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PLOWSHARE GEOTHERMAL
STEAM CHEMISTRY,
INTRODUCTORY STUDIES

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PLOWSHARE GEOTHERMAL STEAM CHEMISTRY,
INTRODUCTORY STUDIES

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PLOWSHARE GEOTHERMAL STEAM CHEMISTRY,
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INTRODUCTION

During May, 1971 Pacific Northwest Laboratories received from Lawrence Radiation Laboratory (LRL) a quantity of granitic rock cored from the chimney area of the Piledriver* underground nuclear detonation. This report describes experimental work conducted during the following June. The Piledriver rock samples were used in a series of tests to determine the potential for water/steam leaching of radioactive and nonradioactive materials from the nuclear blast affected rock. A discussion of the results of these tests within the context of the application of underground nuclear detonations (Plowshare Program) in natural dry geothermal areas for the recovery of heat energy to produce electricity is presented.

The specific goals of the experimental program are:

- to build a system for water and/or steam leaching studies and steam-contaminant transport studies
- to determine suitable analytical techniques for the identification and measurement of concentration of both radioactive and nonradioactive materials leached from nuclear blast affected rock
- to determine the water/steam distribution ratios of chemical elements leached from rock within a temperature range of interest for geothermal steam plant operation.

* The Piledriver project is one of a series of nuclear tests of the Plowshare Program of the Atomic Energy Commission. The Piledriver device was detonated at a Nevada underground test site during June, 1966. The detonation occurred in a granite formation at a depth of about 1500 feet. Post-shot analysis of the nuclear cavity indicated that a 1.3 million cu ft void volume resulted from the 61 ± 10 kiloton explosion.⁽¹⁾

SUMMARY

A two-month exploratory study of Plowshare-geothermal steam chemistry has been completed and the results described. The purpose of the study was a determination of the kinds and concentrations of radioactive and nonradioactive contaminants likely to be brought to the surface by the export steam. An apparatus was constructed for the purpose of contacting with hot water granite samples cored from the region of the Piledriver underground nuclear explosion. Both steam and water phase samples were analyzed for material (elements) leached from the rock. Steam-water distribution rates were calculated for the major radioactive and nonradioactive, leachable species.

For radio-caesium and antimony solubilities are sufficiently high in steam as well as water, that transport could raise operational problems. Low concentrations of europium, cerium, and ruthenium radionuclides were found for the test conditions: 450-650°F, two phase steam water environment. Concentrations in the steam were undetectable. These elements should pose no problems to geothermal steam plants. Silica is the principle constituent dissolved from the rock, representing 80% of the water soluble material. Evidence is presented showing that silica significantly effects distribution ratios of the radionuclides of interest.

Recommendations for further study of these and related topics are presented at the end of the report.

BACKGROUND

Burnham and Stewart^(2,3) have described the application of an underground nuclear detonation (Plowshare Program) in a natural dry geothermal site for subsequent production of geothermal power. The nuclear blast forms a large cavity filled with broken rock from which heat can be removed as high pressure, high temperature steam. It is envisioned that water would be injected through holes drilled into the faulted rock structure associated with the cavity. Steam would be removed from a hole drilled from ground surface to the top of the nuclear blast chimney. The heat energy in the steam would be converted to electrical energy through a steam turbine driven generator. The resulting steam condensate is returned to the blast cavity through the water injection holes.

Natural geothermal power stations rely on the availability of usable natural steam and hot water. Power stations, such as those in Italy, New Zealand, Japan, etc., must function within the limitations of the hydrothermal area. At Wairakei, New Zealand⁽⁴⁾ for example, 40% of the steam used in the turbines is taken from wells (boreholes having an 8 inch diameter and drilled to a depth of 3000 feet) intersecting natural fissures. The pressure range of the steam and hot water is between 180 and 220 psig. The other 60% of usable steam comes from wells located in permeable formations, and the steam pressure ranges from 50 to 85 psig.

Application of the Plowshare-geothermal power concept requires only hot rock and a source of surface or well water. The criteria⁽²⁾ for ideal Plowshare-geothermal siting are:

- rock temperatures of 300° to 500°C at depths of 6,000 to 10,000 feet
- large quantities of water for cooling the steam condenser
- an area remote from large population centers
- an area near major electrical transmission lines.

Geothermal Steam Impurities

The impurity content of steam taken from the nuclear cavity will effect the operation, design and cost of the power plant. Contaminants carried by the steam can be broadly classed as radioactive material, both fission product and induced

activity, and nonradioactive material. Estimates as to the amount of the radioactive material will depend upon yield of the nuclear device, chemical species formed after explosion, activity disposition within the cavity and reaction with the injected water and/or steam phase. The amount of nonradioactive material carried by the steam and deposited on components in the power station will depend on the rock and the steam export line hydraulics. Upper limit estimates can be made from experience with natural wet geothermal power station operations.

Radioactive Material: After detonation of either a fusion or fission nuclear device, a void space is available for the injection of water and the recovery of steam. Radioactivity will be present and distributed throughout the blast cavity. It is generally accepted that the bulk of the radioactivity will be trapped in the fused (melted) rock part of the cavity, and that the radioactive elements expected are those shown in Table I.

The expected distribution of radioactivity in a nuclear blast cavity can be estimated from the results obtained from the Piledriver detonation.⁽¹⁾ The distribution of radioisotopes found is:

- 25% of the Ru-103 and Ru-106 produced was trapped in the fused rock, the balance was volatilized and deposited throughout the cavity
- 12% of the Cs-137 was trapped in the fused rock, and the balance deposited in the cavity
- Sb-125, Pm-147, and W-185 were found in non-melt areas of the cavity
- 95% of the other remaining isotopes were found in the fused rock.

Of the gross amount of radioactivity associated with nonfused rock samples, about 25% could be removed by a water percolation leach test.⁽¹⁾

Krypton-85 and hydrogen-3 (tritium) are also major radioactive species present following a nuclear detonation. While condensable gases will "plate out" in some distribution between fused and fractured rock, Kr-85 and a part of the tritium will remain as noncondensable gases. The amount of noncondensable gas expected can be estimated from the work of Siddons⁽⁵⁾ and also Gasbuggy experience.⁽⁶⁾

TABLE I

POTENTIALLY VOLATILE RADIOACTIVE NUCLIDES PRESENT
180 DAYS AFTER A 1000 KILOTON NUCLEAR EXPLOSION⁽⁷⁾

Nuclide	Half-life	Fission		Fusion (3 kt of Fission)	
		Kilo- curies	MeV/sec	Kilo- curies	MeV/sec
Kr-85	10.7 years	19	1.4×10^{12}	0.057	4.2×10^9
Ru-103	40 days	1150	2.1×10^{16}	3.45	6.3×10^{13}
Ru-106	1 year	1000	3.4×10^{15}	3.0	1.0×10^{13}
Sb-125	2.7 years	60	9.6×10^{14}	0.18	2.9×10^{12}
Te-127m	109 days	90	6.7×10^{11}	0.27	2.0×10^9
Cs-137	30 years	180	3.8×10^{15}	0.54	1.1×10^{13}

Induced activity in soil^a

H-3	12.3 years	220	--	20,290 ^b	--
Na-22	2.6 years	--	--	0.6	4.9×10^{13}
P-32	14.3 days	2	--	2.5	--
S-35	88 days	29	--	40.0	--
Ar-37	35 days	70	--	200	--
Cs-134	2 years	14	7.8×10^{14}	18.3	1.0×10^{15}

^aThe amounts of these activities are derived by a direct linear scaling of amounts produced by 50 kiloton fission and fusion devices calculated by J. Green and R. Lessler. Lawrence Radiation Laboratory, private communication.

