

**Post-Closure Silica Transport in the Proposed High Level Radioactive Waste  
Repository at Yucca Mountain, Nevada**

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Thesis submitted to the Faculty of  
Virginia Polytechnic Institute and State University  
in Partial fulfillment of the requirement of the degree of

MASTER OF SCIENCE

In

Geology

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Defended on May 5th, 1997  
Blacksburg, Virginia

POST-CLOSURE SILICA TRANSPORT IN THE PROPOSED HIGH LEVEL  
RADIOACTIVE WASTE REPOSITORY AT YUCCA MOUNTAIN, NEVADA

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(ABSTRACT)

The United States plans to bury high level radioactive waste from commercial power reactors and from nuclear weapons manufacturing in Yucca Mountain, Nevada. Yucca Mountain, located about 80 miles northwest of Las Vegas, consists of horizontally bedded tuff deposits. Although the region is very arid, enough water exists in the tuffs to create a vapor dominated geothermal system as the pore water evaporates, circulates and recondenses. This study examines how silica leaching might occur as a result of water-tuff interactions in Yucca Mountain after the emplacement of heat-producing nuclear waste canisters. A vertical thermal gradient experiment (VTGE) was designed and built in order to simulate the water cycling scenario where water in the tuff is vaporized by the heat from the canisters, moves to cooler regions along fractures and condenses as a liquid which flows downward toward the hot canisters. This experiment was used to measure the rate of silica leaching from Yucca Mountain tuff at various heat fluxes. The results show that under the experimental conditions silica is leached from the tuff sample very effectively (about  $1.85 \times 10^{-8}$  g per Joule of heat transferred). With such a rate, significant amount of amorphous silica (135 kg per canister for the first 1,000 years after emplacement) could be leached, transported and deposited above the repository horizon; the resulting low permeability zone might change the geological and hydrological properties of the host rock. A significant amount of colloidal silica was formed in the solution soon after the water recycling began. Such colloidal silica could adsorb and transport radionuclides released from breached waste canisters more efficiently than that

when radionuclides act alone. The results indicate that silica leaching is a potential problem for the current designs of the Yucca Mountain repository.

## Acknowledgments

I would like to express my gratitude and appreciation to my major advisor, Dr. Donald Rimstidt for his help, guidance, encouragement and endurance throughout this study. Without him, his solid previous experience with the topic and his excellent scientific instincts, this research and this paper would have not been able to be accomplished at all. I would say that Dr. Rimstidt not only guided me through science, but as well taught me culture, society and everything else about America. I also would like to thank Dr. James Craig and Dr. Lucian Zelazny for their review of this manuscript and helpful comments.

This project was supported by oversight federal funds included by Congress in Department of Energy's budget granted (pursuant to provisions of Public Law 97-425) to the State of Nevada Agency for Nuclear Projects/Nuclear Waste Project Office and Nye County's Nuclear Waste Repository Project Office (Tonopah, Nevada). We thank Geosciences Management Institute, Inc., especially Dr. Don L. Shettel, Jr., for the help in obtaining samples and for administering this grant. We thank them all for letting us doing such an exciting project.

Finally I would like to say "thank you" to my wife, Jing. Without her, I would have achieved nothing.

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## TABLE OF NOTATION

$A_v$	void area of fractures
$m$	concentration of silica, molal
$M_{H_2O}$	mass of water in the flask, kg
$R_h$	heat generation rate, watts
$r_i$	silica leach rate, mol/kg sec
$t$	time, sec
$t'$	time, hour
$T$	temperature, °C
$T_{SiO_2}$	silica transport factor, g/J
$W_{SiO_2}$	molecular weight of $SiO_2$ , 60.08 g/mole



## INTRODUCTION

The United States is currently assessing the feasibility of storing high-level radioactive wastes in a mined repository in the tuffs under Yucca Mountain, Nevada, which is about 80 miles northwest of Las Vegas. High-level nuclear waste is currently in the form of spent fuel rods from commercial power plants and liquid waste from nuclear weapons manufacturing. The fuel rods will be stored in metal canisters with no further processing, and the radionuclides from the liquid waste will be incorporated into glass before it is stored in metal canisters. Current plans call for up to 70,000 metric tons of high-level radioactive waste to be shipped to the proposed Yucca Mountain repository where it must be safely stored for at least 10,000 years (U.S. NRC, 1983; U.S. EPA 1985; Campbell & Cranwell, 1988; U. S. DOE, 1992).

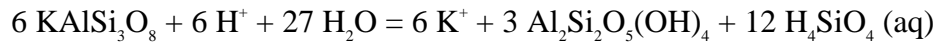
Yucca Mountain is a six-mile long, 1200-foot high, flat-topped volcanic ridge, underlain by a sequence of silicic volcanic rocks, consisting mainly of tuffs (Scott & Bonk, 1984). Several frequently cited characteristics which are potentially favorable for choosing this site are the low population of the area, low average annual precipitation (10.6 inch per year) and its relatively deep water table. The water table in the area is about 540 meters below the earth's surface. The very dry desert conditions have produced this deep unsaturated zone that makes it possible to put a repository about 300 meters underground and yet about 240 meters above the water table (U. S. DOE, 1992).

A major concern is that radionuclides from the nuclear waste could escape from the proposed repository into the groundwater or into the atmosphere, in a way that might expose significant segments of surrounding population. Storing high-level radioactive waste under low-humidity conditions is a particular advantage because liquid water greatly accelerates the corrosion rate of the storage canisters and because liquid water can dissolve and transport radionuclides that might escape from the canisters. Unfortunately the unsaturated zone under Yucca Mountain is not devoid of liquid water; unsaturated simply means that the pore spaces are not 100% filled with liquid. Even in this desert

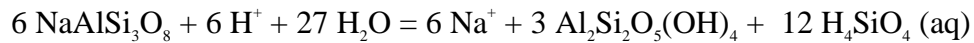
area, there is an average of 10.6 inches of precipitation each year and some of that water infiltrates the surface of Yucca Mountain and migrates downward through its fractured interior to the water table. This water does not migrate as a continuous phase but instead as films on the interior of pores and fractures. It is also held in the smaller pores by capillary effects. Previous studies have documented that in some cases up to 80% of the void spaces of the Yucca Mountain tuffs contained liquid water (Pruess & Wang, 1987, Pruess et al., 1990). In addition, there is a considerable quantity of zeolite (clinoptilolite) in the tuff at Yucca Mountain that could evolve a substantial volume of water upon heating (Carey & Bish, 1996). If canisters of high-level radioactive waste are placed in such a partly saturated tuff, the thermal energy produced by the canisters will evaporate the liquid water in the surrounding rock so that it will dry out. This dry region will extend from the canister surface out to around the 100°C isotherm in the thermal field surrounding the canisters, but as air containing this water vapor moves into cooler regions beyond the 100°C isotherm, much of the water will condense to produce a zone where the void spaces might contain high percentages of liquid water. Due to altitude of the proposed repository at Yucca Mountain, the boiling point of pure water would occur around 95 °C. However, build up of salts in the liquid phase could raise the boiling temperature above 100°C. If this liquid flows back towards the hot zone under the influence of gravity, it would evaporate again and the vapor would expand and recondense in a repetitive cycle. Over the designed lifetime of the repository (10,000 years), this refluxing cycle might dissolve and transport large quantities of silica from the rocks overlying the repository zone. As the solution evaporates, silica will precipitate near the 100°C isotherm where it will fill the pore and fracture spaces, forming a silica cap above the repository. This process could significantly alter the geological and hydrological properties of the surrounding rock. A complete quantitative understanding of this process is vital to the development of a safe repository design. No engineering design of the Yucca Mountain Project can make a convincing case for long term geological and hydrological stability if it fails to consider this scenario.

The purpose of this study was to assess the effectiveness of water reflux process in mobilizing silica. The very high mobility of silica in geothermal and hydrothermal

systems is well known (Rimstidt and Cole, 1983; Saunders, 1990; Herrington and Wilkinson, 1993). The Yucca Mountain tuffs, whose mineralogy is described in Scott & Bonk(1984), contains significant amounts of feldspar. While aqueous silica comes from dissolving glass and silica minerals such as cristobalite, a significant amount will likely be released by accelerated weathering reactions such as:



or



The hydrogen ions needed to drive these reactions can come from the dissolution of  $\text{CO}_2$  from the air in the pore spaces and the subsequent hydrolysis of  $\text{H}_2\text{CO}_3$ . The leaching of Yucca Mountain tuffs via these and other reactions is documented by Rimstidt et al. 1991.

