

TEC-3

A HYDRO-GEOCHEMICAL
STUDY OF THE SOUTHERN HALF
OF THE SANTA CRUZ BASIN NEAR
COOLIDGE, ARIZONA

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Pima Farms Well No. 1 and Selected Irrigation Wells----- in pocket

SUMMARY

Geochemistry reveals that the Pima Farms Well #1 is marginally geothermal. Fluid chemistry and temperature showed little change from 16 to a final 193 elapsed hours of pumping. The thermodynamic characteristics of the fluids are similar to those found in oil wells, i.e. high hydrostatic pressure and low temperature-enthalpy conditions. In general, the chemical concentrations of fluids are distinctly impoverished compared to the chemical concentrations of known producing reservoirs. Maximum subsurface equilibrium temperatures are about 120°C. This temperature agrees well with final well log temperatures. The Pima Farms water is similar to the water from a distant hot irrigation well (X90354). The Pima Farms water may fairly represent the deep waters of the Lower Santa Cruz basin.

The Coolidge area lies on a deep lacustrine basin containing a large volume of hot water, probably conate in part. The heat source is probably the natural gradient of the area. The anomalously hot water found near the surface in irrigation wells probably arose from depth to fill the hydrologic vacuum created by years of surface irrigation.

In spite of the superior reservoir characteristic, i.e. fluid production, low fluid temperature will resign fluid use to space or process heating, irrigation, and possibly air conditioning. This assumes that the calculated 120°C water exists and can be pumped at sufficient rates. The elements present in this water should not present serious corrosion problems.

INTRODUCTION

Temperature and chemical measurements were made during eight days of interrupted pumping at the Pima Farms Well #1.. This report discusses chemical methodology, fluid temperatures, temperature logs obtained before and after pumping, fluid chemistry, and subsurface temperatures, system modeling, and possible problems in industrial utilization of fluids.

Methodology

Temperature measurements were made with a maximum reading thermometer (BT6410 MAX) and a Weston probe thermometer (#4303). Agreement was better than 0.2 percent.

Samples were collected at approximately 12 hour intervals. Field chemical determinations were generally made within a maximum of 12 hours and a minimum of 2 hours after sampling. Precipitation and deterioration of samples was not a problem in this time scale.

Approximately four liters of fluid were collected in plastic bottles at each sampling. The fluid was then filtered through a 0.45 micron filter and analysed for F, Cl, SiO₂ and SO₄. Four 125ml samples were also collected at each sampling and were analyzed for pH, NH₃, HCO₃, and H₂S without filtering. A portion of the filtrate was then acidified with 2 ml of high purity nitric acid. The acidified sample, HCO₃ sample, and the remaining filtrate were flown to Denver and analyzed by C. M. Jensen of Amax Exploration, Inc. Precision (relative error) and accuracy for chemical analyses is better than 5 percent except for SO₄ which is better than 10 percent.

Analytical procedures for thermal waters are summarized as follows:

pH	electrometric
F	specific ion electrode
Cl	mercurimetric titration
SO ₄	turbidimetric
SiO ₂	colorimetric and AA
B	colorimetric
HCO ₃	potentiometric titration
CO ₃	calculated from HCO ₃ and pH
Na	AA
K	AA
Ca	AA
Mg	AA
Li	Flame emission
Fe	AA
Cu	AA
Zn	AA
Mo	colorimetric
NH ₃	colorimetric
H ₂ S	iodimetric titration
T.D.S.	evaporation of 300 ml at 180°C

Fluid thermodynamics

Fluid temperatures measured at the surface are plotted with respect to pumping time on Figure 1. Fluid temperature increased from 60 to 158°F in one hour and thereafter increased very slowly to a maximum of 181°F eight days later when pumping ceased. Pumping was interrupted twice owing to problems in containing the hot water on the surface. The final temperature-time slope is near horizontal.

Three temperature surveys were conducted on September 5, August 21, and October 28, 1974. Results are plotted on Figure 2 along with a "normal" temperature gradient line of 35°C per kilometer (28.8°F per 1000 feet) and the boiling point curve for pure water. The September 5 survey reveals a smooth line almost parallel to the normal gradient line down to about 5800 feet. Temperatures dropped sharply below 5800 feet due to a strong zone of permeability and its acceptance of large quantities of cold make-up water. Another cold permeable zone is visible at 7250 feet. The October 28 survey, conducted just after cessation of pumping shows a sharp increase in slope from the surface to 750 feet and a decrease in slope from 750 to 6500 feet. This phenomena can be explained as a heating effect on the well bore and surrounding rock as a result of pumping. Both of the cold permeable zones seen on the September 5 survey achieved ambient temperatures because they are probably the hot water aquifers. Even after pumping the slope of the October 28 survey below 6500 feet is about parallel to the normal gradient line.

The boiling point curve for pure water is seen on the upper left side of Figure 2. Extrapolation of the visible slope of any of the temperature surveys or the normal gradient line lends assurance that deep flashing of fluids is impossible at normal depth pressure conditions.

Figure 3 is a phase diagram for water showing the relationship of pressure, enthalpy and temperature up to and past the critical point of water. From the left side of the diagram to the lump-shaped envelope, water exists as a liquid with relatively low enthalpy. A mixture of vapor and liquid exists in the envelope with the vapor fraction increasing from 0 to 100 percent from the left to the right most boundary of the envelope. From the right side of the envelope to the right side of the diagram water can exist only as a vapor. The critical point is loosely defined as the pressure-temperature condition where a vapor and a liquid have the same physical properties. The positions of natural hot water-steam and dry-steam systems are shown on Figure 3.

