CHEMICAL TRANSIENTS DURING PRODUCTION OF HIGH GAS WELLS AT THE NORTHERN GEYSERS STEAM FIELD, CALIFORNIA, USA

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ABSTRACT

Non-condensible gas and stable isotope data from the extreme northwest end of The Geysers steam field indicate that this part of the reservoir consists of a deeper zone. below about -8,000 feet msl, where gas concentrations are as high as 100,000 ppm-wt, and a shallower zone with steam containing 15,000 ppm-wt gases, generally conforming to stratification of the reservoir previously reported from a production area several miles to the east. Production wells may tap the shallow zone. the deep zone, or both, depending upon the positions of their production zones with respect to the interface. In addition to high gas content, the deeper zone is characterized by anomalously high temperatures, heavy isotopes of oxygen (and perhaps hydrogen) in the steam, and high total carbon in the gases. Shifts of gas composition during production can be interpreted in terms of dilution of steam in the shallow zone by boiling of reservoir liquid. and mixing between deep and shallow steam. Reservoir steam saturation after 1-1/2 years of production is calculated to be about 0.3 in the shallow zone, and about 0.9 in the deep zone. There is some problem with saturation calculations which involve the concentration of hydrogen. which yields deep zone saturation values as high as 2.5, which is impossible. This is discussed in relation to the possible presence of "excess" hydrogen in the steam.

1. INTRODUCTION

The Aidlin geothermal project is a 20 MW (net) installation located at the northwest tip of The Geysers steam field, offset by more than two miles from adjacent production areas to the east and southeast (figure 1). Four production wells supplied the power plant when operations began in 1989, another was added at the end of 1990, and a sixth came on-line at the end of 1992. One of the six wells was used intermittently for production until March 1993. when it was converted to injection, replacing another injector which is now shut-in. For convenience, this well is henceforth referred to as the "deep" well even though it is not actually the deepest in the leasehold. Three **of** the five current producers have multi-leg completions (Henneberger *et al.*, 1993).

As in the adjacent CCPA production area (figure 1), production in the Aidlin leasehold is relatively deep (vertical depths 8,500 to 11,000 ft) and there is a "high temperature reservoir" (HTR) with higher gas content which underlies the "typical" reservoir (Walters *et al.*, 1988). The produced steam at most Aidlin wells is superheated, and the superheated steam tends to carry corrosive volatile chlorides (*e.g.*, 4 - 60 ppm-wt Cl in January 1993). The corrosion mitigation system at the Aidlin project has been described by Hirtz *et al.* (1990). This paper describes the Aidlin wellhead steam chemistry and discusses transients observed during production. To facilitate comparisons, the Aidlin HTR steam is described as "deep" and the Aidlin "typical" steam is named "shallow", whereas the terms "**HTR** steam" and "typical steam" are reserved for data from the CCPA area (Walters et *al.*,1988; Haizlip, 1985). The term Aidlin "mixed" steam refers both to mixtures of deep steam and shallow steam, and to mixtures between shallow steam and injection-derived steam.

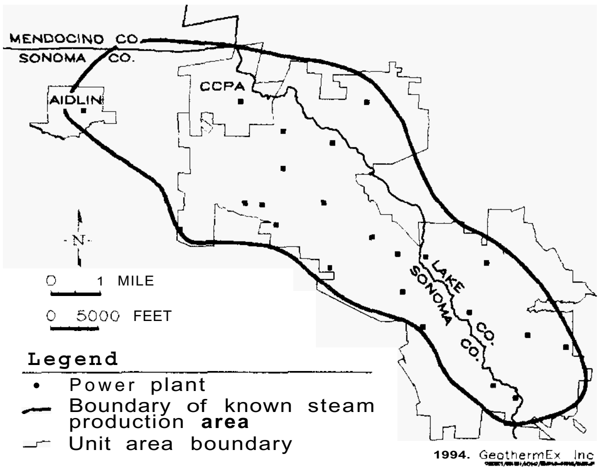

Figure 1: Location of Aidlin Project Area

2. GASES IN STEAM

Total gases in steam at the Aidlin production wells have ranged from about 5,000 ppm-wt to 110,000 ppm-wt (figure 2). Gases were extremely high at the deep well, which is at the northwest edge of the producible area, where the top of the reservoir is deepest. (Another well further to the northwest was dry.) The flow history of the deep well (see figure 2) shows that gases