This paper describes a specially designed experiment to simulate the water reflux process and its coupling to silica leaching and transport. The goal was to determine how fast the silica might be leached and how much silica might be deposited during the lifetime of the proposed repository. The mathematical model to predict the amount of silica deposited above the repository is the first quantitative estimate dealing with this specific problem.

## METHODS

### Experimental Design

A vertical thermal gradient experiment (VTGE, FIG. 1) was designed and constructed in order to simulate the situation that might occur in the Yucca Mountain after the emplacement of heat-producing waste canisters. The device has three parts: a steam-generating unit, a sample chamber and a water-condensing unit. The steam is generated in a two-neck 1000 mL Erlenmeyer flask heated by a power-controllable electrical heater. Steam moves upwards into the sample chamber through a connection between sample chamber and the flask which is made of 1.7 cm-diameter (internal) PVC pipe with several Inconel alloy screens in it. The screens prevent sample grains from falling down into the flask while allowing liquid water and steam to flow freely. A sample of crushed tuff is placed in the sample chamber so that steam moving upward through the sample either condenses directly on the tuff or enters the condenser at the top of the device. In the condenser the steam changes into liquid and the condensate flows downward because of gravity back through the sample chamber where it leaches the sample. The steam flux is controlled by an adjustable power controller which directly controls the power of the heating device. A correlation between the reading of the power controller and the actual heat generation rate was established (Appendix I) in order to estimate heat generation rate of each experiment more accurately. By sampling the solution in the flask (through the second neck of the flask using a syringe), the concentration of dissolved silica is monitored.

The sample chamber was filled with 150 g crushed Yucca Mountain tuff (5 - 10 mesh). The flask contained 500 g of distilled deionized water. Experiments were carried out for heat generation rates of 29 watts, 58 watts and 93 watts. (Details about measuring water flux and heat generation rate in VTGE are given in Appendix I). Samples were taken from the flask at intervals, filtered through Gelman™ 0.20 µm, 3 cm diameter nylon acrodisc syringe filters, and analyzed for pH and dissolved silica. The formation of

colloidal material was detected by Tyndall effect and the colloid itself was analyzed under SEM. The dissolved silica concentration was determined by the molybdate yellow procedure (Appendix II, Govett, 1954).

### *Preparation of Tuff Samples*

Tuff samples used in the leaching experiments were collected from outcrops of the nonlithophysal zone of the Topopah Springs Member of the Paintbrush tuff on the surface of Yucca Mountain (see Scott & Bonk, 1984, for a lithologic description). They were crushed to the size of 5 - 10 mesh. All of the samples were rinsed with distilled water to remove fine particles clinging to the surface of the samples. The specific surface area of the grains was estimated to be  $4.50 \times 10^4 \text{ m}^2/\text{g}$ , assuming each sample grain has the same shape and dimension of 4 mm x 1 mm x 1 mm, and one gram of sample has 90 grains. The  $\text{N}_2$  BET surface area of the sample was measured as  $1.81 \text{ m}^2/\text{g}$ . This relatively high specific surface area arises from internal voids in the grains.

### **Data Analysis Procedures**

The rate of silica accumulation in the boiling flask was estimated using the initial rate method. This was necessary because as the silica concentration in the boiling flask increased, some was removed from solution by adsorption onto aluminum and iron oxyhydroxide colloids and eventually by the condensation of silica colloids. As a result, the rate of dissolved Si increase at the beginning of the experiment gave the best estimate of the rate of Si release from the tuff. The silica concentration versus time data were fit to an equation of the form

$$m = a + bt + ct^2$$

and the derivative of this equation

$$dm/dt = b + 2ct$$

was evaluated at  $t = 0$  where the initial reaction rate for silica leaching is  $r_i = dm/dt = b$ . For example, the original ppm-hour data for the 4th experiment is listed in Appendix III. The unit of ppm then was converted to molal, which is moles/kg. The relationship

between silica concentration in the flask and time for that run is illustrated in FIG. 2. The regression equation fitting data points of 4th experiment is:

$$m = - 5.46 \times 10^{-7} + 2.72 \times 10^{-8} t - 3.00 \times 10^{-14} t^2$$

The derivative of the above equation,

$$r = 2.72 \times 10^{-8} - 3.00 \times 10^{-14} t$$

gives the reaction rate of silica leaching in molal/sec. At  $t = 0$ , the initial rate of this reaction is  $r_i = 2.72 \times 10^{-8}$  mol/kg sec.

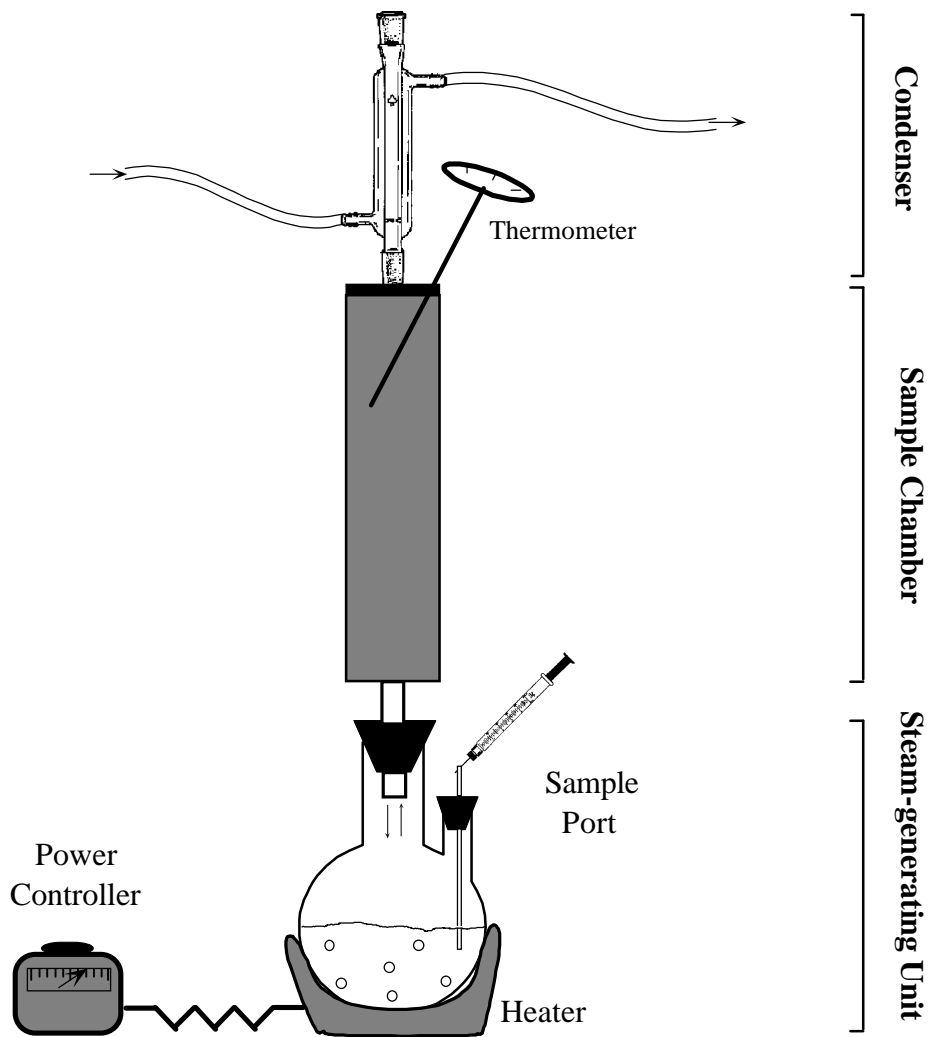


FIG. 1. Apparatus used to simulate water refluxing in Yucca Mountain

## RESULTS

The monomeric (molybdate reactive) silica concentration in the boiling flask as a function of time for five runs is shown in FIG. 2 and the silica leaching rates ( $r_i$ ) in the unit of “mol/kg sec” calculated for each experiment are listed in TABLE 1. Each  $r_i$  corresponds to a specific heat generation rate ( $R_H$ ) which was measured (Appendix I) in the unit of watts. We used these data to find the amount of silica transported per Joule of heat passed through the experiment, which is expressed as  $T_{SiO_2}$ :

$$T_{SiO_2} = \frac{r_i \cdot W_{SiO_2} \cdot M_{H_2O}}{R_H}$$

The silica transport factor,  $T_{SiO_2}$  in units of gram/Joule, describes the amount of silica transported when 1 Joule of heat passes through the experiment. TABLE 1 indicates that  $T_{SiO_2}$  is independent of  $R_H$  for the range of heat flows considered in these experiments and it has a value of approximately  $1.85 \times 10^{-8}$  g of  $SiO_2$  transported per Joule of heat cycled through the experiment.