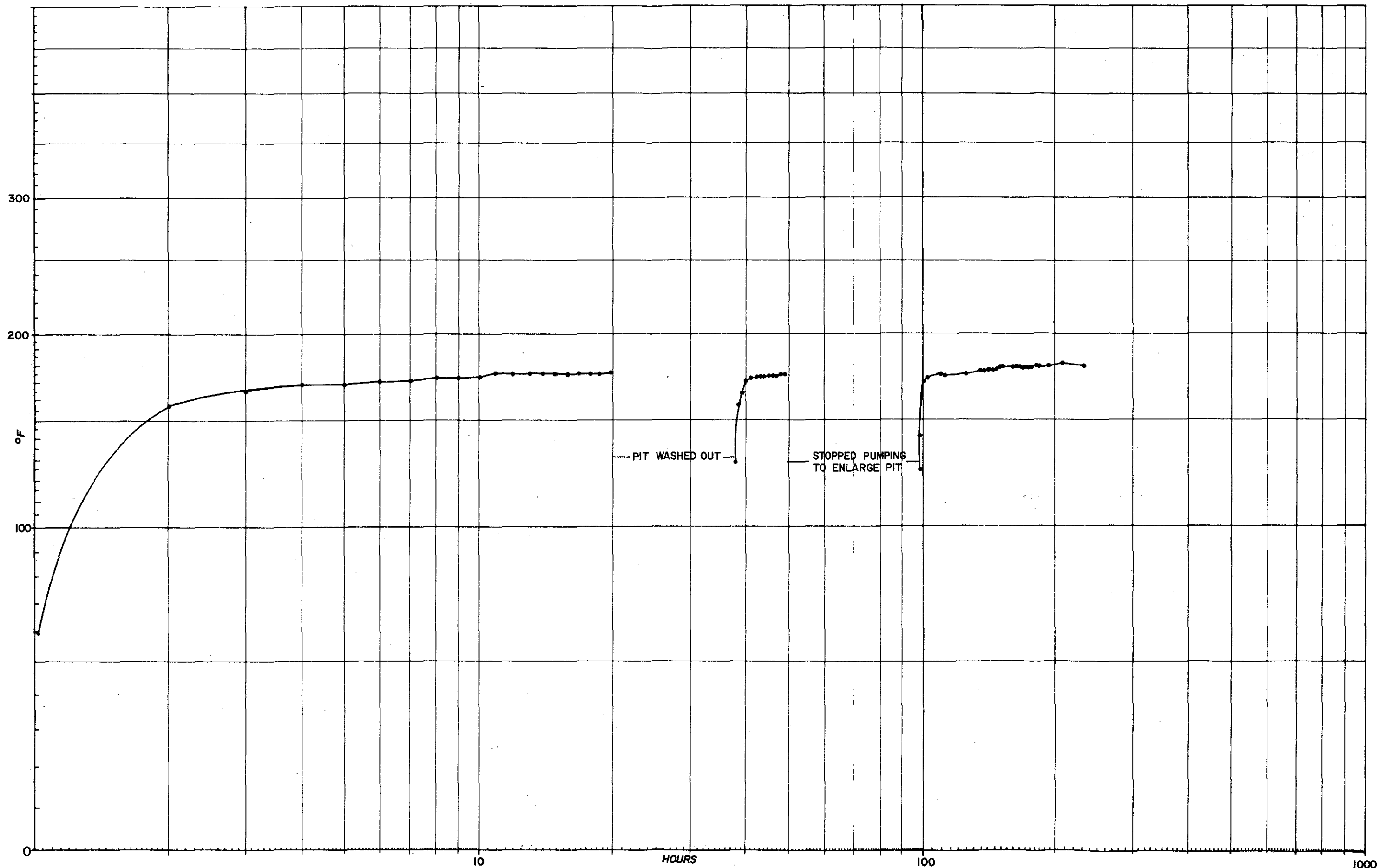


FIGURE 1. FLUID TEMPERATURE AT THE SURFACE PLOTTED AGAINST PUMPING TIME IN HOURS.

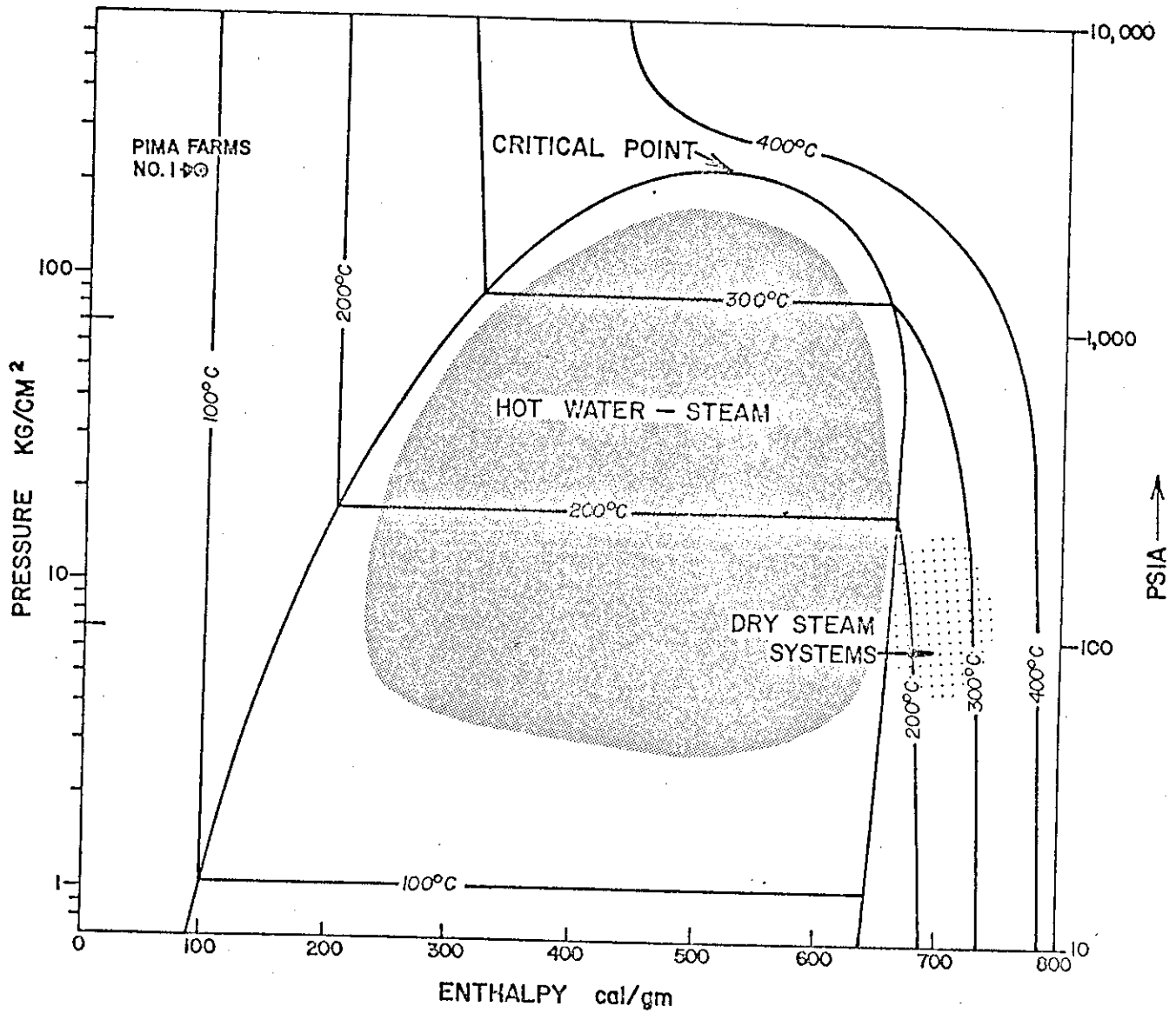


FIGURE 3. A PHASE DIAGRAM FOR WATER, SHOWING THE RELATIVE POSITION OF NATURAL GEOTHERMAL SYSTEMS AND PIMA FARMS WELL # 1.

Calculated bottom hole pressure for the Pima Farms Well is 216 kg/cm², based on a water density of 1 and the hole depth. This figure agrees well with a pressure log conducted on September 4, 1974. Assuming 216 kg/cm² and 82°C the Pima Farms Well falls in the realm of oil wells as seen on Figure 3, i.e. high hydrostatic pressure and low temperature-enthalpy conditions.

Fluid Chemistry

Chemical analyses for 13 samples from the Pima Farms Well #1 and selected hot and cold irrigation wells are reported in Table 1. All of the 13 samples are chemically similar except the first two (X90340 and X90341) collected on October 17. These two samples are a mixture of make-up water, drilling mud, iron rust and a small fraction of deep thermal water. Sample X90340 is very similar to the make-up water well sample X90347. The remaining Pima Farms' samples reflect equilibrium conditions at depth. The Pima Farms' samples collected after October 17 have a distinct sodium-chloride character, basic pH, higher than background levels (see make-up well sample X90347) of silica, alkalis and metals. These chemical conditions are characteristic of hot water systems.

The chemical "potency" of thermal waters can be assessed by a comparison of other thermal waters and cold surface waters. In Table 2, the chemical concentrations of a hot irrigation well, sample X90354 and the Pima Farms sample X90356 are shown as factors of the cold irrigation well X90347. This comparison assumes that the cold irrigation well X90347 fairly represents the local ground water. Thermal waters that contain large concentrations of F, Cl, SO₄, SiO₂, Na, K, B, Li, H₂S, and NH₃ are usually considered attractive. SO₄ is sometimes an exception for it may be produced near surface through oxidation of H₂S. Li is generally considered a magmatic contribution. However, the source of Li in the Coolidge area is probably lacustrine sediments. NH₃ is also considered a primary magmatic gas but it can easily be produced from nitrogen compounds (present in sediments) and catalysis with iron, i.e. the drill pipe and casing. NH₃ anomalies found in areas underlain by degassing igneous rock (The Geysers) are generally 10 to 20 times the level found in the Pima Farms' water. H₂S and B can be produced by passing very hot water over S- and B rich sediments or metasediments, or through primary degassing of igneous rocks.