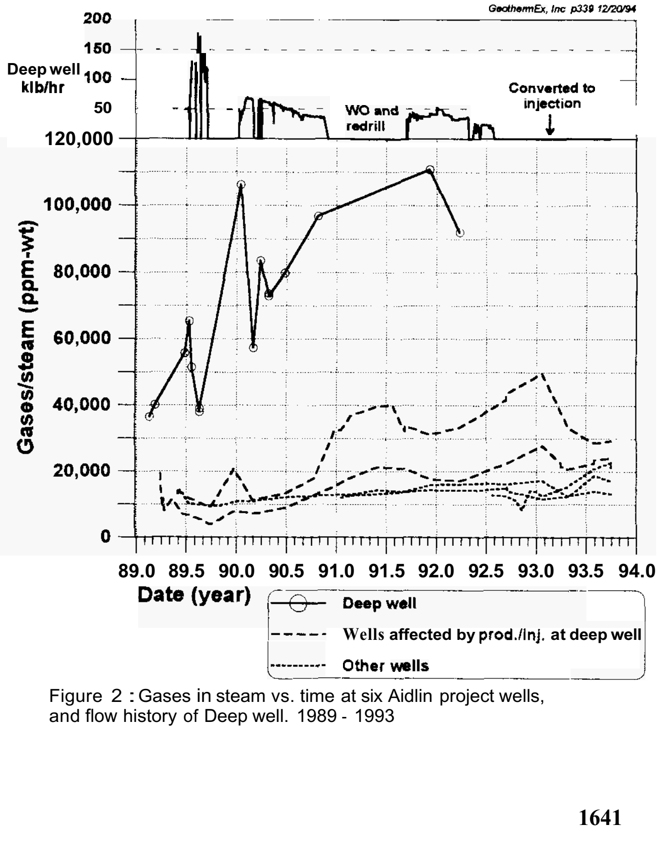

Figure 2 : Gases in steam vs. time at six Aidlin project wells, and flow history of Deep well. 1989 - 1993

increased over time as flow rate decreased. There is no evidence to show that the highest gases measured at this well were a result of casing collapse or formation bridging such as might cause a decline in flow rate and wellbore condensation, and it is notable that the high gases persisted after a workover and redrill in 1990. However, it is reasonable to suspect that gases in steam above c.90,000 ppm-wt were affected by some wellbore condensation at high wellhead pressures, which were applied to restrict overall gas production to the power plant. Three of the four gas measurements at more than 90,000 ppm-wt were collected when the flowing wellhead pressure was at or above 400 psi. Some of the other gas samples were collected at similar high pressures, but others (with gases to 83,000 ppm-wt) were collected in the range 100-144 psig. Two wells adjacent to the deep well showed increased gas production during periods when the deep well was shut-in (see figure 2), and depressed gases after it was converted to injection (March, 1993). At all wells the gases have increased over time, but the two located furthest to the southeast have been the most stable, with only a few thousands of ppm-wt change since 1989. The top of the reservoir, based on elevation of first production, has the shape of a nose which plunges to the northwest, and the legs of the two southeast wells penetrate this nose at highest elevation (-6,700 to -7,000 feet msl), whereas the deep well encountered the top of the reservoir at -8,100 feet msl.

3. STABLE ISOTOPES AND GASES IN STEAM

Only one analysis of the stable isotopes of hydrogen and oxygen was obtained from the deep well, in March 1992. This is shown on figure 3, along with samples from the other production wells (Aidlin shallow steam and Aidlin mixed steam), the injection condensate holding tank (Aidlin injection), the composition of HTR steam in the CCPA production area several miles to the east (Haizlip, 1985), and several mixing trends (M1-M4) which are discussed below. The samples of Aidlin steam on figure 3 cover years 1989 through 1992. Only one injectate sample was analyzed during that time, so three subsequent injectate samples are displayed also, to illustrate the variability of composition.

The deep well sample was collected when the well was producing about 40,000 lbs/hr of steam at a wellhead pressure of 400 psig. These conditions probably allowed some wellbore condensation, which may (partly) explain why the isotope composition of the deep well sample is somewhat offset from the composition of CCPA HTR steam. However, it also is uncertain whether the sample represents a mixture of reservoir steam and injection-derived steam along line M4. The Aidlin injection well which was then active was closer to the deep well than to others in the area. Some Aidlin samples, from well legs which approach or penetrate the HTR, are mixed along line M3 between Aidlin shallow steam and CCPA HTR steam. This implies that the Aidlin area has deep steam with the CCPA HTR composition, and that the Aidlin deep well sample is indeed affected by condensation and/or by mixing with an injectate.