During the experiments, the pH of the solution changed from about 6.5 at the beginning to about 9.5 at the end. This increase in pH resulted from the consumption of  $H^+$  by mineral hydrolysis reactions. After the silica concentration exceeded the amorphous saturation which is 372 ppm at 100 °C, the silica determinations became much less precise because of variable amounts of colloidal silica that passed through the filter.

In subsequent modeling we assumed that the surface of the reacting tuff did not become coated with secondary precipitates because of the washing effects of cycling water, and that the initial reaction rate for silica leaching remained constant during the heat-generation lifetime of canisters containing nuclear waste. In order to test these ideas, we performed the 6th-Run experiment where we washed a sample that had been



leached in the earlier experiment and re-leached it. The resulting initial silica leaching rate, which is listed in TABLE 2, was nearly the same as the others.

Very soon, after the beginning of each experiment (within 3 days), colloidal material was observed in the boiling flask and thereafter significant amounts of milky, gelatinous material gradually accumulated on the bottom of the flask. SEM observations, including Energy Dispersive Analysis (EDA), of the deposited material showed that more than 80% of it was amorphous silica and about 15% was an aluminum compound. During the experiments, the color of the solution in the flask became yellowish red, suggesting that amorphous ferric hydroxide also formed. However, silica leaching and colloidal silica transport was always much greater than Fe, Al or Mn transport. This occurs because of the high silica content of the tuff and relatively high solubility of silica compared with these other elements. We expect that continued leaching would produce a moderately alkaline carbonate brine (Walton, 1993) containing colloidal silica.

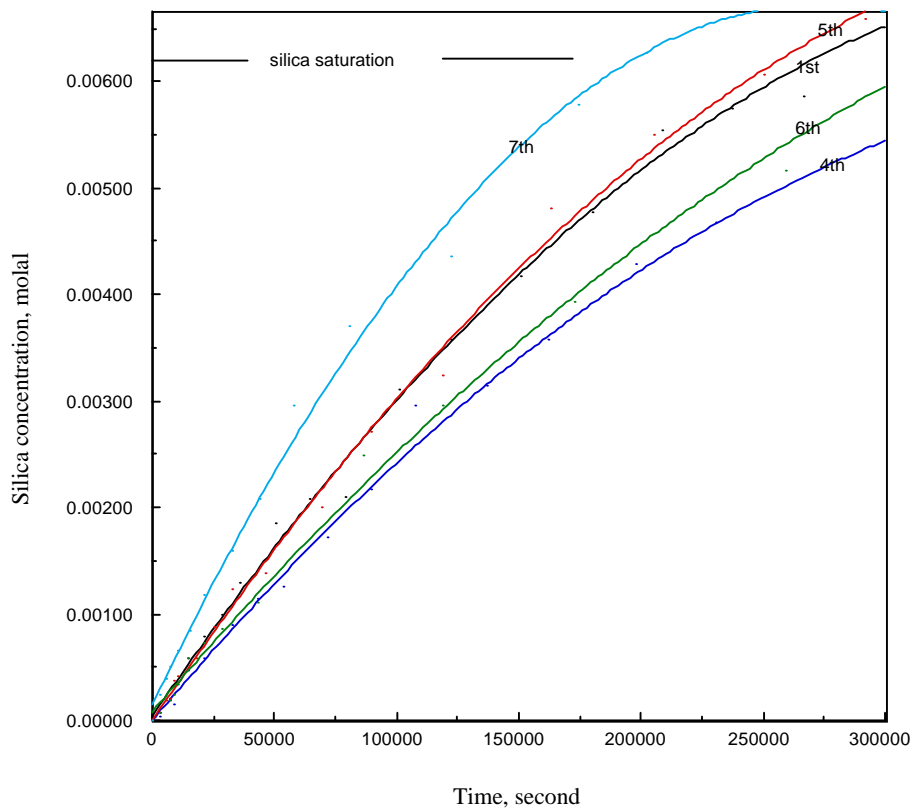


FIG. 2. Experimental results for five runs of experiments

TABLE 1. Initial reaction rates of silica leaching calculated from concentration versus time data in FIG. 2.

Run No.	$R_H$ (watts)	$r_i$ ( molal / sec)	$T_{SiO_2}$ (g / J)
1st-run	58	$3.36 \times 10^{-8}$	$1.74 \times 10^{-8}$
4th-run	29	$2.72 \times 10^{-8}$	$2.81 \times 10^{-8}$
5th-run	58	$3.40 \times 10^{-8}$	$1.76 \times 10^{-8}$
6th-run *	58	$2.67 \times 10^{-8}$	$1.38 \times 10^{-8}$
7th-run	93	$4.83 \times 10^{-8}$	$1.56 \times 10^{-8}$

**Average  $T_{SiO_2}$ :  $1.85 (\pm 0.56) \times 10^{-8}$   
(g / J)**

\* Sample used in this run had been leached earlier in 5th-run. It was washed with distilled and deionized water and then re-run. The purpose for this was to test whether the initial reaction rate changed if the leaching material being washed away “instantly”.

## DISCUSSION

The results of this study indicate that approximately  $1.85 \times 10^{-8}$  g of  $\text{SiO}_2$  will be transported from the overlying tuff to the boiling interface by each Joule of heat cycled in the system. Therefore, the silica transport in the real situation is linked to the heat generation history of canisters containing nuclear wastes. A simplified heat generation history for a canister containing nuclear waste was produced using the thermal models and data of Johnson and Montau, 1988 and Moujaes and Lei, 1995 by fitting heat generation rate for a single canister for the first 1,000 years after emplacement (FIG. 3) to the equation

$$R_H = 1.62 \times 10^{-7} - 9.69 \times 10^{-5} \ln t'$$

The maximum heat generation rate is about 4.5 kw (45,000 J/sec per canister) at the beginning of the storage life cycle. Although some of the spent fuel may have different heat generation histories, it is expected that none will exceed the initial rate of 4.5 kw. By integrating the above equation between 0 and t, we can estimate the total amount of heat generated over certain period of time after emplacement of the canisters (TABLE 2). We assume that half of this energy is conducted upwards from canisters and the other half is conducted downwards. From our experimental results (TABLE 1) we know that  $1.85 \times 10^{-8}$  gram of  $\text{SiO}_2$  is leached and transported for every Joule of energy fluxing up through the system, so we can calculate the amount of silica that might be transported during a certain period of time after the emplacement of the canister (TABLE 2).

