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STATUS REPORT ON WASTE DISPOSAL IN NATURAL SALT FORMATIONS: III

F. M. Empson, Editor

OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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Errata

STATUS REPORT ON WASTE DISPOSAL

IN NATURAL SALT FORMATIONS: III

Substitute the attached corrected pages 14, 28, 42, 45, and 48 for the present ones.

Page 74 in Eq. (2) change lower limit of integration from $a/\sqrt{ak}$ to $a/\sqrt{kt}$

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STATUS REPORT ON WASTE DISPOSAL IN NATURAL SALT FORMATIONS: III

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SUMMARY

The continuing study of waste disposal into natural salt formations is designed to define and solve the problems involved in the storage of liquid and solid wastes in natural salt deposits. The program has included experimental studies in the laboratory and in the mine of the Carey Salt Company at Hutchinson, Kansas. The variables studied include the reactions of salt-saturated Purex wastes, both cold and in the presence of gamma radiation fields, the stability of cavities excavated in the salt structure when influenced by heat, and thermal studies aimed at determining the rate of heat flow both experimentally and through computations.

Heat transfer rates measured in the field experiments agree very well with computations on which the experiments were based. It was found that the production of nitrosyl chloride (NOCl), hydrogen chloride, and nitrogen oxides produced by chemical action in salt-saturated, acid Purex waste could be controlled by maintaining acid strength below 4.0 M and/or temperature below 60° C. There was no significant difference in gaseous reaction products from experiments in pure salt and in a part of the structure containing significant quantities of anhydrite.

Laboratory studies of radiolytic gas production in the salt-acid Purex waste system indicate that the gas production can be controlled by suspending the waste solutions as surface films on crushed salt or by fixing them as absorbed water in the lattices of certain minerals.

Further analytical studies of the thermal problems associated with disposal of wastes in salt show that a cooling period of at least 3 years before ultimate disposal is desirable because of the rapid decrease of maximum temperatures with increased cooling times out to about 1000 days.

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I. INTRODUCTION

The major problems of radioactive liquid waste disposal in natural salt formations have been defined as those related to the combined effects of pressure, temperature, radiation, and chemical interaction on the structural properties of salt and the control of reactive and radioactive gases which may emanate from the wastes. Preliminary studies have indicated that the effects of radiation on the structural properties of rock salt are minor (1)(2)(3). Theoretical studies have shown that the temperature of radioactive liquid wastes stored in salt cavities can be kept within acceptable limits by controlling the age of the wastes and the size of the cavity (4)(5)(6)(7). Laboratory studies of the chemical compatibility of Purex waste and salt have demonstrated that the principal reaction gases, Cl_2 and NOCl, can be eliminated, at temperatures below the boiling point, by limiting the acidity to 4.0 M HNO_3 (8)(9).

These studies have been described in two previous status reports: ORNL-2560 and ORNL-2700. The first status report defined the waste disposal problem in a nuclear power economy, discussed the availability and nature of salt deposits in the United States, and outlined the anticipated problems of disposal into natural salt formations. The second report presented the results of laboratory experiments and theoretical calculations of the mechanism and rate of heat dissipation through rock salt. In addition, the design of proposed field-scale experiments was presented.

This report, Status Report on Waste Disposal in Natural Salt Formations: III, presents the results of work on all phases of the problem

from February 1959 to the present time. Included are model experiments with salt blocks in the laboratory, small field tests in the Carey mine, two large experiments in the Carey mine, and studies of the interaction of Purex waste with salt. The model experiments were used in developing the design of field experiments, while the small-scale field experiments were operated to determine the effects of impurities in the salt and to "shake-down" the equipment and operating procedures for the larger tests.

One large-scale test (using 3000 gal) was carried out with 7 M acid Purex waste and the other with neutralized Purex waste. The acid waste experiment was terminated (power turned off) after 197 days. Evidences of corrosion of the cover had been observed, and it was necessary to avoid possible failure of the cover while the experiment was in operation. The system was allowed to cool to ambient, following which the waste was removed and inspection of the cavity begun. The experiment with neutralized waste was terminated after 392 days and is now in the process of cooling. Examination of these two cavities will yield information on the effects of Purex waste solutions on salt-shale-anhydrite structures.

As the large-scale waste experiments have approached termination, several smaller experiments of a different nature have been initiated. Such experiments are needed to obtain information on (1) cavity alterations in full and partially-filled cylindrical cavities completely surrounded by salt, (2) the effect of decreasing thermal conductivity of salt with increasing temperature on the temperature rise predicted by summing the contributions from a number of cavities, (3) the effect of shale and anhydrite bands on the temperature rise in long cylindrical cavities, (4) the possibility of storing liquid waste in thin layers in sealed rooms, and (5) the

effect of elevation of the temperature of an entire room on the structural stability of the room.

In addition to field experiments, laboratory work on the means of inhibiting or eliminating gas production, theoretical studies of the effect of heat on the structural stability of salt cavities, and theoretical studies of temperature rises to be expected in an actual mine-disposal operation will continue.

II. MODEL EXPERIMENTS

To evaluate the design of several components of the field experiment, small-scale models were operated in salt blocks taken from the Carey mine and the Grand Saline salt mine in Texas.

The first model (10), a 7.5 x 7.5 x 9.5-in.-deep cavity, one-twelfth scale, in a 2-ft cube of salt from Grand Saline, was filled with 6 liters of salt-saturated, synthetic, neutralized Purex waste and covered with a flat sheet of 1/2-in.-thick Teflon. Thermocouples in the liquid and the salt, a quartz-sheathed electric resistance heater, and a reflux condenser were placed in the block.

The test was run for two months, during which time a "bridge" of pure recrystallized salt 2 in. thick completely covered the waste liquid. Below the liquid level there was no apparent chemical interaction other than the deposition of a hydrous iron oxide film approximately 1/16 in. thick. Above the liquid interface there was dissolution of the side walls, and later recrystallization above the liquid surface. The temperature in the liquid phase was not uniform, and the quartz-sheathed electrode was partially dissolved by the neutralized waste.

This test showed that while Purex wastes could be contained in salt, a different cover design (to prevent condensate dissolution of the salt) and more uniform heating of the waste were required.

Electrolytic heating seemed to be the most promising method for providing uniform heating, and, consequently, several electrode materials were

tested. Stainless steel electrodes corroded badly, even in neutralized waste; and tantalum developed an insulating film. Graphite electrodes, however, were unaffected by either neutralized or acid Purex waste, and, therefore, graphite was selected as the electrode material.

A second model test in a 6-1/2-in. cavity was operated to test the effectiveness of electrolytic heating of neutralized waste. This test proved that it is possible to achieve essentially uniform heating of the precipitate with a total of eight graphite electrodes.

In model experiments, using graphite electrodes to heat acid Purex waste, it was found that there was essentially no waste temperature variation in any given horizontal plane; but there was some temperature variation with depth. This was found to be due to the electrical resistance of the electrodes as shown below.

Equation 1, which takes into account the electrode resistance, is used to calculate the vertical power distribution. The equation is exact except that the effective resistance per unit depth of solution, R_S, is not constant as a function of depth when there is a temperature variation with depth:

$$I_E(X) = I_0 \cosh \sqrt{\frac{R_E}{R_S}}\ X - \frac{E_0}{\sqrt{R_E R_S}} \sinh \sqrt{\frac{R_E}{R_S}}\ X . \qquad (1)$$

where

X = depth in solution,

$I_E(X)$ = current in the electrodes at point X,

I_0 = input current,

E_0 = input voltage (at zero solution depth),

R_E = effective resistance per unit length of the electrode installation,

R_S = effective resistance per unit depth of solution (assumed constant with depth).

Figure 1 shows the calculated power distribution in acid waste in a 10-in.-sq salt cavity and the temperature distribution obtained with this power input. The power and temperature distributions for the 7-1/2-ft-sq acid field cavity are also shown. The effect of the electrode resistance is negligible in the neutralized solution.

There will also be some power dissipation in the electrodes above the acid solution and above the neutralized precipitation. For the cases of interest, the distribution of the total power input is indicated in Table 1.

Another series of experiments, using acid Purex wastes in a 24-in.-cube salt block at one-tenth scale, was made to determine gas production, to find a satisfactory gas seal, and to evaluate the performance of a corrosion-resistant cover.

The experiment, assembled and ready for operation, is shown in Fig. 2. The graphite electrodes, by which electrolytic heating is accomplished, may be seen on opposite sides of the cover. Teflon-sheathed thermocouples are inserted in the salt block. The glass reflux condenser discharges the uncondensed gases to polyethylene bags. The titanium cover rests in the annular groove around the cavity. The cavity is sealed from the atmosphere by filling the groove with saturated brine solution. During operation the block and cover are insulated with approximately 2 in. of glass fiber mat.

The experiment was operated for 20 days, during which time the temperature of the solution in the cavity was between 80 and 85° C for four

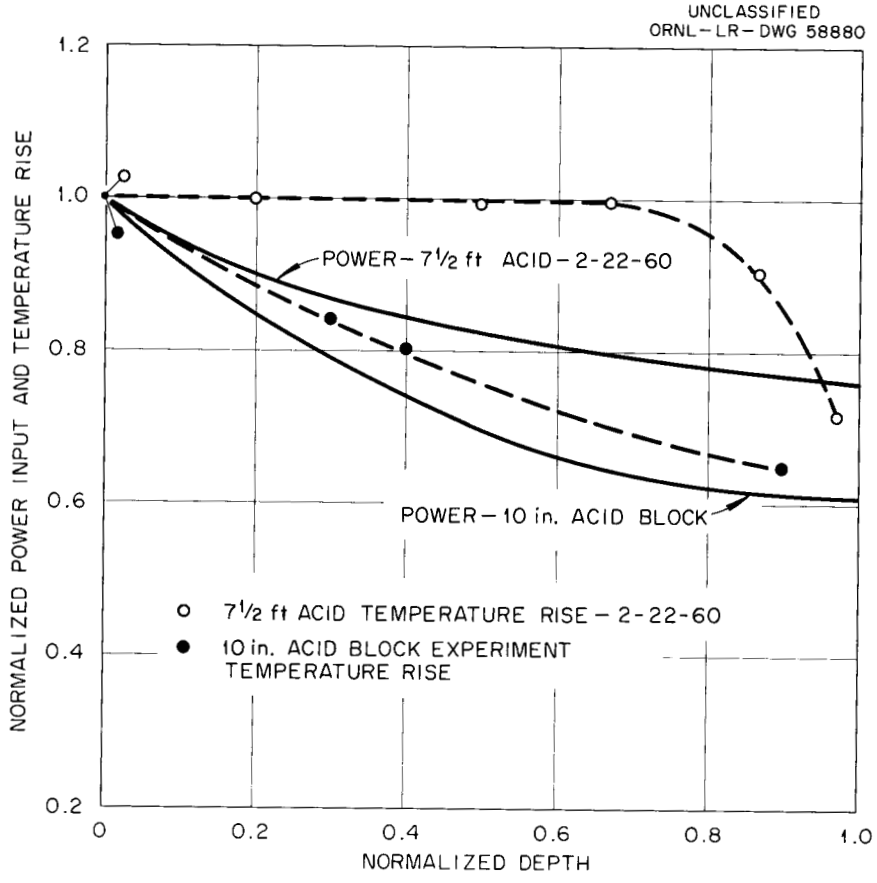

Fig. 1. Variation of Power Input and Temperature Rise with Depth.

Table 1. Effective Power Input - Model and Field Experiments

Experiment	Solution Input (Electrolytic Plus Electrode) (w)	Electrodes Above Solution (w)	Total (w)
10-in. acid	245	46 (air)	291
7-1/2-ft acid	5,340	460 (air)	5,800
7-1/2-ft neutral	5,375	175 (supernatant)	
		150 (air)	5,700

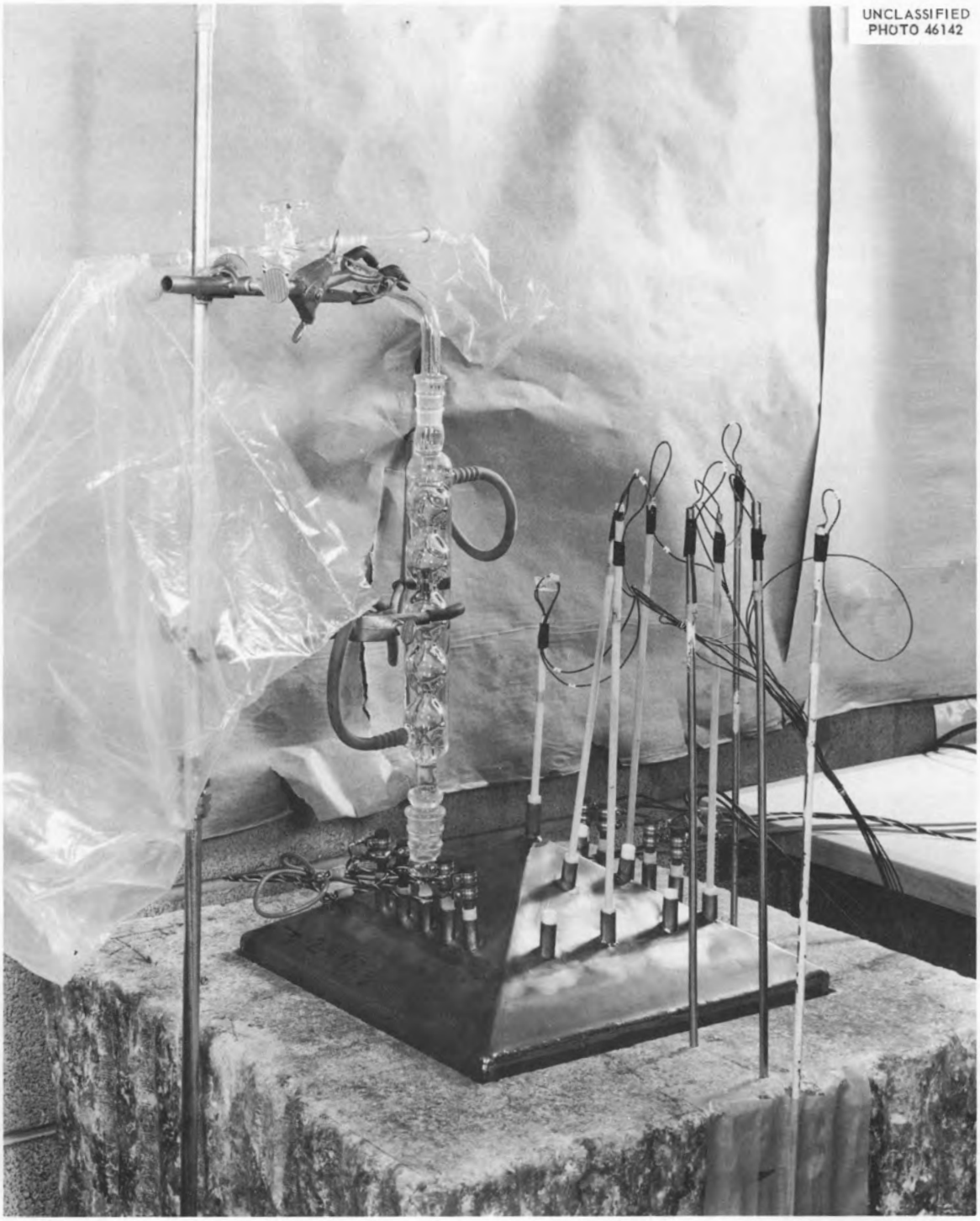

Fig. 2. Experimental Setup – Model No. 3.

days. Off-gases collected during early operation at lower temperatures were largely air and nitrogen oxides (less than 1%). During operation in the range of 80 to 85° C the nitrogen oxide concentration increased to 12%. Saturated brine solution in the annular groove proved to be unsatisfactory as a gas-tight seal because of its evaporation and the need for frequent replenishment. When brine was added, the trench filled with recrystallized salt. When water was added, the trench enlarged by dissolution of the salt.

When the experiment was terminated and the cover removed, a large amount of recrystallized sodium chloride was found in the bottom of the cavity. When the crystals were removed, it was found that the dimensions of the lower part of the cavity were unchanged. However, deep undercutting had occurred at the liquid level, becoming less pronounced with increasing depth and diminishing to no undercut at approximate mid-depth.

The experiment was repeated for 16 days to evaluate G-E silicone fluid [SR-96 (100)] as a gas seal. The silicone did not evaporate but migrated over the surface of the salt into the cavity. When the experiment was concluded and the equipment disassembled, the cavity contained a large amount of silicone polymer.

Dissolution of the upper part of the cavity wall had continued, with recrystallization of the material in the bottom of the cavity. Figure 3 shows one-half of the block after the rerun experiment. The sharp undercut at the liquid level had progressed about 1 1/2 in. The inner apron of the metal cover effectively protected the extreme upper edge of the cavity in the vapor space. These tests showed that acid wastes could be electrolytically heated and that a titanium cover was corrosion-resistant to the waste vapors.

Fig. 3. Cross Section of Block – Model No. 3.

A final one-tenth-scale model experiment in a 24-in. salt block showed that a dry gas seal of sand, silica gel, and charcoal was satisfactory.

III. FIELD EXPERIMENTS

Small-Scale

Purpose and Operation.-- The small-scale tests were designed to determine the effect of impurities in the salt on temperature rise in the wastes and on gaseous reaction products, and to "shakedown" the equipment and operating procedures for the large tests. Two experiments with acid waste were operated, one in pure salt and the second in salt containing about 25% anhydrite and traces of shale. A single experiment with neutralized waste was operated in pure salt. The cavities were 18 x 18 x 25 in. deep, and were one-fifth the scale of the large experiments. Metal covers fabricated of Haynes Alloy No. 25 were used to cover the pits. Figure 4 shows the arrangement of the two experiments in pure salt. Heat was applied by impressing an a-c voltage across graphite electrodes inserted through the cover into the synthetic waste solution.

Heat Transfer.-- Power was supplied in such a manner as to simulate the energy output of a 10,000 Mwd/ton burnup, 33 Mw/ton specific power, and 800 gal/ton waste. For the one-fifth-scale tests, power was supplied at an initial rate of 40 w/gal, which is equivalent to 50 days cooling, and was decreased daily in accordance with the decay curve for 50-day-cooled waste. The temperature reached, as well as the predicted temperatures in the neutralized waste in pure salt, are shown in Fig. 5A. The predicted temperatures are for a 2.2-ft-diam sphere with approximately the same surface area as the cube and the same power input per unit volume. The measured power

Fig. 4. One-Fifth-Scale Experiments in Salt.