^bTo this 290 kilocurie of soil-induced activity has been added the residual tritium from the thermonuclear fuel. Assuming 2 grams of residual tritium per kiloton of fusion yield, this is an additional 20,000 kilocurie.

In the natural steam operation at Wairakei,⁽⁴⁾ noncondensable gases are passed through the turbine and vented from the condenser to the atmosphere. The gases released from the Plowshare-geothermal operation could be handled in much the same manner. However, rather than venting the noncondensable gases to the atmosphere, they would be stored and released at a controlled rate compatible with nuclear safety requirements.

In summary the major gamma activity emitters expected in the steam are:

- Kr-85 present as a permanent gas
- Ru-103 and Ru-106 expected to be highly volatile in an oxidizing atmosphere and essentially nonvolatile under reducing conditions
- Sb-125 expected to be highly volatile
- Cs-134, and Cs-137 of expected low volatility in the presence of CO₂, provided the cesium can be initially tied up in a carbonate matrix. If the atmosphere is oxidizing (forming CsOH), the volatility will be high. If CsCl forms, the volatility will also be high.

Radionuclides have the potential for transfer from the nuclear blast cavity to the steam plant as volatile species, steam soluble species or entrained in water droplets. Presently the only experience on steam soluble nuclide transfer is from the operation of direct cycle nuclear reactors.^(9,10,11,12) Table II shows the ratios of nuclide activity in the reactor water to steam condensate for Borax,^(9,12) EBWR^(9,10) and VBWR.^{(11)*}

The activity distribution ratios cited reflect only limits for radioactivity transfer in the system, provided geothermal steam is at saturation (i.e., a two-phase system). It is interesting to note that cesium and iodine activity observed in a fuel element failure in the BORAX reactor⁽⁹⁾ was not effectively reduced between the reactor and the steam condensate sample point, about 200 feet of steam path. Whether or not this observation can be extrapolated to a geothermal system is a point of conjecture. But, this observation does point out that high cesium transport may be expected in the proposed geothermal experiment.

* These data are also used as reference points in the RESULTS section of this report.

TABLE II

DISTRIBUTION COEFFICIENTS FOR RADIONUCLIDES
BETWEEN STEAM AND WATER

<u>Facility & Date</u>	<u>Temperature, & Pressure</u>	<u>Water Quality</u>	<u>Nuclide</u>	<u>Act. Steam/Act. Water</u>
VBWR 1956	546°F ~1000 psi	pH 7 TDS 1 to 12 ppm	Cr-51	1×10^{-4}
			Mn-54	1.4×10^{-4}
			Co-58	3.3×10^{-4}
			Fe-59	8×10^{-4}
			Na-24	1×10^{-4}
			Na-24 ^(a)	1×10^{-2}
BORAX III 1956	--	Distilled Water	Cs-137 ^(b)	$(0.3 \text{ to } 2) 10^{-5}$
			Cs-137 ^(c)	$(2.4 \text{ to } 4.8) 10^{-5}$
			Na-24	$(0.7 \text{ to } 1.6) 10^{-4}$
BORAX IV 1958	400°F ~ 250 psi	pH 6 to 7	Cs-138 ^(d)	0.1 to 0.8
			Mo-99	not detected
			I-131	0.03
EBWR 1957	489°F ~ 650 psi	pH 7	Na-24 ^(e)	$(3 \text{ to } 6) 10^{-4}$
			Na-24	$(6 \text{ to } 13) 10^{-4}$
			Na-24	0.006 to 0.2

- (a) Water level in the reactor was higher than normal when this data was taken.
- (b) Laboratory test conducted at pressures of 0, 20, and 40 psig and boiling water containing Cs-137 Cl.
- (c) High Pressure laboratory test, 600 psig and steam rates of about 0.72 ft/sec, again using CsCl to monitor activity carryover.
- (d) Fuel element rupture. About 200 feet of steam pipe separates the sample points used in determining the distribution coefficient.
- (e) Activity carryover as a function of percent moisture in steam before and after steam drier. Before drier content ranged from 0.06 to 23%, after drier content ranged from 0.03 to 0.6%.

Nonradioactive Material: Silica and salt content of the steam entering the steam turbines are also important to geothermal steam plant operation. Potential deposition of hard-to-remove solids on the turbine blades from contaminated steam can increase plant maintenance time lowering power generating efficiency.⁽⁸⁾ Conventional steam power stations control the quality of boiler water (see Table III) to maximize the life and efficiency of the power generating steam turbines. Natural geothermal steam power stations, however, have had to design around the water (steam) quality. The Plowshare-geothermal power generation concept will, like natural geothermal power generation, have to live with contaminated steam or provide for a steam cleanup cycle which would reduce the operational thermodynamic efficiency.

TABLE III

<u>Feedwater</u>	<u>WATER SPECIFICATIONS FOR VARIOUS UTILITY</u> <u>POWER PLANTS</u>		
	<u>Once-Through Fossil Fuel⁽¹³⁾</u>	<u>Pressurized Water Reactor⁽¹⁴⁾</u>	<u>Boiling Water Reactor⁽¹⁵⁾</u>
pH	9.3 - 9.6	6.0 - 8.0 (no pH adjust.)	5.5 - 8.5
Cl ⁻ , ppm	<10	0.15 ppm	0.2 max
Silica, ppb	< 5	not specified	<0.1 ppm max (makeup)
TDS, ppb	<25	not specified	not specified
Conductivity micromhos/cm	-	1 max	1 max

The Plowshare-geothermal site requires hot rock, i.e., hot intrusive or plutonic masses, located within several thousand feet of the earth's surface. (See Figure 1 for the kinds of rock formations expected.) Chemical and mineralogical analysis of a granitic formation at the Hoggar test site (a French underground test area in the central Sahara desert) is appended as an example of the rock in which a geothermal cavity might be formed. Also appended is an elemental analysis of a typical granitic rock. The composition of the typical granite is somewhat different from that reported for the Hoggar granite, but appears to be closer to the composition of the Piledriver granite which we used in this investigation as shown in Table IV.

Figure 1 CLASSIFICATION OF ROCK TYPES (Taken in part from L.V. Pirsson, Rock and Rock Minerals, John Wiley and Sons, New York, 1947.)

TABLE IV

COMPOSITION OF GRANITE IN WEIGHT PERCENT

<u>Constituents</u>	<u>Hoggar (a)</u>	<u>Typical(b)</u>	<u>Table IX(c)</u>
SiO ₂	75.8	71	65
Al ₂ O ₃	12.5	14.5	14
K ₂ O	4.8	4.1	-
Na ₂ O	3.8	3.5	1.8
Fe ₂ O ₃	1.3	3.5	2.9
CaO	0.59	2.0	7.0

(a) Values obtained from Appendix A

(b) Values calculated from elemental analysis in Appendix B

(c) Values calculated from elemental analysis of test rock in Table IX, this report.