It seems reasonable that this transported silica will accumulate in or near the boiling zone in such a way that it will seal the most permeable zones. The exact distribution of this silica cap depends upon the repository design. Different designs regarding how to space the nuclear canisters have been proposed. Some designs leave as little as 20 to 40 meters between drifts (Roush, 1995). Moujaes and Lei (1995) constructed a thermal model based on a computational domain that is 30 m between each

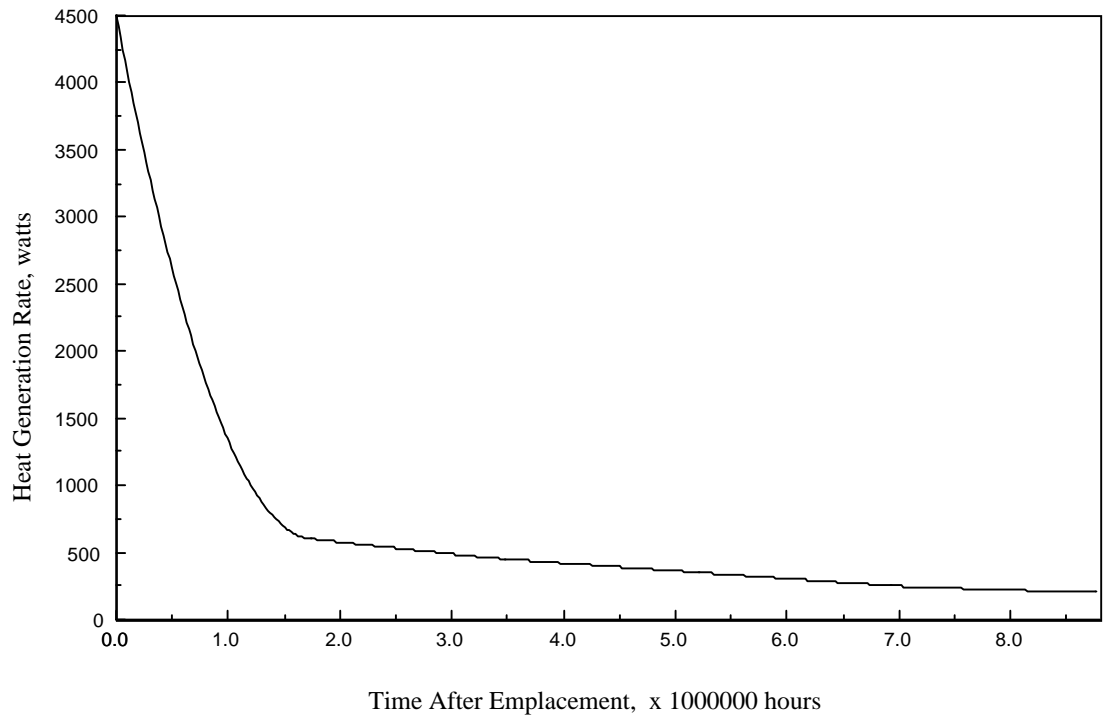


FIG. 3. Heat generation rate of single canister as a function of time

canister and 16 meters between each tunnel. In their model, the canisters were assumed to be placed in horizontal drifts on a rectilinear grid and spaced 30 m apart. In this case, single canister would affect a spatial area of 30 m x 30 m (FIG. 4). Leached silica would be deposited near the 100 °C isotherm within fractures in that area. Assuming that this part of the tuff body has a fracture density of 10 per meter along both the x and y direction and each fracture is in ideal shape with a width of 0.5 mm in this case, the total fracture void area above each canister (out of 900 m<sup>2</sup>) is about

$$A_v = (300 \times 0.5 \text{ mm} \times 30 \text{ m}) \times 2 = 9 \text{ m}^2$$

TABLE 2 lists some of the modeled results of SiO<sub>2</sub> leaching corresponding to different time periods. Only amorphous silica formed in our experiments, not quartz. The average density of amorphous silica in siliceous sinter deposits is about 1.66 ± 0.3 g/cm<sup>3</sup> (Rimstidt and Cole, 1983). Based on this we can estimate the amount of silica deposited in the fractures (FIG. 5) and further calculate the thickness of silica cap formed above the canister(FIG. 6).

There is no doubt that the silica deposited at around the 100°C isotherm will significantly alter the hydro-geological properties of the host rock. Exactly how the rock permeability might change over time is a very difficult issue to address because it would be difficult, if not impossible, to set up an experiment to simulate the situation of the repository conditions for the long times required to cause significant permeability changes in the rock. The best way to investigate this effect is to use natural analogues. Geologists and geochemists have investigated, both theoretically and practically, many natural hydrothermal systems such as porphyry copper deposits, hot springs and mid-ocean ridges, trying to determine a relationship between hydrothermal fluids and the hydro-geological properties of the host rock (Helgeson, 1968; Wood & Hewett, 1982; Wells & Ghiorso, 1991, Lowell, et al, 1993). They concluded that in many geologic situations mass transportation of silica is capable of accounting for a significant amount of the alteration of the host rock, such as decreasing the local porosity on the time scale of decades for Mid Ocean Ridge (Wells & Ghiorso, 1991). Lowell et al (1993) have set

up a model to calculate the scale of fracture closing and permeability changing as a result of simultaneous thermal expansion and silica precipitation. In Yucca Mountain, decreasing porosity and permeability and fracture closing of the host rock as a result of silica precipitation (and thermoelastic stress) may form a thin but impermeable amorphous silica cap near the 100°C isotherm, which will produce a perched water table above the repository. The perched water table could produce several unexpected results. First, as time goes by, the heat generation by the canisters will decrease and the isotherm at which water boils will migrate towards the canister. This would allow the brine (Walton, 1993) perched over the silica cap to migrate closer and closer to the canister, increasing the danger of interaction between it and the canister. Second, after a fracture is sealed, the rock above it would tend to cool because the hot vapor is no longer able to flow through it. Thermoelastic stress would then tend to reopen the fracture and even form some new fractures. With a close perched water table hanging above the canister, the reopening of the fractures (and new fractures) could create a direct channel between the water table and the canister. Third, repository designers are planning to use the heat generated by the waste's own radioactive decay to boil corrosive moisture out of the surrounding rock, so called "extended dryout" (Buscheck & Nitao, 1993, 1994a, 1994b). In this design, the tunnels would be placed as little as 20 to 40 meters apart so that the heat released from the canisters will be able to keep a thick slab of rock above and below the tunnels boiling hot, and thus dry, for thousands of years. From the reasons stated above, this approach, which puts a large group of canisters in a relatively small place with closer spacing between each canister and each tunnel (high thermal load), might result in a even larger perched water table above the canisters, because the intense heat will drive the water upwards but it has no where to go except hanging above (some near the repository boundary may escape laterally). Buscheck et al. (1995) have suggested a "localized dryout" design. This plan puts drains into the repository by spacing the tunnels farther apart (up to 100 meters). This would keep the zones of boiling-hot rock created by each tunnel from overlapping. So, condensed water from each zone could drain through the cooler rock in between, and canisters in a single tunnel could be placed closer to generate

