically not found in the treated volume. The concentration of solids corresponded to 50 ppm of potassium permanganate at the beginning of the experiments, but it was 100 times lower after 5 min.

It was concluded that this scavenging system is suitable for field application. There is enough time after delivery of the system to the contaminated area to adsorb the radioactive fission and corrosion products and form large flocs. The resulting solids, which are then dispersed by turbulent diffusion and transported by currents, settle and are deposited on the bottom of the ocean. The settling rates of flocs formed in Lake Michigan in calm water are given in Table 12. The precipitates were flaky and about 1-4 mm thick.

Table 12

SETTLING TIME OF HYDRATED FERRIC OXIDE
PRECIPITATED IN LAKE MICHIGAN IN CALM WATER

Depth, m	Settling Time			
	Depth, mm			
	1-2	2-3	3-4	6-8
1	3 min 42 sec		2 min 11 sec	1 min 10 sec
2	5 min 30 sec	2 min 39 sec	3 min 59 sec	2 min 35 sec
3	7 min 20 sec	5 min 40 sec	6 min 4 sec	4 min 15 sec
4				
5		10 min 7 sec	10 min 25 sec	7 min 9 sec
6		12 min 57 sec		8 min 29 sec
7		15 min 38 sec		9 min 55 sec
8				
9		20 min 15 sec	17 min 23 sec	12 min 53 sec
10		23 min 11 sec	19 min 15 sec	14 min 21 sec

In summary, the present studies indicated that the scavenging system composed of pellets of anhydrous or monohydrate ferrous sulfate or ferrous chloride dihydrate and potassium permanganate is suitable for field application. Ferric hydroxide-manganese dioxide hydrate is precipitated in the course of the chemical reaction during the scavenging operation. Since the precipitate is practically insoluble in water, it will ultimately be deposited on the bottom of the ocean and will not endanger marine life. An excess of one of the components of scavenging system causes the formation of the insoluble solid of ferric hydroxide as a hydrolysis product or the manganese dioxide hydrate forms as a result of oxidation of organic matter present in the ocean and especially in harbor water. These solids will be precipitated in rather finely divided form and may remain in the mixed layer of the ocean for a long period of time. Their concentration will be high at the point of dispersion but will diminish rapidly due to turbulence. Biological life will undoubtedly influence the deposition of this precipitate.

V. PHASE IV - ESTIMATION OF RADIOACTIVE WASTE CONCENTRATION IN THE WAKE OF THE NUCLEAR-POWERED SHIP

The dilution and dissipation of materials which are either soluble in water or are in a finely divided state when released into the ocean by a ship was studied. The completed investigation is present in Scientific Report No. 4, entitled "Radioactive Waste Concentrations in the Wake of a Ship." The results of the work are also applicable to the intentional disposal of materials in open waters.

Theoretical work and the results of model experiments showed that leakage directed to an outlet in front of the propeller will be immediately diluted to a great extent by the action of the propeller. The resulting concentration depends on the distance the ship travels while releasing a quantity of waste. If 1 c of waste is released over a distance of 1 mile, the maximum concentration at any point in the wake is 6.6×10^{-7} $\mu\text{c/ml}$. Further dilution by mixing due to natural turbulence of the surface layer of the water may reduce the concentration by a factor of 10 in 1 day or of 100 in 3 months. However, the extent of this natural mixing is known to vary greatly according to local conditions and cannot be relied upon unless extensive studies have been made in the region where the ship is to operate. Conversely, such studies may demonstrate that certain regions exist where the mixing rate is highly favorable for waste disposal.

VI. CONCLUSIONS AND RECOMMENDATIONS

Scavenging systems capable of adsorbing radioactive fission and corrosion products from liquid and gaseous dispersions were developed. The original concept involving the formation of a finely divided scavenging agent in the environment of the radioactive aerosol or hydrosol was found to be applicable to the general problem of scavenging.

Most of the radioactive fission and corrosion products in liquid dispersions was scavenged by a potassium permanganate-ferrous sulfate scavenging system. A precipitate of manganese dioxide hydrate-ferric hydroxide formed in the water dispersion containing cations, colloids, and particles. Cesium, sodium, strontium, and barium could not be scavenged by the simple process of adsorption. The idea of formation of solid solutions capable of incorporating cations in the crystalline lattice of the precipitate led to the development of a potassium permanganate-potassium oxalatoferate(II) system. This system improved the scavenging of metals of the alkaline earth group considerably. The potassium permanganate-ferrous salt systems were tested in substitute, natural, and harbor waters, and no significant difference in scavenging of radionuclides was found in the three media.

The desired scavenging system should not only adsorb radioactive cations, colloids, and particles, but should also separate from the water phase. Separation due to sedimentation is believed to be the most advantageous for field application. The highly radioactive solids first will be dispersed by turbulent diffusion, then carried away from the point of release, and finally deposited on the ocean floor. Studies of sedimentation in the presence of additives showed that it is possible to form a fast-settling floc of manganese dioxide hydrate-ferric hydroxide precipitate. The additives improved sedimentation

to such an extent that under quiescent conditions practically all the solids settled below 1 m in less than 5 min. This settling velocity is applicable to field conditions and will cause flocs of scavenging agent to be deposited ultimately on the bottom of the ocean. Much more extensive research is needed in the field of sedimentation, deposition, and transport of materials in ocean waters.

Scavenging of radioactive cesium was improved by the use of ion exchange materials. Because of the high cost of the usual ion exchange resins, the possibility of using inexpensive processed bark ion exchangers is economically attractive. The main criterion for this scavenger is the rate at which it can exchange ions; for field application the rate must be as high as possible.

Radioactive gaseous dispersions were most effectively scavenged by using hydrolysis products of silicon tetrafluoride in the presence of an excess of water vapor or water spray. Because of the highly corrosive nature of hydrogen fluoride, however, this system should be used only in the presence of a neutralizing agent.

It is possible to design a scavenging operation for application inside the containment vessel or in connection with the ventilating system. Silicon tetrafluoride could be ejected into the affected volume, mixed with water spray containing neutralizing agent, and then circulated. The particle size of the hydrolysis products and the water spray are such that practically all the particles can be removed by conventional equipment. The radioactive aerosols are thus removed from the atmosphere and immobilized in the liquid by scavenging all of them with a mixture of droplets. Large-scale tests are needed to establish basic principles for operation aboard nuclear-powered ships.

Although the two major phases of the research program were directed toward the scavenging of radioactive particles released into the ocean or the atmosphere, the possibility of preventing the formation of radioactive aerosols from fuel elements should also be investigated in order to avoid or at least minimize the hazards connected with accidental release. In the case under consideration it can be assumed that in 13 min the fuel elements reach temperatures of 2550°F, at which cladding of the fuel elements will fail. A research program should be directed toward developing a mixture of chemicals which upon adherence to fuel elements will react with radioactive cesium, barium, strontium, etc., thus immobilizing these elements in the reactor. An excess of chemical reactants must be used. The mixture should form a viscous fluid at high temperatures to enable a long contact time of bubbles of metal vapors with the liquid flux. The use of foams seems applicable here. The technical difficulties involved are tremendous. However, the development of a prevention system justifies an extensive research program.

In general, the information in this report can be utilized in formulating design criteria for incorporating scavenging systems aboard passenger-cargo nuclear-powered ships. The proposed systems can scavenge and confine radioactive hydrosols and aerosols and thus play an important role in the safety of the ships. It is recommended that the present systems be improved through further research.