It should be obvious that the quality of the water and/or steam taken from a nuclear formed cavity may be far from ideal. Some indication of the kinds and amounts of expected contaminants in the geothermal steam can be seen in Table V.

Because the Plowshare-geothermal steam system is to operate at temperatures and pressures well above those presently found in natural geothermal steam areas (Figure 2 shows these parameters in relation to the silica solubility at various temperatures and pressures), direct extrapolation of the quality of the steam from these wet geothermal wells represent only approximations. Also, the technology in recovering ground heat from a nuclear formed cavity is to be expanded significantly above that employed in wet geothermal areas. For example, the Plowshare-geothermal steam recovery hole is expected to be 18 inches in diameter and from one to two miles deep. The deepest holes for natural geothermal steam are about 5000 feet in the Salton Sea, California field,⁽¹⁶⁾ about 4000 feet in the Matsukawa, Japan field⁽¹⁷⁾ and about 3000 feet in the Wairakei, New Zealand field.⁽⁴⁾

Contamination of Geothermal Steam

The high pressure, high temperature Plowshare-geothermal steam is potentially contaminated by volatile materials, by nonvolatile compounds dissolved in entrained moisture droplets and by the solubility of various compounds in saturated steam.

Steam Contamination by Volatile Materials: From the point of view of steam turbine efficiency it is recognized that noncondensable gases are to be avoided

TABLE V
CHEMICAL ANALYSES OF GEOTHERMAL WATERS
FROM SEVERAL SOURCES^(a)

	Hengill, Iceland	Krysuvik, Iceland	Wairakei New Zealand	Waiotapu, New Zealand	Matsukawa, Japan
Maximum Source Temperature, °C	230	230	180-220 psi ≅190-200°C	295	195
Rock Type	Basaltic Lava	Basaltic Lava	Ignimbrites & Pumiceous Breccias	Ignimbrites & Pumiceous Breccias	Dacite Lava Tuff
Total Solids, ppm	913	2030	~5000	~3500	-
Na ⁺	174	500	1285	825	280
K ⁺	10	68	201	122	180
NH ^{++b}	0.1	0.0	0.2	1.0	-
Mg ⁺⁺	0.0	0.5	2.6	3.5	8.7
Ca ⁺⁺	2.8	8.7	12.0	9.0	21.2
H ₃ BO ₃	4.9	9.7	160	85	-
Al ⁺⁺⁺	0.4	0.1	-	-	8.6
Fe ⁺⁺⁺	0.1	0.0	-	-	495
SiO ₂	283	425	602	470	633
Cl ⁻	152	735	2178	1380	9.2
HCO ₃ ^{-b}	24	0	71	145	-
CO ₃ ^{*b}	57	50	35	106	-
SO ₄ ⁼	72	67	34	52	1708.1
Total Sulfide as H ₂ S, ppm	5.2	7.0	2.4	11	10.0 to 52.2
Well Depth	3000 ft max				

^a Except for Matsukawa, Japan analysis^(17,18) the above data was taken from various reports in "Proceedings of the United Nations Conference on New Sources of Energy, Solar Energy, Wind Power, and Geothermal Energy. Rome, August, 1961. Vol 2. Geothermal Energy: I," United Nations, New York. 1964

^b Analyses for total ammonia, total carbon dioxide, and total H₂S will vary according to the method used to separate water from steam. The values determined by chemical analyses are lower than the actual concentrations in the underground water.

Figure 2. TEMPERATURE AND PRESSURE DEPENDENCE OF SILICA CONCENTRATIONS IN STEAM AND STEAM-SATURATED WATER EQUILIBRATED WITH SILICA GEL⁽⁷⁾

to the degree possible. However, low pressure turbine systems used with natural geothermal steam have successfully coped with the problem. The presence of fission gases notably krypton-85 and tritium complicate the problem primarily in that storage or controlled release of the radioactive constituents is required. This problem will be most apparent in the early stages of plant operation. Since transport of radioactive krypton to the well head is foreseeable and methods are at hand for its isolation and storage, this subject will not be further discussed. It is our presumption that uncombined tritium will be oxidized to water and returned to the cavity.

Steam Contamination by Steam Soluble Species: In addition to the contamination of steam by volatile compounds, contamination can occur due to the solubility of various compounds in saturated steam.

In previous investigation by Styrikovich,⁽¹⁹⁾ it has been shown that the relative solubility of an impurity in steam can be described by the equation

$$\ln \frac{C_S}{C_W} = m \ln \frac{\rho_S}{\rho_W} - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

Where

C_S & C_W = the concentrations of the compound in saturated steam and in the boiling water, respectively

m = a constant for a given compound in solution

ρ_S & ρ_W = the densities of the steam and water

R = the universal gas constant

T = temperature of steam and water

ΔH = the difference between heats of solution of the compound in steam and water

ΔS = the difference between the entropy for the compound in steam and in water

Near the critical point, ΔH and ΔS approach zero and equation (1), reduces to the approximation

$$\frac{C_S}{C_W} = \left(\frac{\rho_S}{\rho_W} \right)^m = K_D \quad (2)$$

K_D , the "distribution coefficient," has been found to be a constant, varying with the degree of ionization of the compound in solution. In general, K_D has

been found to be higher for slightly dissociated hydrated oxide molecules, and to be considerably lower for easily ionized compounds.⁽²⁰⁾ We expect that the distribution coefficients will be fairly high for the principle constituents of granite (SiO_2 , Al_2O_3 , etc.) dissolved in the high-temperature water.

Practically all of the previous investigations of the distribution coefficients have been conducted on simple systems, that is a single compound dissolved in pure water. An "apparent distribution coefficient," K_d^i has been obtained from the total concentrations of an element in the steam-condensate (C_S) and water (C_W) phases, without regard to the ionic state of that element, i.e.,

$$K_d^i = \frac{\left[\sum_{i=1}^{\eta} (C_S)_i - K_C \sum_{i=1}^{\eta} (C_W)_i \right]}{\sum_{i=1}^{\eta} (C_W)_i} = \frac{\sum_{i=1}^{\eta} (C_W \cdot K_d)_i}{\sum_{i=1}^{\eta} (C_W)_i} \quad (3)$$

In the above equation subscript i refers to different ionic states of the molecules containing the element of interest, and K_C is the fraction of steam condensate which is due to mechanical entrainment of water droplets.

Under these conditions, K_d^i can be highly dependent on such things as pH and oxygen ion concentration, which influence the relative concentrations of the ionic species containing the element being investigated. However, for a single compound dissolved in pure water, K_d^i has generally been found to exhibit the behavior predicted by equation (2), from near the critical temperature, where $\rho_S/\rho_W \approx 1$, to $\rho_S/\rho_W \approx 10^{-2}$ or 10^{-3} .

Steam Contamination by Water Entrainment: The greater fraction of solids exported to the well-head in natural geothermal steam plants is carried to the surface by hot water. In "steam" wells hot water substantially exceeds in weight the geothermal steam. Without effective phase separation, the mineral content of well-head "steam-water" is substantially the same as that at the source.