Table 1. Chemical Analyses for Samples from the Pima Farms Well #1 and Selected Hot and Cold Irrigation Wells*

	Pima Farms Well #1													Cold Irrigation Wells		Hot Irrigation Wells	
	X90340	X90341	X90342	X90343	X90344	X90345	X90346	X90348	X90349	X90350	X90351	X90355	X90356	X90347	X90352	X90353	X90354
Temperature °C	60	158	176	174	176	142	176	177	178.6	179.6	180	181	181	80	77	98.6	149
Collection date	10/17	10/17	10/18	10/19	10/19	10/21	10/22	10/22	10/23	10/23	10/24	10/25	10/25	10/22	10/25	10/25	10/25
Collection time	3:30pm	4:30pm	7:30am	9:00am	5:10pm	6:10pm	9:30am	9:00pm	11:00am	10:00pm	10:00am	9:30am	5:00pm	10:20am	10:30am	11:00am	1:00pm
Elapsed time (hrs.)	0	1	16	41.5	49.5	98.4	114	125.5	139.5	150.5	162.5	186.0	193.5	--	--	--	--
Discharge (gal/m)	~300	~300	~300	~300	~300	~300	~300	~300	~300	~300	~300	~300	~300	~1000	~750	~1000	~1000
pH	6.23	8.12	8.40	8.20	8.61	8.51	8.40	8.49	8.42	8.50	8.48	8.45	8.45	7.58	7.52	9.04	8.70
F(ppm)	0.40	0.56	4.18	4.13	4.40	4.40	4.41	4.35	4.45	4.40	4.42	4.40	4.45	0.42	0.41	3.70	6.20
Cl (ppm)	253	169	1250	1280	1330	1320	1380	1350	1350	1405	1400	1380	1390	240	289	159	796
SO ₄ (ppm)	89	74	155	146	150	135	155	160	155	145	145	145	145	120	240	95	215
HCO ₃ (ppm)	19	45	32	24	19	19	19	22	--	17	16	16	14	131	12	51	29
CO ₃ (ppm)	0	0	0	0	0	4	0	0	--	<1	<1	<1	<1	0	0	10	12
SiO ₂ (ppm) Total	6	4	54	54	52	43	56	55	57	56	55	60	61	32	32	26	36
Na (ppm)	140	96	720	740	740	780	750	770	--	770	780	750	740	79	140	180	580
K (ppm)	4.3	5.6	9.0	9.0	9.1	9.7	9.7	9.7	--	9.8	9.8	9.7	9.7	3.6	4.2	1.4	3.6
Ca (ppm)	38	34	169	174	180	197	191	240	--	240	230	230	240	128	155	5.4	230
Mg (ppm)	6.9	8.6	1.2	1.2	1.0	1.1	0.9	0.8	--	0.4	0.4	0.4	0.4	19	16	0.1	0.3
B (ppm)	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	1.0	--	<1.0	<1.0	<1.0	1.1	<1.0	<1.0	<1.0	<1.0
Li (ppm)	0.2	<0.1	1.3	1.3	1.4	1.5	1.5	1.3	--	1.4	1.4	1.4	1.4	<0.1	0.1	0.2	0.9
Fe (ppm)	2.5	<0.1	0.2	0.1	0.1	0.1	<0.1	0.1	--	0.1	0.1	0.1	0.1	<0.1	<0.1	<0.1	<0.1
Cu (ppm)	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	--	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mo (ppb)	3	10	75	62	75	75	75	75	--	62	62	62	62	2	<1	35	75
Zn (ppm)	0.1	0.1	0.1	0.1	0.1	0.1	<0.1	0.1	--	0.1	0.1	0.2	0.1	0.1	0.1	0.1	0.1
NH ₃ (ppm)	2.37	3.00	0.96	1.00	1.00	1.40	1.10	0.87	1.25	1.40	1.40	1.40	1.39	0.03	0.02	0.00	0.01
H ₂ S (ppm)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

*See map for geographic locations

TABLE 2. A comparison of chemical concentrations between a cold irrigation well, a hot irrigation well and the Pima Farm Well #1. (See text for explanation.)

	COLD IRRIGATION WELL X90347	HOT IRRIGATION WELL X90354	PIMA FARMS WELL #1 X90356
Values higher than background levels are favorable.			
F	1	14.	10.6
Cl	1	3.3	5.8
SO ₄	1	1.8	1.2
SiO ₂	1	1.1	1.9
Na	1	7.3	9.4
K	1	1.	2.6
B	1	-	-
Li	1	9.	14.
NH ₃	1	0.3	46.
Values lower than background levels are favorable.			
HCO ₃	1	0.2	0.1
Mg	1	0.016	0.021
Ca	1	1.8	1.9

The Pima Farms' water is anomalous in neither H₂S nor B. The concentrations of Cl and F appear high but considering their solubilities and considering that lake sediments are rich sources of both elements, their concentrations are in tune with calculated and measured temperatures. The solubilities of HCO₃, Mg and Ca are inversely related to temperature. Low concentrations of these ions in thermal waters are considered attractive. It is interesting that the Pima Farms and the hot irrigation water have near identical levels of HCO₃, Mg and Ca. It is clear that the Pima Farms' water is similar to the local ground water in SO₄, SiO₂, K and B and similar in Cl, F, Na, HCO₃, Mg, and Ca to a hot irrigation well, Sample X90354. This well is 8 miles distant and probably no deeper than 2000 feet.

Figures 4, 5, 6 and 7 demonstrate the change in concentration of selected elements with time during pumping. These curves are similar to the temperature-pumping time curve (Figure 1), i.e. a very low slope was achieved after 16 hours of pumping. The probability of increasing these slopes with further pumping is very low.

Table 3 contains a listing of calculations by Solmneq (Kharaka, 1973), a solution-mineral equilibrium computer program and Mixture (Truesdell et al, 1973), a dilution program. The Pima Farms' sample X90346 was considered representative and selected for computation. The atomic ratios listed in Table 3 are qualitative indicators of water genre and quality. The high Cl/F (136.6) and Cl/SO₄ ratios (16.9) indicate a hot water system at depth. Both of these ratios would approach 1 in a steam system or a steam heated hot water system. The calculated value of dissolved CO₂ (2.97ppm) is also very low. A hot water system heated by geothermal steam (a rich source of CO₂) might approach CO₂ saturation. A relatively cool hot water system is also indicated by low concentrations of NH₃, H₂S and B already mentioned (see Table 1). The Na/Ca ratio for a high quality thermal water should be very high due to the solubilities of these elements at high temperatures. The Pima Farms' water displays low Na/Ca ratios (6.84). The Na/Li ratio in most thermal waters is between 60 and 120. The same ratio is generally greater than 1500 for normal ground waters. The Na/Li ratio of 151 in the Pima Farms' water however, is the result of Li rich reservoir rocks which are probably lake sediments and low subsurface temperatures.