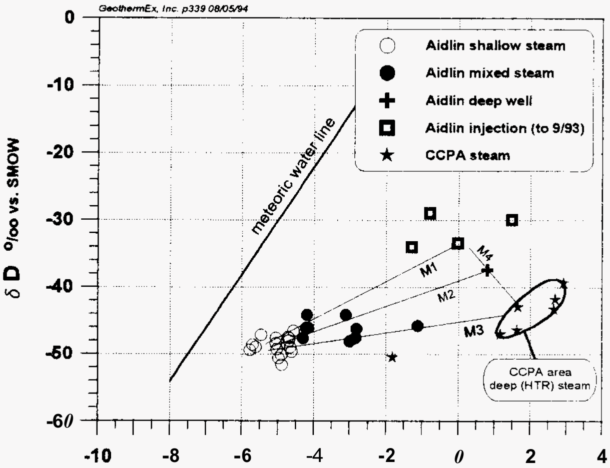

Figure 3 : Stable isotopes of O and H at Aidlin project wells through December 1992, compared with Aidlin injectate and isotopes in the CCPA area (Haizlip, 1985)

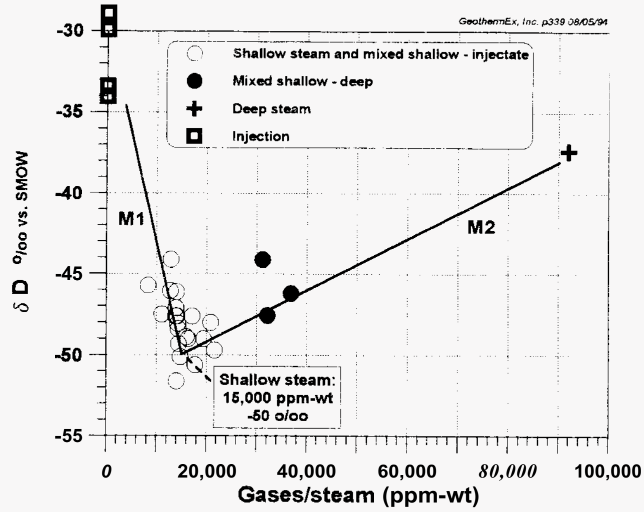

Figure 4 . Isotope deuterium versus gases in steam at Aidlin project wells through December 1992

Line M2 represents mixing between Aidlin shallow steam and the deep sample. and M1 represents mixing with injectate. Some mixing along M1 is clearly indicated by low gas concentrations, as shown on figure **4**. Lines M1 and M2 on figure **4** correspond to the same lines on figure *3*, and their intersection suggests that the shallow steam in the area has an average 15,000 ppm-wt gases. Gas concentrations at the two southeastern wells have been stable at 13,000 to 17,000 ppm-wt since early 1992. Previously lower concentrations can be attributed to a period of dilution by boiling **of** reservoir liquid, which will be discussed further below.

Among the mixed steam samples on figures **3** and **4** there are no unambiguous anomalies of ammonia such as those generally associated with injection returns at The Geysers (Klein and Enedy, 1989; Beall, 1993). However, the injection well in use was at a relatively distant location to the north, perhaps allowing segregation of injected gases from injection-derived steam. More recent injection into the deep well has produced strong ammonia anomalies at nearby wells.

Studies of steam isotopes throughout The Geysers have shown a large shift of ^{18}O and a small shift of D from south to north (*e.g.* Truesdell ***et** al.* 1987). Figure 5 includes steam samples from the south, central and north Geysers, showing this trend, and establishes that δ-^{18}O in the Aidlin shallow steam is somewhat lower than would be expected. The average is about δ-^{18}O = -5.5 o/oo, compared to -4.5 o/oo to 0 o/oo reported from Central Geysers steam (Truesdell ***et** al.*, 1987), -2 o/oo reported from a single (relatively) shallow well in the CCPA area (Haizlip, 1985) and an average -0.2 o/oo in CCPA "typical" steam (Walters *et al.*, 1987).

