

## GEOCHEMISTRY AND HYDROLOGY OF THE ZUNIL GEOTHERMAL SYSTEM, GUATEMALA

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## ABSTRACT

The chemical and isotopic relationships of fluids from wells and springs in the region of the Zunil geothermal field follow a clear and consistent pattern with respect to their location. The chemical data define a plume of high-temperature water that originates in the western part of the existing well field. As this high-temperature fluid travels south and east, it boils and mixes with shallow steam-heated waters. The shallow fluids, which overlie and extend beyond the deeper sodium chloride reservoir, discharge as sulfate- and bicarbonate-rich thermal springs. Cl-enthalpy relationships suggest that the deep fluid may have a temperature as high as 335°C and a chlorinity of up to 1550 ppm.

## INTRODUCTION

Zunil is located in an area of active volcanism that contains numerous hot springs and fumaroles. Since the first thermal gradient holes were drilled in 1976, the area has been under investigation as a source of geothermal power. More than 700 chemical analyses of spring and well fluids have been collected from the Zunil geothermal area (Fig. 1) during the past ten years. In this report, we describe the chemical and isotopic relationships among these fluids and then use these data to develop a hydrogeochemical model of the geothermal system at Zunil. In addition to the analyses obtained as part of the present investigation, our evaluation of the fluid geochemistry was based on chemical analyses of springs sampled by JICA (1977); chemical data on springs, production (ZCQ) and thermal gradient (Z) wells collected by INDE and compiled by Michels (1988); and the isotopic and chemical analyses of springs and production wells collected by Fournier and Hanshaw (1981), and Giggenbach (1986). The locations of the wells and springs in the immediate vicinity of the wellfield are shown in Figure 2.

## DISTRIBUTION OF FLUID TYPES

The thermal fluids that have been sampled in the region encompassing the Zunil geothermal area show an obvious division into sodium chloride, sodium bicarbonate-sulfate, and sodium sulfate fluid types (Fig. 3). Fluids produced by the production and thermal gradient wells are sodium chloride in character whereas the springs discharge fluids that are dominantly sodium bicarbonate-sulfate and sodium sulfate. One exception is spring z-20 (Fig. 2), which is a sodium chloride fluid similar to that of production well ZCQ-2.