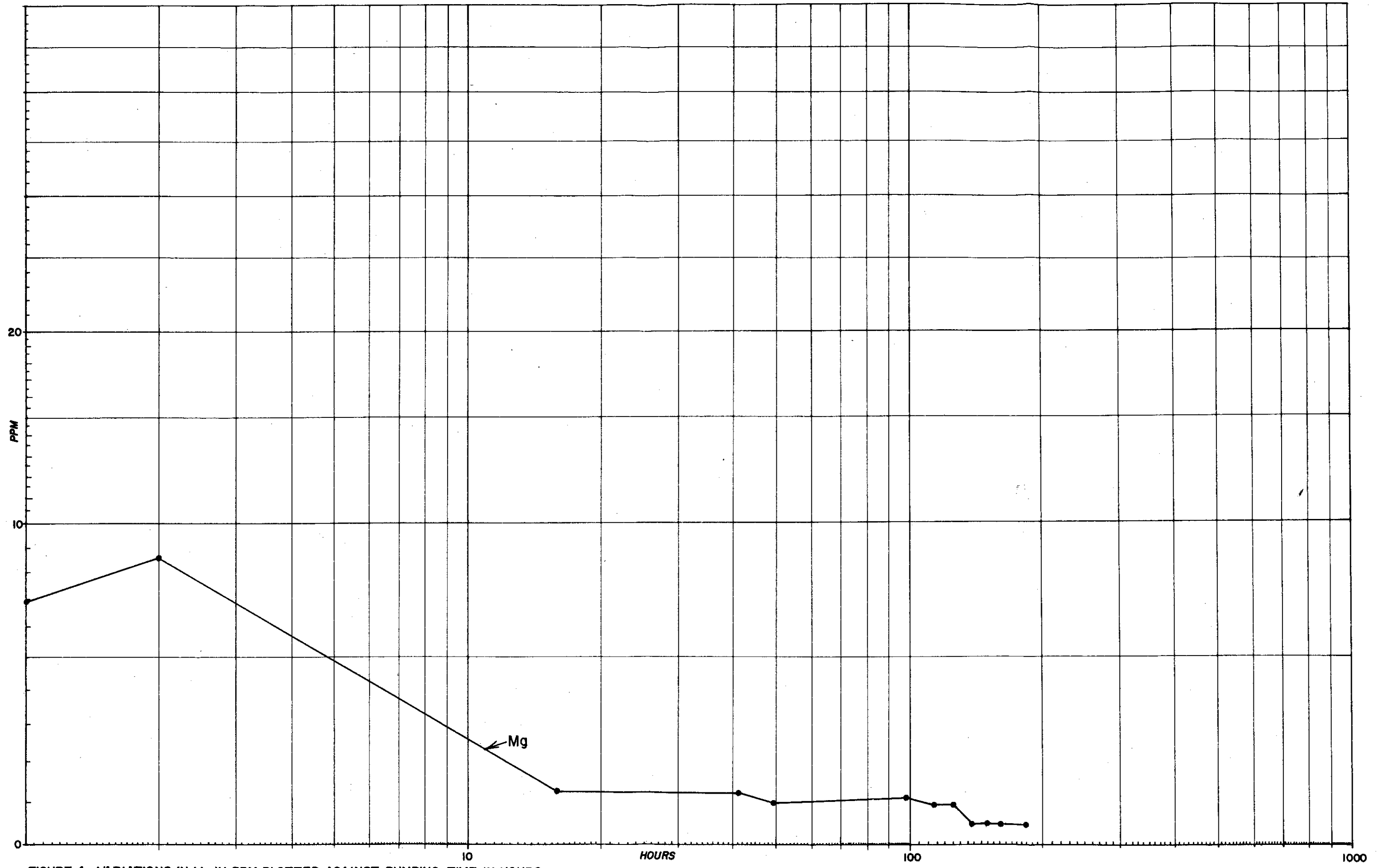


FIGURE 4. VARIATIONS IN Mg IN PPM PLOTTED AGAINST PUMPING TIME IN HOURS.

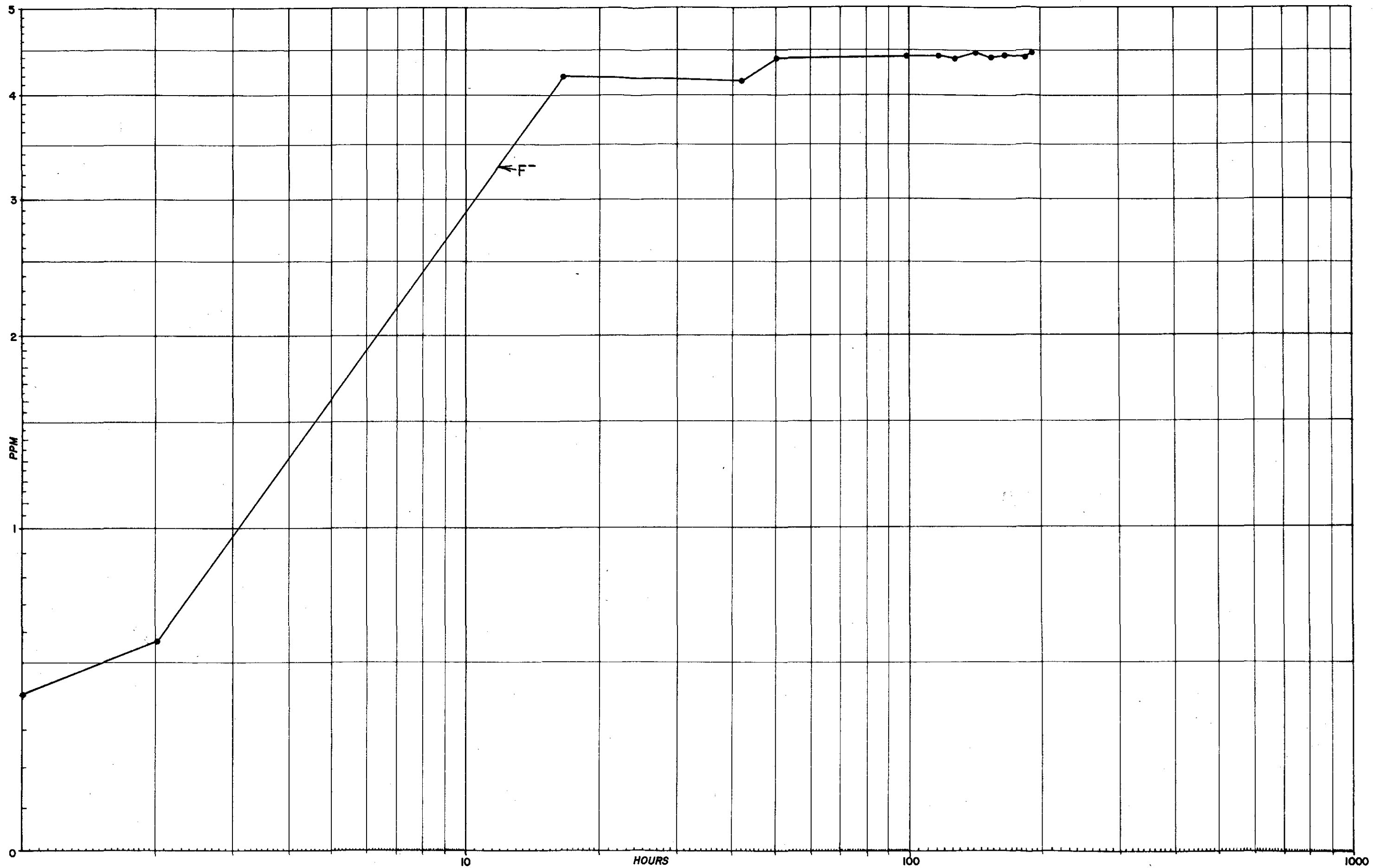


FIGURE 5. VARIATIONS IN F^- IN PPM PLOTTED AGAINST PUMPING TIME IN HOURS.