In Plowshare-geothermal plants reasonably effective phase separation can be anticipated in the nuclear cavity. With good management of the water inventory, we can expect the amount of radioactive and nonradioactive solids introduced into the base of the steam export pipe to be described by the appropriate steam-water distribution coefficients. Since some degree of adiabatic expansion and cooling

of the export steam can be expected in a mile long steam column, some condensation of steam to water will occur. As a result, redistribution of steam dissolved solids should take place, tending to diminish the concentration of solids dissolved in the steam. If the condensed water drains back into the nuclear cavity, the steam that reaches the surface should be relatively free of solids. If on the other hand, the condensed water is entrained in the rising steam column, the solids content will be essentially that of the steam entrant to the export column. On the assumption that a multi-stage steam-water contacting process occurs, the radioactivity at the well-head should be negligible or at least manageable. If the system approximates to a one stage distillation process, considerable radioactivity and other solids will be brought to the surface and scrubbing techniques will probably be required. As indicated above natural geothermal plants provide little guidance in this matter.

EXPERIMENTAL

With the limited time available to conduct the introductory study on geothermal steam chemistry (approximately two months between receipt of the funding and the end of the fiscal year) quite circumscribed experimental objectives were established. These objectives included: design and construction of a system to determine the steam and water distribution coefficients of rock constituents, development of analytical procedures for trace concentrations of solids in water and methods for sampling steam and water phases equilibrated with Pile-driver rock samples. In the following sections the test apparatus, test material, mode of operation, and analytical methods are described.

Test Apparatus

The system constructed to determine distribution of selected chemical species is shown in a schematic drawing in Figure 3 and in a photograph in Figure 4. It consists of three basic sections, (1) the electrically heated 5 liter Inconel autoclave contained the water, rock samples and a demister for separating water droplets from the exported steam, (2) the constant temperature 3/8 in O.D. Inconel steam riser maintained at a temperature of 3 to 5°C above the autoclave temperature by encasing it with a heating unit and asbestos covering, and (3) the 1/4 in O.D. air cooled Inconel steam condensate leg used for condensing steam and returning it in liquid form to the autoclave.

As shown in Figure 3, provisions were made for necessary monitoring operations including: sampling ports, pressure gauge, and thermocouples for measuring temperature at various points in the apparatus. Both water and steam sampling ports included a water cooled condenser and two regulating valves for a controlled sample withdrawal rate. A water pump was used to replenish the system after each sampling operation. For monitoring pressure, a gauge designed to operate at a maximum pressure of 5000 psi was employed. To ensure safe performance of the system, a rupture disc, designed to operate at a maximum pressure of 3500 psi was placed between the autoclave and the constant temperature steam riser. Eight thermocouples were used for monitoring the temperature of the system. Thermocouple 1 was used to monitor the temperature of the water phase, thermocouple 2 placed just above the water level monitored the temperature of the steam, thermocouples 3 and 4 monitored the temperature of the steam at the bottom and top of the steam riser section, thermocouple 5 monitored the steam condensate temperature

Figure 3. SCHEMATIC OF APPARATUS FOR DISTRIBUTION COEFFICIENT MEASUREMENT

Figure 4. APPARATUS FOR DISTRIBUTION
COEFFICIENT MEASUREMENTS

at the end of the steam condensate leg, thermocouples 6 and 7 monitored the temperature of inlet and outlet air on the steam condenser and thermocouple 8 monitored the wall temperature of the steam riser. A demister device was placed in the autoclave above the boiling water surface to minimize water droplet entrainment in the steam riser section.

Test Material

About 3 kilograms of granitic rock were obtained from Lawrence Radiation Laboratory. The rock samples are small sections of drill core taken from the lower hemisphere portion of the Piledriver cavity. They represent rock from the cracked or crushed zone of the blast area and into the cavity zone proper.

Core sections of both melted (fused) and nonmelted rock were placed in the test vessel in the as-received condition. No attempt was made to wash or clean the rock. No attempt was made to increase the rock surface area by crushing or grinding. Figure 5 shows the individual core samples and Figure 6 shows the core samples in the test section "bucket."

Before testing a representative fragment of the dark, fused rock (similar in appearance to that shown at the top, left corner of Figure 5) and a fragment of nonfused rock (similar to the rock at the top right corner of Figure 5) were counted for the major gamma emitting isotopes fixed on or within the rock. Both fragments showed the presence of the same major isotopes, but, as expected, the fused fragment showed orders of magnitude greater activity than did the non-fused fragment. The following gamma emitting isotopes were found: Co-60, Ru-106, Sb-125, Cs-134, Cs-137, CePr-144, Eu-155, Eu-154, Eu-152.

Operating Procedure

During a test run, the autoclave was filled with 1800 ml of water, sealed and electrically heated to the desired operating temperature. The system was allowed to equilibrate at temperature for 18 hours before sampling. The constant temperature steam riser was turned on two hours before sampling and adjusted to maintain the temperature of thermocouple 8 at 2 to 5°C above that of thermocouple 1. Air flow through the steam return leg was adjusted to assure essentially complete condensation but little or no supercooling of the condensed water. The condensation rate of steam in the steam condensate leg was calculated from the

Figure 5. APPEARANCE OF PILEDRIVER ROCK PRIOR TO AUTOCLAVING

Figure 6. PILEDRIVER ROCK READY FOR AUTOCLAVE EXPOSURE

relationship:

$$\text{Condensation Rate of Steam} = \frac{C_p \Delta T}{\Delta H_v} \cdot \text{air flow ft}^3/\text{min} \quad (4)$$

$$C_p (\text{air}) = 8.21 \text{ cal/ft}^3 \text{ } ^\circ\text{C}$$

ΔT = difference between air temperature, $^\circ\text{C}$, at condenser inlet and outlet

ΔH_v = heat of vaporization of water at given temperature

Observed water condensation rates were 350, 350 and 250 gms $\text{H}_2\text{O}/\text{min}$ at 650°F (343°C), 550°F (288°C) and 450°F (232°C).

The sampling procedure used was the following:

- cold water flow to sample cooler turned on
- #2 valve on sample line closed
- #1 valve on sample line slowly opened
- polyethylene sample bottle placed under sample line and #2 valve adjusted for flow of ~ 10 ml/min
 - Sample 1, 50 ml, marked for discard
 - Samples 2-5, 50 ml each, retained for analysis
- on completion of sampling, valve #2 and then valve #1 were closed and valve #2 reopened to drain sample line

Water samples were always taken before steam samples. Steam and water sampling procedures were essentially the same, except that the water sampling line was disconnected at valve #1 and the cooling line flushed with cleaning solutions to guard against loss of materials through deposition in the line. The flushing sequence for the disconnected sampling system consisted of 20 ml of 20% HCl, 20 ml demineralized water, 20 ml of 20% NH_4OH and 20 ml of demineralized water. Analysis of the flush solutions indicated only minor deposition took place during cooling of the water samples.

The water supply in the autoclave was replenished after both water and steam samples had been obtained. Replenishment was accomplished by pumping a volume of water equivalent to the sampling withdrawals through the water addition valve to the autoclave. When the desired amount of water had been added, system conditions were reestablished and the system allowed to equilibrate at the selected temperature before sampling again.