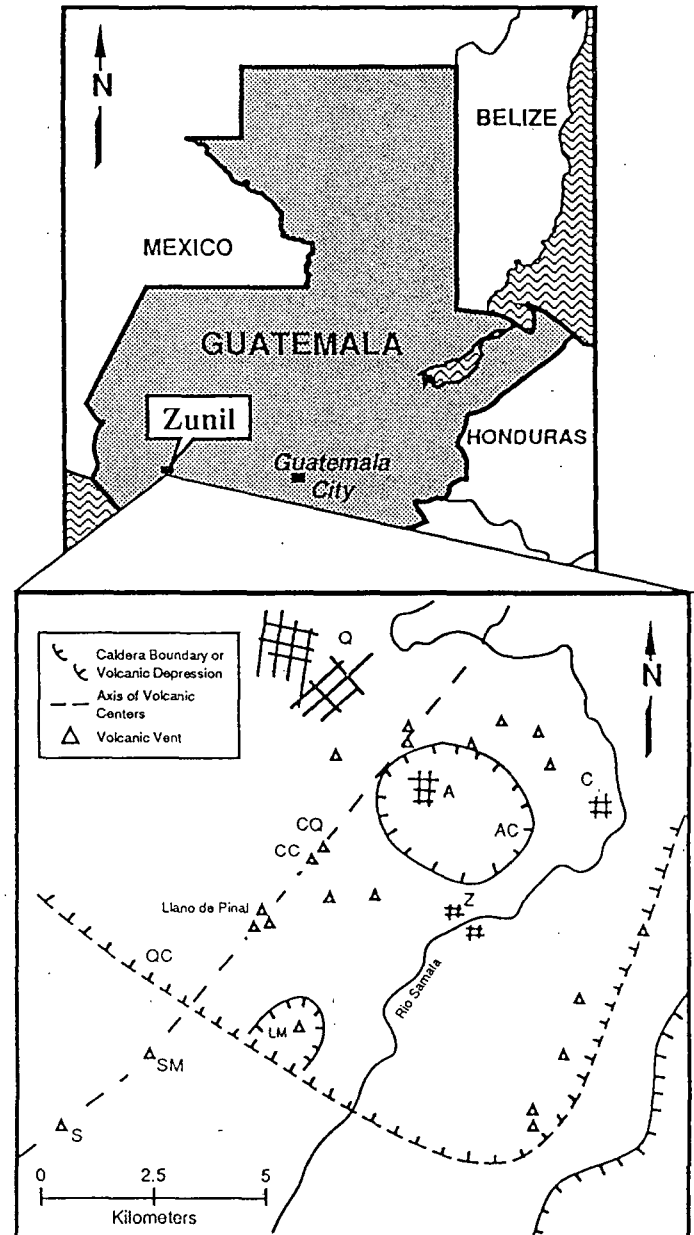


Figure 1. Location map and general geologic features of the Zunil geothermal system. A = Almolonga, AC = Almolonga Caldera, C = Cantel, CC = Cerro Candelaria, CQ = Cerro Quemado, LM = Las Majadas, QC = Quetzaltenango Caldera, S = Santaquito, SM = Santa Maria. The geologic map was modified from Foley et al. (1990).

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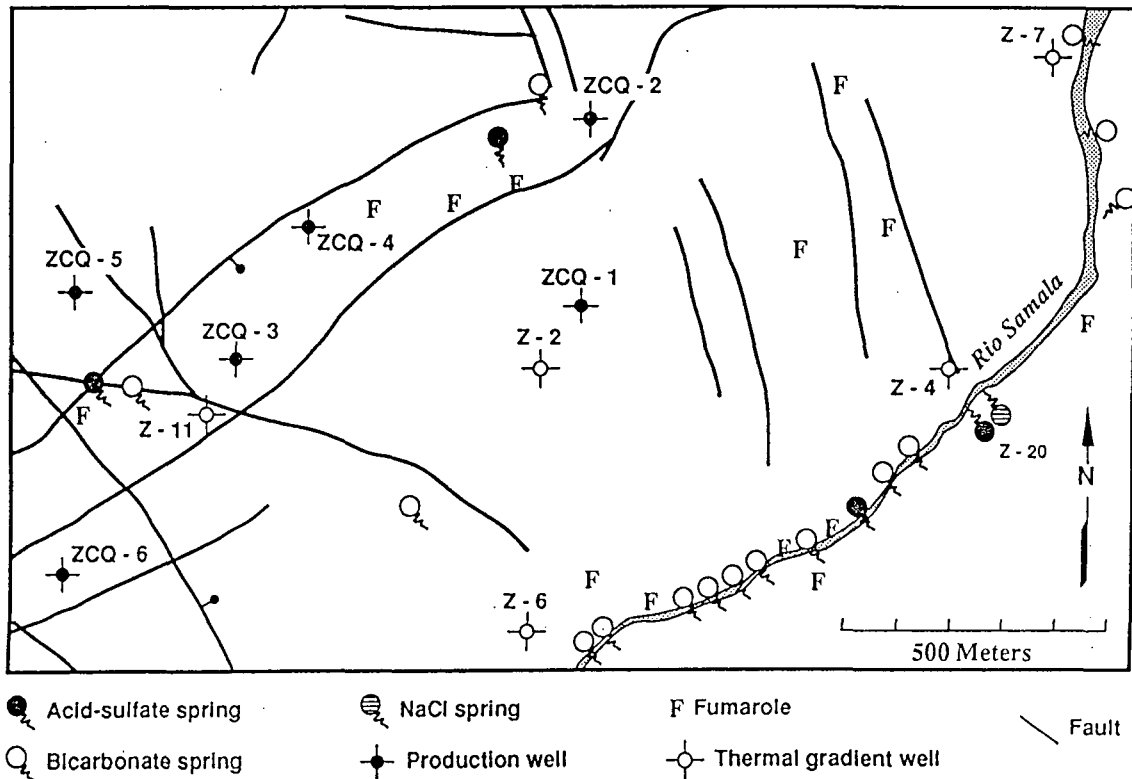


Figure 2. Location of thermal fluid types in the Zunil geothermal system. Fluid produced by thermal wells are sodium chloride in character.