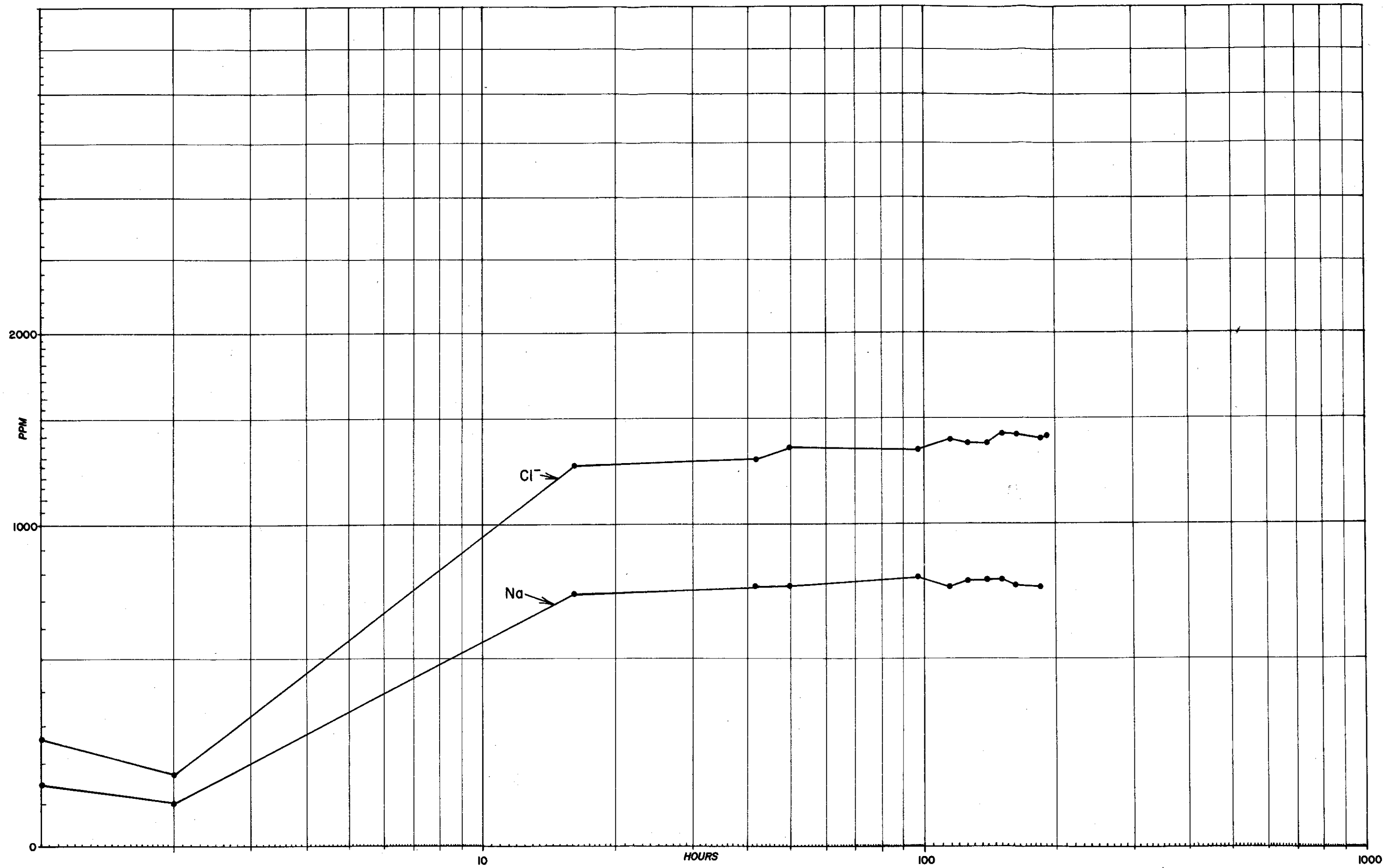


FIGURE 6. VARIATIONS IN Na AND Cl⁻ IN PPM PLOTTED AGAINST PUMPING TIME IN HOURS.

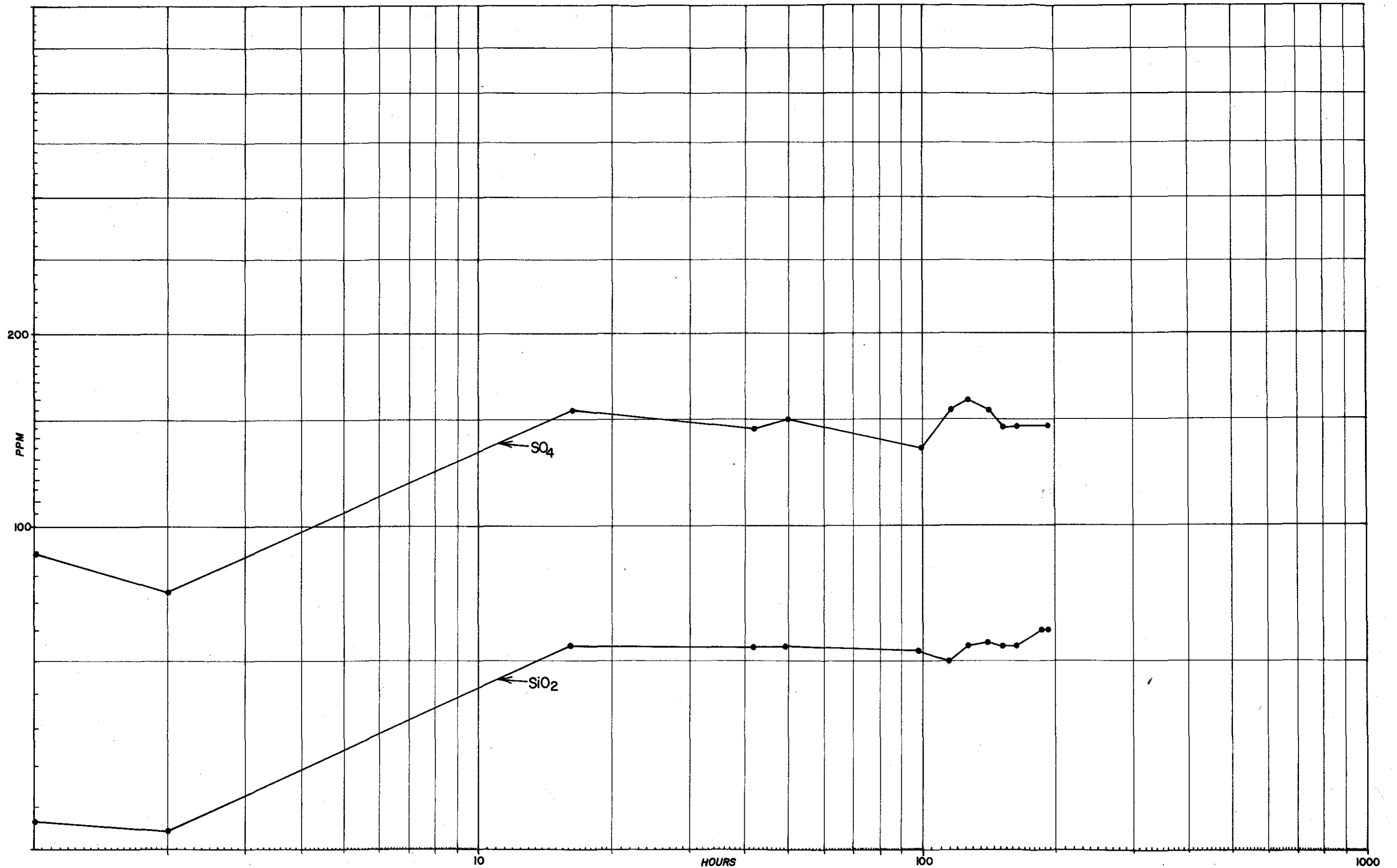


FIGURE 7. VARIATIONS IN SO_4 AND SiO_2 IN PPM, PLOTTED AGAINST PUMPING TIME IN HOURS.

TABLE 3. Calculated species, atomic ratios and equilibrium temperatures for the Pima Farms Sample X90346 and Sample M-3 from the Cerro Prieto field.

