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CORROSION AND SCALING BY STEAM IN NUCLEAR GEOTHERMAL POWERPLANTS*

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ABSTRACT

The quality of steam produced in a nuclear geothermal well will significantly affect the design, operation, efficiency, and expense of a steam-turbine powerplant. Problem areas related to steam quality are: the carrying and deposition of minerals (scaling) by steam, the carrying of radioactive contaminants by steam, the amount and types of noncondensible gases, and the corrosion of alloys.

Minerals carried by steam are usually salts (such as NaCl, NaOH, or sodium silicates) and silica. Deposition of minerals in the piping or turbine can reduce flow, give inefficient turbine operation, or cause material damage to the turbine. The salt deposits are water soluble and can be washed away as an operational procedure. Silica, however, poses serious problems because of its insolubility. The maximum permissible concentration of silica in steam is about 0.05 ppm, in order to reduce silica deposition to a negligible level. If temperatures of 620°K and steam pressures of 80 atm were to be used, the silica content of steam would be about 9 ppm, i.e., more than 2 orders of magnitude higher than the maximum

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permitted concentration. It is clear that such impure steam would need to be purified, either by scrubbing with water or by some other means, before introducing it into the turbine.

Radioactive contaminants from fusion or fission explosives that may be volatile after 180 days are given as the fission products: $\underline{^{85}\mathrm{Kr}}$, $\underline{^{103}\mathrm{Ru}}$, $^{106}\mathrm{Ru}$, $\underline{^{106}\mathrm{Rh}}$, $\underline{^{125}\mathrm{Sb}}$, $\underline{^{127m}\mathrm{Te}}$, and $\underline{^{137}\mathrm{Cs}}$; and induced activities: $^{3}\mathrm{H}$, $\underline{^{22}\mathrm{Na}}$, $^{32}\mathrm{P}$, $^{35}\mathrm{S}$, $^{37}\mathrm{Ar}$, and $\underline{^{134}\mathrm{Cs}}$. Significant gamma emitters are underlined. For 1 Mt of yield, the amount of gamma radiation for the above species is 3.0×10^{16} MeV/sec for all-fission explosives, and 1.1×10^{15} MeV/sec for fusion explosives with 3 kt of fission. Fusion explosives also produce a high level of beta activity in the form of tritium.

A thermodynamic model is used to roughly assess the volatilities of the main gamma emitters in steam. The approach used is to estimate the composition and amounts of volatile rock components and radioactivity retained in the steam when the major portion of the melted rock has cooled and separated from the steam phase. The radionuclide $^{85}\mathrm{Kr}$ is, of course, a permanent gas while $^{125}\mathrm{Sb}$ and $^{127m}\mathrm{Te}$ are also expected to have high volatilities. For $^{103}\mathrm{Ru}$ and $^{106}\mathrm{Ru}$, high volatilities are expected under oxidizing conditions with low volatilities expected under reducing conditions. The radionuclides $^{134}\mathrm{Cs}$ and $^{137}\mathrm{Cs}$ are believed to be significantly volatile, with their actual volatilities affected by the chloride and carbonate content of the rock formation. Radioactive impurities carried by steam are likely to coprecipitate with salts and silica in the turbine system, if the steam quality is poor.

Noncondensible gases present in geothermal steam lead to three problems: (1) enhanced corrosion to alloys; (2) increased pumping costs to maintain turbine efficiency; and (3) possible enhancement of carrying of minerals in steam. The noncondensible gas content of geothermal steam ranges from 0.01 to 5 wt%, with more typical values of 0.1 to 1 wt%. The gas CO_2 represents about 70 to 90% of the noncondensible gas. Next in importance are H_2S and H_2, with lesser amounts of CH_4, NH_3, and N_2.

Limited information is available on the corrosion resistance of common alloys and other materials to geothermal water and steam. Tests have been performed on alloy coupons with water at 320 to 510°K and steam at 370 to 470°K for periods up to 150 days. The alloys most resistant to corrosion are titanium, austenitic stainless steels, and chromium-plated steels. Corrosion of alloys can occur from the presence of NH_3, H_2S, CO_2, and especially chlorides in steam. Also, corrosion is generally enhanced by the presence of oxygen.

INTRODUCTION

The purity of the steam produced in a nuclear chimney or surrounding fractured region will have a major effect on the design, cost, and operation of a Plowshare geothermal plant. Both the quantity and the type of contaminants carried up by the steam may affect the well life, the turbine-condenser design, the operating efficiency of the plant, and even the safety requirements.

For calculational purposes the total yield of nuclear explosives used in a well is assumed to be either 1 Mt of fission or 1 Mt of fusion including 3 kt of fission. The well is assumed to be put into operation 180 days after detonation and to produce steam at approximately 623°K and 80 atm pressure in the chimney. The corresponding well-head pressure would be about 50 atm.

The steam quality problems can be divided into three areas.

- Mineral content of the steam
- Radioactive content of the steam
- Noncondensible gas content of the steam and the related corrosion problems.