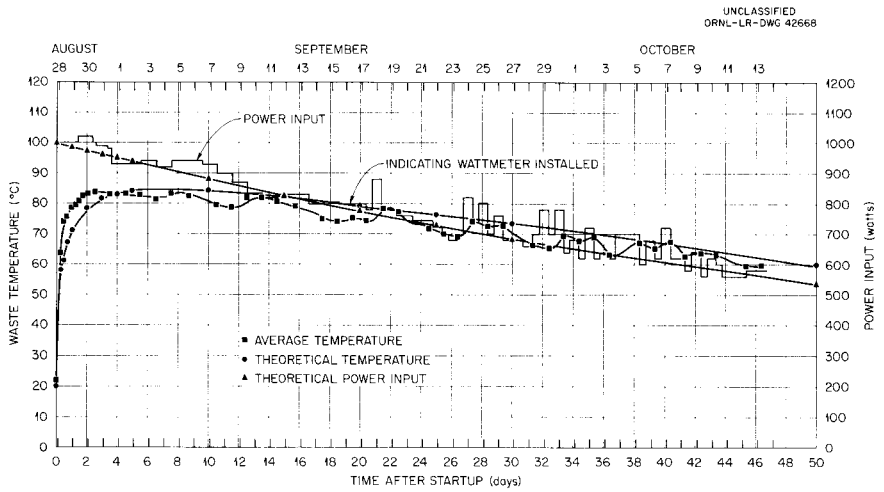

Fig. 5A. Synthetic Neutralized Purex Waste in 18-in. Cavity in 100% NaCl.

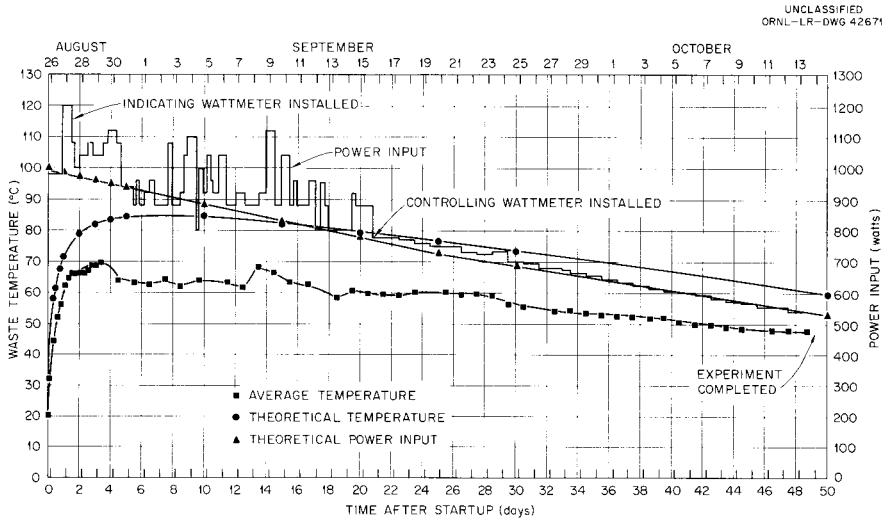

Fig. 5B. Synthetic Purex Waste in 18-in. Cavity in 100% NaCl.

input, as well as the design power input, are also shown in this figure. The power inputs do not coincide, because large fluctuations in line voltage made it impossible to set the correct power input.

Figure 5B shows the temperature of the acid waste in the cavity excavated in pure salt. The power input varied widely until a controlling wattmeter was installed, as the manual controls were not as sensitive as the variable transformer controls used for the neutralized pit. The maximum temperature reached was approximately 20° C below that predicted or 30% below the predicted temperature rise. Figure 5C shows that the maximum temperature of the acid pit in the floor of the mine was also about 20° C below the predicted maximum.

On the basis of these preliminary tests, it was concluded that the anhydrite in the floor of the mine had no major effect on temperature rise in the waste. Temperature rise in the neutralized waste pit was considerably higher than the acid-waste pit, probably due to the lack of convection currents in the precipitate phase of the neutralized waste.

Gas Production.-- The wastes used in the small field experiments were from the solutions prepared for the large field experiments. These solutions were prepared by an outside vendor, delivered to the experiment site in the Carey mine, and saturated with salt by agitation in the shipping container (polyethylene carboys for acid waste and steel drums for neutralized waste). The analyses of the synthetic Purex waste, both before and after the experiments, are given in Table 2. Note that a change in composition of the waste is produced by saturation with NaCl. The nitrate content is reduced without a change in volume, and the sodium ion concentration is approximately half of the chlorine concentration. This is believed to be due to the precipitation of $NaNO_3$ from the saturated solution.

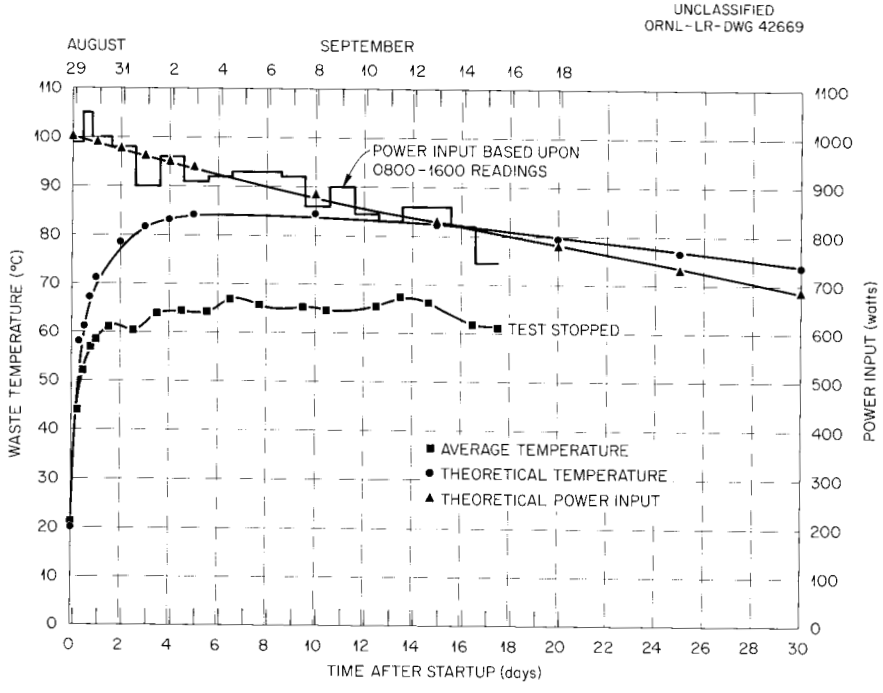

Fig. 5C. Synthetic Purex Waste in 18-in. Cavity in 75% NaCl, 25% $CaSO_4$.

Table 2. Field-Waste Solutions - One-Fifth-Scale Experiments

Sample	Cations (equivalents/liter)			Anions (equivalents/liter)			Total		Specific Gravity
	H^+	Na^+	Fe^{+++}	Cl^-	SO_4^{--}	NO_3^-	Cations	Anions	
Initial Composition									
Acid waste composite	7.21	0.25	1.40	0.01	1.55	7.31	8.86	8.87	
Neutralized waste (after saturation with salt)									
Pit 1	0.5 (OH^-)	7.69	0.93	3.05	1.02	4.37	8.62	8.94	1.3823
Acid waste (after saturation with salt)									
Pit 2	7.09	1.72	1.50	3.44	1.48	5.38	10.31	10.30	1.3251
Pit 3	7.22	1.74	1.50	3.55	1.53	5.42	10.46	10.50	1.3262
Final Composition									
Pit 2	5.99	2.08	1.53	3.74	1.42	4.45	9.60	9.61	
Pit 3	5.40	2.21	2.17	3.88	1.60	4.17	9.78	9.65	

The contact of synthetic Purex waste with NaCl establishes conditions for the aqua regia reaction (11). Nitrosyl chloride (NOCl) and other gases are produced, resulting in an off-gas which would be hazardous in the confined atmosphere of a mine. Neutralized Purex waste saturated with salt and heated above 80° C produces only water vapor. The gas problem in the disposal of neutralized waste in salt would, therefore, result only from water vapor and the radiolytic decomposition of water.

The experiments with acid waste produced substantial quantities of the end products of the aqua regia reaction. The gases were identified as nitrosyl chloride (NOCl), nitrous oxide (N_2O), chlorine, and carbon dioxide. Semiquantitative analyses of off-gas samples taken during the operation of small-scale field experiments are given in Tables 3 and 4. Analytical data are given only for the small field experiments with acid waste, since no gaseous reaction products were produced in the neutralized experiment.

Samples were collected in three ways: Samples of the gas in the vapor space were obtained by pulling 250 ml from the vapor space of the cavity into an evacuated gas-sample bottle after flushing the sample connection. The bottles were sealed by dipping the stopcock on each end in hot paraffin. To secure large quantities of the gases, freeze traps were used. A carbon dioxide-methanol (-78.5° C) trap was followed by a liquid-nitrogen (-195.8° C) trap. Samples were recovered from the freeze traps by allowing the condensed material to evaporate into the evacuated 250-ml gas-sample bottles. Composition of the samples represented an average composition of the gas evolved during the period of collection. All reactive components of the gas were condensed and/or frozen by the two cold traps.

Table 3. Off-Gas Composition, One-Fifth-Scale Experiment, Pit 2 Acid Waste in Pure Salt

Temperature Range (°C)	Sampling Method	Gas Concentration (vol %)			
		CO_2	NOCl	Cl_2	N_2O
20-60	Evacuated bottle			< 2	
	CO_2-methanol trap	1.6	60	2	0.8
	Liquid N_2 trap	2.5			0.6
60-70	Evacuated bottle	2.6	17.0	7.8	1.5
	CO_2-methanol trap	1.1	36.4		1.0
	Liquid N_2 trap	17.0		27.9	12.3
66-64	CO_2-methanol trap	0	76	4.8	0
	Liquid N_2 trap	~ 7	~ 18.5	~ 18	~ 2

Table 4. Off-Gas Composition, One-Fifth-Scale Experiment, Pit 3 Acid Waste in Salt and Anhydrite

Temperature Range (°C)	Sampling Method	Gas Concentration (vol %)			
		CO_2	NOCl	Cl_2	N_2O
55	Evacuated bottle	4.1	9.5		3.6
20-60	CO_2-methanol trap	40.0	43.7		7.5
20-60	Liquid N_2 trap	64.0			36.0
60-65	Evacuated bottle	25	19.6		6.9
	CO_2-methanol trap	5.8	90.6		1.0
	Liquid N_2 trap	51.0	> 2.0		14.5
65-68	Liquid N_2 trap	48.0	~ 7.0	29.8	3.4
68-75*	Evacuated bottle	3.1	13.9	13.9	1.5
	CO_2-methanol trap	1.9	65.8	11.6	> 0.6
	Liquid N_2 trap	6.7	< 2	~ 12.0	1.4
75-72*	CO_2-methanol trap	5.8	44.2	27.6	Tr
72-77*	CO_2-methanol trap	3.0	55.9	25.4	0.8
	Liquid N_2 trap	9.2	< 2		3.1

*These temperatures were reached after September 15, during intermittent periods of high-power operation, designed to test trench-seal materials.

The conclusions drawn from these experiments are: (1) significant quantities of NOCl are produced only after the solution temperature rises above 60° C; (2) the quantity of gas produced by conducting an experiment in mixed salt and anhydrite was not significantly greater than that produced in a pure salt environment; (3) the CO_2 produced at low temperatures in the third experiment was attributable to the interaction of waste and shale.

Large-Scale

Engineering Design.-- Facilities for the large-scale tests consist of two 7.5-ft square by 10-ft-deep cavities in the floor of the mine with a corrosion-resistant metal cover for each cavity, off-gas collection and scrubbing equipment, electrical equipment for application and control of heat to the solution, and instrumentation for the measurement of gas pressures and temperatures in the cavities and in the surrounding salt structure (Fig. 6). Cavity dimensions were selected so that the surface area, with the cavity filled to a 7.5-ft depth, will equal that of a 10-ft-diam sphere. Thus, thermal data from the theoretical heat calculations could be correlated with thermal data from the experiments.

The operating level of the Carey Salt Company's Hutchinson Mine is 640 ft below the surface, and is connected with the surface by a single shaft which restricts the maximum dimensions for any component to 5 ft by 6 ft. This was a severe limitation, particularly in design of the metal closures (off-gas covers) for the cavities. Large pieces of equipment were fabricated in sections for bolting together at the experiment site.

Off-Gas Containment.-- In practice, acid Purex waste solutions are safely contained in austenitic stainless steels. However, when this solution is saturated with NaCl, the resulting solution and its vapor have the

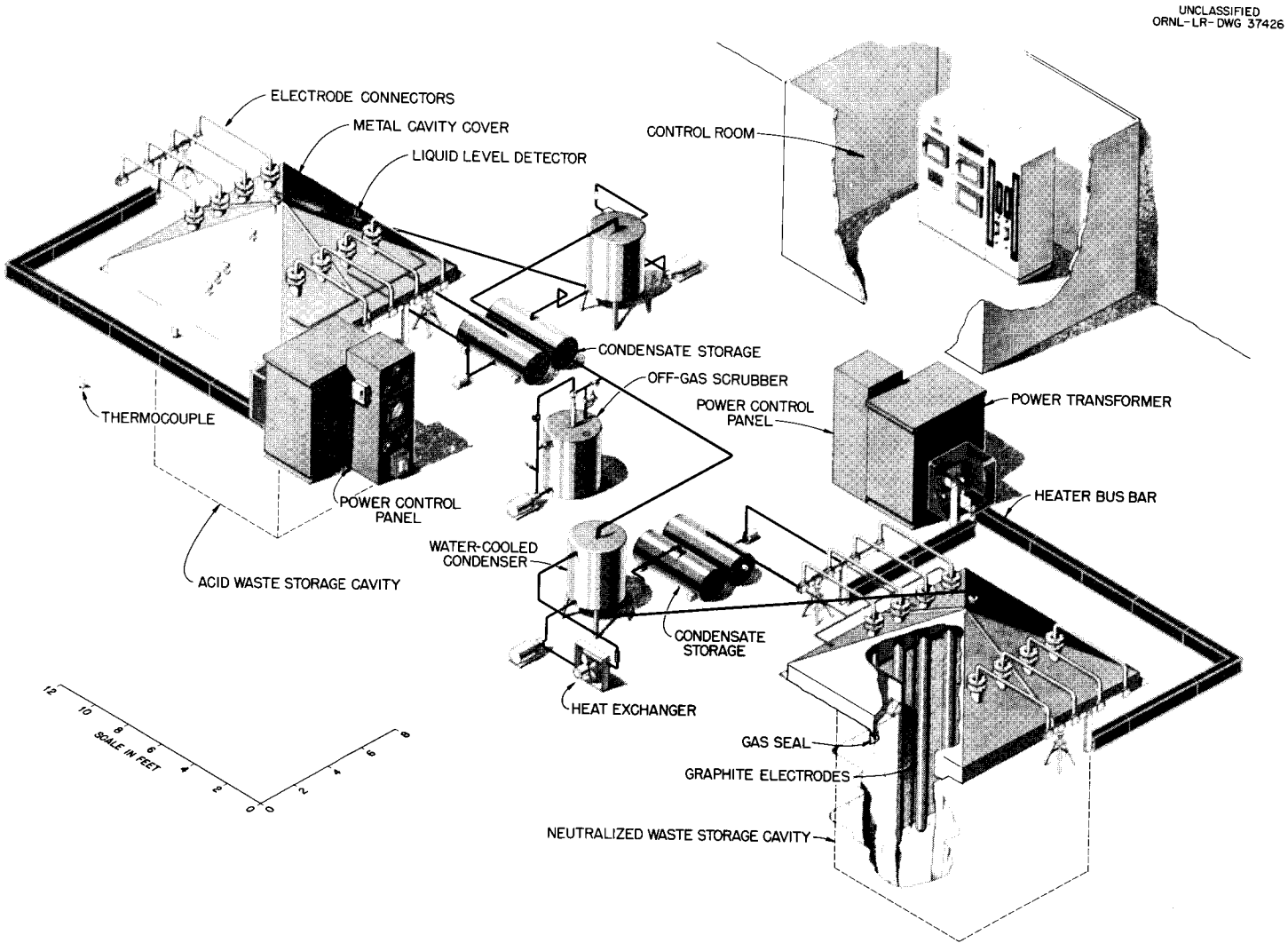

Fig. 6. AEC-ORNL Waste Disposal Field Test, Carey Salt Company — Hutchinson Mine.

characteristics of aqua regia and are extremely corrosive. The solution contains the same ions as aqua regia, and the vapor from the solution contains free chlorine, nitrogen dioxide, and nitrosyl chloride. Most base metals and several noble metals, i.e., gold and platinum, are dissolved by the mixture. Previous work at Battelle Memorial Institute (12), in connection with Zircex and Darex process development, had shown that titanium and Haynes Alloy No. 25 were resistant to nitric acid solutions containing high chloride concentrations under some conditions (The composition of Haynes Alloy No. 25 is 50% cobalt, 20% chromium, 15% tungsten, 10% nickel, 2% maximum iron, 15% manganese.).

An investigation was made of the corrosion resistance of titanium and Haynes 25, as well as a number of other alloy and nonmetallic materials in a vapor-liquid environment of salt-saturated waste solutions. Samples (1 in. x 3 in. coupons) were exposed to salt-saturated solutions of acid aluminum nitrate and acid Purex wastes and, in a number of cases, neutralized aluminum nitrate and Purex wastes. A complete list of the materials, exposure times, temperatures, and corrosion rates are listed in Table 5.

All the metallic materials listed show negligible corrosion in contact with salt-saturated neutralized solutions of Hope and Purex waste. However, all the samples exposed to salt-saturated acid Purex waste, with the exception of titanium and Haynes 25, either dissolved immediately or showed severe corrosion within 48 hr. Tantalum, not listed in Table 5, was tested and found to be corrosion-resistant to all the solutions, but the uncertainty of the fabrication properties and the high cost of tantalum precluded its use in this case. Further testing of welded specimens of titanium and Haynes 25 showed that both materials were subject to slightly increased corrosion rates in the welded areas.

Table 5. Corrosion Data in Salt-Saturated Simulated Waste

All samples partially immersed except as noted

Samples at 80° C (and higher) under refluxing conditions

Material	Corrosive Medium (salt-saturated)	Approximate Temperature (°C)	Exposure (days)	Corrosion Rate (in./year)	Remarks
410 SS	Hope	22	238		Failed
	Hope, neutralized	22	238	Negligible	
	Purex - 7 M HNO_3	22	238		Failed
	Purex, neutralized	22	238		
316 SS	Hope	22	238	Negligible	
	Hope, neutralized	22	238	Negligible	
	Purex - 7 M HNO_3	22	238		Failed
	Purex, neutralized	22	238	Negligible	
347 SS	Hope	22	238	0.0025	
	Hope, neutralized	22	238	Negligible	
	Purex - 7 M HNO_3	22	238		Failed
	Purex, neutralized	22	238	Negligible	
Inconel	Hope	22	238	0.013	
	Hope, neutralized	22	238	Negligible	
	Purex - 7 M HNO_3	22	238		Failed
	Purex, neutralized	22	238	Negligible	
INOR	Hope	22	238	0.008	
	Hope, neutralized	22	238	Negligible	
	Purex - 7 M HNO_3	22	238		Failed
	Purex, neutralized	22	238	Negligible	

Table 5. Corrosion Data in Salt-Saturated Simulated Waste (contd)

Material	Corrosive Medium (salt-saturated)	Approximate Temperature (°C)	Exposure (days)	Corrosion Rate (in./year)	Remarks
Hastelloy C	Purex - 7 M HNO_3	22	139	0.0004	
	Purex - 7 M HNO_3	80	19		Failed
Haynes 25	Purex - 7 M HNO_3	80	77	0.0007	Stamped sample
	Purex - 7 M HNO_3	80	34	0.00147	Sample cut from sched 40 pipe
	Purex - 7 M HNO_3	80	34	0.004	Sample from sched 40 pipe containing butt weld
	Purex, neutralized	80	77	Negligible	Stamped sample
Titanium	Purex - 7 M HNO_3	80	63	0.0008	
	Purex, neutralized	80	63	Negligible	
	Purex - 7 M HNO_3	22	127	Negligible	
Teflon	Purex - 7 M HNO_3	100	70		No change; slight weight gain
Polyvinyl chloride (unplasticized)	Vapor above Purex - 7 M HNO_3	80	24	Negligible	Approx. 1.4% weight gain without apparent swelling
Polyvinyl chloride	Purex - 7 M HNO_3	80	21	Negligible	Totally immersed in medium; 1% weight gain without apparent swelling
Graphite	Purex, neutralized	80	30		No corrosion; slight weight gain
	Purex - 7 M HNO_3	80	30		No change; no weight loss during use of graphite as electrode in heating experiments

Graphite and Teflon were not susceptible to corrosion by any of the salt-saturated waste solutions. Unplasticized polyvinyl chloride also demonstrated corrosion resistance but was subject to swelling and discoloration. Teflon, though corrosion-resistant, is of limited utility in this case because of the difficulty of fabrication and of its limited structural strength. Based on these studies, Haynes 25 was selected as the material for the off-gas covers with Teflon to be used for gaskets. For external vapor and condensate piping, unplasticized polyvinyl chloride was used together with a limited amount of stainless steel.