	<u>Pima Farms Well #1</u>	<u>Cerro Prieto - Sample M-3</u>
Cl/F atomic ratio	136.6	5864
Cl/SO ₄ atomic ratio	16.9	1493.5
Na/Li atomic ratio	151.0	106.3
Na/Ca atomic ratio	6.84	32.2
CO ₂ ppm	2.97	Not Determined
PCO ₂ (atmospheres)	3.61 x 10 ⁻⁵	Not Determined
TSiO ₂ (amorphous)	-12.6°C (-54.7°F)	Not Determined
TSiO ₂ (conductive)	107.2°C (225°F)	222°C (431.6°F)
TSiO ₂ (maximum)	120°C (248°F)	Not Determined
TNa/K atomic	27°C (80.6°F)	270°C (518°F)
TNa-K-Ca	71.1°C (160°F)	Not Determined

Qualitative subsurface temperatures are also listed in Table 3. The calculated temperature contributed by amorphous silica (TSiO₂ amorphous) is -12.6°C and therefore should not affect the quartz silica temperatures. The minimum quartz silica temperature (TSiO₂ conductive) is 107.2°C. The undiluted quartz silica temperature (TSiO₂ maximum) calculated by computer program Mixture is 120°C and the proportion of hot water (120°C) mixed with cold water (25°C) is reported as 40 and 60 percent, respectively. The subsurface equilibrium temperature derived from the Na/K atomic ratio is 27°C. This temperature is unreasonably low due to the large concentration of Ca (191 ppm). The Ca corrected Na/K temperature (TNa-K-Ca) is 71.1°C. The alkali thermometers generally work qualitatively rather than quantitatively when reservoir temperatures are below 175°C. The aforementioned geothermometers show good correlation and indicate subsurface temperatures quite similar to the 10⁴°C temperatures recorded by the drill logs.

Modeling

Several models exist that could explain the data collected thus far. First, let us assume that with nonselective pumping at less than 3000' the maximum temperature of water brought to the surface is 82°C. Second, let us assume that the maximum water temperature at depth is 120°C, that computed by the dilution program Mixture,

Figure 8 demonstrates a possible model where an aquifer producing 25°C water is mixed with another aquifer producing 120°C water in the drill hole. The proportions of hot 120°C and cold 25°C water mixed must be 40 and 60 percent, respectively. In this model selective pumping could possibly produce 120°C water.

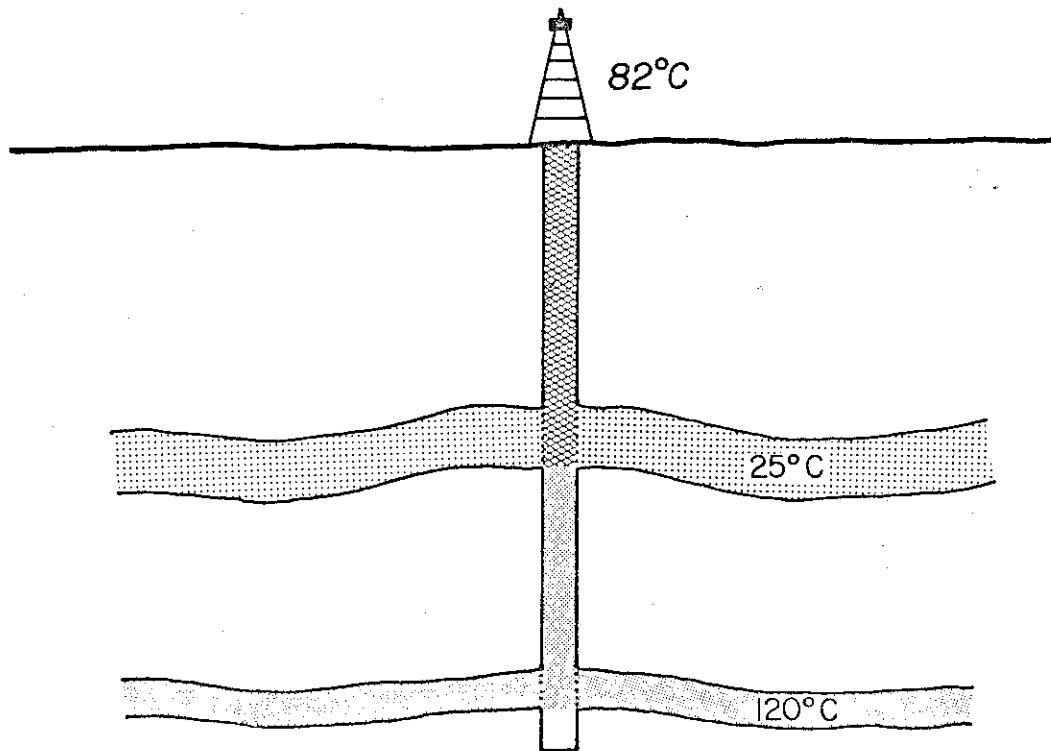


Figure 8. A model for mixing water from hot and cold aquifer in the well hole.

Figure 9 is similar to Figure 8 except that mixing occurs in the aquifer(s) at some unknown location and not in the drill hole. This situation would severely limit the utility of the Pima Farms Well because the maximum temperature of fluids derived would be 82°C regardless of pumping technique.

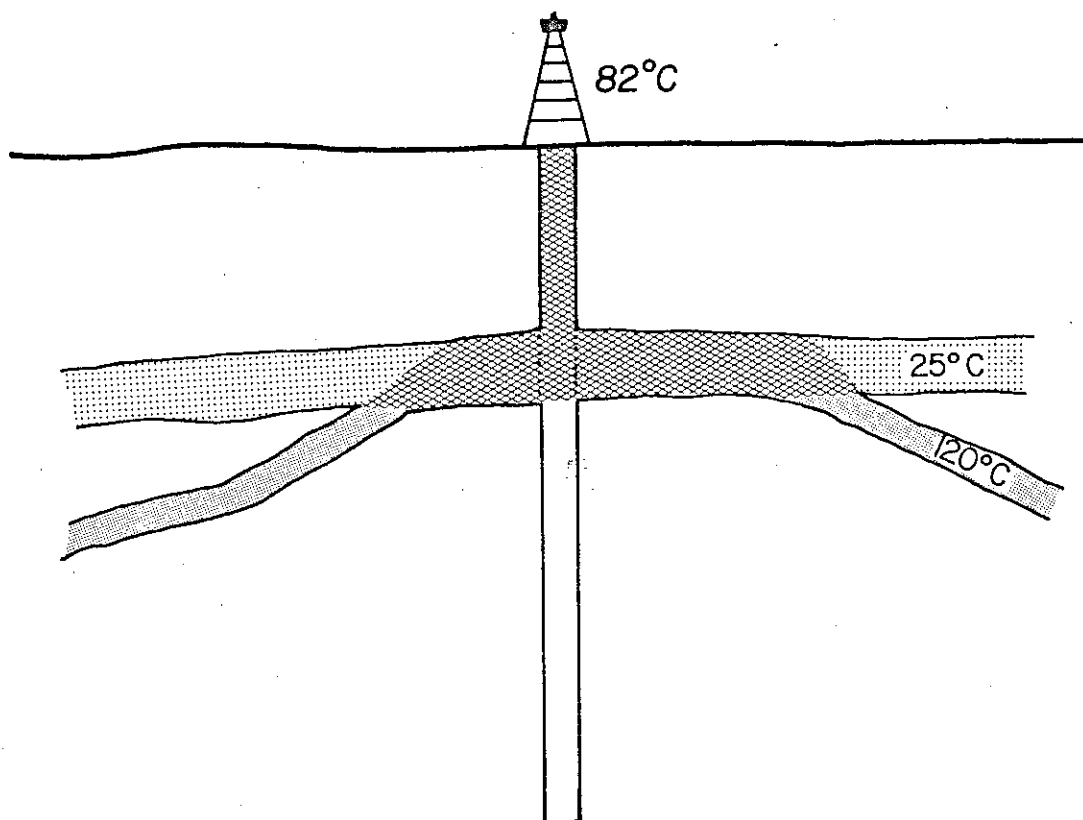


Figure 9. A model for mixing of hot and cold water in an aquifer.