Sodium chloride waters are generally recognized as being primary reservoir fluids in geothermal systems (Henley et al., 1984). Fluids that are sodium bicarbonate-sulfate or sodium sulfate may form secondary reservoirs over and around the deep sodium chloride fluids. These reservoirs develop through the heating of shallow groundwaters by steam containing H<sub>2</sub>S and CO<sub>2</sub> (Mahon et al., 1980). The formation of sulfuric acid from H<sub>2</sub>S and the dissolution of CO<sub>2</sub> can result in high acidities and disequilibrium with the enclosing rocks. Consequently, the chemistries of steam-heated waters are frequently difficult or impossible to interpret in terms of equilibrium reservoir parameters. The chemical data shown in Figure 3 indicate that most of the springs are indeed steam-heated waters with significant HCO<sub>3</sub>.

Giggenbach (1988) has attempted to quantify the degree of chemical equilibrium reached by thermal waters through the application of geothermometers based on Na-, K-, and Mg-bearing minerals. He suggests that a chemically mature fluid, defined as a fluid which is in equilibrium with the reservoir rocks, will have identical temperatures predicted by the K/Mg and K/Na geothermometers. When these predicted temperatures differ widely, the fluid is defined as immature. The most immature fluid will be one produced by the acidification and heating of a groundwater by steam. Because acid fluids can quantitatively dissolve some rocks, transferring the elemental ratios of the rock to the fluid, the

compositions of these fluids may produce spurious geothermometer temperatures.

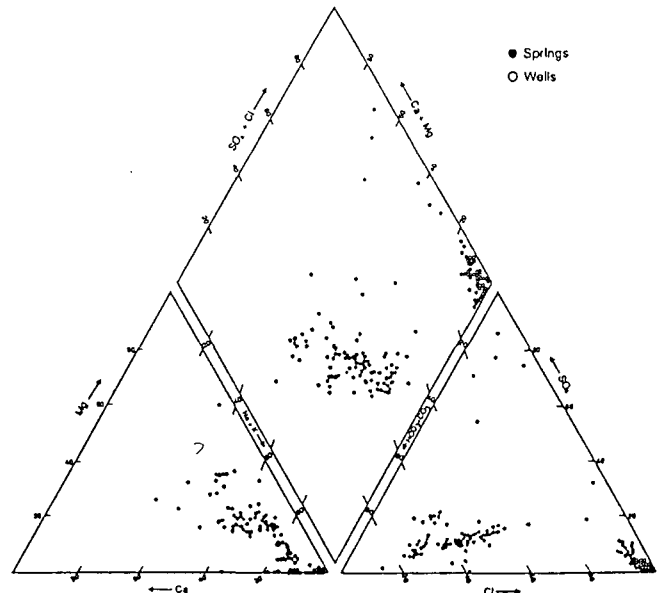


Figure 3. Piper plot of hot springs and thermal well fluids from the Zunil geothermal system.

The maturity relationships of the Zunil fluids are summarized in the ternary plot of Na, K, and Mg shown in Figure 4. Points that plot below the lowermost curved line are immature fluids. Most of

## AUTHOR'S LAST NAME

the springs from the Zunil area plot in this region. The indicated immaturity of these fluids is in agreement with the high acidity and sulfate contents found in some of these fluids. Fluids that plot between the lower and upper curved line have intermediate maturities, whereas those that plot on the upper curved line are fully mature, with concordant K/Na and K/Mg geothermometer temperatures. The predicted temperatures of the geothermometers that Giggenbach (1988) uses for this method are marked on the upper curve. These geothermometers have not yet been extensively tested, and therefore the discussion of chemical geothermometry presented below relies on more established geothermometers.