MINERAL CONTENT OF STEAM

Scaling of Turbines

A number of minerals are known to form volatile gaseous species by reacting with steam and are, thereby, transported by steam. The main interest in previous work on mineral transport by steam has been to obtain a better understanding of hydrothermal phenomena; also, considerable interest has been shown in the scaling processes of steam-turbine blades. Experimental information in these two areas, especially on scaling of steam-turbine blades, is useful in interpreting and predicting the steam transport behavior of minerals in geothermal applications. The information is applicable not only in interpreting the scaling behavior of turbine blades but also in predicting the mineral transport behavior in the underground well. Transport of radioactive species and their relationship to mineral transport are discussed in the next section.

The potential problems that result from mineral deposition on the pipes, steam-turbine, and in the condenser of a nuclear geothermal powerplant may be extremely important. Straub[1] has shown that the deposition of salts and silica (and hence associated radioactivity) on turbine blades is dependent on the impurities in steam and on the steam pressure. Salt deposits on steam-turbine blades are water soluble and, with proper operational procedures, can be washed off with water. The most important of these salts are NaCl, NaOH, sodium silicates, Na_2CO_3 and sometimes Na_2SO_4. Deposits that are insoluble in water are most commonly silicic acid, amorphous silica, and the various crystalline forms of silica. Deposits of iron oxides and $CaCO_3$ that are insoluble in water may also occur.

The water insoluble deposits, in particular the various forms of silica, present the most serious problems. The deposits can lead to distortion of turbine blade configurations and hence lower the turbine efficiency. More seriously, they can lead to imbalance of the turbine and vibrations that will cause material damage to the turbine. It may be possible to wash off the water insoluble deposits with NaOH solutions, if the rate of deposition is not high. The operation is time-consuming, however, and requires considerable care to avoid damage to the turbine.

To reduce silica deposits to a negligible level for a nuclear geothermal application, the maximum permissible silica concentration in steam with 80 atm of steam pressure at the turbine inlet is about 0.05 ppm.[1] In agreement with this, Styrikovich[2] concludes that the total dissolved solid content (salts plus silica) of steam used in normal turbine operations should not exceed 0.05 to 0.2 ppm. Steam of such purity is difficult to achieve, even in the best boiler systems.

Silica-Steam System

An estimate of the silica concentration in steam for geothermal applications may be obtained from Heitmann's work,[3] in which silica gel, silicic acid, or quartz were equilibrated with high-pressure steam. Results on silica gel are presented as smoothed data in Fig. 1. Silica gel and the various silicic acids will interconvert, depending on temperature and steam-pressure conditions. Hence, no distinction has been made among them in the figure. Quartz shows a lower solubility in water than does silica gel by a factor ranging from 10 at 370°K to 2 at 600°K. In steam, volatilized silica concentrations are lower for quartz than for silica gel, but the differences are usually small. The maximum difference amounts to a factor of 2 at about 600°K and 30 to 50 atm of steam pressure. From Fig. 1, the silica concentration in steam is found to be 9 ppm at 623°K and 80 atm of steam pressure. Therefore, it is estimated to be in the range of 5 to 9 ppm for the underground nuclear cavity condition, since either quartz or the more active forms of silica may be present. It becomes apparent that the silica content of the 80-atm steam from the underground cavity is too high by about 2 orders of magnitude for normal turbine operations and that severe deposition will occur on the turbine blades if the steam is fed directly into the turbine. The situation is further complicated by the presence of radioactivity in the steam, since species such as ^{125}Sb, ^{137}Cs, and ^{134}Cs may coprecipitate on the turbine blades with the silica and various salts.

Natural steam fields operate with "dirty" steam but at lower temperatures and pressures, as shown in Fig. 1, so that scaling is only a marginal problem. The turbine cycles are correspondingly less efficient, but this inefficiency is counterbalanced by the low cost of natural steam.

Scrubbing of Steam

If geothermal steam from a nuclear cavity is to be used directly in turbine operations at high pressures, it is likely that it will need purification to prevent inefficient turbine operation and excessive radioactive buildup. A method of purification suggested by Straub[1] is to scrub the steam with high-purity water before passing it through the turbine. Unfortunately, such a process cools the steam, degrades its energy, and lowers the efficiency. Also, after scrubbing, the steam is at its saturation point and, if used in the turbine, could lead to erosion of the turbine blades by impinging water droplets. Consequently, the steam would need to be reheated.

The effectiveness of such scrubbing treatments may be evaluated from Styrikovich's data on distribution ratios of various "solute" materials in saturated steam and in water.[2] In Table 1, the distribution ratios representing concentrations of silica in steam compared to those in water (C_{st}/C_w) are given for several temperatures. Also given are: the concentrations of silica in steam, assuming equilibrium with condensed phase silica in the nuclear cavity (from Fig. 1), and the predicted silica content of the steam after scrubbing.

From Table 1, it may be concluded that scrubbing is a feasible method of purifying steam up to temperatures in the vicinity of 569 to 585°K, corresponding to saturation pressures of 80 to 100 atm. Styrikovich also gives distribution ratios for NaCl, NaOH, and a variety of other salts and hydroxides. The C_{st}/C_w ratio is about 10^{-4} or less for these compounds; therefore the various salts and hydroxides should be removed even more effectively by scrubbing than is SiO_2. By preventing the formation of deposits on the turbine, any radioactive materials that are not removed by the scrub water will end up in the condensate of the turbine discharge, and not accumulate in the turbine.

