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Fate of Sodium Sulfide and Sodium Bisulfide

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in Steam Muffler Effluent

DEPT. OF WATER &
LAND DEVELOPMENT

The chemical species generated by the treatment of geothermal steam with sodium hydroxide (NaOH) include sodium carbonate (Na_2CO_3), sodium bicarbonate (NaHCO_3), sodium sulfide (Na_2S), and sodium bisulfide (NaHS). The former two chemicals are environmentally benign and their disposal will have no significant effect on groundwater quality. Sodium sulfide and bisulfide can, however, have substantial impacts on water quality due to their toxicity at moderate concentrations and their potential for odor generation at extremely low concentrations. Hence, the fate of these chemicals under normal environmental conditions is of concern in considering their production and disposal as a result of treatment of geothermal steam.

Hydrogen sulfide abatement from geothermal steam has been accomplished in Hawaii by the injection of a 10% solution of sodium hydroxide into the steam phase at a mole ratio of three moles of sodium hydroxide to one mole of hydrogen sulfide. The pH of the resultant solution will be in the range of 12 to 13 and hence the predominant sulfide species in solution will be sodium sulfide. Because a quantitative reaction of hydrogen sulfide to sodium sulfide would require only two moles of caustic to one mole of sulfide, an excess of caustic will be present that will maintain the pH at a high level for a substantial period after the scrubber effluent is exposed to atmospheric air. Upon exposure of the sodium sulfide solution to air, the most important reaction that will occur is the oxidation of the sodium sulfide. Although the precise mechanism for the oxidation

the sodium sulfide. Although the precise mechanism for the oxidation of the sulfide involves a number of intermediate sulfur compounds (polysulfides and thiosulfates), the ultimate reaction product under conditions of high pH is sodium sulfate (Na_2SO_4). This compound is found in most natural systems and is present at moderately high concentrations in seawater and hence it is not considered to present a significant hazard to water quality.

Even though the ultimate reaction product of the oxidation of sodium sulfide may not be a problem, the rate of oxidation requires some analysis. A number of studies of sulfur oxidation rates have been conducted under laboratory conditions; this research has been reviewed by F. Millero in Marine Chemistry, Volume 18, 1986, pages 121-147. This work has shown that the rate of oxidation of sulfide is quite variable but, in general, is very high. The half-life of sulfide in oxygenated water (the time required to oxidize one-half of the total sulfide present) ranges from 0.3 hours to a maximum of 65 hours with the times varying according to the temperature, pH, oxygen availability, and concentrations of other ions in the water. The experimental data that seems most relevant to the current case (high pH and high temperature) suggests that the oxidation half life of sulfur would be less than a few hours in the presence of adequate oxygen.

Because the oxidation rate is so high, it is likely that oxygen will be the limiting factor in the conversion of sulfide to sulfate. The magnitude of the oxygen demand can be calculated from the estimated quantity of sodium sulfide generated. In the case of a well test, sulfide production would amount to 61 pounds per hour for a

total of 480 hours (20 days). The mass of sulfide generated would be 2.93×10^4 lbs or about 4.2×10^5 moles which would require about 8.4×10^5 moles of oxygen to oxidize the sulfide completely to sulfate. This volume of oxygen is contained in 9.41×10^4 cubic meters of air; given that the elevation of the discharge point is approximately 200 meters, this would be equivalent to the volume of air contained within a percolation radius of approximately 22 meters down to the depth at which the effluent would encounter the water table. The time over which the effluent would be exposed to oxidation in the unsaturated zone would, on the basis of rainfall percolation rates reported by Stearns and MacDonald of about 22 meters per day in the Puna area, amount to at least nine days. Given that the half-life of sulfide oxidation is only a few hours, the combination of lateral dispersion of the percolating effluent and normal ground air mobility should be sufficient to oxidize virtually all of the sodium sulfide discharged during a well test prior to its encountering the water table.

If a portion of the sulfide survives the descent to the water table, oxidation of the sulfide can continue as the effluent mixes with the groundwater. Rainfall recharge to the basal lens will contain approximately 2.8×10^{-4} moles of dissolved oxygen per liter. Hence, each mole of sulfide that survives must mix with approximately 5.6×10^4 litres of rainfall recharge in order for complete oxidation to occur. Lateral groundwater migration rates have been estimated by Drueker and Fan (Ground Water, Volume 14, 1976, pp. 340-350) to be approximately 1.5 to 3 meters per day. Because the nearest well down-gradient from the project site is approximately 2 kilometers away (well number 2881-01) and the nearest source of drinking water is

about 4 kilometers, mixing of the effluent will occur over a period of at least 660 days before the sulfide could impact an existing groundwater source. During this interval, 5.74×10^3 liters of rainfall recharge will enter the groundwater table per square meter of surface area of effluent plume. If the plume area amounts to slightly more than 0.5 km^2 , then the oxygen contained in the rainfall recharge will be sufficient to completely oxidize the the sulfide produced by a 20 day well test before it can reach the nearest existing groundwater well.

A major unknown at present is the actual direction of groundwater flow in the Puna district. This presents a difficult problem for monitoring the effect of geothermal discharge on the basal groundwater system. At the present time, the only way to be certain of encountering a discharge plume would be to drill monitoring wells that completely encircle the injection point. A possible method of determining the direction of groundwater flow would be to inject a highly conductive solution (salt water) into the basal lens and perform either a mis-a-la-masse survey around the injection well or perform a time domain electromagnetic survey around the injection point.