Methods of Analysis

Analytical methods were required for trace element analysis of water and steam equilibrated with radioactive (very low level) rock samples. Analytical methods appropriate to elements selected for analysis are listed, along with what we consider to be our lower detection limits. The basis of the element selection is the literature data on granitic rock composition listed in Appendix A and the anticipated fission products shown in Table I. Factors which must be considered in selecting the analytical methods include: low concentration of elements of concern in the rock, radioactive decay of short lived and intermediate half life radioisotopes, e.g., $t_{1/2} \approx 6$ months, and finally interference of one element with analytical methods otherwise useful for other constituents.

The distribution coefficients of radionuclides are clearly of major importance in Plowshare-geothermal steam systems. Both direct gamma analysis of radioactive species and of augmented samples (50 ppm spike + neutron activation) were tried.

In the determination of nonradioactive species, modifications of established analytical methods, were employed. Atomic Absorption, Flame Emission Spectroscopy, Emission Spectroscopy and Colorimetric methods of analyses were used. Listed in Table VI are the elements determined, method of analysis and lower detection limits.

Analytical results are reported as simple averages of results obtained from one or more analytical procedures. Development of meaningful confidence levels for analytical data will require more information on reproducibility of both the sampling method and the analytical procedure than we now have.

TABLE VI

ANALYTICAL METHODS FOR DETERMINATION OF ROCK CONSTITUENTS
DISSOLVED IN HIGH TEMPERATURE STEAM AND WATER

<u>Element</u>	<u>Method of Analysis</u>	<u>Detection Limit</u>
Aluminum	Chroazural S (colorimetric) ²¹	3 ppb (10 cm cells)
	Atomic Absorption Spectroscopy	0.3 ppm
	Eriochrome Cyanine R (colorimetric) ²²	10 ppb (1 cm cell)
Antimony	Gamma Spectroscopy	20 ppb to 10 ⁻⁶ ppb*
Boron	Azure C (colorimetric) ²³	20 ppb (1 cm cell)
	Atomic Absorption Spectroscopy	0.5 ppm
Calcium	Flame Spectroscopy	10 ppb
	Atomic Absorption Spectroscopy	10 ppb
Cerium	Gamma Spectroscopy	20 ppb to 10 ⁻⁶ ppb*
Cesium	Gamma Spectroscopy	20 ppb to 10 ⁻⁶ ppb*
Cobalt	Atomic Absorption Spectroscopy	10 ppb
	Activation Analyses	20 ppb to 10 ⁻⁶ ppb*
Copper	Flame Spectroscopy	25 ppb
	Atomic Absorption Spectroscopy	10 ppb
Iron	Flame Spectroscopy	200 ppb
	Atomic Absorption Spectroscopy	25 ppb
	Ferrozine (colorimetric) ²⁴	2 ppb (10 cm cell)
Magnesium	Flame Spectroscopy	100 ppb
	Atomic Absorption Spectroscopy	1 ppb
	Eriochrome Black T (colorimetric) ²⁵	10 ppb (1 cm cell)
Manganese	Flame Spectroscopy	20 ppb
	Atomic Absorption Spectroscopy	1 ppb
Potassium	Flame Spectroscopy	1 ppb
Ruthenium	Gamma Spectroscopy	20 ppb to 10 ⁻⁶ ppb*
Silica	Molybdenum Blue (colorimetric) ²⁶	3 ppb (10 cm cell)
	Atomic Absorption Spectroscopy	0.5 ppm
Sodium	Flame Spectroscopy	0.2 ppb
Strontium	Atomic Absorption Spectroscopy	1 ppb
	Flame Spectroscopy	20 ppb

Determinations were made for all of the above elements. In cases where water samples contained less than 100 ppb of the element, no steam analyses were made, except where gamma spectroscopy techniques were applicable.

* Sensitivity of Gamma Spectroscopy determination varies widely, depending on interferences from other radionuclides present, total gamma signal of sample, activation time, counting time, half life, etc.

RESULTS AND DISCUSSION

System Qualification

From equation 3 it can be seen that the value of K_C , the fraction of steam condensate transferred as mechanically entrained water droplets, fixes the lower bound beyond which K'_d , the apparent distribution coefficient, becomes undeterminable. Therefore, before loading the Piledriver rocks into the autoclave system, we ran an initial series of tests to ensure that K_C was small enough not to interfere with the determination of K'_d . The autoclave was loaded with 10 g Na_2SO_4 , 3.8 g aluminum foil and 2 liters water. Na_2SO_4 was chosen because it is a highly soluble, readily ionized compound with very low values of K'_d ; the aluminum foil rapidly corrodes to relatively soluble forms of hydrated Al_2O_3 and $\text{Al}(\text{OH})_3$, these are not easily ionizable, however, and the values of K'_d are quite large.

In Figure 7, our results are compared with values of K'_d reported by Styrikovich, et al^(27,28). We can conclude that K_C is not larger than 4×10^{-5} at 650°F (343°C), under the final conditions established for operation of the autoclave system. It should be noted that the values of K'_d , measured in this experiment, are considerably different from those reported previously. However, the referenced results were obtained with a single solute system. In a system containing more than one compound, as is the case for our studies, the ionic state may be considerably altered. Under such conditions, K'_d could change by several orders of magnitude, as can be seen by consideration of equation 3. Due to the press of time, we did not pursue this subject further. We did observe that the total concentration of dissolved aluminum in the autoclave was 30 to 100 times higher than the equilibrium concentration in pure water,⁽²⁹⁾ which is presumably related to the presence of Na_2SO_4 in solution.

Water and Steam Leached Contaminants from Piledriver Rock

Figure 8 compares our measured values of K'_d for silica with values obtained from investigations on SiO_2 solubility. Within experimental error, the data obtained at 650°F (343°C) and 550°F (288°C) follow the behavior predicted by equation 2. The value of the slope, m , is only slightly higher than that obtained by other investigations for SiO_2 . The value of K'_d obtained at 450°F

Figure 7. RESULTS OF ENTRAINMENT STUDIES FOR DETERMINATION OF K_c . APPARENT DISTRIBUTION COEFFICIENT VERSUS RATIO OF WATER AND SATURATED STEAM DENSITIES.

Figure 8. COMPARISON OF APPARENT DISTRIBUTION COEFFICIENTS FOR SILICA. APPARENT DISTRIBUTION COEFFICIENT VERSUS RATIO OF WATER AND SATURATED STEAM DENSITIES.

(232°C) does not follow the same relationship; moreover, it is an order of magnitude higher than the maximum value of K_C obtained in our preliminary tests and is therefore probably not associated with water droplet entrainment.

In general the K'_d values obtained on other elements show a greater tendency to deviate from the theoretical relationship of equation 2. Since these deviations are of different orders of magnitude for the various elements, they are not explainable by assuming a higher value of K_C than that which was obtained from our preliminary test and shown in Figure 7.

The chemistry of a mixed oxide-hydroxide system one obtains under our conditions is quite complex, the ionic state of any element in solution being dependent on the ionic states and solubilities of all other compounds in the solution. Based on this hypothesis, and bearing in mind that SiO_2 is relatively soluble and the major constituent of granite, it seems reasonable to assume that the K'_d of silica would be least affected by changes in the ionic state or solubilities of all other constituents, as is observed from our results.