Other alternatives warrant consideration. A solid phase scrubber such as limestone might prove effective in removing silica. Another solution is to add a heat exchanger in which water would be boiled and the steam from the nuclear chimney condensed. While this additional equipment would decrease the thermal efficiency of the process, it would concentrate the scaling and radioactivity. The economic trade-off in using this approach lies in the ability to use more conventional equipment in the rest of the plant. If scaling in the heat exchangers proves severe, either two heat exchangers could be provided, or chemical or mechanical descalers could be added.

If the steam is cleaned, the contaminants will be present in the scrubbing systems. The disposal of radioactivity and contaminants present in the scrubbing system could possibly be carried out by reinjection into the nuclear chimney if a fluid scrubbing system is used.

RADIOACTIVE CONTENT OF STEAM

Volatile Radioactive Species

Levy[4] gives the radioactive contaminants that might be volatile in steam after 180 days from either fission or fusion nuclear explosives. The fission products are $\underline{^{85}\mathrm{Kr}}$, $\underline{^{103}\mathrm{Ru}}$, $^{106}\mathrm{Ru}$, $\underline{^{106}\mathrm{Rh}}$, $\underline{^{125}\mathrm{Sb}}$, $\underline{^{127m}\mathrm{Te}}$, and $\underline{^{137}\mathrm{Cs}}$; the induced activities are $^{3}\mathrm{H}$, $\underline{^{22}\mathrm{Na}}$, $^{32}\mathrm{P}$, $^{35}\mathrm{S}$, $^{37}\mathrm{Ar}$, and $\underline{^{134}\mathrm{Cs}}$. (Significant gamma emitters are underlined.) For 1 Mt of yield, the amount of gamma radiation after 180 days for these is 3.0×10^{16} MeV/sec for an all-fission device and 1.1×10^{15} MeV/sec for a fusion device having 3 kt of fission (see Table 2). Although the fusion device shows a lower level of gamma radiation for volatile species, it has a very high level of beta activity in the form of tritium.

It should be noted that the induced activities indicated in Table 2 are for an explosive without neutron shielding. Calculations show a factor of about 10 reduction in soil activation for every 15 cm of boric-acid neutron shielding.[5] The induced activities also depend on soil composition (calculations in Table 2 are for Hardhat granite) and details of the explosive design.

Noncondensible gases (including radioactive species) that are present in the steam will be separated in the condenser. In natural steam fields, noncondensible gases are exhausted from the condenser and vented to the atmosphere. For the Plowshare geothermal application, the gases could be collected and radioactive contaminants, such as ^{85}Kr, ^{37}Ar, and ^{3}H, separated or concentrated and then stored underground. Low levels of volatile chemical and radioactive contaminants could be vented to the atmosphere.

Fusion explosives, if used, would result in several orders of magnitude less krypton but much more argon. They would also produce much more tritium. Once the tritium has exchanged with the hydrogen in the water or steam it would be most difficult to remove, and adequate measures to ensure its safe containment would be needed.

A Thermodynamic Model of Radioactive Transport

Actual volatilities of the various gamma-emitting species, estimated with a thermodynamic model, can be used to either qualitatively or semiquantitatively estimate the gamma activity of the steam, since the assumption of complete volatility of these species appears to be unnecessarily extreme. To apply thermodynamic calculations to the problem, certain assumptions need to be made about processes and reactions occurring during formation of the explosion cavity. At short times after the nuclear event, virtually all of the vaporized rock and explosive materials will have condensed (except for steam and permanent gases) to form a molten glass. Refractory radioactive species and some portion of the more volatile radioactive species will be in this glass. The glass will form both as droplets within the cavity and as a surface layer on the walls and will tend to settle into the bottom of the cavity to form a puddle of glass. This puddle glass will cool at a rapid rate at first, because of convective and radiative losses, but the rate will slow down as the temperature drops. A significant decrease in the cooling rate is expected if minerals begin to crystallize out. The crystallization range for a typical basalt at 80 atm steam pressure is from about 1350 to 1500°K and for a typical granite from 1200 to 1400°K. Whether or not crystallization occurs, the viscosities of silicate melts in these temperature regimes are very high, and thus limit the extent of the rates of gas-liquid interactions. From these considerations, it seem appropriate to assume that the late-time condensation, which is critical to the disposition of volatile radioactivity, occurs at temperatures below about 1500°K.

A number of factors are expected to contribute to variations in the amount and composition of the late-time condensate. Perhaps the most important factor is the time of chimney collapse. With an early collapse, the melt would be quenched at high temperature and the cavity would release steam containing a high proportion of moderately volatile rock components (and also the moderately and highly volatile radionuclides) into the chimney. With late collapse, and consequently lower melt temperatures, a greater amount of the moderately volatile rock constituents and radionuclides would remain in the melt phase.

Other factors such as steam pressure, oxidizing or reducing conditions, and amount of nuclear yield are expected to affect the amount of late-time condensation.