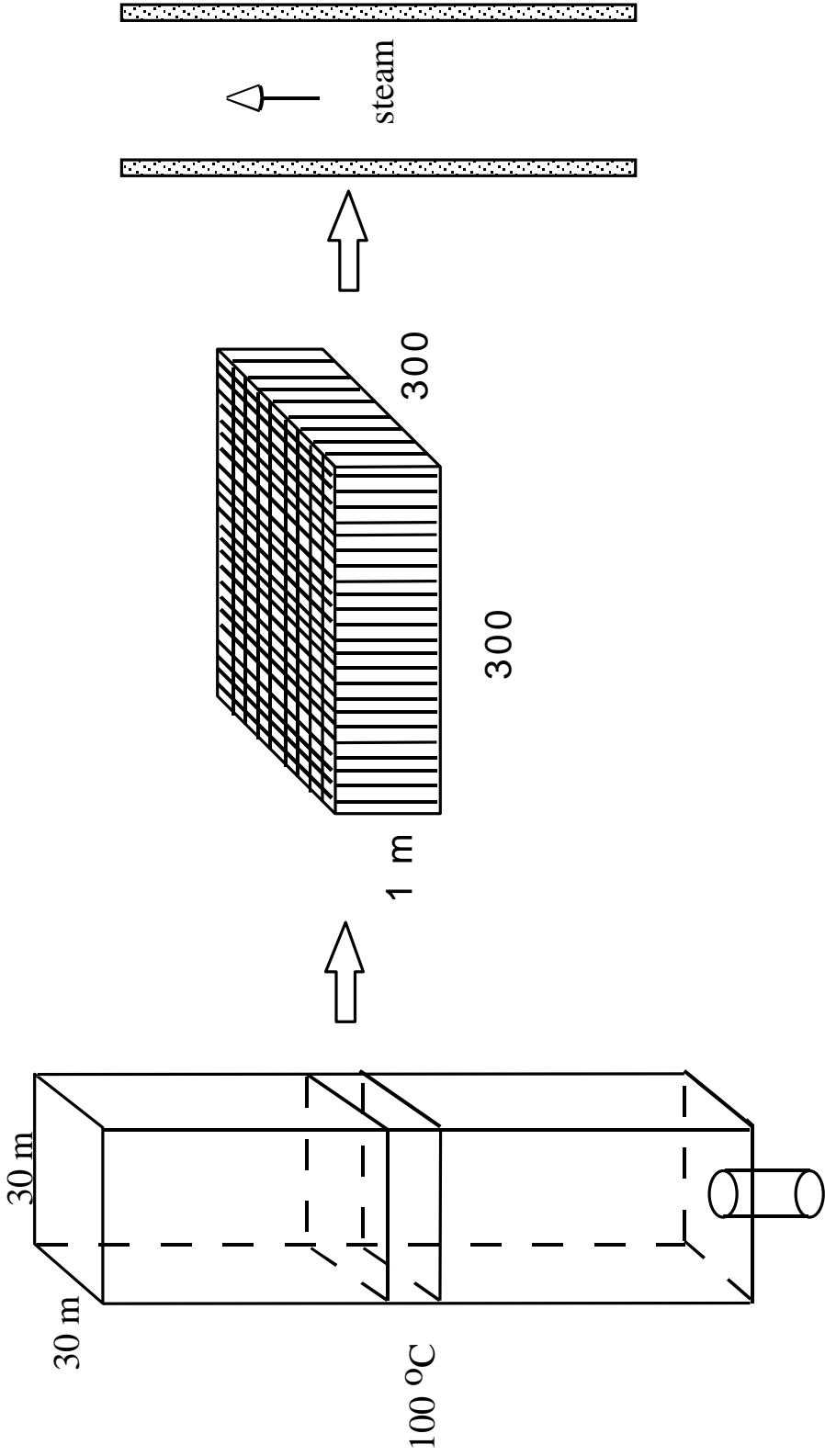


Fig 4. Computational Domain and Fracture density assumption



TABLE 2. Calculated results of amount of silica leached as a function of time and their corresponding thickness if Deposited as cap above canisters in 30 m by 30 m area.

time after emplacement (Years)	Heat Generated (Joules)	amount of silica * (kg)	thickness of silica cap** (mm)
100	$3.43 \times 10^{12}$	31.73	2.12
200	$5.67 \times 10^{12}$	52.45	3.51
300	$7.48 \times 10^{12}$	69.19	4.63
400	$8.99 \times 10^{12}$	83.16	5.57
500	$1.03 \times 10^{13}$	95.28	6.38
600	$1.14 \times 10^{13}$	105.45	7.06
700	$1.24 \times 10^{13}$	114.70	7.68
800	$1.33 \times 10^{13}$	123.03	8.23
900	$1.40 \times 10^{13}$	129.50	8.67
1000	$1.47 \times 10^{13}$	135.98	9.10
2000	$1.76 \times 10^{13}$	162.80	10.90

\* Amount of silica = ( Heat Generated in Joule / 2 ) x  $(1.85 \times 10^{-8})$  / 1000