The only known investigation of such a complex system is the work done by Martynova, et al,⁽³⁰⁾ on corrosion products from boiling water reactors. There are several ambiguities, such as whether the water chemistry is truly comparable among the different reactors, which make the different observations difficult to interpret. We can say, however, the results obtained by Martynova, et al,⁽³⁰⁾ display a much more complex behavior than that of equation 2. Figure 9 compares sodium distribution coefficients obtained from our results with those obtained from single compounds and from the mixtures of reactor corrosion products.

Figures 10 and 11 show our results as a function of saturated steam temperature. The data is presented in this manner, rather than that suggested by equation 2 because: the K'_d values for a complex system generally do not obey the theoretical relationship of a single ionic specie, the ultimate use of this data recommends presentation of K'_d values as a function of saturated steam temperature, rather than as a function of $\ln(\rho_W/\rho_S)$ and for this study $\ln(\rho_W/\rho_S)$ is nearly a linear function of temperature.

Preliminary investigations of the leaching of the rock samples at 650°F (343°C) indicated that the radionuclides of prime importance, such as Eu, Ru, Ce, and Co, were not leached from the samples in sufficient quantity to be directly detectable by gamma spectroscopy. Moreover, the radioactive species

Figure 9. COMPARISON OF APPARENT DISTRIBUTION COEFFICIENTS FOR SODIUM IN COMPLEX SYSTEM. APPARENT DISTRIBUTION COEFFICIENT VERSUS RATIO OF WATER AND SATURATED STEAM DENSITIES.

Figure 10. APPARENT DISTRIBUTION COEFFICIENTS FOR CHLORIDE ION AND ALKALI METALS

Figure 11. APPARENT DISTRIBUTION COEFFICIENTS
FOR A1, B, Sb and SiO₂

which did leach, such as Sb and Cs, were present in the water in such minute quantities that they were barely above detection level in the steam samples. It was not clear whether the low concentration of these radionuclides were due to (1) radioactive decay due to sample age (~6 years), (2) a slow leaching process, or (3) the insolubility of compounds containing the radionuclides. If the low concentrations of the radioactive species were due to processes (1) or (2), isotopic dilution followed by neutron activation would make possible the determination of distribution coefficients for the desired radioactive species. Therefore, fifty parts per million (50 ppm) of the elements Cs, Sb, Ru, Co, and Ce were added in the form of oxide or nitrate compounds. In a separate series of runs, 50 ppm Eu was added as the oxide. Separation of the Eu from the other isotopes was required to avoid anticipated counting interferences arising from the complex Eu gamma spectra.

Results obtained from the activation analysis indicated that essentially the same species dominated the solution, i.e., small amounts of Sb, ~2 ppm maximum and Cs, 0.1 ppm maximum. Small amounts of Co were also found in the water and steam phase samples, however, Co was at a concentration level which might be relatable to Inconel or stainless steel corrosion product. Other elements added, Ru, Ce, and Eu were not present in detectable quantities. We conclude, therefore, that the low concentrations of these elements in steam and water is attributable to the low solubility of the chemical compounds in which they are present.

Calculated distribution coefficients are given in Table VII and Figures 10 and 11. As discussed above, distribution coefficients in a simple system are expected to remain concentration and temperature independent near the critical temperature. Due to the complex chemical nature of our system, our results do not follow such a simple relationship. Some species analyzed exhibited an inverse water solubility. This was evident in the case of sodium. The result is not very surprising since it is known that sodium silicate does exhibit an inverse solubility. It is not expected that the results of Figures 10 and 11 can be generally applied to rocks of differing chemistry. Furthermore, it is not expected that all possible troublesome species have been defined. However, it is expected that if rock samples of similar composition were allowed to equilibrate at the temperatures investigated the constituents of major interest will follow a relationship similar to that shown in Figures 10 and 11.

TABLE VII
LIQUID PHASE CONCENTRATION AND APPARENT STEAM-WATER DISTRIBUTION COEFFICIENTS

	650°F (343°C)		550°F (288°C)		450°F (232°C)	
	Concen- tration (L)	Distrib. Coeff.	Concen- tration (L)	Distrib. Coeff.	Concen- tration (L)	Distrib. Coeff.
Silicon (SiO ₂)	1000 ppm	10 ⁻²	800	5 x 10 ⁻⁴	600	5 x 10 ⁻⁴
Sodium	20	3 x 10 ⁻³	50	8 x 10 ⁻⁴	60	9 x 10 ⁻⁴
Potassium	10	4 x 10 ⁻³	20	2 x 10 ⁻³	30	2 x 10 ⁻³
Chloride	12	6 x 10 ⁻²	14	8 x 10 ⁻²	20	4 x 10 ⁻²
Aluminum	5	4 x 10 ⁻²	6	4 x 10 ⁻²	8	8 x 10 ⁻²
Antimony*	2	6 x 10 ⁻³	1	4 x 10 ⁻³	1	10 ⁻³
Boron	1	6 x 10 ⁻¹	0.7	3 x 10 ⁻¹	0.8	2 x 10 ⁻¹
Cesium*	0.08	10 ⁻³	0.1	3 x 10 ⁻⁴	0.1	4 x 10 ⁻⁴
Iron	0.1	-	0.05	-	0.04	-
Cobalt*	0.05	-	0.03	-	0.03	-
Manganese	0.02	-	0.01	-	0.01	-
Calcium	<0.01	-	<0.01	-	<0.01	-
Copper	<0.005	-	<0.005	-	<0.005	-
Strontium	<0.005	-	<0.005	-	<0.005	-
Magnesium	<0.002	-	<0.002	-	<0.002	-
Cerium*	<0.02	-	<0.02	-	<0.02	-
Ruthenium*	<0.02	-	<0.02	-	<0.02	-
Europium*	<0.02	-	<0.02	-	<0.02	-

* Experiment spiked with 50 ppm of specified element as oxide or nitrate

Autoclave Deposit Analysis

Upon conclusion of the rock leaching studies, the autoclave walls were observed to be coated with a hard, flaky material extending above the water level. This material was resistant to concentrated hydrochloric acid, nitric acid, aqua regia, and 50% caustic solution even when heated to ~90°C. The only effective method of dissolving the species was a 3 to 5 hour exposure to 48% hydrofluoric acid solution. To identify this autoclave deposit, chemical and radiochemical analyses were performed. Results are indicated in Table VIII and IX.

TABLE VIII
RADIOCHEMICAL COMPARISON OF AUTOCLAVE DEPOSITS
WITH ROCK AND WATER SAMPLES

<u>Substance</u>	<u>Ratio</u>	
	$\text{Cs}^{137} / \text{Cs}^{134}$	$\text{Sb}^{125} / \text{Cs}^{134}$
Water Sample	2.7	3.6
Rock Sample	1.4	0.53
Autoclave Flakes	2.6	3.0

TABLE IX
FLAKE COMPOSITION COMPARED TO OTHER SAMPLES (Emission Spec)

<u>Element</u>	<u>650°F (343°C) H₂O Sample</u>	<u>650°F (343°C) Steam Sample</u>	<u>Rock</u>	<u>Flakes</u>
Ag	0.0004 ppm	-	-	0.001%
Al	4.8	0.09 ppm	7.4%	2.0
B	1.3	0.7	0.85	1.1
Ca	0.2	<0.02	5	0.5
Cr	0.02	0.002	-	0.02
Cu	0.008	0.0008	0.0005	0.01
Fe	0.1	0.08	2	0.2
Mg	0.008	0.004	0.02	0.005
Mn	20	0.1	1.3	0.42
Sb	1.7	0.009	-	0.2
Si (as SiO ₂)	1000	15	65	90
V	0.08	-	0.02	0.05
Ru	<0.02	<0.02	?	Trace

The results in Table VIII suggest that the formation process for these flakes was primarily one of concentration by evaporation and possibly spattering just above the water level. This is evident from the fact that the radioactive species present had approximately the same elemental ratio as that in the water sample.