An estimate of the amount of late-time condensate may be made based on 80 atm steam pressure* and 1500°K as the conditions during separation from the melt region. The last of the vaporized rock constituents to condense in the presence of steam would be residual amounts of the alkali metals and silica. (See earlier section on Mineral Content of Steam.) The principal alkali vapor species are believed to be NaOH(g) and KOH(g) under the above conditions.** The condensed forms are probably carbonates and silicates that can be assumed, for purposes of thermodynamic calculations, to be $Na_2Si_2O_5$, Na_2SiO_3, K_2CO_3, $K_2Si_4O_9$, and $K_2Si_2O_5$. The compound Na_2CO_3 is not stable under the conditions considered here. Whether an alkali condenses as a carbonate or reacts with a rock to form a silicate will depend upon the partial pressure of CO_2 in the gas and upon kinetic factors. Condensed NaOH and KOH will not form because of their high vapor pressures under these conditions. Based on available thermodynamic data,[6-8] and assuming a steam pressure of approximately 80 atm, the gaseous alkali hydroxide vapor pressure is calculated to be approximately 10^{-3} atm at 1500°K. The vapor pressure of volatile silicon hydroxide species under these

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*The steam pressure in the cavity will depend upon the amount of water in the rock and the depth of the explosion. A steam pressure of 80 atm at a cavity temperature of 1500°K is obtained if it is assumed that the rock contains either 3 wt% water at 0.5 km depth or 1 wt% at 3 km and that 1.2×10^9 kg of rock lose water per Mt of yield. The corresponding cavity void volumes are estimated at 3×10^6 m^3/Mt and 1×10^6 m^3/Mt.

**Alkali chlorides are also believed to be very volatile, especially in the presence of steam. Data are not available, however, on volatilities of these chlorides in rock melts at the low chlorine concentrations (~ 100 ppm) typically found in igneous rocks.

conditions exceeds 10^{-3} atm[9] so that direct gas-phase reactions can also lead to silicate formation. Thus, either gas-surface reactions or gas-gas reactions can occur, which will lead to late-time condensation of alkali silicates and carbonates at temperatures of about 1500°K or less.

Assuming that the vapor phase contains a total of 10^{-3} atm of alkali hydroxide molecules such as NaOH(g) and KOH(g), in a volume of 10^6 m^3 means that about 2×10^4 g-atoms of alkali will condense at temperatures below about 1500°K. This rough estimate of late-time condensate can be compared in Table 3 with the amounts of potentially available volatile gamma emitters from 1 Mt of all-fission explosives. It is apparent that the concentrations of radionuclides are low compared to the total amount of late-time condensate. All of the potentially volatile species listed in Table 3, with the exception of permanent gases, are proposed to be associated with the late-time condensation of alkali silicates and carbonates. It is further assumed that this condensation occurs over a time scale of minutes. Because of the late-time nature of this condensate, it will probably extend into the chimney region and coat rock surfaces.

Powerplant Operation

Some predictions can be made of the volatilities of the gamma emitters listed in Table 3 under powerplant conditions. The steam produced in the nuclear chimney is assumed to be at 80 atm and 623°K.

Volatilities of NaCl, KCl, and NaOH in steam under the conditions of interest were studied by Spillner[10]; volatilities of NaCl and NaOH were studied by Straub.[1] Results of the studies have been examined by Elliott.[11] The results of

Straub and Spillner are reasonably consistent for NaCl, and KCl appears to have an identical volatility. At 80 atm steam pressure and 623°K, the alkali halide partial pressures in steam are approximately 1×10^{-4} atm above the pure halide salts. For pure liquid NaOH, Spillner found the partial pressure of gaseous alkali hydroxide to be about 1×10^{-3} atm under these steam conditions. Straub worked only with water solutions of NaOH but noted that the NaOH volatilities in steam were higher than for identical concentrations of NaCl in water. Elliott showed that the gaseous species accounting for the volatilities of alkali halides and hydroxides under these conditions are very complex. He tentatively proposed species such as $NaCl \cdot 7H_2O(g)$ and $NaOH \cdot 7H_2O(g)$. Although a positive identification of these species has not been made, they are useful in showing the marked dependence (~ 7th power) of alkali halide and hydroxide volatilities on steam pressure. Such complex species would not be expected to be important at much higher temperatures as, for example, at 1500°K, where simpler molecules such as NaCl(g) or NaOH(g) would be expected to predominate.

In the nuclear chimney, alkali hydroxides are not stable as condensed phases, although alkali halides may be. If alkali halides are present as pure phases, they would contribute about 1×10^{-4} atm partial pressure to the steam. Any gaseous alkali hydroxides that are transported into the chimney as part of the late-time condensate are predicted to form either condensed silicates or carbonates. They would thus have a lower NaOH activity than the pure NaOH studied by Spillner.

The thermochemical NaOH activity in the rock can be estimated by comparing the calculated vapor pressure of NaOH(g) from a reaction such as,

$$Na_2SiO_3(\text{glass}) + \frac{1}{2} H_2O(g) = \frac{1}{2} Na_2Si_2O_5(\text{glass}) + NaOH(g),$$

with the NaOH(g) vapor pressure over pure NaOH(l). The activity of NaOH(l) is thus found to be 1.3×10^{-2}. Applying this factor to Spillner's value for the volatility of pure NaOH in steam gives a value of about 10^{-5} atm for the sodium volatility in steam above the sodium silicates.

It does not seem fruitful at this time to pursue a more complete consideration of the possible volatility reactions that can occur. The alkali metals will all be assumed to have about the same volatilities, either as hydrated halide or hydroxide species, with a partial pressure of 10^{-5} to 10^{-4} atm at 80 atm steam pressure and 623°K.