Figure 10 demonstrates a combination of the aforementioned models. This model would permit selective pumping of 120°C fluids at some unknown flow rate and depth.

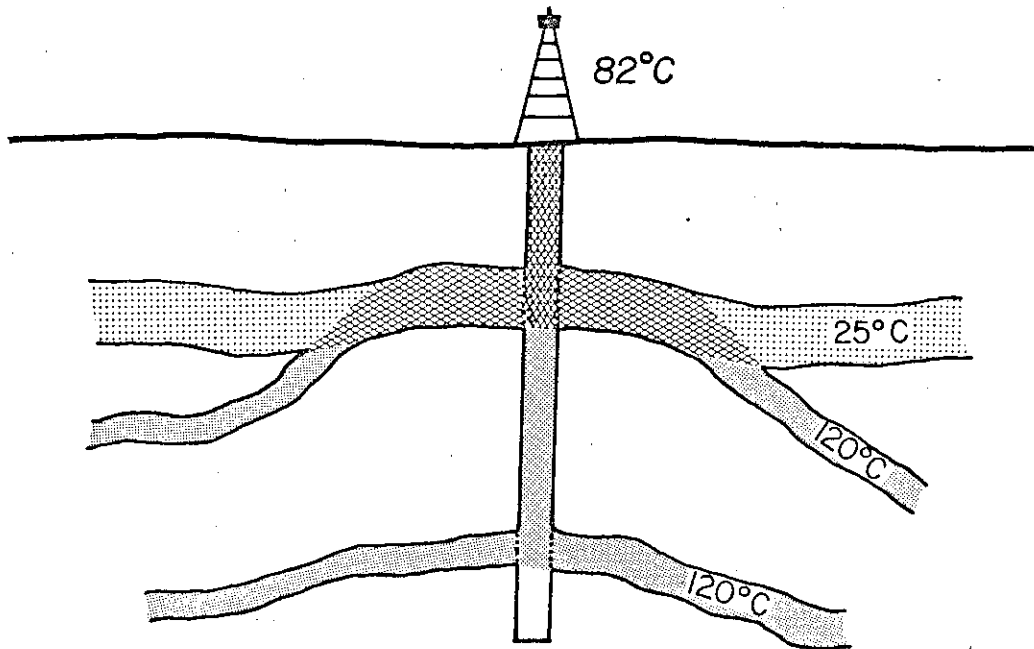


Figure 10. A model for mixing hot and cold water in an aquifer and in the well hole.

All three models are possible but the model described in Figure 9 or a similar model is most probable based on the chemical data. The Pima Farms Well will be limited to irrigation or space heating if Figure 9 accurately describes the situation at depth.

Mineral Precipitation

The following data may be useful in the design and maintenance of space heating or air conditioning equipment in the event that selective pumping proves the existence of 120°C fluids at depth. The total dissolved solids derived from Sample X90356 through direct analysis and calculation are listed in Table 4. The percent of each ion expected on evaporation is also listed. The Pima Farms' water contains approximately 2700 ppm of total dissolved solids and may be used for irrigating. The lower limit for brine is 10,000 ppm. The largest constituents are in descending order Cl, Na, Ca, SO₄, and SiO₂.

TABLE 4. Total dissolved solids and percent ion of TDS for Pima Farms Sample X90355.

TDS @ 180°C (sample X90356) 2700 ppm

TDS calculated by Solmneq 2603 ppm

Percent ion of TDS (calculated)

F	0.17%
Cl	54.20%
SO ₄	6.08%
HCO ₃	0.75%
CO ₃	0.00%
SiO ₂	2.20%
Na	29.45%
K	0.38%
Ca	7.70%
Mg	0.03%
B	-----
Li	0.06%
Fe	-----
Cu	-----
Mo	-----
Zn	-----

TOTAL 101.02%

Solmneq has calculated various minerals in the Pima Farms' water which are saturated to some degree and may precipitate at one atmosphere pressure and at 82°C. The mineral name, formula and Gibbs free energy are shown in Table 5. A negative Gibbs free energy implies undersaturation, 0 energy implies equilibrium and positive energy implies saturation and possible precipitation at the T-P conditions mentioned. The minerals listed, Tremolite for example, may not form but amorphous sinters with the same general formula may be deposited. Therefore, at 82°C calcium-magnesium-silicates may deposit in piping. Chlorides are not expected to precipitate because of their high solubilities.

TABLE 5. A listing of saturated mineral species calculated by Solmneq for Pima Farms Sample X90346.

<u>MINERAL NAME</u>	<u>FORMULA</u>	<u>GIBBS FREE ENERGY</u>
Aragonite	CaCO ₃	0.4834 kcal/mole
Calcite	CaCO ₃	0.6027 kcal/mole
Chrysotile	H ₄ Mg ₃ Si ₂ O ₉	5.4684 kcal/mole
Diopside	CaMg(Si ₂ O ₆)	5.9444 kcal/mole
Quartz	SiO ₂	0.2168 kcal/mole
Talc	Mg ₃ (Si ₄ O ₁₀)(OH) ₂	13.3918 kcal/mole
Tremolite	Ca ₂ Mg ₅ (Si ₈ O ₂₂)(OH) ₂	28.3405 kcal/mole
Wollastonite	Ca(SiO ₃)	0.2453 kcal/mole
Zinc White	ZnO	2.0472 kcal/mole

Further Exploration

All of the preceeding data comes from a limited number of sample points. The possibility of misrepresenting the system through inadequate sampling exists. A thorough program of water sampling from all available irrigation wells in the area would be useful in detecting regions of greater interest around the Coolidge area and substantiating the data gathered thus far. The proposed hydrogeochemical survey should be conducted in the month of January or February, 1975, and would require one to two weeks field work.

A heat flow survey of the Coolidge area by Rob Roy will be submitted shortly. Results thus far substantiate conclusions reached by geochemical analysis and indicate the low temperature nature of the area.