### GEO THERMOMETRY AND CL-ENTHALPY RELATIONSHIPS

The geothermometer temperatures and chemical analyses of production fluids from the Zunil system are listed in Table 1. The Na/K (Fournier, 1981) geothermometer temperatures indicate maximum reservoir temperatures of approximately 290°C. Production of fluids with these temperatures through deeper drilling is considered reasonable because both ZCQ-5 and 6 recorded maximum downhole temperatures of approximately 288°C.

Table 1. Chemical analyses of production fluids from the Zunil geothermal system. The analyses have been restored to their reservoir compositions using the measured enthalpy for fluids from ZCQ-3 and ZCQ-6, and the K/Mg geothermometer temperature for fluids from ZCQ-2 and ZCQ-4. NP = not preserved, ND = not detected, NA = not analyzed, and Tnk = Na/K geothermometer temperatures (Fournier, 1981).

Well	ZCQ-3	ZCQ-6	ZCQ-2	ZCQ-4
Na	525	545	501	1187
K	111	106	74	190
Ca	7	4	4.6	33.3
Mg	ND	ND	0.04	0.04
SiO <sub>2</sub>	484	451	NP	NP
B	21.8	22.8	24.6	46
Li	4.92	4.47	3.07	12.32
SO <sub>4</sub>	17.8	28.5	191	65
Cl	900	897	686	2071
CO <sub>2</sub>	1867	2905	NA	NA
H <sub>2</sub> S	51.3	40.2	NA	NA
N <sub>2</sub>	8.57	11.7	NA	NA
NH <sub>3</sub>	1.35	1.81	NA	NA
H <sub>2</sub>	0.0925	0.0757	NA	NA
CH <sub>4</sub>	0.0976	0.0706	NA	NA
Ar	0.0320	0.0258	NA	NA
Tnk	290	281	253	261

Enthalpies derived from geothermometer temperatures can be used in conjunction with the concentration of Cl in the fluids to predict maximum reservoir temperatures and to define areas of mixing and boiling. A Cl-enthalpy plot for the Zunil fluids, based on the Na/K geothermometer (Fournier, 1981), is shown in Figure 5. The trends expected for boiling, mixing, and conductive cooling are also shown on this

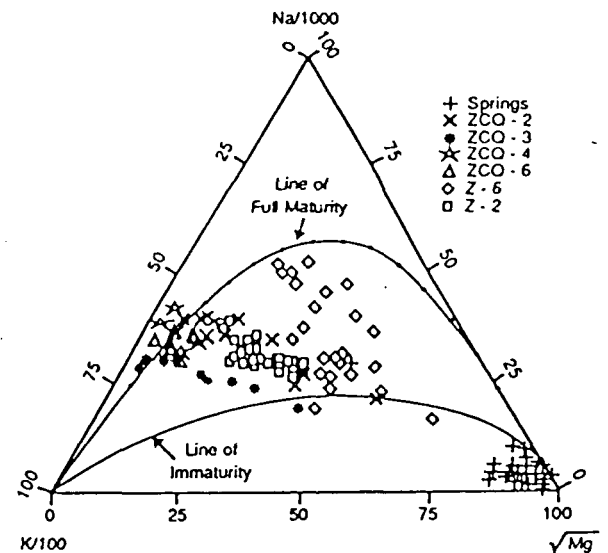


Figure 4. Maturity indices of thermal fluids from the Zunil geothermal system.