The cavity closures, or off-gas covers, are required to contain the corrosive and noxious gases released from the heated waste-salt mixture. The covers were gas tight and were sealed into the floor of the mine by a dry seal so as to give a completely closed cavity. The seal (Fig. 7) consisted of approximately 10 in. of dry masonry sand in which the flange of the off-gas cover rests. In the outer annulus, 2 in. of sand are replaced with 1 in. of activated carbon and 1 in. of silica gel covered by a layer of asbestos paper sealed to the metal cover and to the salt floor by several coats of an alkyd enamel (Glyptal 1201). The seals are essentially gas tight and, with the scrubbing system, prevent contamination of the mine air. No trouble was experienced with the seal except for a brief period when the jet exhauster-scrubber, because of a loose nozzle, failed to evacuate the vapor under the cover. Sufficient acidic condensate collected to fill the trench and caused the alkyd enamel to break down. Repair of the jet and removal of the condensate from the trench corrected the problem.

The covers are pyramidal in shape and are 10 1/2 ft on each edge and 4 ft high (Fig. 7). Penetrations of the cover include a nozzle used as an

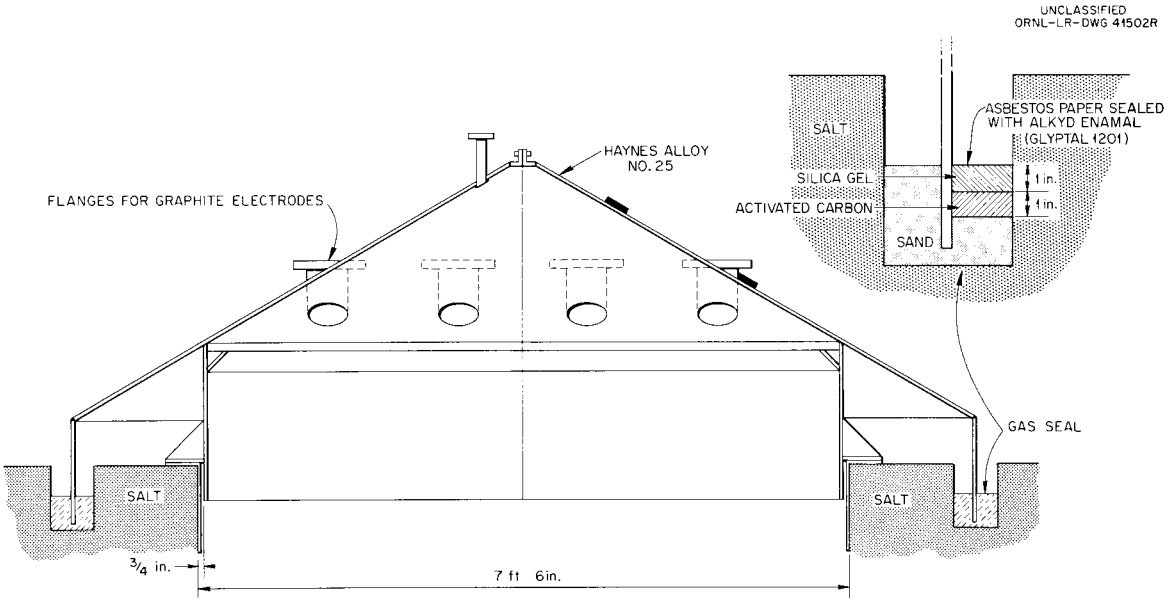

Fig. 7. Cavity Cover for Field Experiment.

off-gas outlet, a nozzle for a liquid-level probe assembly, eight nozzles for insertion of graphite heating electrodes, nozzles both for removal of condensate from the inner surface of the cover and for return of condensate to the experiment. There are also threaded openings for insertion of thermocouples and for attachment of pressure-sensing lines. The cover also includes a gutter on the inner surface for collection of condensate and an apron for protection of the cavity side wall.

Off-gas equipment, external to the cover, consists of a water-cooled condenser, followed by a recirculating caustic scrubber-exhauster. A stream of dilute caustic is pumped as the actuating fluid through a vacuum jet made of rigid polyvinyl chloride. This operation serves both to maintain a small negative pressure on the cavity and to scrub acidic vapors from the off-gas. The combined gas and liquid stream is discharged into a stainless steel drum, vented to the atmosphere through a small activated carbon bed. The recirculating water supply for the condenser is cooled by passing through an air-cooled heat exchanger.

Instrumentation.-- Instruments for the experiment include thermocouples, moisture probes, off-gas liquid level, and pressure measuring devices. All thermocouples (60 for each experiment) record on one 144-point Minneapolis-Honeywell Data Logger recorder (Fig. 8). The moisture probes (12 for each experiment) are designed to detect the presence of moisture in the salt structure adjacent to the experiments, but the permeability of the shale layers below the floor made them unusable. An alarm system is provided for the detection of high temperature, high off-gas pressure, and power failure. Visual and audible alarms are installed in the control room at the experiments and were telemetered to the surface in a cable with an

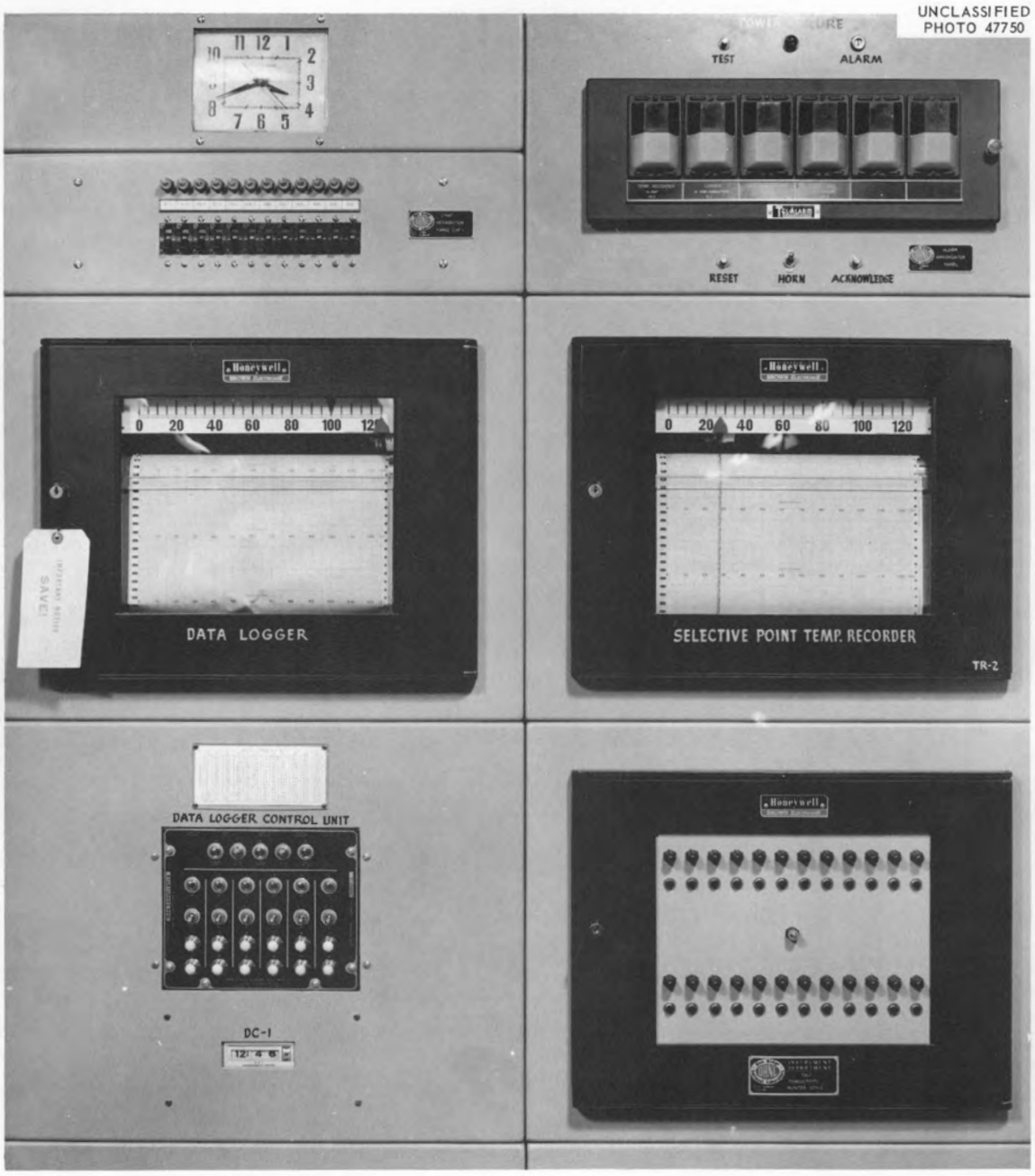

Fig. 8. Instrument Panel for Field Experiment.

intercommunication system. Failure of the cable to the surface early in the experiment made the alarm system inoperable except at the control room. The control panel for liquid-level measurement and off-gas pressure is shown in Fig. 9. A 12-point recorder is also included for recording temperatures needed infrequently or for repeating readings more frequently than they appear on the 144-point logger.

Other instrumentation for the off-gas system included a static pressure manometer on the annunciator panel. No measurable pressures have been observed. Small rotameters were installed on the off-gas line to give a qualitative indication of the off-gas flow.

Simulation of Fission Product Heating.-- In neutralized Purex waste there is a precipitate which, after heating, occupies approximately 30% of the solution volume. In the actual case, the major portion (90-99%) of Sr^{90} and the rare earths are in the precipitate, producing a concentrated heat source in the bottom of the container. Acid Purex waste has no precipitate, and the fission products are uniformly distributed. Thus, to simulate fission product heating in the field experiments, it was necessary to produce uniform heating in the acid waste and concentrated heating in the sludge of the neutralized waste.

Uniform heating may be achieved electrolytically by means of flat-plate electrodes on opposite walls of the salt cavity. An a-c voltage applied between the electrodes results in a heat-producing current flow through the solution. Due to corrosion problems with acid waste and poor thermal convection in neutralized sludge, resistance heating is not feasible.

While plate electrodes would be ideal, practical considerations favored the use of four vertical graphite electrodes per electrical pole; that is,

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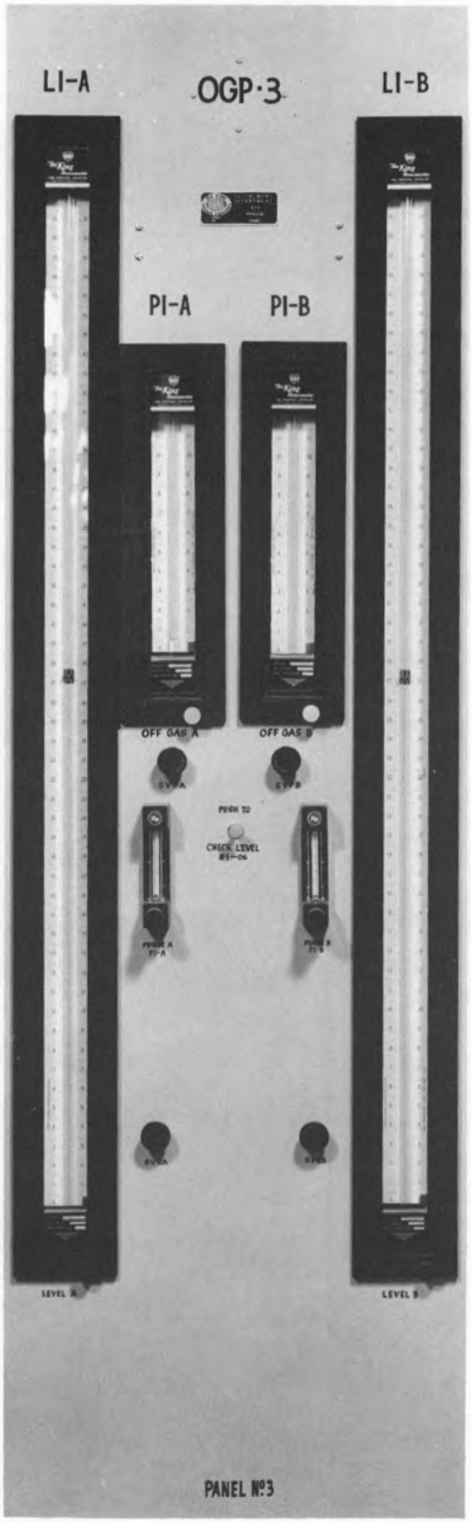

Fig. 9. Control Panel for Liquid-Level Measurement and Off-Gas Pressure in Field Experiments.

eight per cavity. Electrodes for the 7-1/2-ft-square cavities were 4 in. in diameter and 12.3 ft long.

Graphite electrodes were used in an identical manner for neutralized and acid wastes, with the exception that electrodes in the neutralized waste were insulated over the upper three-fourths of their length (in the solution) to provide concentrated heating of the settled sludge. Insulation was provided by means of a Teflon tape wrap.

The neutralized waste has a resistivity greater than acid waste by a factor of 2 to 3, and the resistivities change by a factor of 2 to 3 over the range of temperatures experienced (13). In addition, the comparative effective resistance of the neutralized waste cavity is about twice as large as indicated by these resistivity figures, since the electrodes are exposed only to the sludge. To supply the necessary power input with an adequate safety margin under all operating conditions, two identical power supply units with ratings of 3000 amp ac at output voltages from 5 to 20 v and 1500 amp from 10 to 40 v were obtained.

A preset power input to follow a particular fission product power decay scheme was maintained, in the face of solution resistance and line voltage changes, by means of a recording, controlling wattmeter feeding a saturable reactor in the power supply.

Current was conveyed from the supply to the electrodes by means of two 1/4 by 6 in. bus bars. At each electrode, connection was made by means of copper tubing inserted in an oversize hole in the electrode end. The hole was then filled with Cerrolow 117, a low melting alloy, which is liquid under operating conditions, assuring a low-resistance contact.

Site Preparation.-- On March 9, 1959, field work was initiated in the Carey mine to prepare the site for the field experiments. The area around each cavity was leveled to provide a uniform bearing surface for the off-gas covers. The room was whitewashed to provide better illumination, and all loose salt and rock was removed from the ceiling. Prior to excavating the two large cavities, core holes were drilled in the corners of each cavity. A plot of the structure from the recovered cores is shown in Fig. 10. After core drilling, the cavity excavation was started by means of drill holes spaced on 3-in. centers around the perimeter of the cavities. These holes were drilled to an 18-in. depth, and the material was then removed down to 12 in. with jack hammers. Figure 11 shows the first 12 in. of salt and anhydrite being removed from the No. 1 pit. After removing the upper layer, the holes were then drilled and the salt removed in 12-in. increments. This procedure was followed until the 10-ft depth was reached. At this point the walls were smoothed by means of special tools until the deviation from the required dimensions was less than 1/2 in. Table 6 compares the distribution of salt, anhydrite, and shale in the cavity walls as determined by chemical analysis and x-ray diffraction. The average salt concentration is 72% for Pit 1 and 78% for Pit 2. However, in vertical distribution, shale, salt, and anhydrite bands differ in continuity and thickness (Figs. 12 and 13). Selected samples of the material were examined by x-ray diffraction for quartz, vermiculite, illite, and kaolinite.

After the cavity had been excavated, the gas-seal trenches were cut. The side walls of the seal trenches were not smoothed, since irregularities were not critical.

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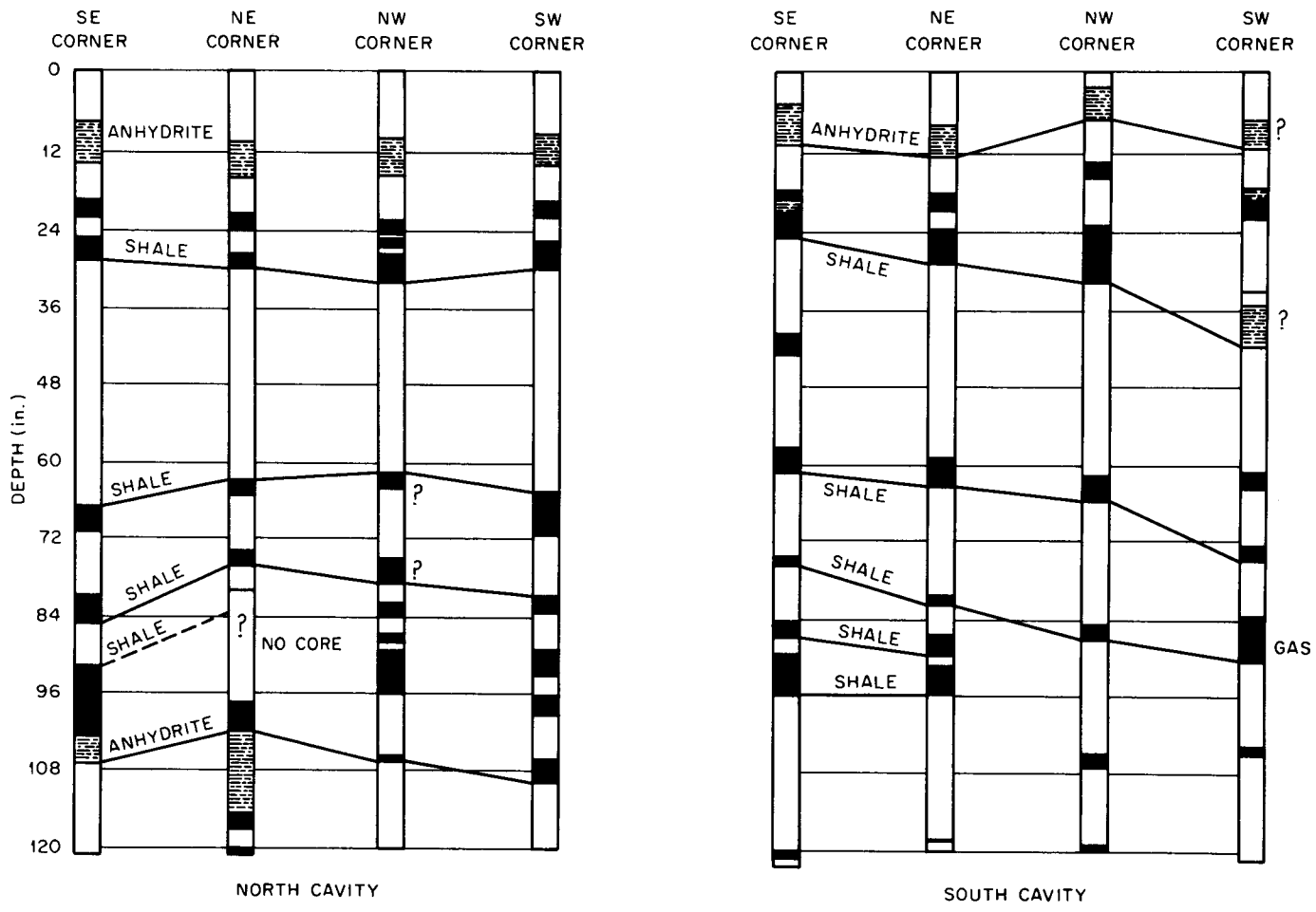

Fig. 10. Core Logs from Corners of Field Cavities Showing Anhydrite and Shale Bands Interstratified with Salt.