CONCLUSIONS

During this study a system was constructed and used to investigate the leaching and steam transport of rock constituents over a temperature range of interest for geothermal steam power plant operation. Suitable techniques have been selected for the analysis of radioactive and nonradioactive materials leached from nuclear blast affected rock and transported in the steam phase. Steam-water distribution ratios of these compounds have been measured at temperatures of 650°F (343°C), 550°F (288°C), and 450°F (232°C).

The results indicate that the chemistry of the rock-water system is quite complex. It appears that both the total solubility of an element and the ratios of the ionic species containing that element may be influenced by solubilities and ionic states of other rock constituents as well as by pH and oxygen ion concentrations. These complex interactions result in apparent steam-water distribution coefficients which, in general, do not follow the linear relationship observed for single solute system. Several radioactive products, such as the isotopes of Eu, Ru, and Ce, were found to have such low solubilities, under the conditions of this investigation, that they should present no problems for future geothermal steam plants. For other isotopes, such as Cs-137 and Sb-125 solubilities are sufficiently high that their transport in geothermal steam could be a problem.

Silica is the principal dissolved constituent of the rock, representing 80% or more of the water soluble material. Of the species studied, silica solubility characteristics are, predictably, most like those observed in simple, one solute systems.

RECOMMENDATION FOR FUTURE WORK

A number of technical questions remain to be resolved concerning the kinds and amounts of impurities which will be brought to the surface with Plowshare geothermal steam. These are in part anticipated problems, but outside the scope of the exploratory studies described here. They also include questions uncovered or at least better defined as a result of our preliminary results. These problem areas are listed below in three categories along with an explanatory sentence or two for each item.

A. Further Investigation of the Steam-Water Leaching Process

- 1) Effects of Higher Temperature. It is highly likely that during the early stages of plant operation the rock temperatures in the blast cavity and surrounding fissured rock zone will provide steam at temperatures considerably above 650°F. Minor modifications in the experimental system will be required to achieve goal operating conditions, 850°F and 3500 psi.
- 2) Effects of Rock Chemistry on Transport Processes. Our results have clearly shown that solubilities in steam and water are modified by the presence of rock constituents. Considerable variation in both chemical and mineralogical compositions occur among the various types of igneous rocks. These differences in composition may effect the ionic state and solubility of transportable species. Initial studies would be directed toward igneous rocks with differing ratios of acid and basic constituents.
- 3) Effects of Oxygen on Steam-Water Solubilities. Control of oxygen ion concentration either through introduction of air or degassing of return water offers a potential means of controlling solubility and transportability of critical elements. We believe this concept should be investigated.
- 4) Better Understanding, Better Predictive Capability for Steam-Water Solubility of Individual Elements in Siliceous Waters. As data is accumulated on the solubilities of various elements under differing

chemical conditions, we expect some of the governing principles effecting solubility to become apparent. On the basis of these principles, predictive capabilities should develop applicable to untested rock chemistries.

- 5) Leaching ^{RATE} ~~Rock~~ Data. Studies to date have been directed to equilibrated systems. It is very much to the point to inquire as to the rates at which rock constituents are leached from rock. Beside the obvious possibility of refreshed autoclave studies at various temperatures, BIIW has very elegant techniques in thin section petrography which could be used to study the effects of leaching on rock structures. These techniques could provide considerable information on the importance of mineralogical as contrasted to chemical composition of the rock as it effects leaching rates.
 - 6) Evolutionary Chemical Processes Within the Heat Extraction Zone. Natural geothermal hot water and steam ^{are} ~~is~~ commonly characterized by the presence of species like CO_2 and H_2S . H_2S , particularly is potentially corrosive to the steam supply system and turbines. There is need to know if reduction of sulfate constituents of igneous rocks to sulfide is likely to occur during prolonged operation of the system.
- B. Engineering Studies Relating to the Steam Export Process
- 1) Theoretical Analysis of the Thermodynamics and Hydraulics of Long Steam Columns. The point has been made at several places in the text of this report that the entrainment of water droplets in steam brought to the surface is likely to be the principal source of both radioactive and nonradioactive contaminants. An engineering study of the behavior of long steam columns is necessary to approximate the degree of the water droplet entrainment problem.
 - 2) Evaluation of Possible Experimental Verification Tests of Steam Column Behavior. Following the theoretical prediction of conditions expected to maintain in the steam column, possible laboratory verification tests will be proposed for review and possibly later implementation.

- 3) Identification of Possible Deposition Processes (of Solids) Within the Steam Column. Deposition of solids at the water line of the steam solubility apparatus has been described. The nature of the deposit and the conditions that produced the deposition need review to determine if significant deposition is likely to occur in the steam export line.
- 4) Application of Steam Scrubbing Processes. If the weight of evidence suggests that significant quantities of solids and radioactive materials will be exported to the wellhead, steam scrubbing techniques may be required to assure safe reliable operation of the steam turbines and ready accessibility to all parts of the system.

C. Modifications to the Present Experimental System

- 1) Apparatus. Operational experience with the present autoclave apparatus has enabled us to identify several modifications which could improve the precision of future measurements and convenience of operation. These modifications include water level control, some modifications to piping and improved thermal isolation of the temperature controlled sections. These changes should be completed before beginning additional studies.
- 2) Sampling and Analysis of Water and Steam for Dissolved Impurities. More experience is required in this area to optimize the sensitivity and reliability of analytical results.