figure. It is apparent from these data that the fluids can all be related to a single parent fluid that has undergone varying degrees of boiling, mixing with heated groundwaters, and conductive cooling. The Cl-enthalpy plot shows that fluids from ZCQ-3 and 6 are nearly identical. The position of ZCQ-3 and 6 indicates that these fluids could be derived from the parent fluid by mixing with groundwater having a temperature of about 170°C. The high temperature of the diluent and the fluid inclusion data discussed by Moore et al., (1990) suggest that the diluent is steam-heated groundwater. Fluids from ZCQ-2 and Z-4 are similar to each other and could be produced by further dilution of ZCQ-3 and 6. The composition of ZCQ-4 lies along a boiling trend that extends through the parental fluid to the enthalpy of pure steam. Finally, fluid from thermal gradient wells Z-2 and 6 can be derived by conductive cooling of a fluid that was slightly more concentrated than the reservoir liquid feeding ZCQ-3 and 6. As shown in Figure 5, the parent fluid is predicted to have a temperature of approximately 335°C and a chlorinity of 1550 ppm.

### STABLE ISOTOPES

The O-18 and deuterium contents of fluids from the Zunil area are plotted on Figure 6. Also plotted on these figures are the Western Guatemala local (Fournier and Hanshaw, 1981) and the global (Craig, 1961) meteoric water lines. The isotopic compositions of the deep thermal fluids from Zunil show a 5 part per mil oxygen shift. This is comparable to other high-temperature productive geothermal systems throughout the world (Craig, 1963).

The compositional range of the hot spring fluids is similar to that of cold groundwaters from the vicinity

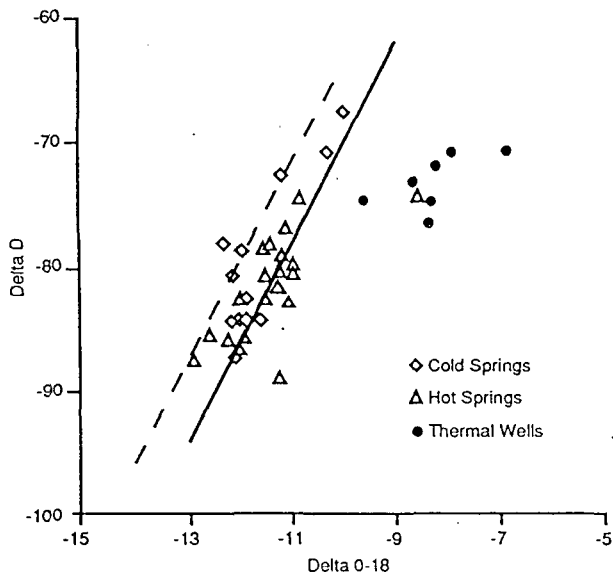


Figure 5. Chloride-enthalpy diagram for the Zunil thermal fluids. Enthalpies are derived from the Na/K (Fournier) geothermometer.

of Zunil as well as from Llano de Pinal (Fig. 1). In addition, steam derived from boiling the deep thermal fluids to temperatures ranging from 140° to 180°C would also produce isotopic values similar to the hot and cold spring fluids. Thus, the stable isotope data alone cannot separate the contributions of steam and groundwater to the hot spring fluids. The low tritium contents of the hot springs discussed below suggest that, if the groundwater component is large, it must be relatively old.

The compositions of the geothermal fluids and some of the groundwaters define a linear relationship suggestive of mixing (Fig. 6). However, the source of recharge for the deep geothermal fluids is not clear. Because the groundwater compositions are significantly lighter in deuterium than the production-well fluids, these groundwaters do not appear to represent the source of recharge for the deep fluids. Analyses of water from the Rio Samala between Zunil and Quetzaltenango (Fig. 1; Fournier and Hanshaw, 1981), however, have deuterium values of -71.5 and -68 parts per mil, which are similar to the deuterium contents of the geothermal fluids. Thus, the waters that recharge the deep geothermal fluids may originate northeast of Zunil, in the regions drained by the Rio Samala.

## TRITIUM

Tritium has been analyzed in samples from the Rio Samala, hot and cold springs, and thermal wells. In contrast to most explored geothermal systems, concentrations of tritium in the thermal well waters are greater than or equal to those in the hot springs. Tritium in the cold springs and the Rio Samala are 5 to 25 times greater than the thermal well waters.