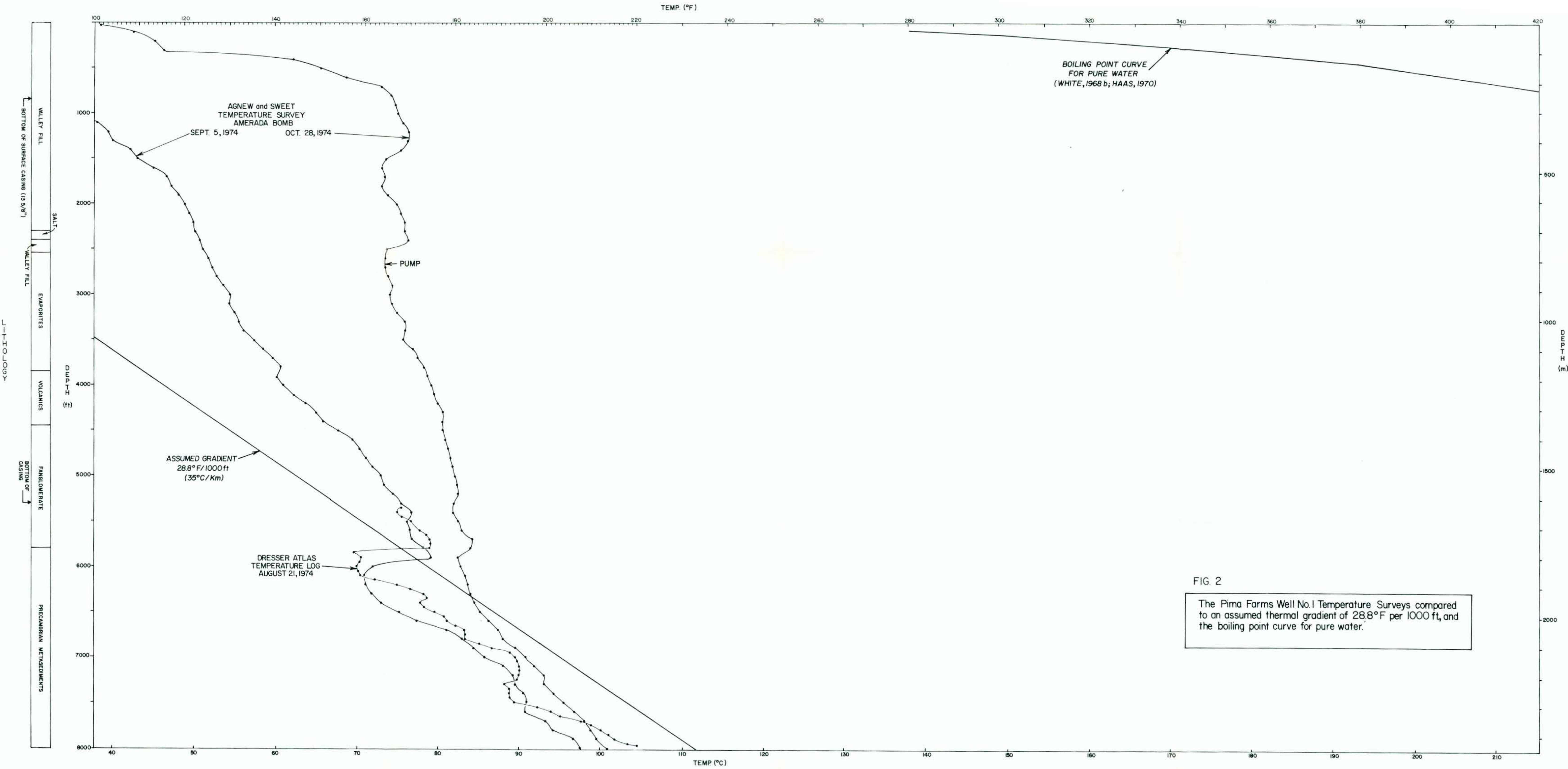
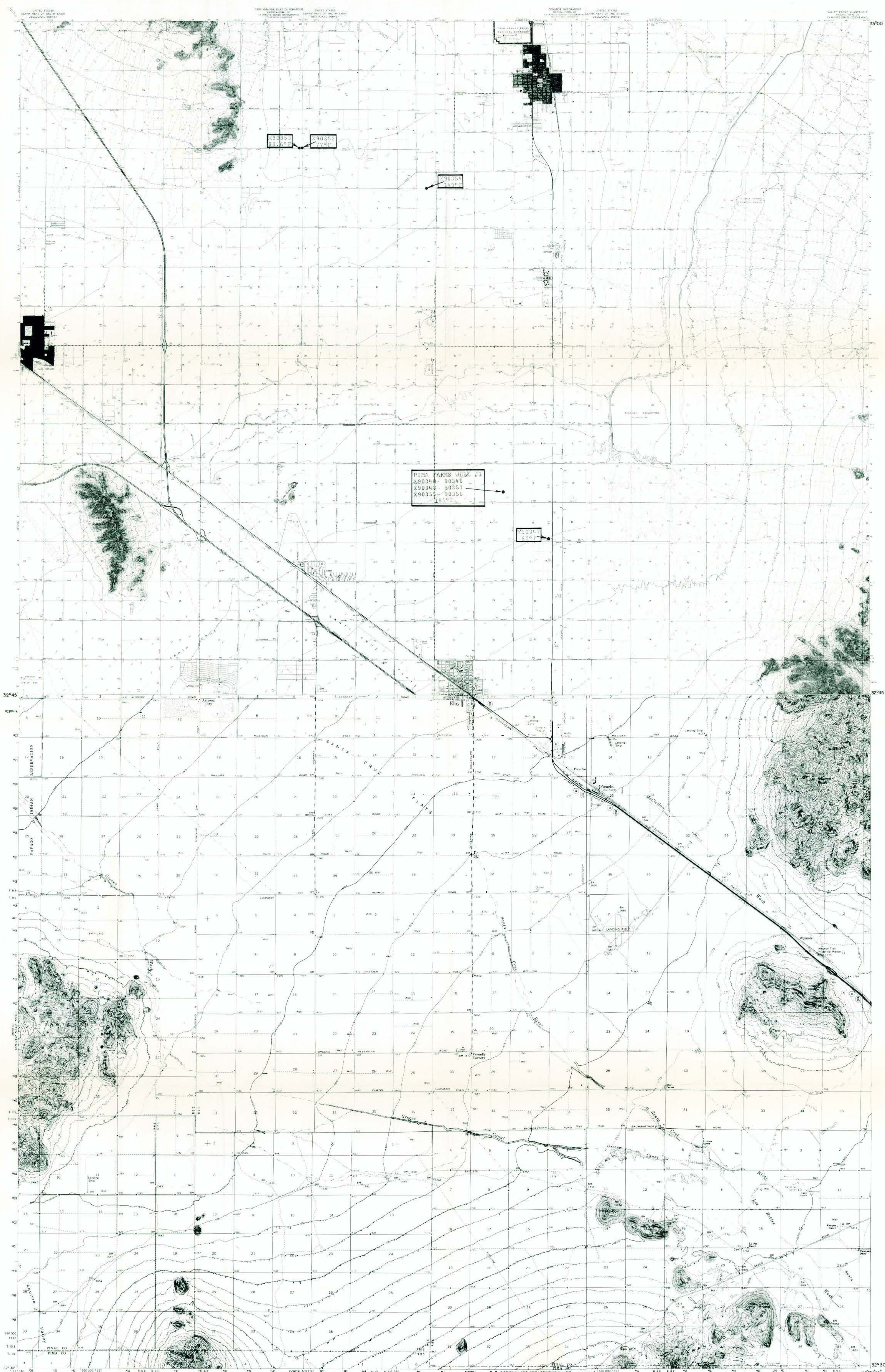


FIG. 2
 The Pima Farms Well No.1 Temperature Surveys compared to an assumed thermal gradient of 28.8° F per 1000 ft, and the boiling point curve for pure water.

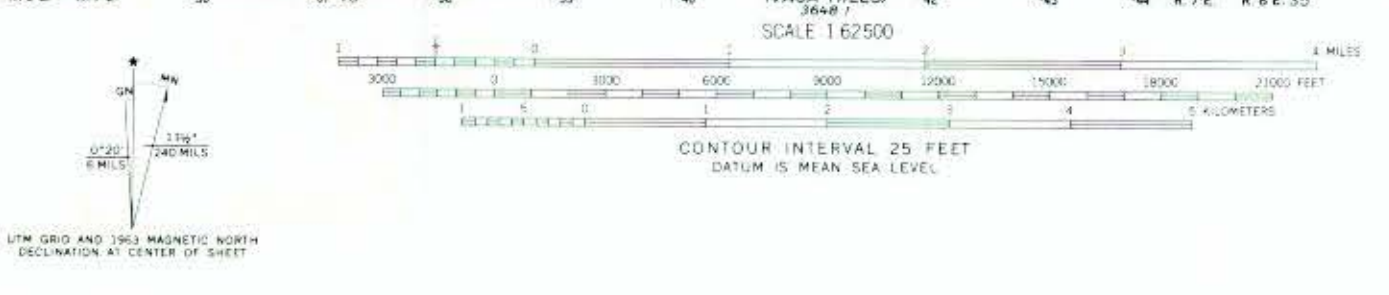


32°45'

32°30'

111°30'

111°22'30"



PIMA FARMS WELL NO. 1
AND SELECTED
IRRIGATION WELLS

AMAX EXPLORATION, INC.
DENVER, COLORADO

CASA GRANDE AREA