Fig. 11. Removal of First 12 in. of Salt and Anhydrite from the Field Cavity.

Table 6. Distribution of Anhydrite, Shale, and Salt with Depth in the Walls of the Field Cavities

Determined by chemical analysis and x-ray diffraction*

Sample Depth (in.)	Distribution (%)					
	Halite	Anhydrite	Quartz	Kaolinite	Illite	Vermiculite
			Pit 1 (South)			
7-10	25-50	25-50			Est < 10	
10-12	0-25	25-50				0-25
21-23	25-50	Est < 10	Est < 10		0-25	0-25
37-39	50-75	Est < 10	Est < 10	Est < 10	0-25	
51-53	75-100	Est < 10				
62-63	0-25		Est < 10	0-25	25-50	Est < 10
73-74	25-50	0-25	Est < 10	Est < 10	0-25	
84-87	0-25	25-50	Est < 10	Est < 10	0-25	
91-91.5	75-100			Est < 10		
104-106	75-100	Est < 10		Est < 10		
115.5-116	50-75	Est < 10	Est < 10		0-25	
			Pit 2 (North)			
9-13	25-50	25-50		Est < 10	0-25	0-25
21-23	25-50		Est < 10	0-25	0-25	
29-30	Est < 10	Est < 10	Est < 10	0-25	0-25	0-25
67-69	0-25		Est < 10	0-25	0-25	
83-84	25-50		Est < 10	0-25		
95-100	0-25		Est < 10	0-25	25-50	0-25
104-106	0-25	50-75				
118-120	75-100	Est < 10				

*X-ray analysis by T. Tamura.

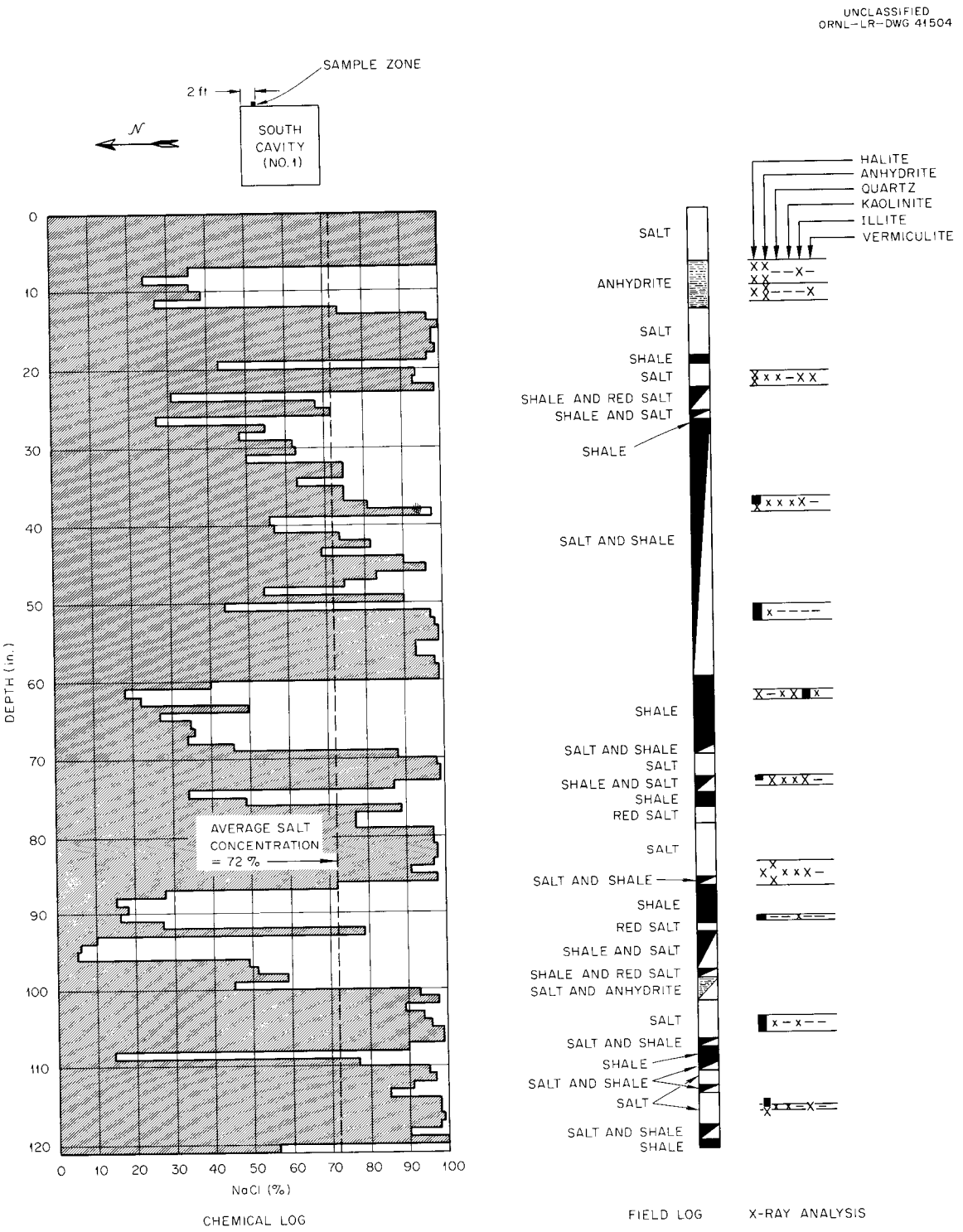

Fig. 12. Mineral Analysis of East Wall of South Cavity (No. 1), Carey Salt Mine.

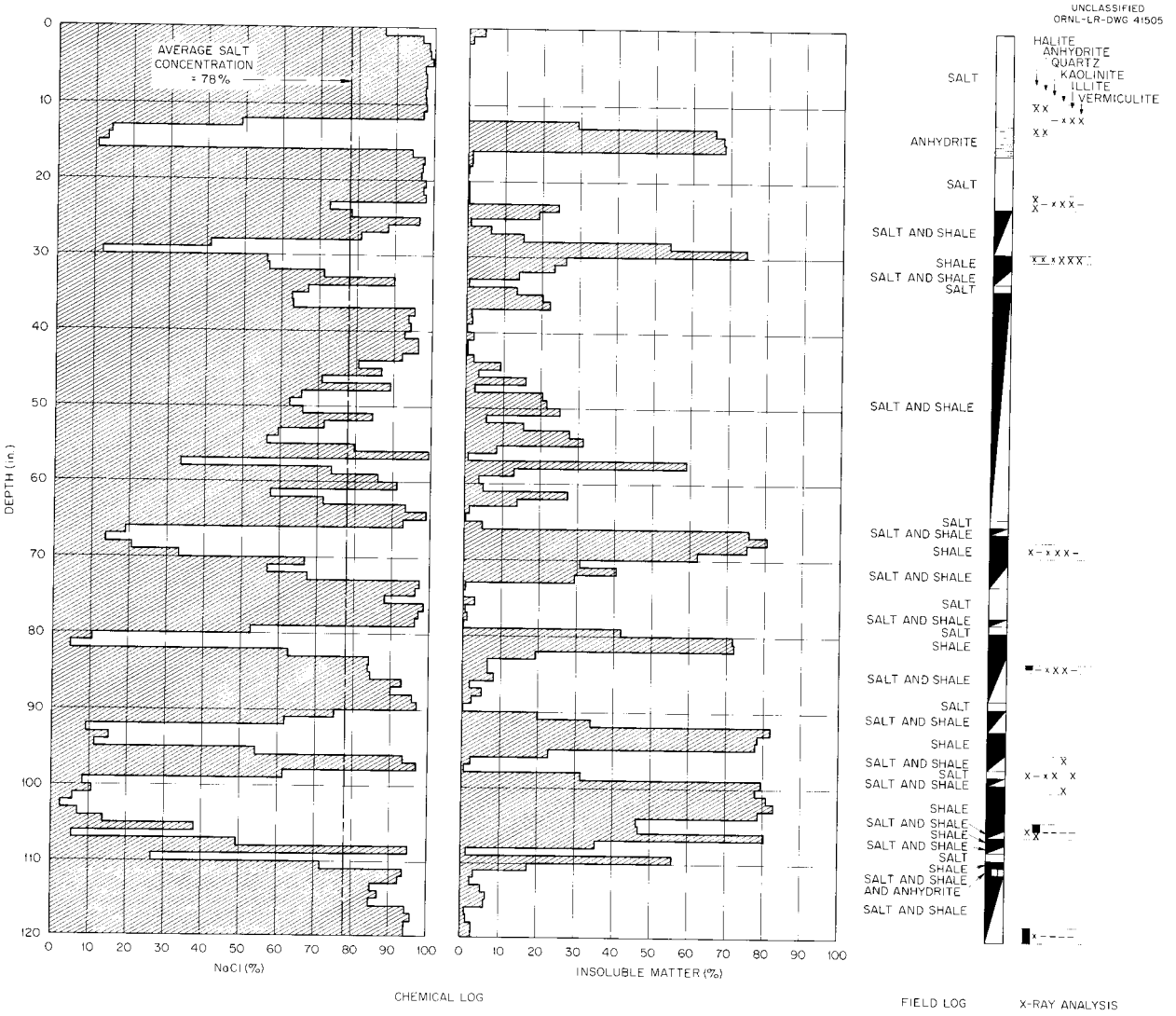

Fig. 13. Mineral Analysis of West Wall of North Cavity (No. 2), Carey Salt Mine.

The cores taken at the four corners of each cavity indicated that a greater amount of shale and anhydrite was present than in the cores obtained during site selection. Gas pockets and loss of drilling fluid were also encountered during the drilling. As a result, additional cores were drilled to define the extent of the gas pockets and the slope and thickness of the shale beds in the vicinity of the experimental cavities. The logs of these core holes indicated that the anhydrite and upper shale bands were continuous, but, at depths below 3 ft, the width of the shale bands varied.

Because of the voids and cracks in the lower salt and shale layers, as shown by the appearance of gas and by the loss of drilling fluid during coring, the cavities were filled with brine in an attempt to seal the cracks and permeable shale layers. A decrease in the water level in Pit 2 and a corresponding increase in Pit 1 indicated a hydraulic connection between the pits. Core holes between the two pits showed that the connection was not oriented regularly and, further, that it was about 8.5 ft below the floor of the mine. The presence of the interconnection did not rule out the use of this location for the experiments. It did, however, require that liquid levels in each pit be kept equal to prevent flow of waste from one cavity to the other. Since this interconnection allowed water to enter the shale formation, the moisture probes were not installed as originally planned.

Operation.-- The experiment with neutralized waste was placed in operation on January 6, 1960, and the acid-waste experiment on January 18, 1960. The acid-waste experiment was terminated on August 2, 1960, after 197 days operation. The neutralized waste experiment was terminated on February 1, 1961, after 392 days of operation. Initial power input to both experiments has been based on an assumed cooling time of 2 years for 10,000 Mwd/ton

burnup, 33 Mw/ton specific power, and 800 gal/ton waste. However, the power input was reduced at a rate corresponding to the decay of 5-year-cooled wastes. For wastes of this age the decay curve is relatively flat. Figure 14 shows the variation of power input with duration of experiment.

Comprehensive temperature data are being collected with a logger system for approximately 125 thermocouples. Maximum average liquid temperatures, which were reached in about 100 days, were 73° C for the neutralized-waste experiment and 64° C for the acid-waste experiment. The temperatures, after reaching the peak, remainded constant, except for drops due to power interruptions resulting from failures in the mine electrical distribution system.

During the course of the experiments, it was found that insufficient thermocouples were available to establish an adequate temperature profile around either pit. To accomplish this, five holes, 30 ft deep, were drilled on a line north of the neutralized pit, and thermocouples were installed at various depths. Thermocouple readings, recorded approximately twice weekly, have made it possible to establish temperature profiles under the neutralized pit. The results of these measurements are included in the section under Heat Transfer.

Operation of the experiments has been relatively trouble free. The recording controller and power supply have operated for a year in the case of the neutralized experiment and more than 6 months in the acid experiment with only routine instrument maintenance. The logger system has required approximately twice monthly maintenance, and some trouble has been experienced with synchronization of the print mechanism and the thermocouple selector switch.

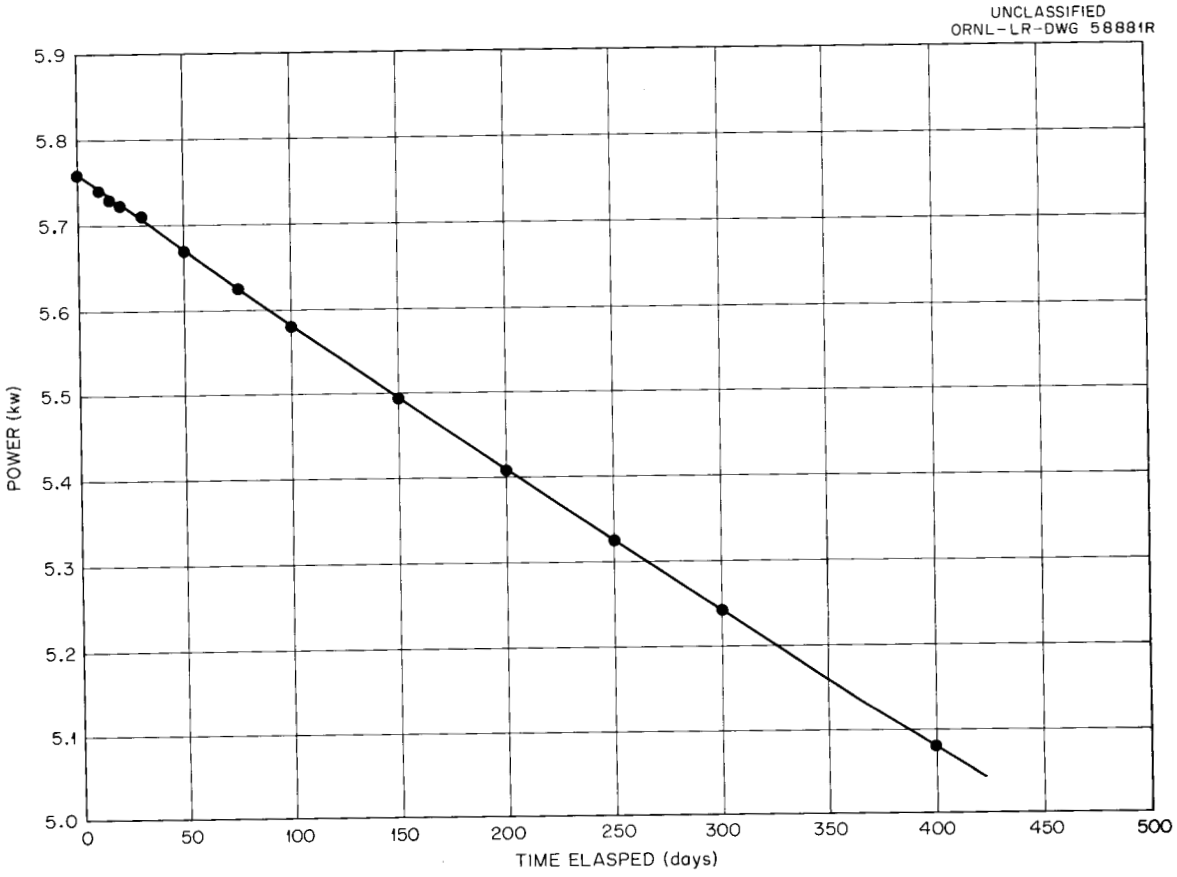

Fig. 14. Power Curve – Large-Scale Field Experiments.

Heat Transfer.-- Temperature rises in both the acid-waste and neutralized-waste experiments have generally followed those predicted for an equivalent sphere in an infinite salt medium. Perfect agreement would not be expected, since (1) the sphere only approximates the cube, (2) heat transfer from the floor to the mine air would not be the same as for conduction in salt, and (3) there are horizontal shale and anhydrite bands in the cavity walls.

Figures 15 and 16 show a comparison of experiment temperatures with those calculated for a sphere whose surface area is equal to the area of a 7.5-ft cube. The salt temperatures shown were obtained from thermocouples located at a depth of 6 ft 3 in. below the mine floor, on a horizontal line through the center of the waste solutions.

In the acid-waste experiment the temperature in the waste was uniform, both horizontally and vertically, with the exception of the lower foot or so which is several degrees cooler than the upper portions. This results in an average waste temperature 1 to 2° C lower than that shown in Fig. 15 for the waste at mid-depth (For the vertical profile see Fig. 1 in the section on Model Experiments.).