It should be noted that the alkali partial pressure at a constant 80 atm stream pressure decreases by only about a factor of 10 to 100 in going from 1500 to 623°K. This means that about 2.5 to 25% of the alkali still remains in the gaseous state after cooling from 1500 to 623°K, if concentrations are calculated according to the ideal gas law. There is quite a change in the types of gaseous species at the two temperatures. Whereas at 1500°K species such as NaOH(g) are important, at 623°K species such as $NaOH \cdot 7H_2O(g)$ are believed to be important.

The radioactive cesium, as a first approximation, may be expected to form an ideal mixture with the principal alkali metal constituents either in the gas phase or in late-time condensate. Thus, as much as 25% of the radioactive cesium may be present in the gaseous state in a nuclear chimney at 80 atm steam pressure and 623°K. Any other radioactive alkali species, such as ^{22}Na, should behave in a similar manner.

Some complicating factors need to be considered. First, it is recognized that ^{137}Cs has volatile precursors that exist during part, if not all, of the early condensation period. Known precursors are ^{137}I with a 24-sec half life, ^{138}I with a 6-sec half life, and ^{137}Xe with a 3.9-min half life. A more realistic explanation of the disposition of the ^{137}Cs might be to assume that a portion of the ^{137}I and ^{138}I isotopes become entrapped in the alkali silicate or carbonate matrix during the early stages of late-time condensation, but that most of the material migrates further up the chimney to convert to ^{137}Xe and finally condenses as it converts to ^{137}Cs. Thus, the final condensate will be further from the puddle region and more highly enriched in ^{137}Cs relative to the alkali matrix. In the region in which the ^{137}Cs is enriched in the condensate, it will tend to form a carbonate rather than a silicate. Although thermodynamic data are not available on cesium silicates, the thermodynamic stabilities of alkali carbonates are known to increase relative to the silicates as the atomic number of the alkali increases.[6,8] In the carbonate form, the cesium volatility will be lowered by about 2 to 3 orders of magnitude relative to the silicate for p_{H_2O}/p_{CO_2} ratios in the range of 1 to 1000.

As steam is extracted from the chimney, the radioactive alkali content of the steam should vary qualitatively as follows. Initially, the radioactive content of the steam will be high, probably not as high as expected on the basis of ideal mixing, but rather of the order of 1% of the total radioactive alkali. During the initial extraction, the ^{137}Cs would be expected to be proportionately lower in steam (compared to ^{134}Cs and ^{22}Na) than its abundance would indicate, as a consequence of carbonate formation. As steam flow progresses, the ^{134}Cs and ^{22}Na, which are expected to be present as silicates, should volatilize first, leading to a gradual decline in the total radioactive alkali content of the steam and an enrichment of the proportion of ^{137}Cs in the gaseous radioactive alkali. At late times, the main species should be ^{137}Cs, which would originate from decomposition of a carbonate phase.

In the cases of ^{103}Ru and ^{106}Ru, the volatile species in the presence of steam are not known, so a calculation cannot be made. Radiochemical observations do indicate the presence of these isotopes in the chimney region in some nuclear events, although the behavior is erratic. The radionuclide ^{103}Ru has 62-sec half-life ^{103}Mo and 50-sec half-life ^{103}Tc as precursors, while ^{106}Ru has 37-sec half-life ^{106}Tc as its precursor. Molybdenum is known to be volatile in steam as $MoO_2(OH)_2(g)$ under oxidizing conditions, and it may be speculated that technetium is volatile as $TcO_3(OH)(g)$ by analogy with rhenium.[12] Ruthenium might also be expected to form volatile species such as $RuO_2(OH)_2(g)$. According to calculations based on estimated data given by Jackson,[12] the lower oxygen-content species, $RuOH(g)$ and $Ru(OH)_2(g)$, are unimportant. Also, experience by Blasewitz and Mendel[13] at Battelle-Northwest in calcining of nitrate solutions of radioactive wastes shows that ruthenium volatility increases as a function of hydrogen ion concentration. Their results can also be interpreted as indicating that the ruthenium volatility is a function of oxygen partial pressure since the HNO_3 present in the acid solutions would decompose to produce oxygen during calcining.

Qualitatively, it may be speculated that under neutral conditions, where the oxygen partial pressure is determined only by the dissociation of steam, species such as $MoO_2(OH)_2(g)$, $TcO_3(OH)(g)$, and $RuO_2(OH)_2(g)$ are probably volatile at 1500°K. If significant amounts of hydrogen are produced by the explosion, the volatilities of these species will drop. At 623°K and 80 atm of steam pressure, it is anticipated that the volatilities of ^{103}Ru and ^{106}Ru will be very low under reducing conditions and probably low under neutral conditions, but may be high under oxidizing conditions.

The precursors for ^{125}Sb are 9.4-day half-life ^{125}Sn and 9.7-min half-life ^{125m}Sn. Tin and antimony undoubtedly have volatile hydroxides, but their molecular species and thermodynamic data are not presently known. The radionuclide ^{127m}Te has 2.1-hr half-life ^{127}Sn and 93-hr half-life ^{127}Sb as its precursors. Tellurium is believed to form $TeO(OH)_2(g)$, which is quite volatile.[12] Fortunately, ^{127m}Te is much less important than the other fission products considered.