\*\* Thickness of silica cap = ( Amount of silica in kg) / 9 / 1660 x 1000

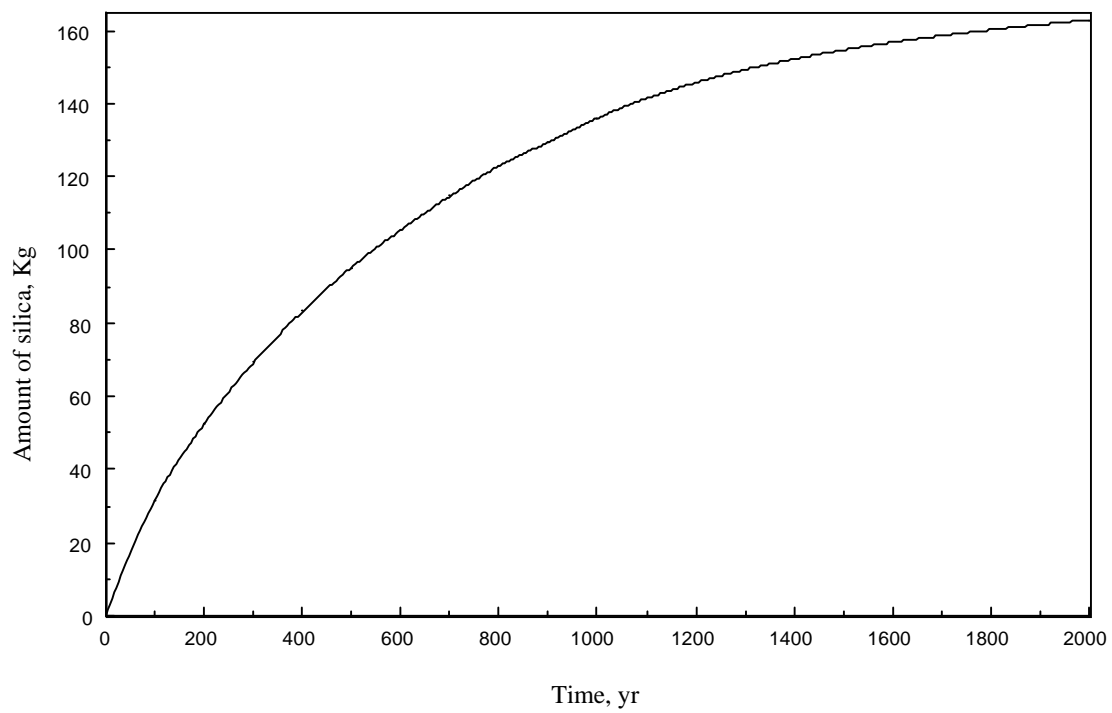


FIG. 5. The amount of silica produced as a function of time

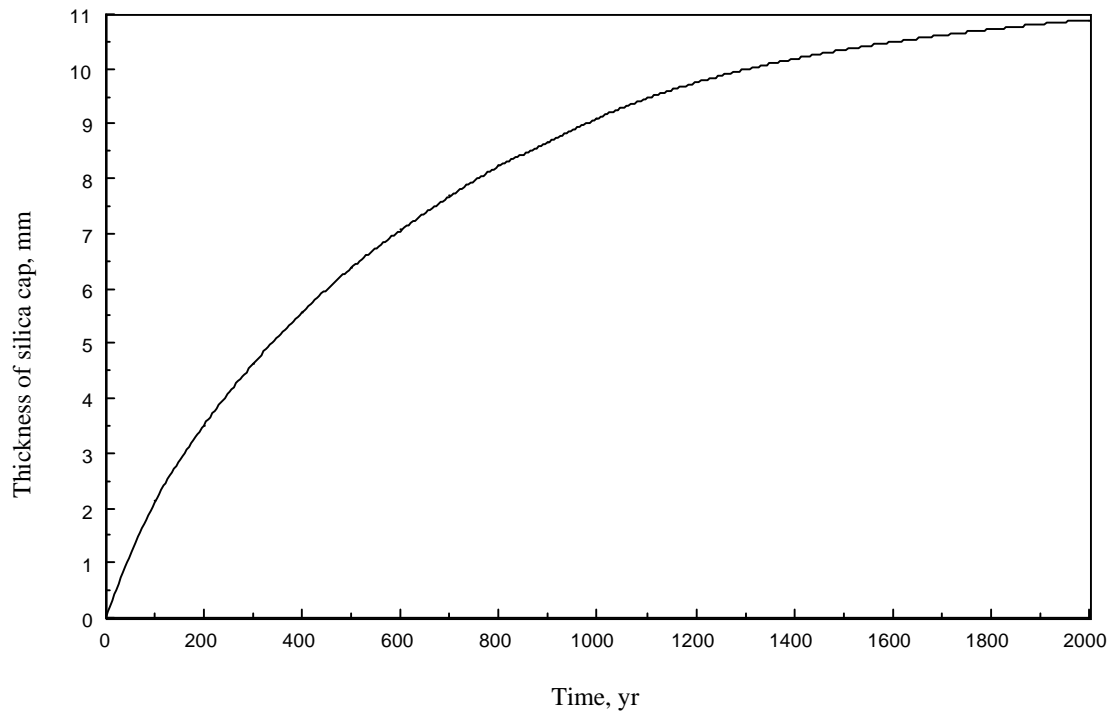


FIG. 6. Thickness of silica cap that might be formed as a function of time

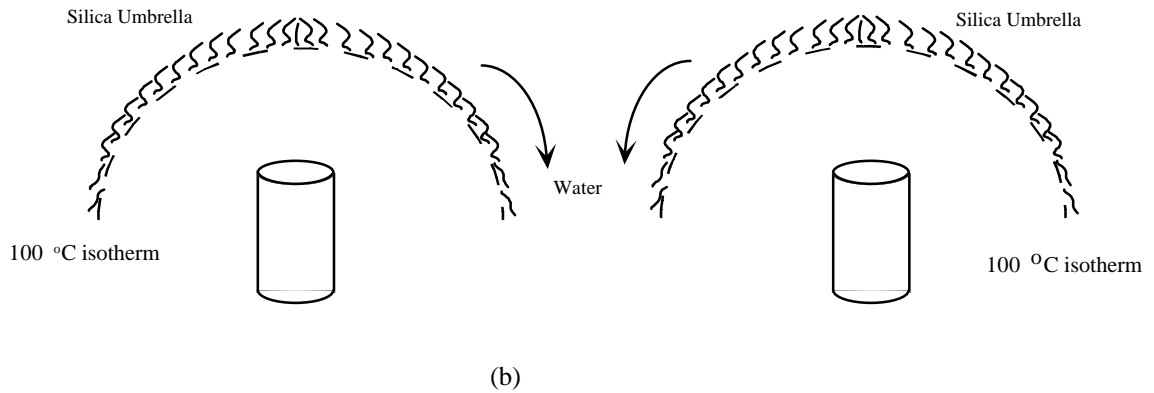
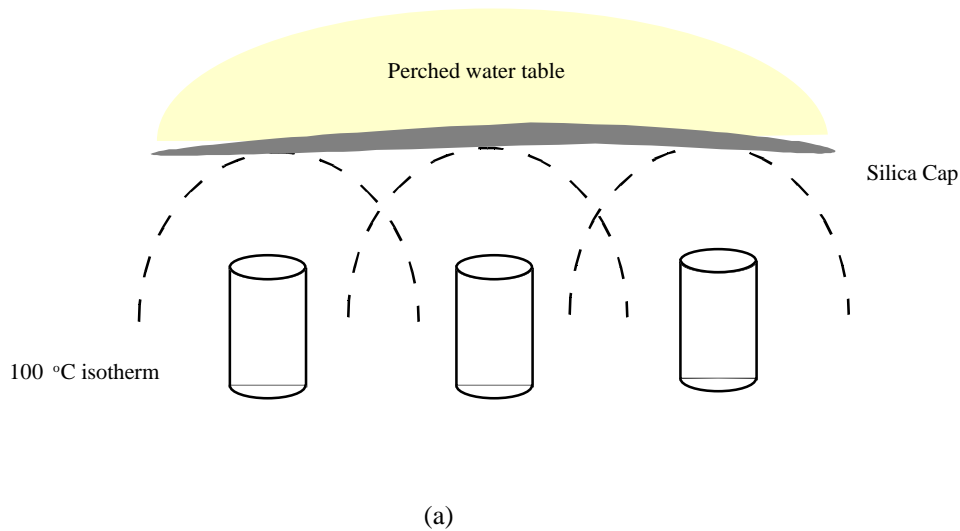


FIG. 7. Comparison of the expected geometries for an “extended dry-out” repository design versus a “localized dry-out” repository design. The extended dryout design may develop a perched watertable above the repository (a) because the overlapping isotherms at where water boils will produce a continuous silica cap above the repository. The “localized dry-out” design would produce an umbrella-like silica cap above each row of canisters (b) that would shed infiltrating ground water into the region between the rows.

a more intense heating zone to keep it dry. Although this design may result in other engineering problems, it does provide an escape route for brines produced by thermal recycling of water. Very possible, instead of forming a single silica cap above the whole repository, a domed silica layer could be formed above each tunnel, like an umbrella covering the tunnels (FIG. 7). The effect of this silica umbrella upon the repository is not known today.

A significant amount of colloidal silica would be produced by this thermal recycling process and this colloidal silica particles can adsorb and transport radionuclides. In our experiments, colloidal silica was produced very quickly and in significant amounts. These colloidal particles which are less than a micron across remained suspended in the solution long after the end of experiments. They are smaller than most rock matrix pores and form a dilute suspension that can be carried quickly by groundwater through rock formations. Colloid transport in geological media is documented (McCarthy & Zacchara, 1989; McCarthy & Degueldre, 1991; Moulin & Ouzounian, 1992, Nuttall, 1989, Nuttall and Long, 1993). In one of his papers, Nuttall (1993) stated that for several test sites, groundwater colloidal particles were responsible for the rapid transport of radioactive waste material. In all cases, nuclear waste particles had rapidly migrated tens of meters (even miles) while laboratory studies predicted only millimeters (Nyhan, et al, 1985). Natural geological analogues also support the importance of element transport by silica colloid. Herrington & Wilkinson (1993) studied some mesothermal gold-containing quartz veins and concluded that the presence of colloidal silica allows further gold transport in suspension in the hydrothermal fluid for a great distance. Unfortunately, only limited studies of colloidal behavior under expected site-specific conditions have been carried out by Yucca Mountain Project. In these studies, no progress was made and “no further work is expected because funding for this activity has been terminated.” (US DOE, 1996).

Finally, if we assume that the hydrothermal system under repository conditions is an open system, in other words it is free to interact with the atmosphere all the time, then the dissolution of the CO<sub>2</sub> in the alkaline solutions becomes important. As stated earlier,

we assume that the  $H^+$  needed for the silicate leaching reactions comes from the hydrolysis of  $H_2CO_3$  which is a result of  $CO_2$  dissolution. Silicate leaching reactions consume basically all the available  $H^+$ , with  $HCO_3^-$  or  $CO_3^{2-}$  left behind. The solutions in our experiments became more and more alkaline (pH ranging from about 6.5 to about 9.5). The accumulated carbonate can significantly increase the solubility of many chemical substances and some of the actinide elements such as neptunium and uranium by forming complexes ( $Np(OH)_2(CO_3)_2^{2-}$ ,  $Np(OH)_4(HCO_3)_2^{2-}$ ,  $U(OH)_2(CO_3)_2^{2-}$ ) with them (Pratopo et al, 1990). This could cause a dramatic increase in the mobility of these elements. Walton (1993, 1994) suggested that such a highly variable water chemistry may occur as a result of temperature and temperature gradient dependent evaporation/condensation of water. This highly variable water chemistry is a significant role in water dynamics at the repository scale and should be studied extensively.

## CONCLUSIONS

Our study shows that:

1. Coupled heat and fluid flow in the proposed Yucca Mountain high level nuclear waste repository can result in the leaching and transportation of large quantities of silica from the rocks above the repository to near the 100 °C isotherm “boiling zone”.

2. The aqueous silica concentration in the “boiling zone” will rapidly rise to saturation and a large quantity of amorphous colloidal silica will deposit.

3. This colloidal silica will likely accumulate as sinter-like deposits in the boiling region to create a low permeability zone. If the repository is constructed according to the “extended dryout” scenario, this low permeability zone along with the thermal recycling will trap carbonate brine above the repository as an extensive perched water table. On the other hand, if the repository is constructed according to the recommendation of Buscheck’s “localized dry-out” design, the silica cap may act as an umbrella and shed the liquid water laterally and downward away from the canisters.

4. The fate of the solution trapped in the perched water table is quite important because it will likely be an alkaline bicarbonate-carbonate solution that can dissolve and transport uranium oxides and because it will contain colloidal silica that can adsorb and transport radionuclides.