In the neutralized waste there is a viscous precipitate which settles to occupy approximately 30% of the solution volume. Heating is essentially confined to this region, since most of the fission products would be scavenged by the precipitate. There is little or no convection in the precipitate, and, consequently, temperatures as high as 120° C were recorded near the center; however, a steep gradient existed, and temperatures at the cavity wall were approximately the same as in the supernatant region. There

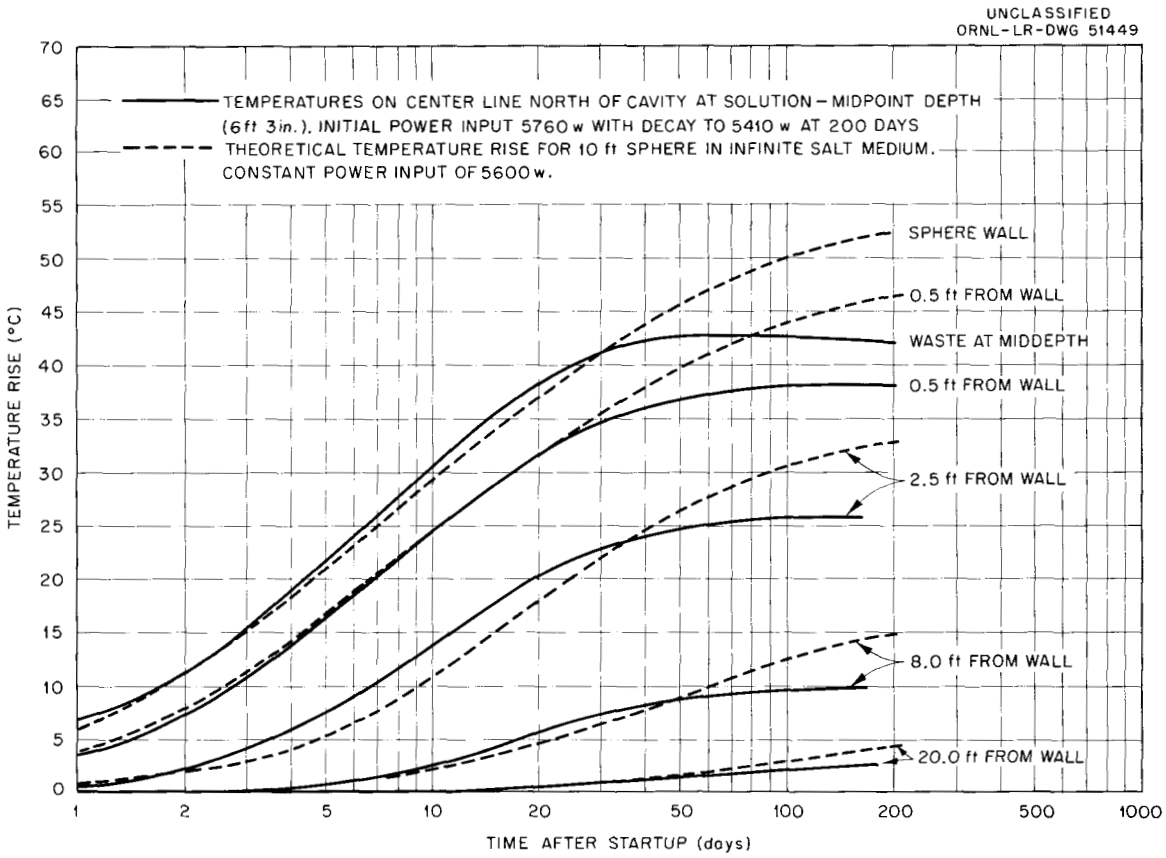

Fig. 15. Temperature Rise in 7-1/2-ft Acid-Waste Experiment.

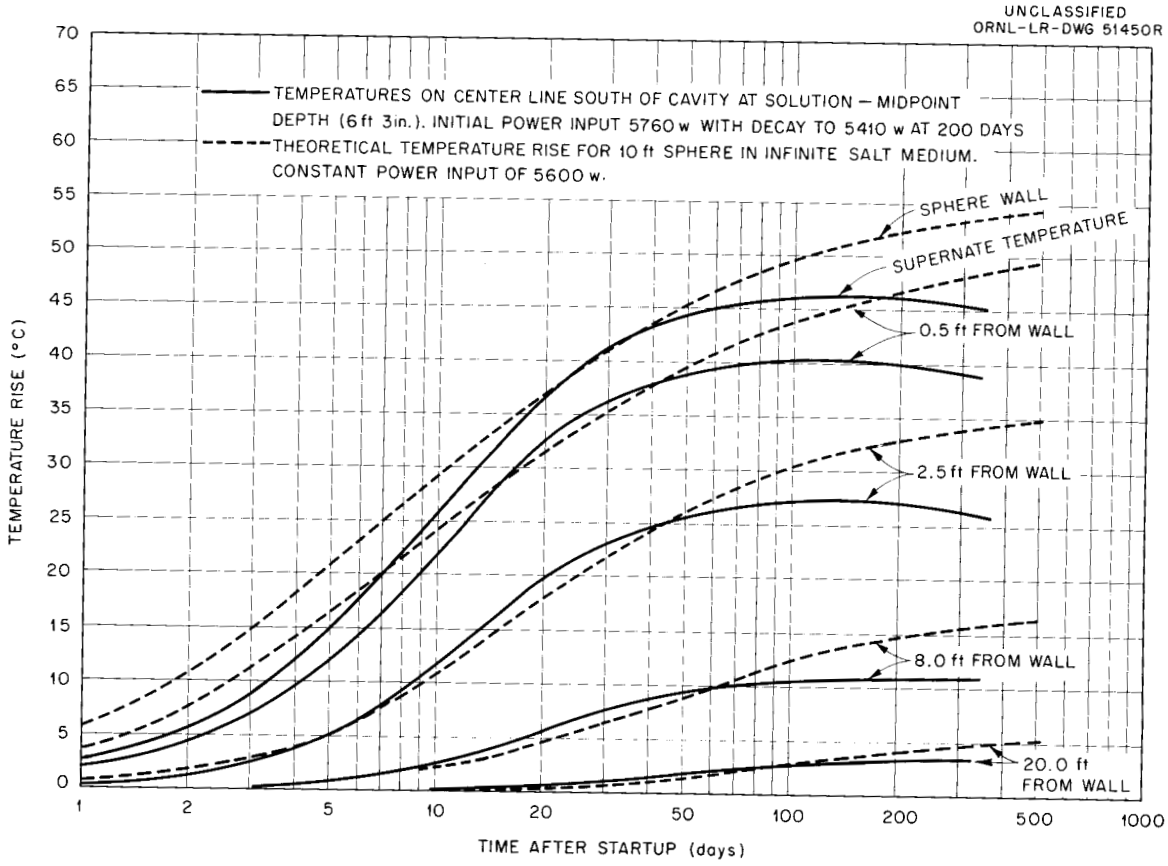

Fig. 16. Temperature Rise in 7-1/2-ft Neutralized-Waste Experiment.

is free convection in the supernatant, and, thereby, a uniform temperature distribution.

Figure 17 shows the vertical temperature distribution obtained within the cavity and out in the salt to the north of the center of the neutralized cavity. Precipitate temperature contours are based on data from only five fixed-position thermocouples and two vertical traverses and, thus, are not as accurate as the salt temperature contours. The salt temperature contours were constructed from data obtained from 44 thermocouples. There were not enough thermocouples to construct salt temperature contours around the acid cavity, but comparison of existing couples indicated that the salt temperature profile was approximately the same as for the neutralized cavity.

Plastic Flow.-- The stresses in a salt formation due to overburden pressure are disturbed during the mining operation, resulting in a process of stress redistribution within the formation. Depending on the volume of salt removed, the stresses in the roof and the pillars supporting the roof can exceed the elastic limit for salt, and plastic flow will result. Plastic flow produces a change in room dimensions, thereby reducing the stresses in the salt surrounding the room and producing a new condition of stability. The size of the plastic zone increases with rising temperature, resulting in an increased plastic flow (creep rate).

Gages have been installed in the Carey mine to measure the plastic flow in the vicinity of the field experiments. Figure 18 shows the gages installed around the neutralized-waste cavity. Two types of gages have been installed: (1) dial-gage extensometers, used to measure the linear movement of salt per unit time between two reference points; and (2) strain seismographs, used to determine if the rate of movement has a constant or

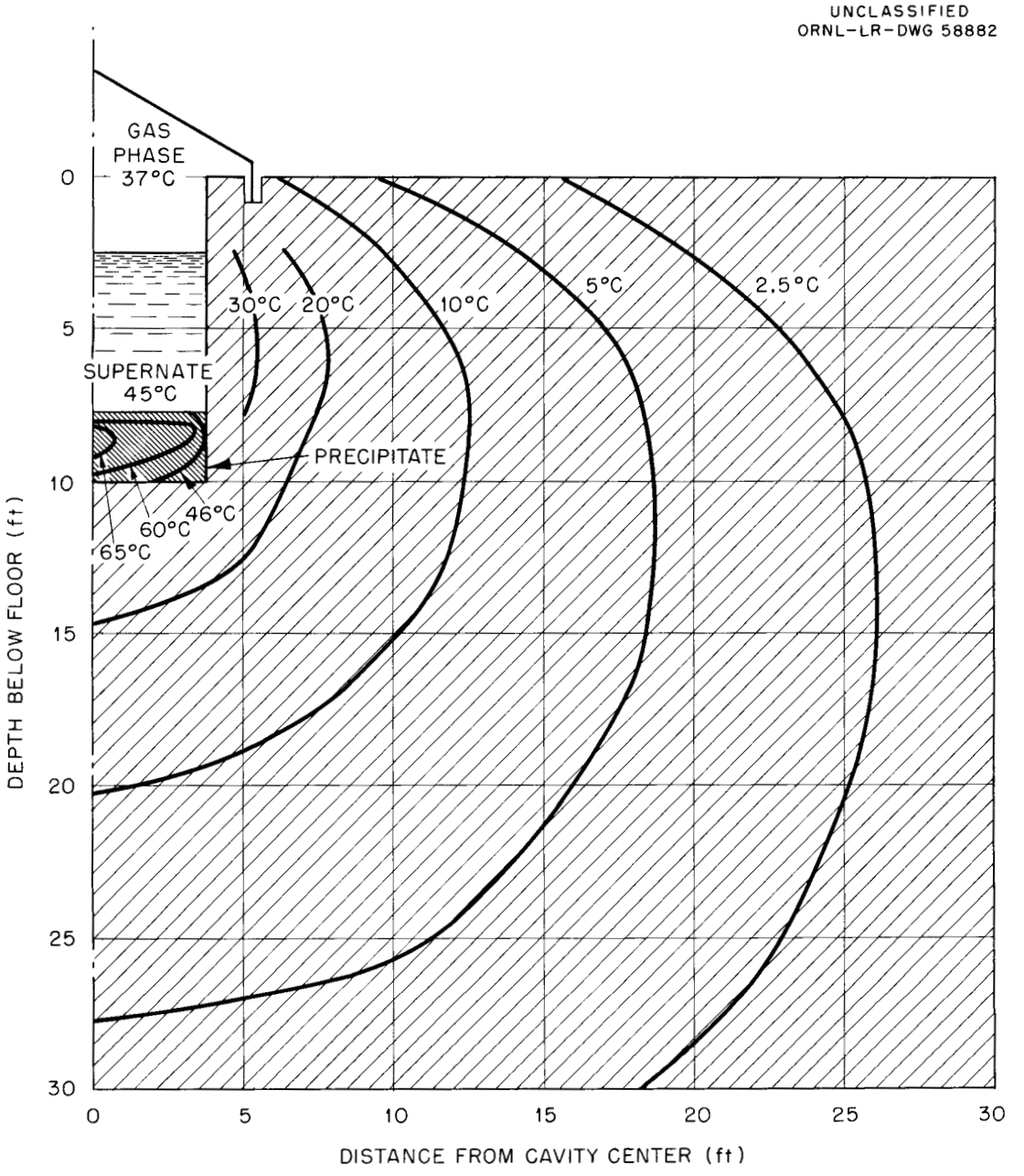

Fig. 17. Vertical Temperature-Rise Contours, 7-1/2-ft Neutralized-Waste Experiment, October 1960.

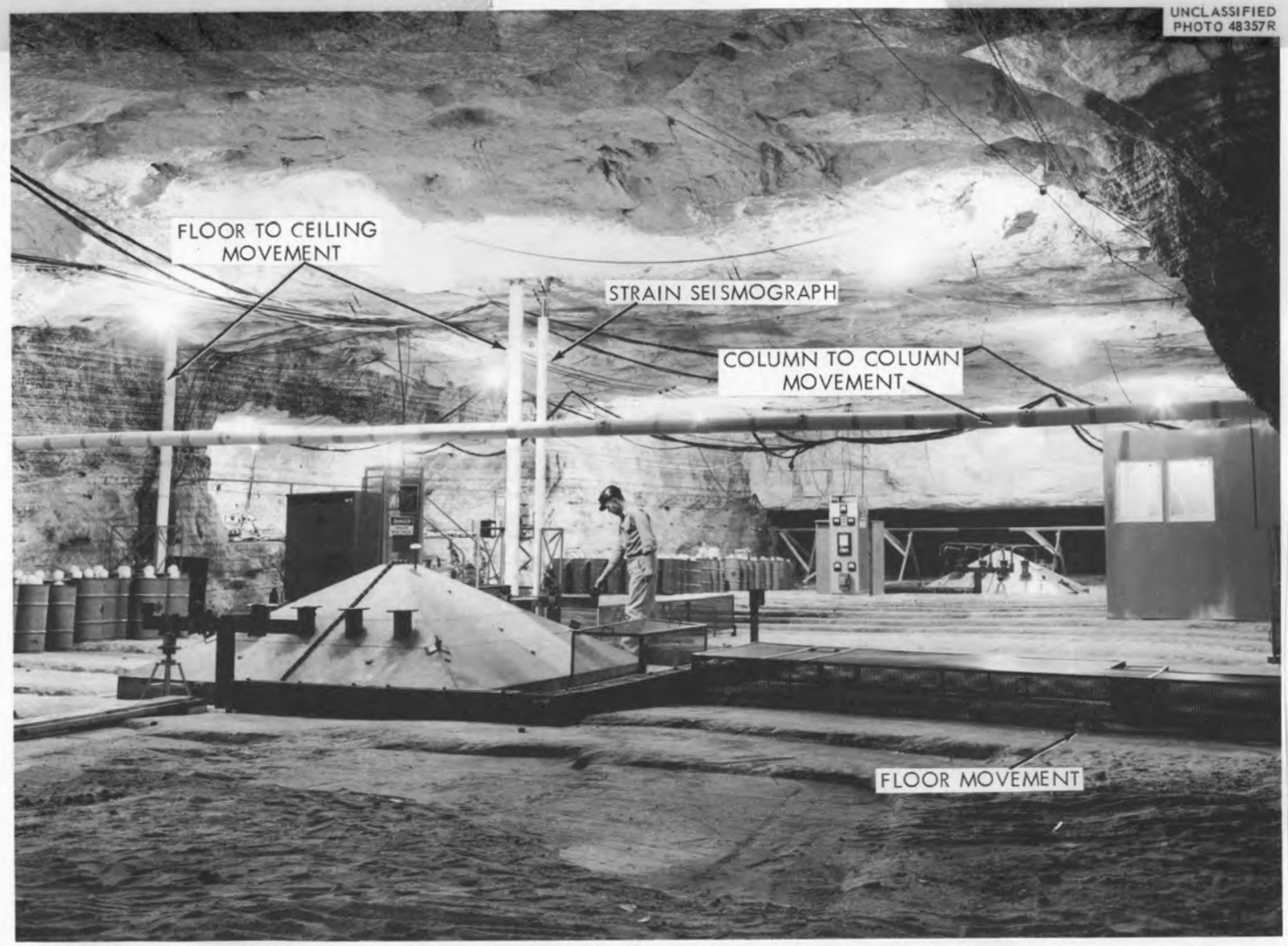

Fig. 18. Location of Devices for Measuring Plastic Flow.

a variable velocity. Measurements are being taken of the floor-to-ceiling movement, column-to-column movement, and floor movement. Measurements began before heat was applied to the cavity. Figure 19 shows the results obtained from the floor-to-ceiling gages and the column-to-column gages. The data plotted in these curves are not corrected for the thermal expansion of salt or of the measuring rod. The vertical gage located in the center of the room has shown an apparent sixfold increase in creep rate due to a rise in salt temperature of approximately 20° C, whereas the vertical gage near the wall has shown an apparent creep rate increase of about three times the initial rate due to a temperature rise of approximately 3° C. In all cases the creep curves show a slope decreasing with time, which is representative of the creep curve for a cavity approaching a condition of stability by adjusting its dimensions, as predicted by the theory of plasticity. Representatives of the Department of Civil Engineering, University of Texas, have installed extensometers in the vicinity of the acid-waste cavity, and similar results are recorded.

Measurements of the movement of the floor in the area surrounding the neutralized-waste cavity show a flow of salt toward the cavity. Due to difficulties in attaching these gages to the salt without disturbing the mine floor, the data are not consistent from gage to gage. Other strain-measuring devices, installed in the mine floor by the Bureau of Mines, similarly show that a movement toward the cavity may exist, but no results have been reported.

Preliminary analysis of the charts from the strain seismographs indicates that the salt is moving with constant velocity. More detailed analysis of these charts is required to separate the information on the movement of

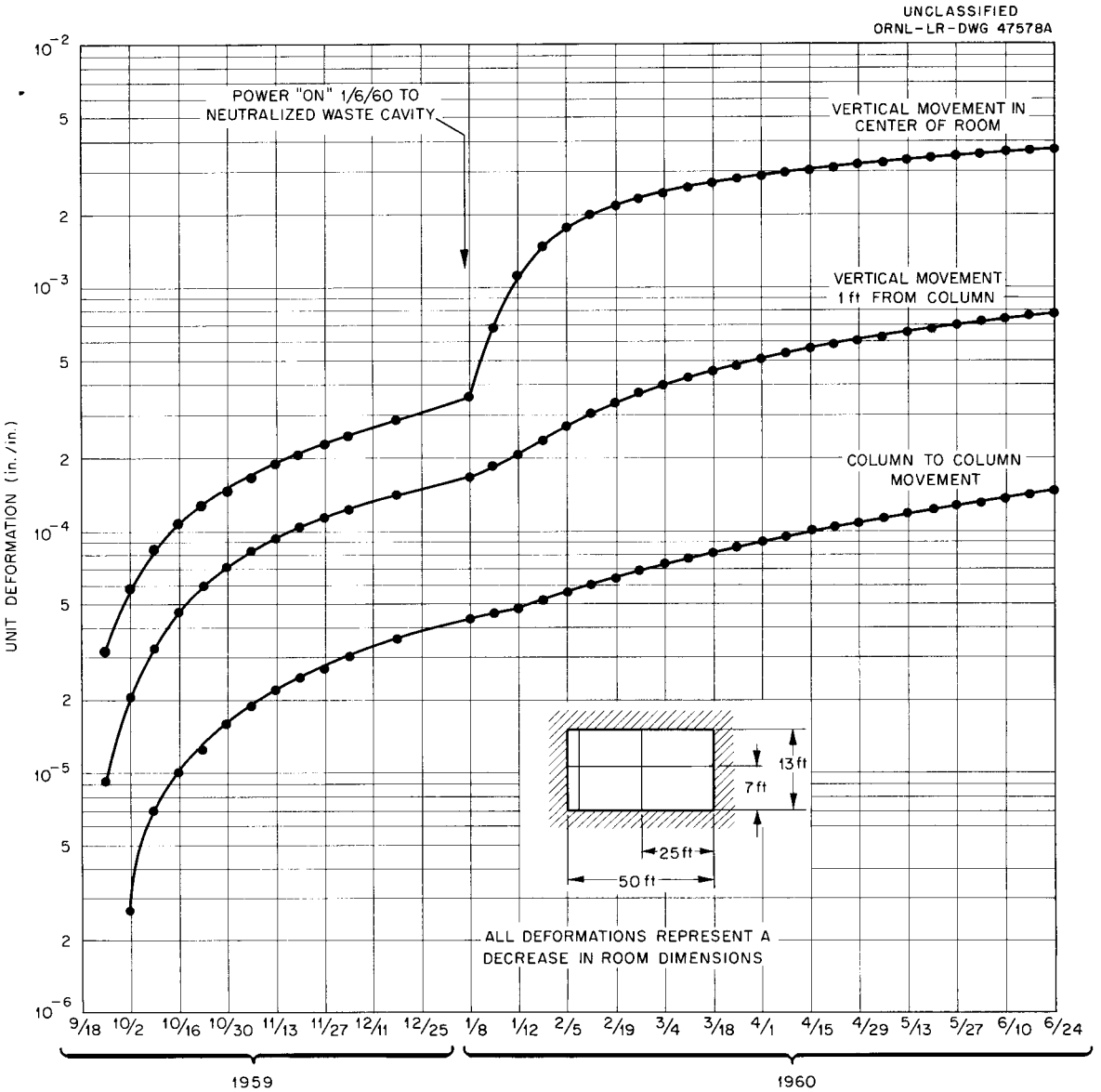

Fig. 19. Unit Deformation in Salt Surrounding Neutralized Waste Cavity.

salt from the background disturbance due to local vibrations and extraneous signals. This work is in progress and a report is in preparation.