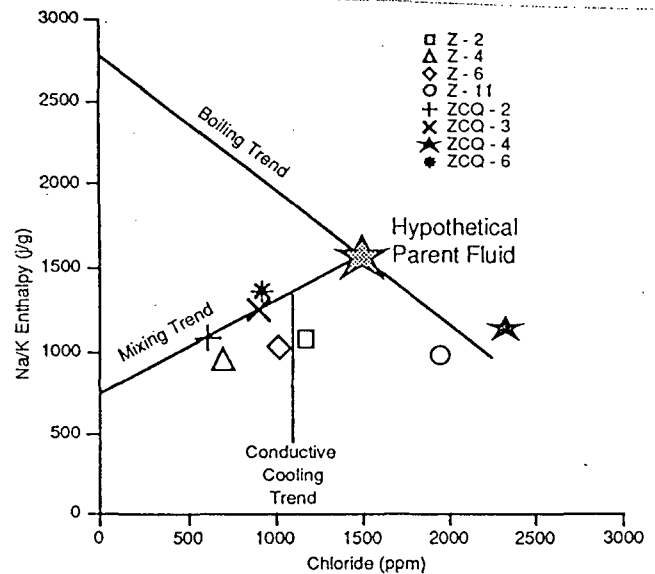


Figure 6. Isotopic composition of Zunil fluids. Data sources are listed in the text.

The low tritium concentrations in the hot springs appear to be caused by the mixing of tritium-depleted steam and groundwater. Because of fractionation during boiling, the tritium concentration of the steam would be lower than that of the boiled liquid. The actual concentration of the mixture would depend on the mixing ratio and the age of the groundwaters. If the steam component is small, the groundwaters must be old.

If we assume that the geothermal fluids contain no component of tritium-enriched groundwater, then the residence time of the thermal fluids can be calculated by the method of Pearson and Truesdell (1978). This method takes into account the hydrodynamic-dispersive mixing that may occur within the geothermal system as well as the possibility of multiple sources of fluid recharge. The ratio of system volume to input or output is taken to be the turnover time, or residence time, of the system. This has been shown to be identical to the average transit time or average age of particles leaving the reservoir.

Data on the tritium levels in precipitation in Central America are required in order to apply the differential equation of Pearson and Truesdell (1978) to the Zunil tritium data. These data have been compiled and integrated for other studies in Central America and are published in Goff et al. (1987). The results of their integration imply a residence time of approximately 200 years for the deep geothermal fluids at Zunil.

## HYDROLOGY

A hydrogeologic investigation of the Llano de Pinal was initiated to determine the potential for groundwater recharge to the Zunil geothermal system. This

investigation consisted of a well inventory, streamflow data review, geochemical sampling, well testing, and the examination of geologic conditions.

Three hydrologic units can be identified in the area encompassing Zunil, Llano de Pinal and Quezaltenango. A shallow groundwater flow system was identified in the Llano de Pinal area (Fig. 1). This flow system occurs at higher elevations than the Rio Samala basin and appears to be limited to the upper more recent pyroclastic and alluvial deposits. An intermediate flow system, which discharges low-temperature steam-heated water, appears to be the source for most of the thermal discharges occurring along the Rio Samala. The deep flow system is represented by fluids discharged from the production wells and some of the thermal gradient wells. The deep hydrothermal system is confined to high permeability fracture zones.

The rocks underlying the upper part of the Llano de Pinal and Quezaltenango basin consist of a thick sequence of air fall tuffs that dip to the northeast. Because the horizontal hydraulic conductivity of volcanic tuffs is generally greater than their vertical hydraulic conductivity, movement of the groundwater will occur in a down-dip direction. The hydraulic gradient becomes shallower as the Quezaltenango basin is approached from the Llano de Pinal until it is nearly flat. The lack of springs and surface drainage features within the lower portion of the Llano de Pinal and within most of the Quezaltenango basin suggests that vertical groundwater movement is dominant in this area. This also indicates that the potential recharge zone may extend throughout most of the Quezaltenango basin.

