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LETTER REPORT

TITLE: Review of "The Dissolution of Rainier Mesa Volcanic Tuffs, and Its Application to the Analysis of the Groundwater Environment," MS Thesis of M. S. Henne, University of Nevada, Reno, NV, 1982.

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This thesis describes research that was conducted to ascertain groundwater travel times in the unsaturated zone beneath Rainier Mesa (NTS). The data obtained by Henne shows that some of the groundwaters that infiltrate Rainier Mesa may be capable of percolating downward very rapidly through the underlying unsaturated tuffaceous rocks.

The research included both laboratory investigations and field studies. The principal objective of the laboratory work was to establish experimentally the effects of pH, temperature, and surface area on the dissolution of glass-rich tuff from Rainier Mesa. Also, the experiments were designed to elucidate the quantitative relationship between: (1) reaction time, (2) tuff surface area to water volume ratio, and (3) the concentration of SiO_2 , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} in Rainier Mesa groundwaters. This quantitative relationship (eventually cast in the form of a rate equation for dissolution of silica from Rainier Mesa tuff) was employed to estimate the retention times of Rainier Mesa groundwaters. The field studies consisted mainly of collecting samples of (1) soil waters from the surface of Rainier Mesa and (2) groundwaters from various tunnel excavations beneath the Mesa. Groundwaters in the tunnels were collected with lysimeters and at the sites of natural seeps.

The laboratory studies showed:

1. The results of tuff dissolution experiments performed at 25, 30, 50, and 70°C for up to 20 d are in fairly good agreement with results obtained previously by White and Claassen (1980). It was found that pH did not affect the dissolution of SiO_2 , had only a slight effect on the dissolution of Na^+ , but had a major effect on the dissolution of Ca^{2+} and Mg^{2+} . (The amounts of dissolved calcium and magnesium were greater at the lower values of pH). By contrast, potassium exhibited irregular behavior: at low values of pH the concentration of K^+ increased at first but subsequently began to decline. However, at values of pH above approximately 6.4, the quantities of dissolved potassium increased steadily during experimentation.
2. It was observed that the rates of mass transfer of SiO_2 , Na^+ , K^+ , Ca^{2+} , and Mg^{2+} from Rainier Mesa tuff to contiguous water were greater for the experiments with higher tuff surface-area-to-water-volume ratio. Therefore, Henne concluded that, in using dissolution kinetics to estimate the retention time of a groundwater in tuffaceous rocks, it is essential to have an accurate value for the reactive surface area of the rocks.

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3. Experiments performed at 25, 50 and 70°C indicate collectively that, for a given tuff surface-area-to-water-volume ratio and reaction time, silica solubility increases sharply with increasing temperature.
4. At 70°C, steady-state concentrations of Na⁺, K⁺, Ca²⁺, and Mg²⁺ were achieved in 40 hr, but the concentration of dissolved SiO₂ continued to rise steadily for up to 284 hr. Similar behavior of silica solubility was observed at 25 and 50°C.
5. The results of all experiments indicate that silica concentrations provide the most reliable means of estimating groundwater retention time.

The field studies showed:

1. Meteoric waters that flow from the soils on Rainier Mesa into the subjacent rocks experience an increase in pH.
2. The chemistries of groundwaters in Rainier Mesa tunnels vary with geochemical environment, but show only slight variation with time.
3. Retention times of Rainier Mesa groundwaters were estimated in two ways. The first method utilized a long-term trend in the cation-to-silica ratio observed in lysimeter 2 and showed that the maximum in this ratio was observed in June. This observation implies groundwater infiltration six weeks to three months prior to this time (i.e., during the annual spring thaw on the surface of Rainier Mesa when infiltrating meltwaters dissolve "extra" cations from the thin soils on the Mesa). The second method employed silica-dissolution kinetics to estimate the retention time of the groundwaters. Assuming that the tuff surface-area-to-water-volume ratio is approximately 100 square meters per liter, and using the minimum silica concentration of the groundwaters collected in the tunnels - 33 mg/L - the retention time of groundwater in the Mesa was calculated to be as short as 3 months. The values obtained by the two methods agree closely but "are approximations made with unproven estimates."

There are three apparent deficiencies of the research described in this thesis:

1. The silica-dissolution rate equation developed by Henne is of uncertain accuracy. There is no discussion of potential sources of error in the data used to derive the rate equation. Also, Henne fails to describe his regression methods in sufficient detail to permit an assessment of his methodology, and appropriate statistical data concerning the "goodness of fit" of his equation are not presented.
2. Henne's calculation of a minimum three-month travel time for groundwater sampled using lysimeter 2 is based on an assumed value of 100 square meters per liter for the tuff surface-area-to-groundwater-volume ratio. Since, no justification is provided for the use of this particular number (and for the reasons discussed above), the accuracy of the calculated three-month travel time is very uncertain.

3. Henne does not state what fraction of percolating groundwaters reach the tunnels beneath Rainier Mesa in just three months. It is almost certain that Henne does not believe that all groundwaters in Rainier Mesa percolate downward that rapidly, but he does not address this important subject at all.

Despite these concerns, the research performed by Henne remains noteworthy. The finding that some groundwaters in tunnels beneath Rainier Meas contain very little dissolved silica is interesting and possibly very significant. Likewise the discovery that the ratio of cations to silica in these groundwaters exhibits an annual maximum in June, an observation that is explained nicely by the hypothesis that "extra" cations released from the thin soils on Rainier Mesa during the annual spring thaw reach the tunnels beneath Rainier Mesa in just a few weeks. Collectively, the data obtained by Henne should be viewed as permissive evidence that some of the groundwaters that infiltrate Rainier Meas are capable of percolating downward very rapidly through the underlying unsaturated tuffaceous rocks.

Reference

White, A. F., and Claassen, H. C., 1908, Kinetic Model for the Short-Term Dissolution of a Rhyolitic Glass, *Chemical Geology*, Vol. 28, pp. 91-109.