Measurements of plastic flow are also being made by the University of Texas in a new working area of the mine. These measurements at ambient temperature give results similar to those observed near the cavities before they were heated; however, due to the relatively short time since the mine opening was made, the flow rate is much greater than that observed near the cavities.

Bureau of Mines personnel have also conducted three stress-relief tests in pillars at various mine locations. These tests were designed to give information on the horizontal and vertical stresses in the pillars. No results have been reported from these tests.

Analysis of the data collected from the gages is underway to determine the flow rates and effect of temperature on flow. These data will be combined with data from further mine experiments and measurements made in other mines in an attempt to derive fundamental relationships useful in the design of stable rooms for the storage of radioactive waste.

Gas Production.-- The synthetic Purex waste solution used in the large-scale experiments was from the same lot as that used in the small-scale experiments (see Table 2). However, the structure in which the large pits are excavated is a complex mixture of salt, shale, and anhydrite in clearly defined strata. The shale contains oxidizable material which will react with HNO_3 at ambient temperature to produce volatile oxides of nitrogen, and carbonates which will react to liberate CO_2. No interaction has been observed between anhydrite and the acid-waste solution. The slight attack

of acid Purex waste solution on the Haynes Alloy No. 25 cover produced small amounts of the oxides of nitrogen.

Samples of the gaseous products were taken at the beginning of the experiment (temperature, 22° C) and at regular intervals up to the maximum temperature reached. Samples were obtained by pulling 250 ml into an evacuated bottle. Table 7 contains a summary of the composition of the off-gas in equilibrium with salt-saturated acid Purex waste at the temperatures listed. No data are given for the neutralized Purex waste, since no gases were produced.

Gas production becomes substantial only between 50 and 60° C. The vapor contained no detectable NOCl at 51° C and reached 7% (by volume) at 60° C. A further rise in temperature to 63.7° C resulted in an NOCl content of 18%. The storage of acid Purex waste in a salt cavity would be simplified if the facility were designed to prevent the temperature from rising above 50° C. Only the gaseous products of radiolytic decomposition would then be a problem.

Routine analysis of off-gases from the acid pit did not show a positive indication of the presence of chlorine. However, when a sample of the gases was collected in a CO_2-methanol trap, chlorine was present.

The off-gases from the experiments were controlled by a water-cooled condenser followed by a vacuum jet-type scrubber which functioned both to provide a flow of gaseous products from the cavity and to absorb the acidic gases by reaction with a 5 M NaOH scrubbing solution (See description under "Off-Gas Containment."). This system has been most effective in the removal of noxious gases, as illustrated in Table 7. No measurable concentrations have been found in the off-gas following the scrubber, even without the activated-carbon filter bed.

Table 7. Analysis of Gases from the Acid Pit

Date	Liquid Temperature (°C)	Vapor Temperature (°C)	Sample Port[a]	Gas Found (vol %)			
				N_2O-NO_2	NOCl	Cl_2	CO_2
January 1960							
18	22	22	I	T[b]	*[c]	*	*
			II	T	*	*	*
			III	T	*	*	*
			IV	*	*	*	*
			V	T	*	*	*
23	42.8	42.0	I	T	*	*	*
			II	T	*	*	*
			III	T	*	*	1
			IV	*	*	*	*
			V	T	*	*	*
27	56.3	49.0	I	1	*	*	1
			II	1	*	*	*
			III	1	*	*	*
			IV	*	*	*	*
			V	1	*	*	1
February 1960							
9	59.9	57.4	I	3	5	*	4
			II	3	10	*	4
			III	3	3	*	4
			IV	*	*	*	*
			V	3	5	*	4
March 1960							
31	63.7	60.1	I	10	18.5	*	3
			II	10	20	*	3
			III	8	10	*	3
			IV	*	*	*	*
			V	8	10	*	3

[a]Sample Ports:

I. Under cover, above liquid.
II. Before condenser.
III. After condenser.
IV. After scrubber.
V. Under cover, above seal.

[b]T = trace.

[c]* = not detectable.

Laboratory studies have shown that there is a close relationship between the free-acid content of acid Purex waste and gas production. The free-acid content was monitored at two locations during the rising-temperature phase of the experiment and is shown in Table 8. Samples were obtained from two points within the pit solution: (1) midway between the two rows of electrodes and about 2 ft from the bottom of the pit, and (2) about a foot from one row and a foot below the surface. The samples were withdrawn into tared polyethylene bottles and returned to the laboratory for analysis. Since the hot solution deposits salt upon cooling, it was necessary to weigh and dilute the entire sample to a known volume before the analysis. Density measurements were made at the start of the run and at maximum solution temperature, and values in between were approximated by interpolation. The acid concentrations were converted from the molal to the molar scale by using the density values thus derived.

Cooperative Studies

The Geotechnical Corporation.-- W. B. Heroy, Sr., president of the corporation, has served as a consultant to the Laboratory on problems related to disposal of radioactive waste into salt. This has included investigation of sites for the present experiments and for possible future experiments. In addition, the corporation, under contract, designed and installed instrumentation for the measurement of plastic movement of the salt surrounding the experiments. These data are presented in the section on Plastic Flow.

University of Texas.-- The Department of Sanitary Engineering of the University of Texas, under the direction of E. F. Gloyna, is carrying on a study of plastic flow in the area around the waste experiments and also in

Table 8. Free Acid of Acid Pit

Sampling Date	Sample	Temperature (°C)	Concentration of Free Acid	
			Molal	Molar
January 1960				
18		21	5.793	7.015
21	I*	35.7	6.417	8.047
	II**	36.7	5.576	7.003
22	I	39.4	5.554	7.020
	II	40.4	5.443	6.902
24	I	39.2	5.446	6.884
	II	40.3	5.755	7.297
27	I	49.7	5.314	6.876
	II	49.7	5.302	6.866
31	I	54.3	5.274	6.893
	II	55.4	5.324	6.974
February 1960				
9	I	60.0	5.169	6.833
	II	60.7	5.212	6.895
March 1960				
31	I	63.4	4.914	6.560
	II	64.3	4.940	6.595

*I = Center of pit, 2 ft from bottom.
**II = One foot from electrodes, 1 ft from surface.

a remote area of the mine. The data are being collected by ORNL personnel, but will be correlated by the University of Texas.

U. S. Bureau of Mines.-- The Applied Physics Laboratory of the U. S. Bureau of Mines, under the direction of L. Obert, is also making strain measurements in the vicinity of one of the experiments. The instruments are read by ORNL personnel, and the data will be correlated and reported by the Bureau of Mines.

The Carey Salt Company.-- The field experiments are being carried on in an unused section of the Hutchinson, Kansas, mine of the Carey Salt Company. The company has furnished labor, utilities, and mechanical facilities for operating the field experiments.

IV. CHEMICAL LABORATORY STUDIES

Chemical Gas Production

The chemical compatibility of simulated 7 M acid Purex solution and salt was studied in the laboratory with equipment designed to closely duplicate the conditions of the field experiment. The solutions were in a glass system in which all vapors issuing from the solution were air-refluxed, permitting noncondensible gases to diffuse out of the system, thus, maintaining atmospheric pressure over the liquid. One major difference was the application of heat through the walls of the containing vessel, rather than directly into the solution.

A large portion of 7 M acid Purex is HNO_3, and the ions which predominate in the mixed solution are hydrogen, sodium, nitrate, and chloride. This composition suggests that any reaction which might occur would be similar to that between HNO_3 and HCl, the aqua regia reaction (14). This similarity was verified by laboratory tests using (1) NaCl and HNO_3 and (2) NaCl and simulated 7 M acid Purex waste solution. The identifiable products of both reactions were NOCl and Cl_2. Taking the idealized over-all reaction to be

$$NO_3^- + 3Cl^- + 4H^+ = NOCl + Cl_2 + 2H_2O$$

and noting that both nitrate and chloride are always present in abundance, it was found that the hydrogen ion concentration is the condition that limits

the extent of the reaction. There is also a marked temperature effect upon both speed and degree of the reaction. The influence of hydrogen ion concentration and temperature on the reaction is shown in Fig. 20. From the stoichiometry of the aqua regia reaction, the gas production is calculated to be 11.2 liters of gas per equivalent of acid consumed. The approximate maximum gas production that could be expected from a 7 M Purex-salt system at different solution temperatures is given in Table 9.

When the acid molarity at which the rate of reaction becomes imperceptible is plotted against the corresponding temperature, the points describe a line which extrapolates to 4 M (3.2 m) and 60° C. These two intercepts indicate the minimum conditions below which gas production ceases at 1 atm of pressure. Thus, chemical gas production in a 7 M acid Purex-salt solution can be inhibited by decreasing the acidity of the solution through denitration or neutralization, or by cooling the solution. These conclusions were confirmed by laboratory tests.

A thermochemical balance of the chemical reaction shows a net endothermic uptake of 42 kcal for the balanced reaction or about 10 kcal absorbed per equivalent of acid ion consumed. This is equivalent to a 10° C cooling per equivalent of acid consumed.

In order to develop a method for directly measuring the volume of gas produced by heated mixtures of NaCl-saturated synthetic waste solutions, two gas-measurement systems were studied. The first system studied, cold trap fractionation, used helium gas to sweep the product gases, Cl_2, NOCl, and water vapor, from a heated synthetic waste-salt sample through a series of of water, CO_2-methanol, and liquid-nitrogen-cooled condensers. The condensers were arranged in the order listed to selectively remove water in the 0° C

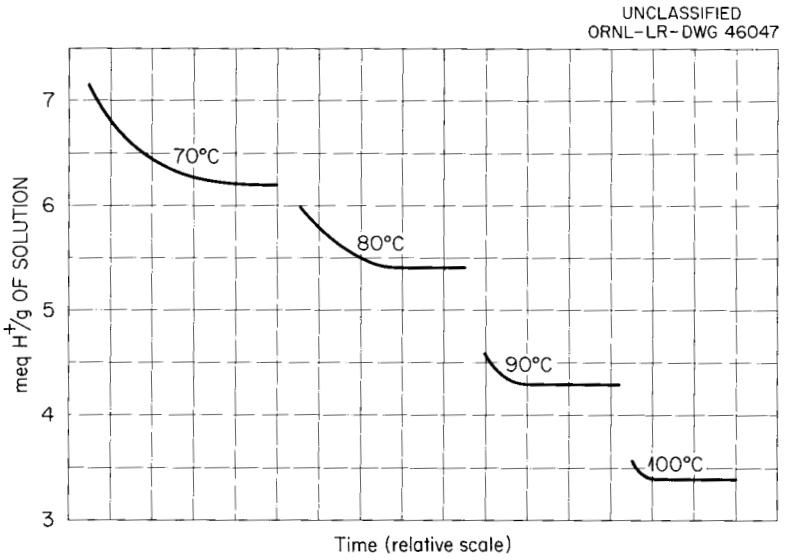

Fig. 20. The HNO_3-NaCl Reaction as a Function of Temperature.

Table 9. Calculated Maximum Gas Production from 7 M Acid Purex-Salt Solution

Temperature (°C)	Acid Consumed (equivalents/liter)	Volume of Gas Produced, STP (liters per liter of solution)	Volume of Gas Produced, STP (ft^3/gal)
70	< 0.05	Trace	
80	0.5	6	0.6
90	1.8	20	1.9
100	3.2	36	3.5

water-cooled condenser; NOCl and Cl_2 in the CO_2-methanol condenser; and nitrogen oxides in the liquid-nitrogen-cooled condenser. Following sample collection, a manometric method was used to measure the gas volume of each fraction. Qualitative and quantitative chemical analysis of the fractions showed that NOCl and Cl_2 gases were produced in equimolar amounts of solution samples of salt-saturated 7 M Purex waste. Accurate quantitative measurement of the gas volumes produced by the salt-saturated sample was not attained, because the waste-salt solution system was sensitive to sweep-gas rates. Another factor which contributed to large variance in the quantitative measurement was the reaction of the product gases, Cl_2 and NOCl, with the water vapor.

The principal feature of the second gas-measurement method was the quantitative displacement of helium by the product gases in the apparatus shown in Fig. 21. After introduction of the 50-ml sample, all air in the system was displaced by helium, and the apparatus was adjusted to ambient pressure which was maintained during the heating period by manipulating the volume of the gas burette. During the heating period the gases produced by the sample, as well as water vapor, displaced helium into the calibrated gas burette. A number of preliminary experiments established the optimum sample volume, container size, and amount of helium required to prevent chemical reaction between the product gases and mercury in the gas burette. A calibration curve of the apparatus was prepared by comparing experimentally determined pressures, temperatures, and volumes with calculated values.

Figure 22 shows a typical temperature-vapor-volume curve for 50-ml samples of synthetic 7 M Purex waste solution and salt-saturated 7 M Purex waste solution. Below 65° C the salt-saturated waste solution exhibits

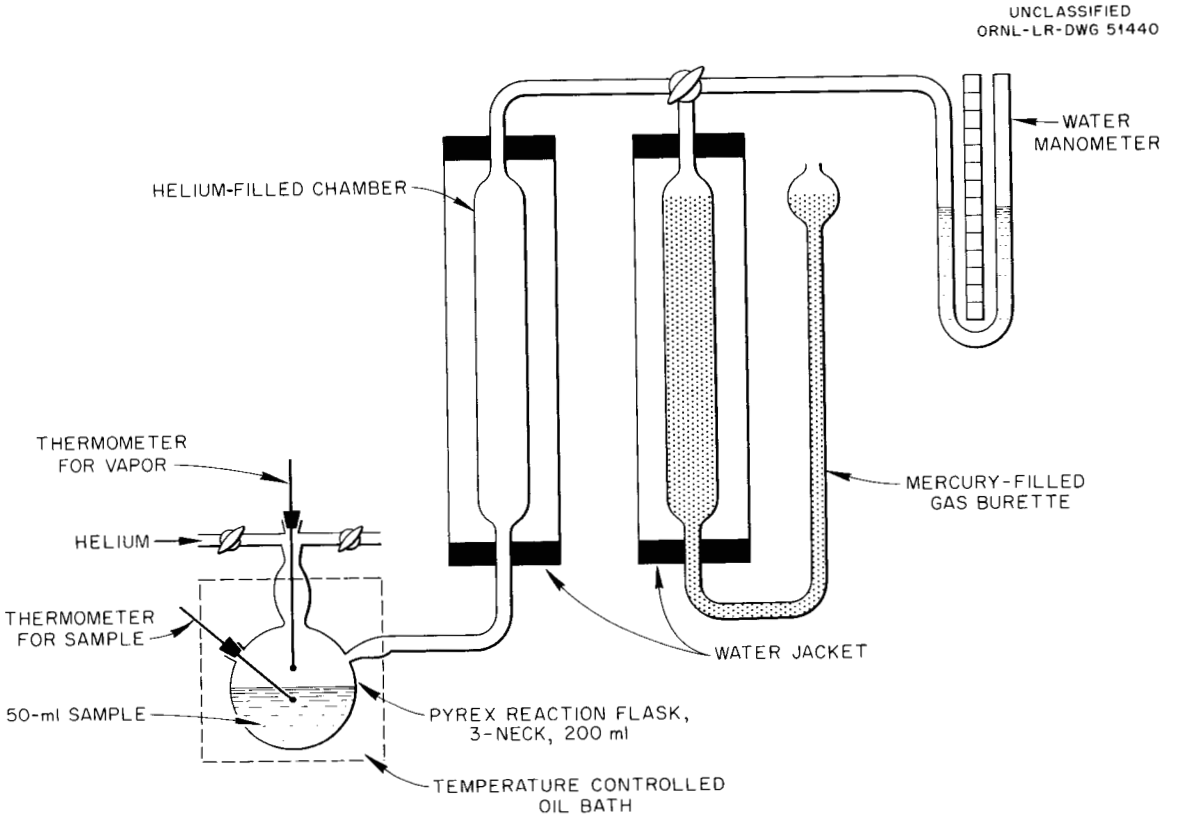

Fig. 21. Helium-Displacement Gas-Measuring Apparatus.

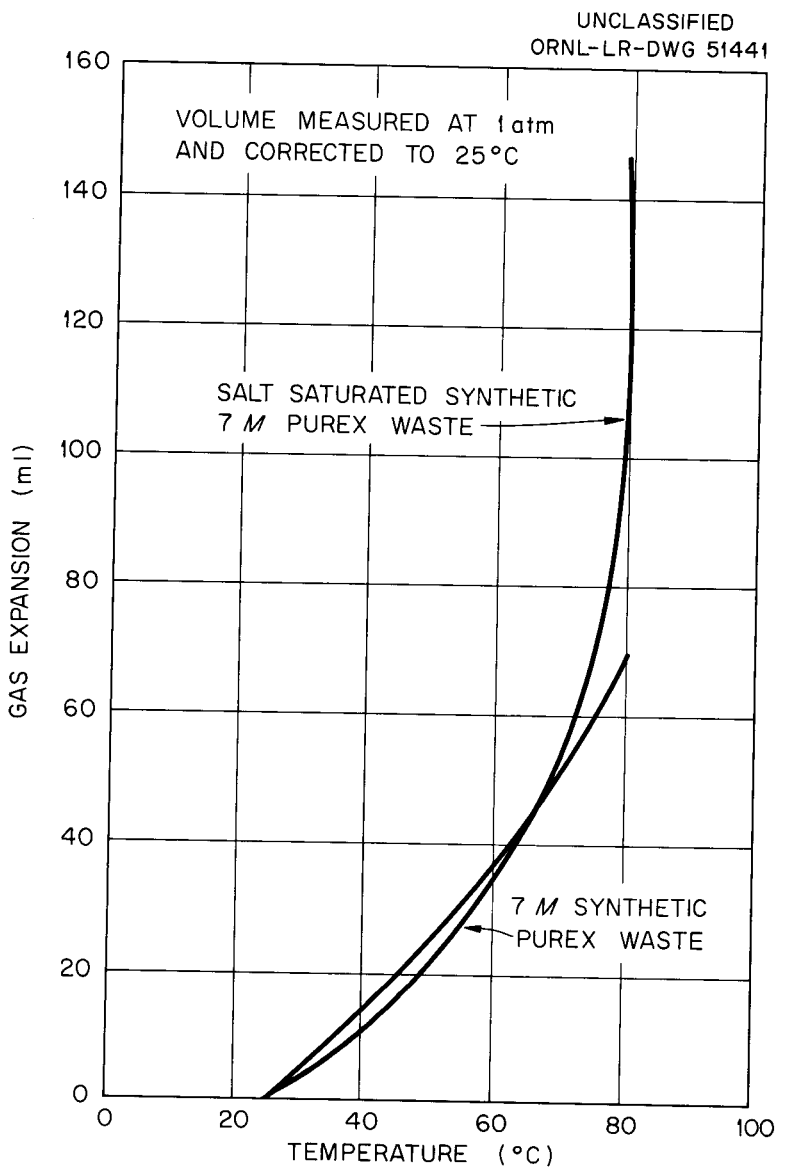

Fig. 22. Experimental Determination of Gas Production.

negligible gas production and reduced vapor volume due to an increased concentration of ionized solute as compared with the 7 M Purex waste solution. When the temperature of the solution is increased above 65° C, vapor volume of the salt-saturated sample increases, due to the production of NOCl and Cl_2. This action, when plotted, results in an intersection of the two curves and accounts for the increased slope of the salt-saturated vapor-volume curve at higher temperatures. Analysis of a series of curves similar to the above for separate samples of synthetic waste and salt-saturated samples are summarized in Table 10. These values show that the gas volumes predicted by the aqua regia study are in close agreement with the experimentally determined volumes. Also listed in Table 10 are the vapor volumes for samples of NaOH neutralized and half-neutralized waste solutions with and without salt, which show that gas production by the aqua regia reaction can be minimized by decreasing the acidity.