The order-of-magnitude nature of the volatility calculations used here should be emphasized. The primary objective has been to make reasonable estimates of the concentration of volatile gamma-emitting species in the steam. As experimental information becomes available, these conclusions may change. The radionuclides ^{137}Cs and ^{125}Sb may be less volatile than anticipated, or at least less available in the chimney region for volatilization to occur. Other activities that have been considered refractory here may actually be more significant. It is clear that these complex chemical interactions must be studied in the laboratory and the field before they can be defined accurately.

NONCONDENSIBLE GASES IN STEAM

Chemical Analyses of Geothermal Fluids

To evaluate the corrosion behavior of geothermal steam, an assessment must be made of the impurities present in the rocks and source waters of the wells. It may then be possible to derive some conclusions concerning the condensible and noncondensible impurities picked up by the steam and the chemical effects of these impurities on the steam-turbine system. Much of the information on corrosion and scaling is, of necessity, based on experience with natural geothermal wells. Caution needs to be exercised in extrapolating this information to the nuclear case because different steam conditions and geology may prevail for the nuclear wells.

Chemical analyses of geothermal well waters from Iceland and New Zealand and surface waters from Chile are shown in Table 4. Geothermal steam analyses from several sources are shown in Table 5. Except for the Showa-shinzan Volcano,[14] analyses were taken from various reports in the 1961 Proceedings of the United Nations Conference on New Sources of Energy.[15-20] A number of minor constituents have not been included in the tables. The rock types represented are primarily igneous in origin.

In Table 4, analyses for solutes that can form gaseous products are not representative of the actual solute concentrations in the underground well waters because of losses incurred during separation of the geothermal waters from steam. During the separation, volatile solutes tend to concentrate in the steam phase, whereas nonvolatile solutes tend to concentrate in the water. As an example, the actual CO_2 content of Wairakei, New Zealand, well waters is about 200 to 600 ppm in the underground condition, and for Waiotapu, New Zealand, it is about 800 to 2500 ppm,[18] as compared with the much lower values for HCO_3^- and $CO_3^=$ listed in Table 4.

Corrosion of Materials

Tables 4 and 5 show that substances known to cause corrosion are present in significant amounts. Similar substances may be anticipated for the nuclear case.

Whether or not corrosion and scaling reactions actually occur will depend on the specific conditions in each case. Chlorides, NH_3, CO_2, and H_2S are known to be corrosive to metals in certain instances. Steam and hot water are corrosive to all silicate materials such as grouting in pipe joints, reinforced concrete pipes or tanks, and silicate filter beds. All such materials should either be avoided or protected with suitable coatings. Scaling (or deposition) may occur in pipes, turbines, or condensers as a consequence of volatile impurities in the steam such as the chlorides, hydroxides, carbonates, sulfates, and silicates of the alkalies, calcium carbonate, and silica. Noncondensible impurities in the steam such as CO_2, H_2S, H_2, and CH_3, may not necessarily be corrosive, but will need to be exhausted from the turbine discharge in order to have an efficient turbine operation.

A limited amount of information is available on the corrosion resistance of common alloys and other materials to geothermal fluids.[19,21,22] The alloys most resistant to corrosion are found to be titanium, austenitic stainless steels, and chromium-plated steels. Epoxy resins are found to be resistant to corrosion at temperatures up to 373°K. Tests have been performed on alloy coupons with water at 323 to 513°K and with steam at 373 to 473°K for periods up to 150 days.

Although a wide variety of corrosion mechanisms has been identified, the most serious in alloys is probably stress corrosion. It is known that stress corrosion can be induced by trace amounts of either chlorides or sulfides and can lead to formation of fissures and fractures in a variety of alloys that are used in the construction of turbines. A minimum concentration and temperature requirement for chloride stress corrosion is believed to be 5 ppm of chlorides at 323°K. The presence of oxygen accelerates the rate of stress corrosion.

There is no limiting stress below which cracking will not occur. Sulfide-induced stress cracking can occur in the presence of H_2S at temperatures up to at least 463°K. The gas, H_2S, also causes a phenomenon known as hydrogen infusion, which can lead to the embrittlement, blistering, and fracture of stainless steels.

Other corrosion mechanisms that should be mentioned are chemical corrosion and mechanical erosion. Chemical corrosion can occur from the presence of NH_3, H_2S, CO_2, and chlorides in geothermal steam. In special circumstances, such as in early experiences at The Geysers, mercury may also be present as a corrosive agent. Generally, the corrosive action of these chemicals is enhanced by the presence of air. Chemical corrosion has been minimized or avoided in most natural geothermal powerplants by the proper selection of alloys and by avoiding aeration. At the higher steam pressures and temperatures proposed for the nuclear application, however, chemical corrosion may be a more serious problem.

The problem of mechanical erosion is encountered when wet steam at high velocities impinges on the turbine blades. Such impingement can lead to a combined corrosion-erosion process that can seriously damage the turbine blades. A certain amount of success has been achieved in erosion resistance through the use of 13 Cr-stainless steel alloys.

The experiences gained on corrosion and scaling in natural geothermal powerplants make it apparent that similar problems are likely to be encountered in the nuclear case. These problems can be explored more fully by performing exposure tests on alloy coupons in geothermal steam and water under the proposed nuclear-application conditions. It is important in such tests that the compositions of the steam and the water be representative of the particular geothermal formation. Steam taken directly from a nuclear well would be most desirable or, lacking an actual well, it may be possible to infer the impurities to be expected in the steam from analyses of core samples from the formation. It seems likely, as has been the case for natural geothermal wells,[18,20,21] that suitable alloys and other construction materials for turbine systems can be found through such screening tests.