Most of the groundwater from the intermediate system flows southward, discharging to the surface as thermal springs along the Rio Samala. A smaller, shallow component may flow northward toward the Quezaltenango basin.

The exact character of the deep hydrothermal flow system is difficult to define since deep subsurface drillhole data is limited to a relatively small area. Several possible sources of recharge exist for the hydrothermal system. Isotope data discussed above suggest that the most likely source of the deep hydrothermal fluids is downward leakage along faults from the area northeast of the well field. Foley et al. (1990) have shown that this is a structurally complex area which is underlain by a large caldera and transected by a major N40 to 50E trending fault zone. The intersection of the caldera ring structure with the NE-trending fault zone (located several km NE of Fig. 2) could have resulted in a high density of fracture zones, creating transmissive areas for the vertical migration of the groundwater. The northeast-trending fault may form a transmissive region for groundwater movement from the Quezaltenango recharge area to the well field. Additionally, the high relief of the area creates a hydraulic head which enhances the vertical movement of groundwater.

Hydrologic studies of the upper Rio Samala basin show that there is abundant precipitation. The lack of an integrated surface drainage system in the Llano de Pinal and upper Quezaltenango basin in conjunction with the large streamflow gains along the Rio Samala between Quezaltenango and Zunil, provide evidence that this region contains and discharges large quantities of groundwater.

The hydrological system was modeled using vertical cross-section simulations to investigate the interaction between recharge and discharge sources and to determine whether the deeper granodiorite contributes to the thermal discharge (Fig. 1). The unit thickness used were 1200 meters for the volcanic rocks in the upper unit, and 2300 meters for the granodiorite in the lower unit. The discharge area is represented by a fractured zone corresponding to the high density of faulting observed in this area. Permeabilities for the simulation were  $1.5 \times 10^{-6}$  m/s for the volcanic rocks and granodiorite and one order of magnitude higher for the fractured zone. Log velocity vectors resulting from the simulation are shown in Figure 7.

The simulated regional hydrogeologic system flows in an easterly and southerly direction from a recharge area in the Quezaltenango basin (Fig. 7). The permeabilities required to calibrate the local and regional models were approximately one to two orders of magnitude higher than those values derived from the field tests. This may indicate that the regional permeabilities are somewhat higher than the values measured at selected locations.

All of the numerical simulations that were performed indicated some flow of geothermal fluid in the granodiorite beneath the well field. A wide range of permeabilities was used in the simulations. Although more flow occurred at the higher permeabilities ( $8.0 \times 10^{-7}$  m<sup>2</sup>/s), some flow still exists in the granodiorite even if the lower values ( $8.0 \times 10^{-11}$  m<sup>2</sup>/s) are used. The exclusion of flow in the granodiorite beneath the northern portion of the basin should produce a series of local recharge and discharge sources at the surface on both sides of the regional flow system. Springs have not been observed in the northern portion in the Llano de Pinal area, which indicates that flow must occur in the deep rocks.

Available hydrogeologic data indicate there is sufficient groundwater recharge for the operation of a 15 MW power plant. These data, and the results of geologic and geochemical studies indicate that the hydrothermal fluids persist to depths greater than those penetrated by the production wells.

The simulations may represent only a portion of the total recharge available, based on isotope data. This data indicates a common source for the Rio Samala and the deep thermal system. This, combined with the tritium data that suggest a residence time of approximately 200 years, indicates that the upper