Radiolytic Gas Production

In view of the high radioactivity predicted for the waste solutions, it is necessary to determine whether gas production by radiolysis will preclude disposal in liquid form. It is also pertinent to check whether radiolysis can be controlled by altering certain solution conditions.

From the standpoint of radiation chemistry, the radiolysis of very pure water is thought to consist of a cycle of reactions which results in no net change in the system. With the introduction of small amounts of impurities, as found in good grades of distilled water, there is a measurable production of gas. The G value (molecules of substance destroyed or produced per 100 ev of absorbed radiation) for hydrogen is commonly accepted to be about 0.45

Table 10. Comparison of Calculated (ΔH^+) and Experimental Gas Yield of Synthetic Purex Waste-Salt Solutions

Sample Description	25° C Calculated* Yield (ml of gas per liter of solution)	25° C Experimental Yield (ml of gas per liter of solution)	Temperature ($^\circ$C)
Salt-Saturated 7 M Purex	1200	1560	80
Salt-Saturated 7 M Purex	1220	1600	100
Salt-Saturated (+10 excess salt) 7 M Purex	1300	1590	100
Salt-Saturated NaOH Neutral Purex	0	0	100
Salt-Saturated 3.5 M Purex	0	0	100

*Gas-yield values calculated on basis of measured acidity change of the sample solution.

which is equivalent to about 0.01 cc per gram of water per 10^6 rad. Oxygen also is produced, and the G value for its production when nitrate is present varies with the pH of the medium as well as the nitrate concentration. The G values for the yields of radiolytic products reported in the literature were determined with essentially pure systems and are not generally applicable to this situation, because the presence of even a small amount of other substance can alter the yield by a considerable amount. They are useful, however, in allowing one to estimate approximate possible maximum yields. In a confined system, the build-up of product gases may increase the rate of recombination reactions or alter the radiolytic chain reactions such that a net low-yield steady-state condition may be attained.

A study of the radiolytic stability of representative waste solutions was initiated in order to determine the degree of radiolysis that could be expected under storage conditions, as well as the solution conditions which effect changes in the rate and degree. The solutions were irradiated in the Co^{60} facility, and the results are limited, therefore, to the effects of gamma radiation (1.17 and 1.33 Mev) from an external source. Since the activity of waste solutions is primarily due to Cs^{137} (0.52 Mev β) and Sr^{90} (0.61 Mev β), the absorption of the Co^{60} gamma radiation with the release of an electron with about one Mev energy should involve energetics of about the same magnitude.

The composition of the waste solutions studied are given in Table 11. Each solution type was irradiated under three conditions: (1) no salt added, (2) salt saturated, and (3) salt saturated plus excess salt. The irradiations were carried out in tubes fashioned after a model furnished by the Chemistry Division. Each tube had a sample capacity of about 4 ml and

Table 11. Composition of Waste Solution Types Investigated for Radiolytic Stability

Type	Ionic Concentration (equivalents/liter)				
	Free H^+	Fe	Na	NO_3	SO_4
7 M Purex	7.0	1.0	0.3	7.3	1.5
3.5 M Purex	3.5	0.5	0.15	3.65	0.75
Semineutral Purex	3.61	0.87	3.17	6.35	1.30
Neutral Purex	1.23	0.78	4.84	5.68	1.17
Formaldehyde-denitrated Purex*	0.5	2.4	0.9	0.5	4.0

*Also contains 0.7 equivalent of aluminum.

included a built-in mercury manometer to indicate the internal pressure. A known volume of each solution was put into a tube; the inlet port was sealed; and the tube was irradiated. The pressure within the tube, determined by the height of the mercury column, was recorded as a function of absorbed radiation.

The degree of radiolysis represented by the internal pressure of the irradiation tubes is plotted as a function of absorbed dose for each solution type in Figs 23-27. Since the pressure was determined with closed end manometers, there is a greater uncertainty in the higher pressure readings than the lower readings. Thus, the uncertainty of 4% at 2 atmospheres increases to 5.3% at 4 and 9% at 8 atmospheres.

All the solutions investigated approached steady-state conditions as the dosage approached 10^9 rad. In general, the degree of radiolysis before steady state sets in is increased by saturating the solution with salt and is even more enhanced by the presence of excess solid salt. The data for the neutral Purex is anomalous to the general trend: the minimum steady-state pressure was observed with excess salt present.

The total pressure and the total gas production per milliliter of solution at the steady-state condition are included in Table 12. A comparison of the steady-state pressures and volumes of gas produced by Co^{60} radiation absorption with the volume of gas produced by chemical interaction indicates that chemical gas production is negligible compared with radiolytic gas production, especially if the product gases are allowed to escape.

The analysis of the gases from an irradiated tube containing synthetic denitrated Purex gave 6 vol % hydrogen, 23 vol % oxygen, and the remainder

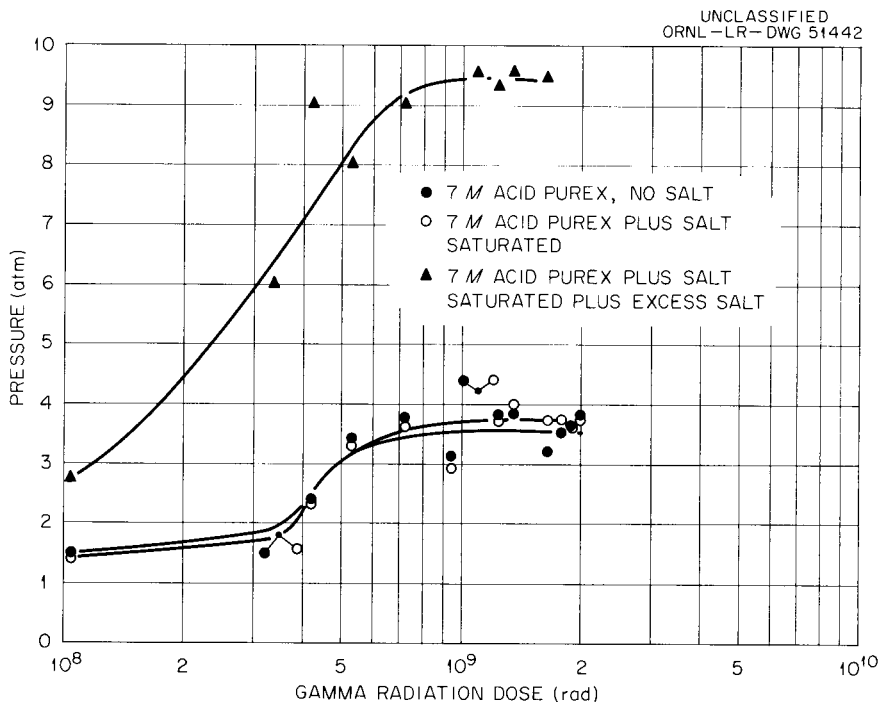

Fig. 23. Vapor Pressure of Co^{60}-Irradiated Waste-Salt Samples, 7 M Acid Purex and Salt.

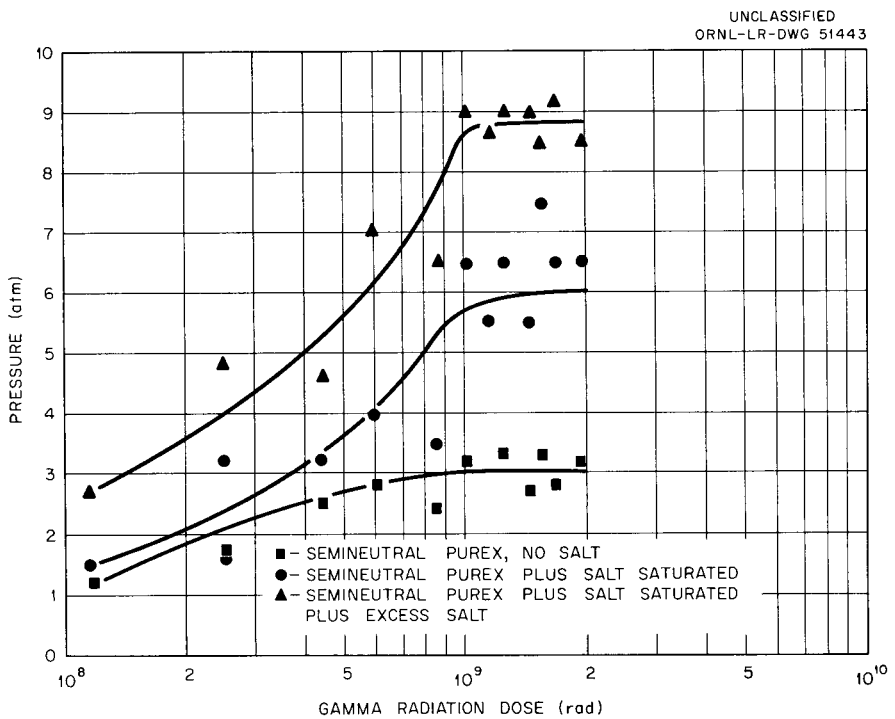

Fig. 24. Vapor Pressure of Co^{60}-Irradiated Waste-Salt Samples, Semineutral Purex.

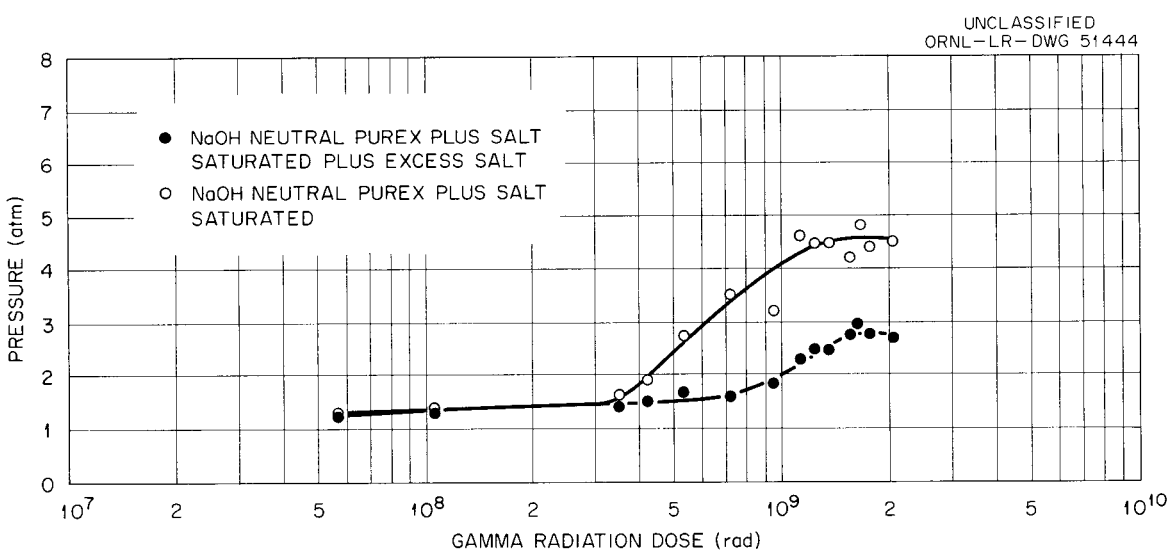

Fig. 25. Vapor Pressure of Co^{60}-Irradiated Waste-Salt Samples, Neutralized Purex Salt.

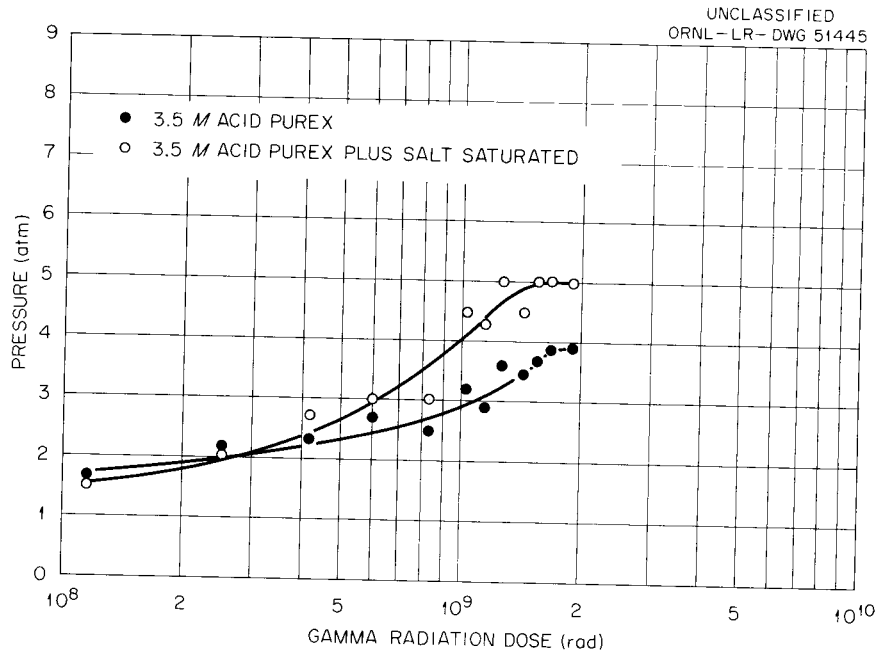

Fig. 26. Vapor Pressure of Co^{60}-Irradiated Waste-Salt Samples, 3.5 M Purex.

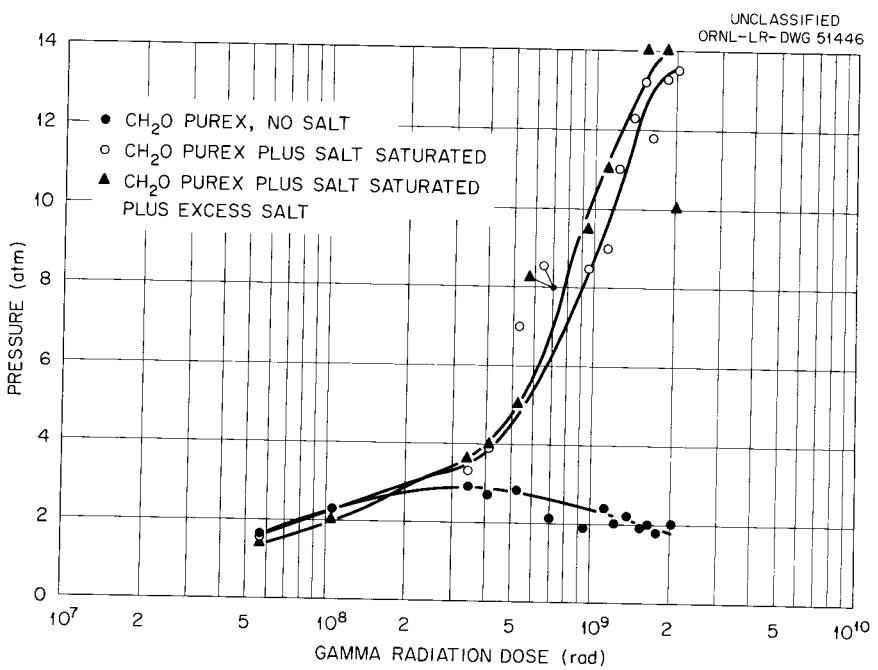

Fig. 27. Vapor Pressure of Co^{60}-Irradiated Waste-Salt Samples, Formaldehyde-Denitrated Purex.

Table 12. Steady-State Pressures and Total Gas Production

Type	Condition	Steady-State Pressure (atm)	Yield (ml of gas per ml of solution)
7 M Purex	A[a]	3.55	1.44
	B[b]	3.64	1.40
	C[c]	9.4	4.90
3.5 M Purex	A	3.85	1.42
	B	5.01	1.90
	C[d]		
Semineutral	A	2.94	1.02
	B	5.68	2.00
	C	8.88	4.28
Neutral Purex	A[d]		
	B	4.58	1.43
	C	2.68	0.91
Formaldehyde denitrated	A	2.06	0.29
	B	11.9	6.35
	C	11.6	6.62

[a]No salt added.

[b]Salt saturated.

[c]Salt saturated plus excess solid salt.

[d]Original samples damaged - data incomplete.

nitrogen. Since hydrogen is normally not a major constituent of the atmosphere, the measurable hydrogen content was significant. The irradiation of 7 M Purex solution kept under a hydrogen blanket showed no change in internal pressure up to a dose of 10^9 rad. The partial pressure of hydrogen seems to be an important factor which governs the degree of radiolysis.

In a different approach to minimizing radiolysis, the effect of suspending waste solutions as surface films on crushed salt and fixing as absorbed water in the lattices of certain minerals was studied. The waste solutions were poured over crushed salt at the ratio of 1 ml per 5 g of salt. No pressure build-up was observed as long as the liquid remained suspended as film. As the total dose approached 10^9 rad, a liquid phase separated over the layer of solid salt. This was accompanied by a build-up of pressure. Solutions absorbed in vermiculite and attapulgite showed no evidence of radiolytic decomposition which would have been indicated by a pressure build-up. The irradiations were repeated in tubes which utilized open end manometers for pressure indicators, and no pressure rise greater than 20 mm of mercury was observed.

V. THERMAL STUDIES

Field Experiments

The initial heat-production rate used in the large-scale (7.5-ft cube) field experiments was equivalent to that of 2-year-cooled wastes from fuel irradiated 10,000 Mwd per metric ton of uranium at a specific power of 33 Mw/ton and yielding 800 gal of waste per ton (15). However, the power input was reduced at a rate corresponding to the decay of 5-year-cooled wastes. Interpolation of previous thermal calculations (16) for 1- and 6-year-cooled wastes indicated that 2-year-cooled wastes could be stored in a 10-ft-diam sphere (surface area approximately the same as a 7.5-ft cube) without boiling.