## REFERENCES

- Buscheck T. A. and Nitao J. J. (1993) Repository-Heat-Driven Hydrothermal Flow at Yucca Mountain, Part I: Modeling and Analysis, Nuclear Technology, Vol. 104, No. 3. 418 -448
- Buscheck T. A. and Nitao J. J. (1994a) The Impact of Buoyant Gas-Phase Flow and Heterogeneity on Thermo-Hydrological Behavior at Yucca Mountain, American Nuclear Society, La Grange Park, IL, Proceedings Fifth International High-Level Radioactive Waste Management Conference, Las Vegas, NV, May 1994
- Buscheck T. A. and Nitao J. J. (1994b) The Importance of Thermal Loading Conditions to Waste Package Performance at Yucca Mountain, Materials Research Society, Pittsburgh, PA, Proceedings Materials Research Society XVIII international Symposium on the Scientific Basis for Nuclear Waste Management, Oct. 23 - 27, 1994.
- Buscheck T. A. and Nitao J. J. (1995) Localized Dryout: An Approach for Managing the Thermal-Hydrological Effects of Decay Heat at Yucca Mountain, Materials Research Society, Pittsburgh, PA, Proceedings Materials Research Society XIX International Symposium on the Scientific Basis for Nuclear Waste Management, Boston, MA, Nov. 27 - December 1, 1995
- Campbell J. E. and Cranwell R. M.(1988) Performance Assessment of Radioactive Waste Repositories, Science, Vol. 239, 1389 - 1392
- Carey J. W. and Bish D. L. (1996) Equilibrium in the clinoptilolite-H<sub>2</sub>O system. American Mineralogist 81, 952 - 962.
- Govett, G. J. S. (1961) Critical Factors in the Colorimetric Determination of Silica, Anal. Chim. Acta, 25 (1961), 69 – 81



- Helgeson J. C. (1968) Geochemistry of Hydrothermal Ore Deposits, *Geochim. Cosmochim. Acta* 32, 568 - 610
- Herrington R. J. and Wilkinson J. J. (1993) Colloidal gold and silica in mesothermal vein systems. *Geology* 21(June), 539 - 542.
- Johnson G. and Montau D. (1988) Thermal Performance of a Buried Nuclear Waste Storage Container Storing a Hybrid Mix of PWR and BWR Spent Fuel Rods, Report UCID 21414, Lawrence Livermore National Laboratory
- Lowell R. P., Cappellen P. V., and Germanovich L. N. (1993) Silica precipitation in fractures and the evolution of permeability in hydrothermal upflow zones. *Science* 260 (9 April), 192 - 194.
- McCarthy J. F. & Zacchara J. M. (1989) Subsurface transport of contaminants. *Environ. Sci. and Tech.*, 23, 496 - 502
- McCarthy J. and Degueldre C. (1991) Sampling and characterization of colloids and particles in groundwater for studying their role in contaminant transport. *Environmental Particles*, van Leeuwen H. P. and Buffle J. (Editors) IUPAC, Environmental, Analytical and Physical Chemistry Series, II
- Moujaes S. and Lei Y. (1995) Thermal considerations in vertically emplaced high level nuclear waste containers. Fifth International Conference on radioactive Waste Management and Environmental Remediation, 867 - 871.
- Moulin V. and Quzounian G. (1992) Role of Colloids and humic substances in the transport of radio-elements through the geosphere. *Applied Geochemistry*, Supplementary Issue 1, 179 - 186

Nuttall, H. E., (1989) Colloid Transport Update – Milestone, R528, LA-UR-87-3742

Nuttall, H. E. and Long R. L. (1993) Mobility of radioactive colloidal particles in groundwater. *Radioactive Waste Management and the Nuclear Fuel Cycle* 17(3-4), 237 - 251.

Nyhan J. W., Drennon B. J., Abeele W. V., Wheeler M. L., Purtymun W. D., Trujillo G., Herrera W. J., and Booth J. W. (1985) Distribution of Plutonium and Americium beneath a 33-yr-old liquid waste disposal site. *J. Environ. Quality* 14(4), 501 - 508.

Pratopo, M. I., Moriyama, H. and Higashi, K. (1990) Carbonate Complexation of Neptunium(IV) and Analogous Complexation of Ground-Water Uranium, *Radiochimica Acta*, 51, 27 – 31

Pruess K. and J. S. Y. Wang (1987) Numerical Modeling of Isothermal and Nonisothermal Flow in Unsaturated Fractured Rock, A Review, Flow and transport through unsaturated fractured rock, Evans D. & T. Nicholson editors, American Geophysical Union, 1987, 11 – 21.

Pruess K. J, Wang J. S. Y., and Tsang Y. W. (1990) On Thermalhydrologic Conditions Near High-level Nuclear Wastes Emplaced in Partially Saturated Fractured Tuff, 1, Simulation Studies with Explicit Consideration of Fracture Effects, *Water Resour. Res.*, 26(6), 1235 - 1248

Rimstidt J. D. and Cole D. R. (1983) Geothermal mineralization I: The mechanism of formation of the Beowarwe, Nevada, siliceous sinter deposit. *A. J. S.* 283(October), 861 - 875.

Rimstidt J. D., Williamson M. A., and Newcomb W. D. (1991) Element redistribution in Yucca Mountain radioactive waste repository produced by evaporation and

- condensation of water in a thermal field. Topical Meeting on Nuclear Waste Packaging, Focus '91, 50-57.
- Saunders J. a. (1990) Colloidal transport of gold and silica in epithermal precious-metal systems: Evidence from the Sleeper deposit, Nevada. *Geology* 18(August), 757 - 760.
- Roush W. (1995) Can Nuclear Waste Keep Yucca Mountain Dry - and Safe? *Science* VOL. 270, 15, 1761 - 1762
- Scott R. B. and Bonk J. (1984) Preliminary Geologic Map of Yucca Mountain NYE County, Nevada with Geologic Sections. US Geological Survey.
- US Department of Energy (USDOE) (1992) Yucca Mountain Studies (ed. Y. M. S. C. Project), Washington, DC, Govt. Print. Off. 7 - 11
- US Department of Energy (USDOE) (1996) Site Characterization Progress Report: Yucca Mountain, Nevada. U.S. Department of Energy, Washington, DC, Govt. Print. Off.
- US Environmental Protection Agency (USEPA) (1985) Environmental Standards for the Management and Disposal of Spent Nuclear Fuel, High-Level and transuranic Radioactive Wastes. 40 CFR 191, Washington, DC, Govt. Print. Off.
- US Nuclear Regulatory Commission (USNRC) (1983) Disposal of High-Level Radioactive Wastes in Geologic Repositories: Technical Criteria. 10 CFR 60. Washington, DC, Govt. Print. Off.
- Walton J. C. (1993) Effects of evaporation and solute concentration on presence and composition of water in and around the waste package at Yucca Mountain. *Waste Management* 13, 293 - 301.

Walton J. C. (1994) Influence of Evaporation on Waste Package Environment and Radionuclide Release From a Tuff Repository, *Water Resour. Res.*, Vol. 30, No. 12, 3497 - 3487

Wells J. T. and Ghiorso M. S. (1991) coupled fluid flow and reaction in mid-ocean ridge hydrothermal systems: The behavior of silica. *Geochim. Cosmochim. Acta* 55, 2467 - 2481.

Wood J. R. and Hewett T. A. (1982) Fluid convection and mass transfer in porous sandstones - a theoretical model. *Geochim. Cosmochim. Acta* 46, 1707 - 1713.

## APPENDIX I: Water Flux Measurements

The water flux was correlated to the power supply readings by measuring the mass of water distilled into a weighed flask over a timed interval. The device used is illustrated in FIG. 8.

The device is used to measure water flux through the experiment apparatus under different power supply readings which are 50, 60, 70, etc. Everything used here are identical with those used in the leaching experiment. By establishing the relationship between time and the amount of water condensed in beaker, water flux were calculated in terms of (grams of water per second ). Knowing that water vaporization energy is 40.866 kJ/mol (Robie, et al, 1979), heat generation rate was calculated. The following table is the result of all of the measurements:

Controller Reading	Time (min)	H <sub>2</sub> O produced (g)	flux (g / sec)	Average Heat Generation Rate (watts)
140	3	28.66	0.16	362
140	2	18.95	0.16	
140	1	9.70	0.16	
120	3	22.06	0.12	276
120	2	14.85	0.12	
120	1	7.14	0.12	
100	5	20.80	0.07	161
100	3	12.62	0.07	
100	1	4.38	0.07	
90	8	25.76	0.05	123
90	7	22.47	0.05	
90	5	16.62	0.06	
80	15	39.91	0.04	93
80	10	22.92	0.04	
80	5	12.09	0.04	
70	240	389.97	0.03	58
70	120	181.37	0.03	
70	60	88.37	0.02	
60	376	301.57	0.01	29
60	247	180.62	0.01	
60	232	173.75	0.01	

Note: The internal diameter of the PVC pipe is 0.017 m (17 mm).  
And the correlation between water flux and power supply is shown in FIG. 9 .