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TABLE 1. Distribution ratios for silica between steam and water and silica contents of nuclear cavity steam before and after scrubbing.

	Steam temperature, °K			
	524	569	585	623
Saturation pressure, atm	40	80	100	163
C_{st}/C_w ratio	1.0×10^{-3}	5×10^{-3}	9×10^{-3}	5×10^{-2}
SiO_2 in cavity steam, ppm	1.7	7	12	50
SiO_2 in scrubbed steam, ppm	0.0017	0.035	0.11	2.5

TABLE 2. Potentially volatile radioactive nuclides present 180 days after a 1-Mt nuclear explosion.

Nuclide	Half-life	Fission		Fusion (3-kt fission)	
		kCi	MeV/sec	kCi	MeV/sec
Fission products					
^{85}Kr	10.7 y	19	1.41×10^{12}	0.057	4.2×10^{9}
^{103}Ru	40 d	1150	2.1×10^{16}	3.45	6.3×10^{13}
^{106}Ru	1 y	1000	3.37×10^{15}	3.0	1×10^{13}
^{125}Sb	2.7 y	60	9.6×10^{14}	0.18	2.9×10^{12}
^{127m}Te	109 d	90	6.7×10^{11}	0.27	2.0×10^{9}
^{137}Cs	30 y	180	3.8×10^{15}	0.54	1.14×10^{13}
Induced activity in soil[a]					
^{3}H	12.3 y	220	—	20,290[b]	—
^{22}Na	2.6 y	—	—	0.6	4.9×10^{13}
^{32}P	14.3 d	2	—	2.5	—
^{35}S	88 d	29	—	40.0	—
^{37}Ar	35 d	70	—	200	—
^{134}Cs	2 y	14	7.8×10^{14}	18.3	1.0×10^{15}

[a] The amounts of these activities are derived from direct linear scaling of amounts produced by 50-kt fission and fusion devices as calculated by J. Green and R. Lessler (Lawrence Livermore Laboratory private communication to H. B. Levy,[4] 1970).

[b] To the 290 kCi of soil-induced activity has been added the residual tritium from the thermonuclear fuel. Assuming 2 g of residual tritium per kt of fusion yield, this is an additional 20,000 kCi.[5]

TABLE 3. Relative volatilities in steam after 180 days of potentially volatile gamma emitters produced by a 1-Mt fission explosion in igneous rock.

Nuclide	Nuclide, g-atoms	Volatility in steam, 80 atm at 623°K
^{85}Kr	0.57	Permanent gas
^{103}Ru	0.35	Oxidizing - high Reducing - low
^{106}Ru (^{106}Rh)	2.8	Oxidizing - high Reducing - low
^{125}Sb	0.45	Probably high
^{127m}Te	0.075	High
^{137}Cs	15.1	Initially high, declining with time, CO_2 decreases volatility, Cl^- increases volatility
^{134}Cs	0.08	Similar to ^{137}Cs

TABLE 4. Chemical analyses of geothermal waters from several sources.

	Hengill, Iceland	Krysuvik, Iceland	Wairakei, New Zealand	Waiotapu, New Zealand	Tatio, Chile	Reykjavik, Iceland
Maximum source temperature (°K)	503	503	538	568	313 to 363[a]	361[a]
Rock type	Basaltic lava	Basaltic lava	Ignimbrites and pumiceous breccias	Ignimbrites and pumiceous breccias	Volcanic origin	Volcanic origin
Total solids (ppm)	913	2030	~5000	~3500	—	285
Na^+	174	500	1285	825	—	159
K^+	10	68	201	122	—	1.4
NH_4^+[b]	0.1	0.0	0.2	1.0	—	0.0
Mg^{++}	0.0	0.5	2.6	3.5	—	0.3
Ca^{++}	2.8	8.7	12	9	7-28	1.9
H_3BO_3	4.9	9.7	160	85	60-1050	0.3
Al^{+++}	0.4	0.1	—	—	3-19	0.1
Fe^{+++}	0.1	0.0	—	—	3-27	0.0
SiO_2	283	425	602	470	11-36	126
Cl^-	152	735	2178	1380	—	30
HCO_3^-[b]	24	0	71	145	—	—
$CO_3^=$[b]	57	50	35	106	—	43
$SO_4^=$	72	67	34	52	—	17
Total sulfide as H_2S[b] (ppm)	5.2	7.0	2.4	11	—	0.2

[a] Surface waters.

[b] Analyses for total ammonia, carbon dioxide, and H_2S 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.

TABLE 5. Chemical analyses of noncondensible gases in geothermal steam.