REFERENCES

1. D.D. Rabb, "Particle-Size Distribution Study: Piledriver Event," UCRL-72078, Lawrence Radiation Laboratory, Livermore, California. November, 1969.
2. D.H. Stewart, J.B. Burnham, "Application of Plowshare to Geothermal Power," Atomic Industrial Forum, BWL-SA-2803, December, 1969.
3. D.H. Stewart, J.B. Burnham, "The Economics of Plowshare Geothermal Power," ANS Symposium on Engineering with Nuclear Explosives, CONF 700101 (Vol II), p. 1376, January, 1970.
4. T.G.N. Haldane, H.C.H. Armstead, "The Geothermal Power Development at Wairakei, New Zealand," Proc. Instn. Mech. Engs., 176, No. 23, pp. 603-634. 1962.
5. R.A. Siddons, "Studies of Radioactivity from Nuclear Explosions for Peaceful Purposes," ANS Symposium on Engineering with Nuclear Explosives, CONF-700101 (Vol I), p. 753. January, 1970.
6. C.F. Smith, "Gas Quality Analysis and Evaluation Program for Project Gasbuggy," Ibid. p. 775.
7. D.H. Stewart, J.B. Burnham, unpublished data. 1971.
8. F.G. Straub, "Steam Turbine Blade Deposits," University of Illinois Bulletin 43, No. 59, Eng. Exp. Station Bulletin Series No. 364. 1946.
9. J.M. Harrer, et al., "Performance Evaluation of Direct Cycle Boiling Water Nuclear Power Plants Based on Recent EBWR and BORAX Data," Paper 2379, 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1958.
10. G.K. Whitham and R.R. Smith, "Water Chemistry in a Direct Cycle Boiling Water Reactor," Paper 946, 2nd International Conference on the Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1958.
11. F.J. Brutschy, et al., "Vallecitos Boiling Water Reactor--Coolant Technology," Ind. and Eng. Chem., 51, p. 1262. 1959.
12. A.J. Shor, et al., "Radioactive Carryover from BORAX-III and Test Systems," Nuc. Sci. and Eng., 2, p. 126, 1957.
13. J.V. White, G.J. Crits, "Producing Low Chloride Effluent with Low Regenerant Waste Volumes by Condensate Mixed-Bed Polishers in Nuclear Cycles," Proc. American Power Conference, Vol 32, p. 772, 1970.
14. RDT Standard, Coolant Composition in PWR's, Draft, February, 1970.
15. RDT Standard, Coolant Composition in BWR's, Draft, November, 1970.
16. D.E. White, E.T. Anderson, D.K. Grubbs, "Geothermal Brine Well: Mile Deep Drill Hole May Tap Ore-Bearing Magmatic Water and Rocks Undergoing Metamorphism," Science, Vol. 139, p. 919. 1963.

17. Takaki, Sin-uhio, Tavaka, Sin-ichi, "Electrical Logging and Temperature Surveys at Matsakawa Geothermal Wells," Japan Geo. Survey Bulletin Vol. 19, No. 8, pp. 507-518. 1969 Geophysical Abstracts, 271-303. August, 1969.
18. H. Yoshida, J. Hoashi, M. Miyazaki, "Corrosion Control in Geothermal Steam Turbines," Proc. of the American Power Conference, Vol. 30. pp. 905-973. 1968.
19. M.A. Styrikovich, O.I. Martynova, I.S. Kurtova, "The Behavior of Feedwater Impurities in the Circuits of Supercritical Units," Thermal Engineering, 13, p. 45. 1966.
20. M.A. Styrikovich, "Investigation of the Solubility of Low Volatility Substances in High Pressure Steam by Radioisotopes," Radioisotopes in Scientific Research, Vol. 1, p. 411. Pergamon Press, New York, NY.
21. P. Pakalns, "Spectrophotometric Determination of Aluminum with Chrome Azurol S," Analytica Chimica Acta, Vol. 32, pp. 57-63. 1965.
22. J.C. Langford, Flamephotometer and Colorimetric Procedures, BNWL-CC-849. Pacific Northwest Laboratory, Richland, Washington, September, 1966.
23. L. Pasztor and J.D. Bode, "Thionin Derivatives in the Extraction and Direct Photometric Determination of Boron," Analytica Chimica Acta, Vol. 24, pp. 467-473. 1961.
24. L.L. Stookey, "Ferozine--A New Spectrophotometric Reagent for Iron," Analytical Chemistry, Vol. 42, No. 7, pp. 779-781. 1970.
25. A.E. Harvey, J.M. Komarmy, and G.M. Wyatt, "Colorimetric Determination of Magnesium with Eriochrome Black T," Analytical Chemistry, Vol. 25, No. 3, pp. 498-500. 1963.
26. O.A. Kenyon and H.A. Berwick, "Photometric Determination of Silica in Alkalies," Analytical Chemistry, Vol. 25, No. 1, pp. 145-148. 1953.
27. M.A. Styrokovich, O.I. Martynova, "Contamination of the Steam in Boiling Reactors from Solution of Water Impurities," Sov. At. Energy, 15, 3, 917, 1963.
28. M.A. Styrikovich, O.I. Martynova, K. Ya Katkovskayas, I. Ya. Dubrovskii, E.I. Mingulina, "A Study of Aluminum Hydroxide Between Water and Saturated Steam," Atomnaya Energiya, 15, p. 161, 1963.
29. R.L. Dillon, "Dissolution of Aluminum Oxide as a Regulatory Factor in Aqueous Aluminum Corrosion," HW-61089, Hanford Laboratories, August 31, 1959.
30. O.I. Martynova, A.E. Nazaron, Yu. V. Chechetkin, E.K. Yakshin, I.G. Kobzar, "Radioactivity of the Coolant in the VK50 Boiling Reactor," Atomnaya Energiya, 23, p. 305. 1967.

APPENDIX A

APPENDIX A

COMPOSITION OF THE GRANITE OF THE
HOGGAR TEST SITE*

Chemical Analyses

SiO ₂	75.80	CaO	0.59
Al ₂ O ₃	12.49	Na ₂ O	3.80
Fe ₂ O ₃	1.30	K ₂ O	4.79
MnO	0.04	Li ₂ O	0.08
MgO	0.03	P ₂ O ₅	0.01

Mineralogical Analyses

Quartz	35
Microcline	37
Plagioclase	25
Biotite	2.1
Muscovite	0.6

* Jean Faure, "Study of the Mineralogical Transformations of Granite by Underground Nuclear Explosions," Symposium on Engineering with Nuclear Explosives, CONF-700101 (Vol II), p. 1407. 1970.

APPENDIX B

APPENDIX E

TYPICAL GRANITE COMPOSITION ASSUMED*
(Averages)

Li	10 ppm	Zn	60 ppm	Sm	9.3 ppm
Be	5 ppm	Ga	20 ppm	Eu	1.1 ppm
C	300 ppm	Ge	1.4 ppm	Gd	6.0 ppm
N	20 ppm	As	1.5 ppm	Tb	2.5 ppm
O	48%	Se	0.05 ppm	Dy	2.8 ppm
Na	2.6%	Br	1.7 ppm	Ho	2 ppm
Mg	0.5%	Rb	200 ppm	Er	4 ppm
Al	7.7%	Sr	300 ppm	Tm	0
Si	33%	Y	34 ppm	Yb	4 ppm
P	800 ppm	Zr	200 ppm	Lu	1 ppm
S	120 ppm	Nb	20 ppm	Hf	1 ppm
F	220 ppm	Mo	1 ppm	Ta	3.5 ppm
K	3.4%	Ag	0.4 ppm	W	1.5 ppm
Ca	1.4%	Cd	0.14 ppm	Re	0.00067 ppm
Sc	3 ppm	In	0.26 ppm	Ir	0.006 ppm
Ti	0.23%	Sn	45 ppm	Au	0.01 ppm
V	17 ppm	Sb	0.26 ppm	Hg	0.08 ppm
Cr	15 ppm	Te	0.001 ppm	Tl	1.5 ppm
Mn	900 ppm	Cs	5 ppm	Pb	20 ppm
Fe	2.4%	Ba	830 ppm	Bi	0.01 ppm
Co	6 ppm	La	60 ppm	U	3.5 ppm
Ni	8 ppm	Ce	100 ppm	Th	(not given)
Cu	1%	Nd	54 ppm	B	<10 ppm

* D.D. Rabb, LRL, Personal Communication

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