An analytical solution for the time-temperature relationship at the surface of a heated sphere of uniform conductivity in a uniform medium with exponential decay of the heating rate is given by Birch (17):

$$T(a,t) = \frac{A_o a^2}{3ck} \left\{ 3e^{-\alpha t} \int_{a/\sqrt{kt}}^{\infty} e^{\alpha a^2/k\beta^2} \left[\operatorname{erf} \beta - \frac{2}{\beta\sqrt{\pi}} \left(1 - e^{-\beta^2}\right) \right] \frac{d\beta}{\beta^3} \right\} , \quad (2)$$

where

A_o = the initial heating rate per unit volume,

a = the radius of the sphere,

c = the specific heat per unit volume of the medium,

k = thermal diffusivity of the medium,

α = the heating rate decay constant,

t = time,

β = variable of integration

This equation was solved by numerical integration for the time variation of temperature at the surface of a 10-ft sphere, equivalent to the 7.5-ft cube field experiments. An analytical solution for the time-space variation of temperatures in the salt medium surrounding the sphere when the heating rate is constant is (18):

$$T(r,t) = (2Aat/cr)\left[i^2 \operatorname{erfc} \frac{r-a}{\sqrt{4kt}} + i^2 \operatorname{erfc} \frac{r+a}{\sqrt{4kt}} + \right.$$

$$\left. + \frac{\sqrt{4kt}}{a}\left(i^3 \operatorname{erfc} \frac{r+a}{\sqrt{4kt}} - i^3 \operatorname{erfc} \frac{r-a}{\sqrt{4kt}}\right)\right] , \quad (3)$$

where

r = the distance from center of sphere to a point in the medium,

i^2 = second integral,

i^3 = third integral.

The other terms are the same as for Equation 2.

In the 7.5-ft-cube field experiments the heating rate is almost constant, starting at 1.8 w/gal and falling to 1.7 w/gal after 200 days. Over this period the effect of the decaying heat-production rate is not great, as may be seen from Fig. 28. A comparison of the experimental data with the theoretical calculations is made in the section on Field Experiments.

Calculations for the surface temperatures of a sphere with surface area equivalent to the 18-in., small-scale experiments were made by utilizing Equation 2. The results will be found in the section on Field Experiments.

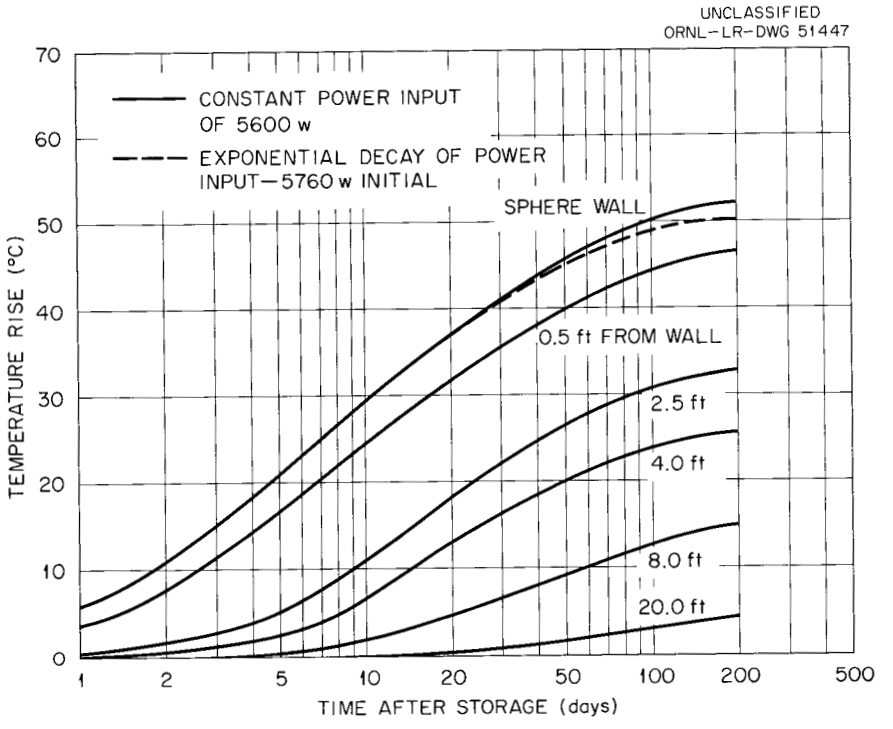

Fig. 28. Ten-Foot Sphere — Theoretical Temperature Rise in Infinite Salt Medium.

Mine Disposal

In a mine-disposal operation each cavity will be affected by heat from other cavities, and, thus, it becomes necessary to investigate maximum temperature rises for various sizes and shapes of cavities in various configurations which might be encountered.

A solution is available for the temperature rise in an infinite slab in contact with an infinite medium and with exponential decay of the heating rate (19). By use of this equation, and approximating the power-decay curve of Blomeke by a series of exponentials, the curve in Fig. 29 was calculated. Inherent in these calculations are the assumptions: (1) The heat source is uniformly distributed in a 10-ft-thick layer of salt, extending infinitely in the horizontal plane. (2) The conductivity of the salt in the heat-generating layer is infinite, although the heat capacity is the same as that of the infinite salt medium. (3) Thermal properties do not change with temperature.

The assumption of the infinite horizontal slab is conservative, since probably no more than 60% of the gross area of a mine would be used for actual waste storage. The assumption of infinite conductivity is approximately true for a layer of freely convecting liquid.

Figure 30 shows the calculated maximum temperature rise in F^{o} in an infinite thin slab of waste in an infinite salt medium as a function of cooling time before storage. The waste is assumed to have a heat-generation rate of 100 w/gal after 120 days of cooling and a concentration in the slab of one gallon per square foot. Curve A is an analytical solution based on the same equation as Fig. 29. Curves B and C are computer calculations for slabs of zero thickness and 10-ft thickness which were performed for this

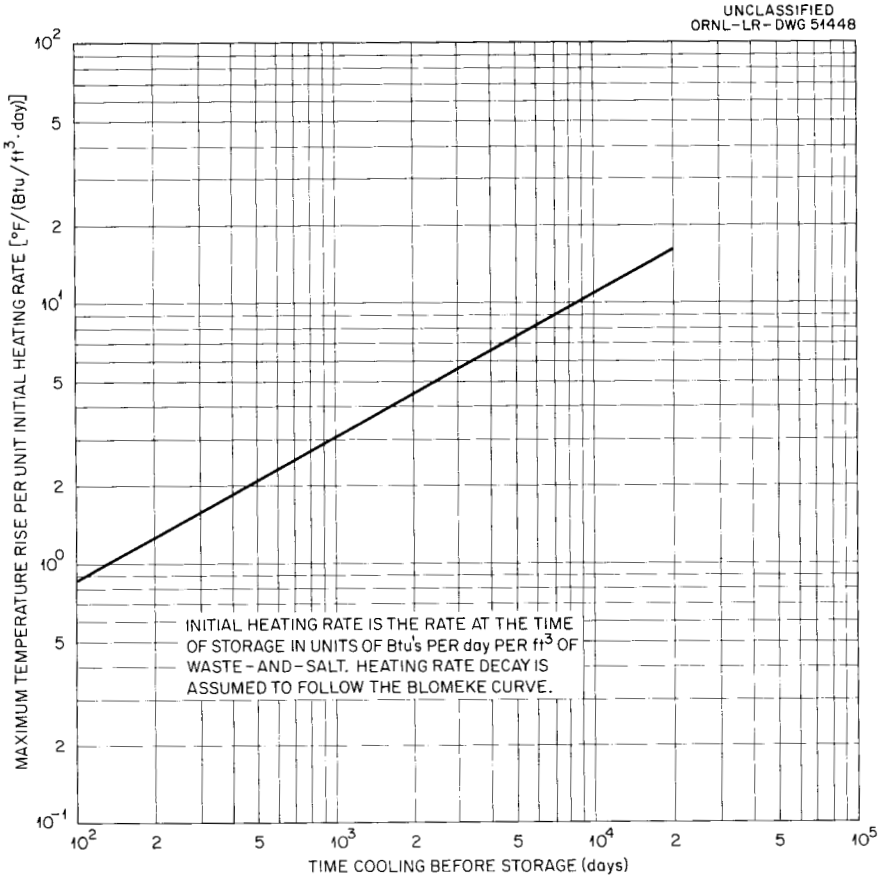

Fig. 29. Maximum Temperature Rise in a 10-ft-thick Infinite Slab of Waste and Salt in Infinite Expanse of Salt.

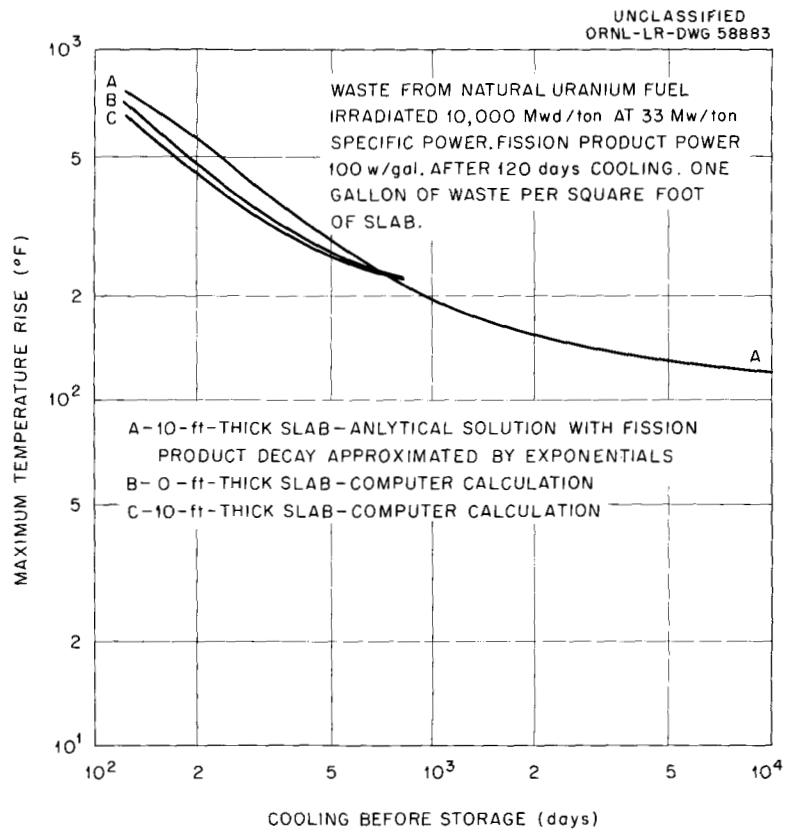

Fig. 30. Temperature Rise in Infinite Slab of Waste in Infinite Salt Medium.

project by W. D. Powers of the Reactor Division. The zero thickness waste slab can be visualized as the result of evaporating one gallon of waste per square foot of salt floor. Note that there is little thermal advantage to be gained from dispersing the waste in depth.

For the most efficient use of a salt formation, the wastes should be cooled at least 3 years before ultimate disposal as indicated by the rapid decrease of maximum temperatures with increasing cooling times out to about 1000 days.

By comparison with the computer calculations, the analytical solution overestimates the temperature rise for short-cooling times and underestimates for long cooling. This is probably due to the use of exponentials to approximate the fission-product power curve in the analytical solution. A new code has been prepared by Powers which will enable the extention of the computer calculations to long-cooling periods. The introduction from a rough draft of a memorandum on the new code follows:

"A code, designed for monitor runs on the IBM-704 computer, has been written to evaluate the temperatures in a semi-infinite slab with a variable heat source. The physical problem motivating this code is the temperature rise associated with the burial of heat-producing radioactive wastes in salt mines. These salt mines consist of a large number of rooms in a horizontal plane. If radioactive waste is placed in each room, the only direction for heat flow is vertical. Approximately one-half of the heat will flow downward, the other half upward. The semi-infinite slab is the simplest geometry to consider in studying this problem. The purpose of this code is to give answers to the following questions: (1) How much waste can be buried without an excessive temperature rise in the waste and the surrounding salt? (2) Should

the waste be buried shortly after its formation, or should it be stored above ground for a period of time before it is buried? (3) This question concerns itself with the method of disposal of the waste in the mine. It may be placed directly on the floor of the mine so that the heat is generated in a layer of small thickness. Alternatively, the waste may be mixed with the salt; for instance, contained in small holes drilled in the floor so that effectively the heat is generated in a relatively thick layer. The code is formulated so that the temperature is evaluated as a function of time for waste whose age at the time of burial varies. The temperatures may be calculated for any number of depths and for any number of thicknesses of the layer in which heat is generated."

VI. NEW CONCEPTS

Previous experimental studies on disposal in salt have been based on wastes from natural or slightly enriched uranium fuel irradiated to 10,000 Mwd/metric ton at a specific power of 33 Mw/ton, and reprocessed to produce 800 gal of waste per ton.

Recent developments in fuel reprocessing indicate that it is quite feasible to reduce the waste volumes to as little as 60 gal or less per ton; the general trend is in the direction of reduced volumes. After a 3-month decay period, wastes from a 60-gal-per-ton plant would have a heat generation rate (based on the aforementioned irradiation history) of 260 w/gal; and after an 8-year decay, the generation rate would still be 8 w/gal.

The projected thermal capacity of power-generating reactors in the United States by 1970 is 33,000 Mw (20). It is of interest to examine a salt-disposal operation to handle the ultimate storage of waste from a plant processing all fuel from these reactors. This plant would process 3.3 tons of fuel, producing 200 gal of waste per day.

Assume tank storage for 8 years before disposal in salt, after which time the specific power would be 8 w per gal or 1600 w per one-day batch. Assume ambient salt temperature of 70° F, and allow a 125° F rise in waste temperature.

A fairly good idea of what is involved in the storage of these wastes in spheres in salt can be obtained by an examination of the equation for the

steady-state temperature rise of a sphere, containing a well-mixed fluid with a constant heat generation rate, located in an infinite medium:

$$T = \frac{A_o a^2}{3K} \tag{4}$$

where

T = steady-state temperature rise - ^{o}F,

A_o = heat generation rate - Btu/hr-ft^3,

a = radius of sphere - ft,

K = thermal conductivity of medium - Btu/hr-ft-^{o}F.

From the above equation, an equation can be derived for the volume in gallons of a sphere which will achieve a given steady-state temperature rise, T, for a constant heat generation rate of A_g watts per gallon:

$$V_g = 1.265 \left(\frac{TKN}{A_g}\right)^{3/2} \tag{5}$$

where

V_g = volume of sphere - gal,

T = desired temperature rise - ^{o}F,

A_g = heat generation rate of undiluted waste - w/gal,

N = dilution factor (unity for no dilution).

For the case in question, A_g will be 8 w/gal, T will be 125° F, and K will be 2.8 Btu/hr-ft-^{o}F. If no dilution is assumed, the allowable sphere volume will be 366 gal (approximately 4-1/2-ft diam); and with a plant output of 200 gal per day, this amounts to a requirement of sixteen and four-tenths 366-gal spheres per month. If the original waste is diluted by a factor of 10, the allowable sphere volume becomes 11,570 gal (14-1/2-ft

diam); and 5.2 such spheres will be required to hold one month's plant output.

Another approach might be to assume that a batch of waste, say one month's plant output of 6000 gal, will be contained in a single sphere. From Equation 4 can be derived an equation to yield the dilution factor, N, required to limit the temperature rise in a single sphere to a value T:

$$N = 0.625 \left(\frac{A_g}{TK} \right)^3 V_g^{\,2} \qquad (6)$$

where

V_g = the undiluted volume of waste, and all other units are as defined previously.

For the case of interest, A_g is 8 w/gal, T is 125° F, K is 2.8 Btu/hr-ft-°F, and V_g is 6000 gal. The dilution factor, N, is thus 268, and the total volume of the single sphere is 1.6×10^6 gal (74-ft diam).

The above equations assume a constant heat generation rate, and thus overestimate the temperature rise which would occur with actual wastes. However, they also assume isolated spheres which would not be practical in an actual disposal operation, and thus the results should only be regarded as qualitative indications of the effects of waste dilution and aging.

In Table 13 are tabulated some calculations using Equation 5 and wastes from the hypothetical processing plant. It is obvious from this table that it would not be practical to dispose of large batches of short-cooled wastes from this plant in a single sphere by diluting them to the extent required to limit the temperature rise to 125° F. For wastes cooled as long as 8 years, it might be feasible to dilute and contain as much as a one-month

Table 13. Effects of Waste Age and Dilution on Allowable Sphere Size And Number of Cavities Required per Month

Waste Age (years)	Heat Generation Rate (w/gal)	Dilution Factor, N	Volume of Sphere[a] (gal)	Diameter of Sphere (ft)	Number of Spheres/Month
8	8	1	3.7×10^2	4 1/2	16
		10	1.2×10^4	14 1/2	5.2
		10^2	3.7×10^5	45	1.6
		5×10^2	4.1×10^6	101	0.7
3	18	1	1.1×10^2	3	56
		10	3.4×10^3	9 1/2	19
		10^2	1.1×10^5	30	5.6
		10^3	3.4×10^6	95	1.9
		10^4	1.1×10^8	300	0.6
0.25	260	1	2.0	0.8	3000
		10	6.2×10^1	2 1/2	970
		10^2	2.0×10^3	8	300
		10^3	6.2×10^4	25	97
		10^4	2.0×10^6	80	30
		10^5	6.2×10^7	250	9.7
		10^6	2.0×10^9	800	3
		10^7	6.2×10^{10}	2500	1

[a]Sphere which will achieve a steady-state temperature rise of 125° F when filled with a fluid having a constant heat generation rate equal to the value listed in column 2 divided by the dilution factor.

batch in a single sphere (74-ft diam), although it seems likely that the 16 small spheres (4-1/2-ft diam) would be more economical.

It thus appears that for storage of the projected high-specific-activity wastes, numerous closely spaced cavities will be required. In fact, from the standpoint of economics and heat transfer, the best configuration for salt-mine disposal of large quantities of long-cooled, high-level, liquid waste would seem to be a single horizontal layer of waste.

The results of the infinite slab calculation discussed in the section on Thermal Studies can be applied to the case of the disposal of the wastes from the same hypothetical plant assumed for the sphere calculations; namely, 200 gal per day of 8-year-cooled wastes having a heat generation rate of 8 w/gal. According to the curve of Fig. 29, it is found that, in an infinite slab, 228 Btu-ft^2-day^{-1} will produce a 125° F rise. Thus, 575 ft^2 of storage area will be required for one day's plant output. On the basis of current salt-mining practice, approximately 60% of the gross area of a mine would be available for waste storage. Gross area requirements are then 960 ft^2 per day or 8 acres per year. If all rooms and passageways are opened to a height of 7 ft, this would require the removal of an average of 330 tons of salt each day. By comparison, the Carey operation at Hutchinson (a relatively small operation) removes 1000 to 1200 tons a day during the peak season.

Future studies and experiments will be directed toward determining optimum conditions, from the standpoint of heat dissipation, structural integrity, and economics, for a practical mine-disposal operation. In addition, primary emphasis will shift from the disposal of liquids to the disposal of solids.

Previous studies on heat dissipation and structural stability are directly applicable to solids disposal. The chief differences between liquid and solids disposal will be the greater allowable temperature rise and the absence of radiolytic or chemical off-gases with solid waste.

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