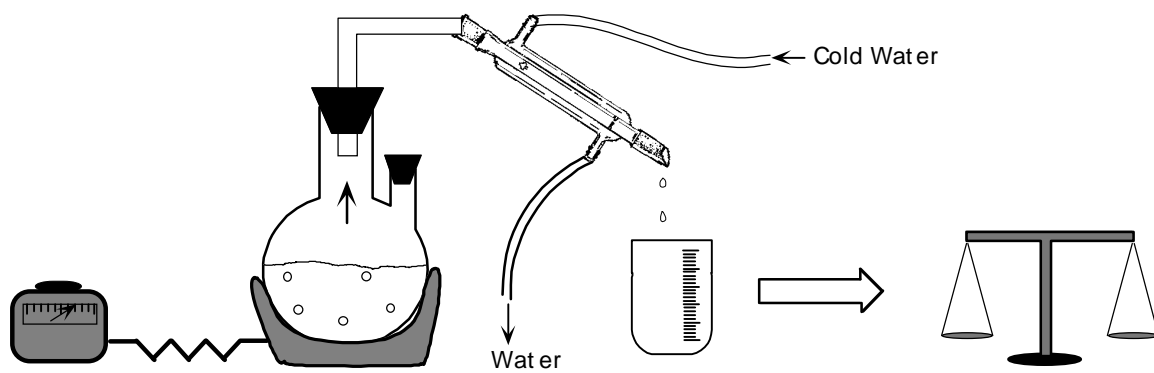


FIG. 8. Devices used to measure water flux in the reflux experiment.

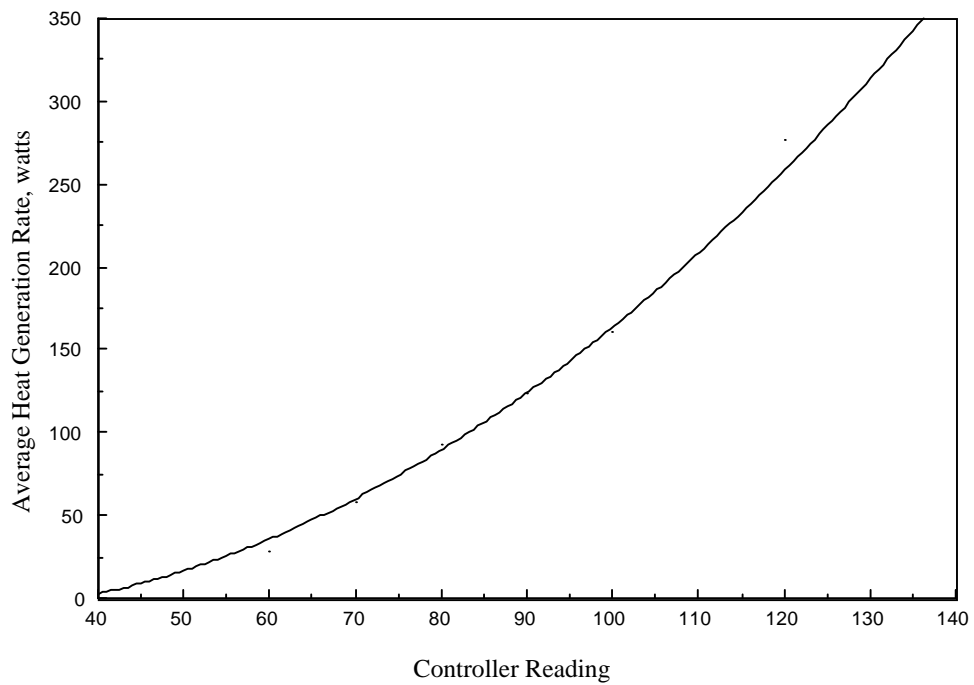


FIG. 9. Relationship between heat generation rate (watts) and power controller readings

## APPENDIX II: Spectrophotometric Silica Assay

A method for the colorimetric determination of silica was adapted from Grovett (1961). Standard absorbance versus concentration curves at 400  $\mu\text{m}$  were prepared using 0 - 300 ppm diluted from Fisher 1000 ppm Silica standard. The average precision of the molybdate yellow method is  $\pm 2\%$ .

### Instruments:

A Bausch & Lomb Spectronic 21 spectrophotometer, Model D, with 10 mm cuvettes, was used for the spectrophotometric measurements.

### Preparation of reagent solutions:

Distilled and deionized water was used for all dilution.

Ammonium Molybdate (0.3 M  $\text{MoO}_4^{2-}$ ): Dissolve 52.97 g  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  in 900 ml water adjust to pH 7-8 with NaOH and bring to 1 L total volume. Store in polyethylene container. Put this solution into a fixed volume 10 ml automatic pipette dispenser as needed for assay.

Sulfuric Acid (1 N): With stirring add 28 concentrate  $\text{H}_2\text{SO}_4$  to about 800 ml  $\text{H}_2\text{O}$ , then dilute to 1 L. Transfer this solution to a fixed volume 10 ml automatic pipette dispenser when needed for assay.

### Procedure:

1. Filter the 1 ml original solution sample with Gelman<sup>TM</sup> 0.20  $\mu\text{m}$ , 3 cm diameter nylon acrodisc. The clear drops were added into a 50 ml class A volumetric flask.
2. Acidify sample with 10 ml 1 N  $\text{H}_2\text{SO}_4$  (giving a pH  $\sim$  2).
3. Add 10 ml Ammonium Molybdate reagent.
4. Dilute to 50 ml with distilled  $\text{H}_2\text{O}$
5. After 3 minutes (2-10 minutes max range), read absorbance at 400  $\mu\text{m}$ .

### Calculation of Results:



Determine the concentration of silica from the standard curve of absorbance at 400  $\mu\text{m}$  versus  $\text{SiO}_2$  content of the assay which is prepared before every analysis.

### APPENDIX III: Original Experimental Data

The following are original silica concentration versus time data, used to calculate initial reaction rates of silica leaching. All experiments applied the same amount of tuff sample (0.15 kg) and same amount of solution (0.5 kg). All silica concentration were expressed as SiO<sub>2</sub>.

4th Run:  $R_H = 29$  watts

Time (hr)	Concentration (ppm)
1	2.14
2.5	8.57
4	27.86
6	34.29
9	53.57
12	68.57
15	75.00
20	102.86
25	130.71
30	177.86
38	188.57
45	214.29
55	257.14
64	280.71
87	321.43
95	342.86
125	375.00

5th Run:  $R_H = 58$  watts

Time (hr)	Concentration (ppm)
0	0
1	4.29
1.5	10.71
2	12.86
2.5	22.71
3	24.64
5	35.14
7	52.71
9	73.93
13	83.57
19.3	120.00
25	162.86
33	195.00
45.25	289.29
57	330.86
69.5	364.29
81	395.56

1st Run:  $R_H = 58$  watts

Time (hr)	Concentration (ppm)
0	0
1	4.29
2	12.86
4	34.29
6	47.14
8	60.00
10	77.14
14	111.43
18	124.29
22	126.43
28	186.43
34	214.29
42	250.71
50	287.14
58	332.14
66	345.00
74	351.43
82	400.71
94	409.29
106	415.71
118	422.14
130	432.86
142	450.00
154	450.00
166	450.00
178	454.29
190	454.29
202	454.29
224	482.14
247	486.43
285	525.00
309	557.14
333	546.43
357	492.86
381	559.29
406	522.86
430	525.00
478	503.57
484	522.86
500	527.14

6th Run:  $R_H = 58$  watts

Time (hr) (ppm)	Concentration (ppm)
0	0
1	4.29
2	11.57
2.5	14.25
3	19.71
4	34.29
6	44.14
8	51.43
12	66.43
24	150.00
33	177.86
48	235.71
72	310.71
96	396.43

7th Run:  $R_H = 93$  watts

Time (hr)	Concentration
0	0
1	14.14
1.5	23.57
2	30.00
3	39.00
4.2	51.00
6	71.00
9	96.00
12.3	124.29
16	177.86
22.5	222.86
34	261.43
48.5	347.14
56.2	377.00
71	407.14

## **Vita**

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