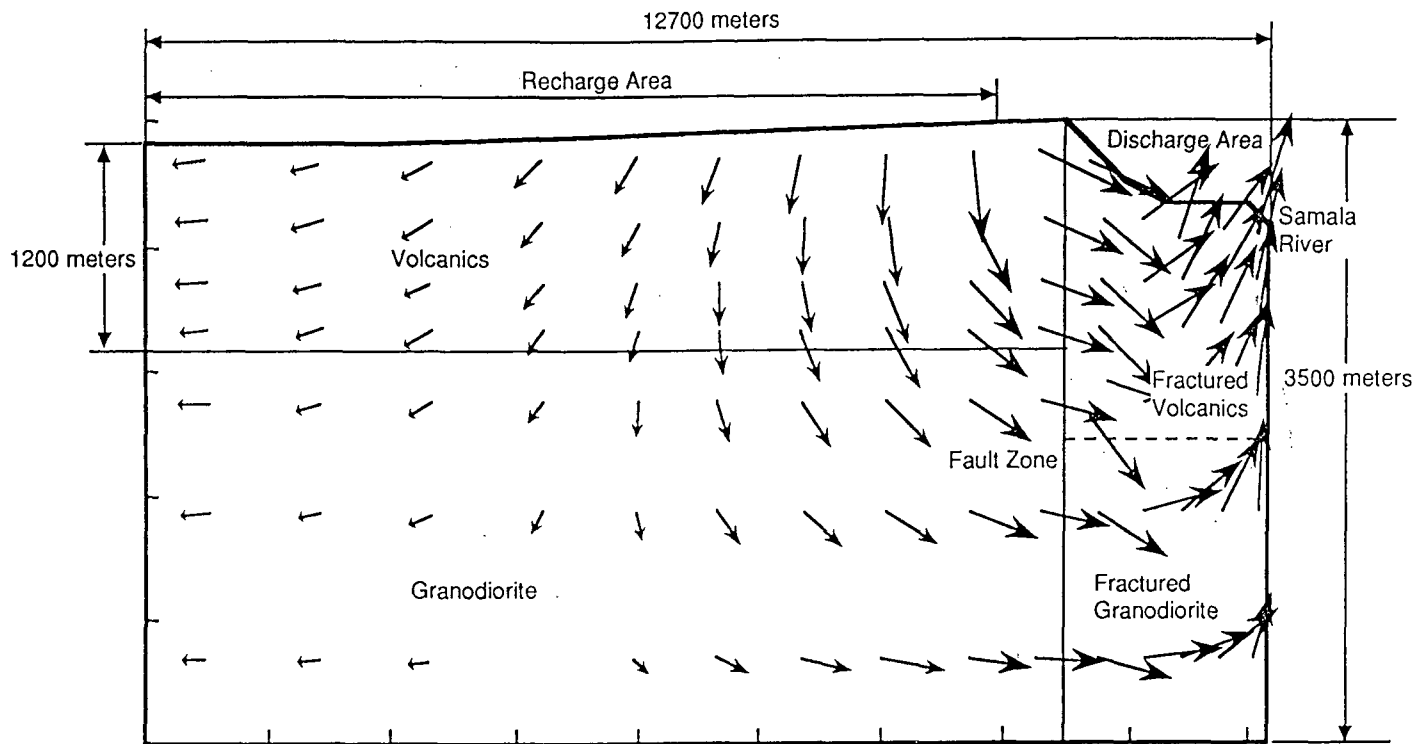


Figure 7. Simulated hydrogeologic cross section. The arrows represent velocity vectors, the size of which are proportional to the log of the velocity.

Quezaltenango basin is most likely the dominant recharge area. However, additional data on the granodiorite is required to confirm the properties of this geothermal system and update the modeling.

#### CONCLUSIONS

The chemical, isotopic, and hydrologic relationships of fluids from wells and springs in the region of the Zunil geothermal field define a complex hydrologic system. A plume of high-temperature water flows upward from granodiorite in the western part of the existing well field and travels south and east through the overlying volcanics. As this fluid travels across the area, it boils and mixes with shallow steam-heated waters, producing an intermediate flow system. These steam-heated fluids overlie and extend beyond the deeper sodium chloride reservoir and discharge as sulfate- and bicarbonate-rich thermal springs, primarily along the Rio Samala. Cl-enthalpy relationships suggest that the deep fluid may have a temperature as high as 335°C and a chlorinity of up to 1550 ppm. The isotopic data indicate that recharge for the deep geothermal fluids may originate in the upper Quezaltenango basin, which is several km NE of the geothermal system. In contrast, the isotopic data indicate that the groundwater component in the steam-heated waters may be locally derived.

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