	Hengill, Iceland	Hveragerdi, Iceland	Krysuvik, Iceland	Wairakei, New Zealand	Waiotapu, New Zealand	Larderello, Italy (1870)	Larderello, Italy (1960)	The Geysers, California	Showa-shinzan Volcano, Japan	Showa-shinzan Volcano, Japan
Maximum source temperature (°K)	503	503	503	538	568	—	518	~478	—	—
Well-head temperature (°K)	~433	~433	~433	~468	—	—	~463	448	467	601
Noncondensible gas content of total discharge (wt%)	0.3	0.1	1.3	0.01 to 0.5	0.07 to 0.2	—	4.5	0.7	0.6	2.2
CO_2 (mole %)	84.6	78.5	83.9	93.0	90.0	90.5	92.4	69.3	69.4	84.9
H_2 (mole %)	2.1	1.1	5.4	0.8	1.5	2.0	1.4	12.7	12.4	6.6
H_2S (mole %)	4.9	17.2	9.6	3.8	7.8	4.2	2.5	3.0	3.9	1.0
CH_4 (mole %)	0.0	—	0.1	0.8	0.3	1.4	1.0	11.8	0.1	0.1
NH_3 (mole %)	—	—	—	~0.2	~0.2	—	1.7	1.6	0.0	0.0
N_2 (mole %)	—	—	—	1.4	0.2	1.9	0.6	1.6	9.1	5.2
Residuals (mole %)	8.4[a]	3.2[a]	1.0[a]	—	—	—	0.4[b]	—	5.1[c]	2.2[c]

[a] Includes N_2.

[b] Primarily H_3BO_3.

[c] Primarily HCl, with lesser amounts of HF and SO_2.

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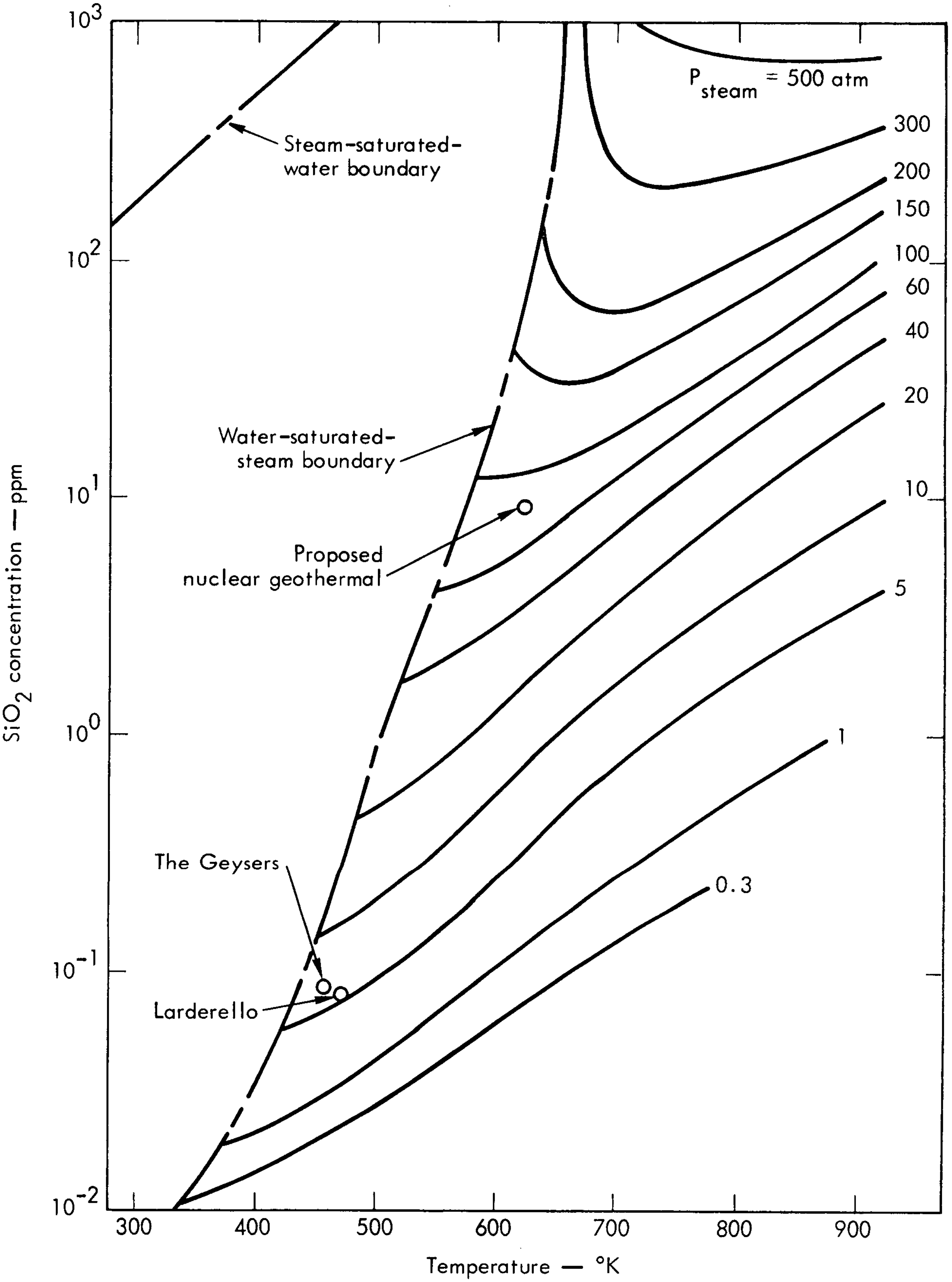
FIGURE CAPTIONS

Fig. 1. Temperature and pressure dependence of silica concentrations in steam and steam-saturated water equilibrated with silica gel.



Krikorian - Fig. 1

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