The seemingly anomalous ^{18}O of Aidlin shallow steam may be an effect of Rayleigh condensation near the field boundary, as discussed by Truesdell ***et** al.* (1987) and Truesdell ***et** al.* (1993). At the temperatures of The Geysers reservoir, this process causes a progressive decline of δ-^{18}O and increase of δ-D in residual steam as condensate is removed. A Rayleigh model does not uniquely establish the initial steam composition and condensation temperature, but reasonable values can explain the origin of the Aidlin shallow steam. For example, 80% condensation at 250°C will strip initial steam at δ-^{18}O = -3.1 *oioo.* 6-D = -55 o/oo to the δ-^{18}O = -5.7 *oioo,* δ-D = -50 o/oo observed in Aidlin shallow steam. **CCPA** "typical" steam (figure 5) does not make a particularly good initial composition for a Rayleigh model, because it has the same 8-D as does the Aidlin shallow steam. If the CCPA "typical" steam is used as the initial composition, then some additional process has affected 8-D. Possible processes include water-rock exchange, as discussed by Haizlip (1985), and mixing with meteoric recharge water (compositions shown on figure *5)*.

4. TEMPORAL CHANGES OF GAS COMPOSITION

All of the Aidlin shallow and mixed steam wells show a distinct shift of gas composition during the first 1-1/2 years of production. This shift is associated with increasing total gases in steam but tends to be more distinct. The basic pattern, in volume percent of dry gas, is an increase of CO, and CH,, **a** decrease of H_2S, **NH,** and H,, and essentially stable N, and **Ar.** Figure 6 shows the shift of CO_2.

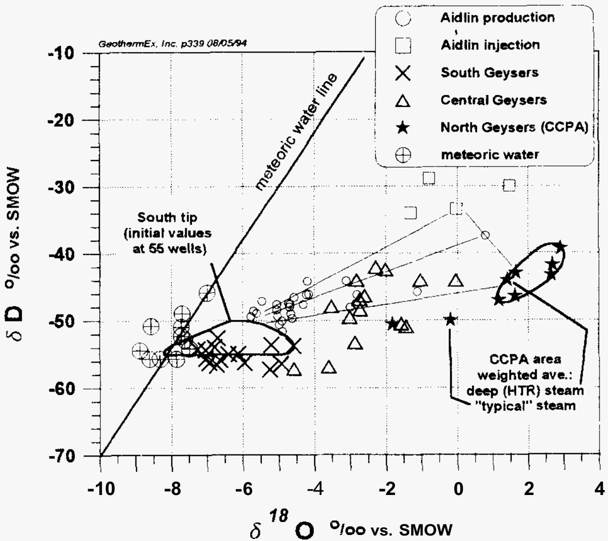

Figure 5 Aidlin stable isotopes compared with steam from other parts of The Geysers (south tip field drawn from data in Klein and Enedy, 1989, south and central steam from Truesdell et al , 1987, north steam from Haizlip, 1985 and Walters et al , 1988)

The composition shift can also be illustrated in terms of the mole fractions of total carbon, nitrogen and sulfur in the dry gas. For example, the combined shifts of carbon dioxide and methane become a shift of mole fraction C, as shown on figure 7. The mole fraction approach avoids the effects on molecular species of hydrogen exchange reactions such as CH, + 2H$_2$O = CO, + 4H$_2$ and 2NH$_3$ = N, + 3H$_3$, although shifts in bulk composition may still occur when gases react with rock minerals. (Examples of such reactions are 2H$_2$ + S$_2$ = 2H$_2$S, where S comes from oxidation **of** pyrite in equilibrium with the high-temperature dissociation of water, and C(graphite) + 2H$_2$ = CH,.)

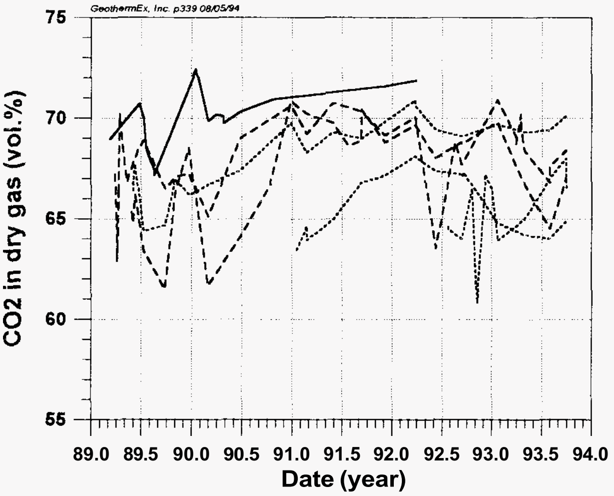

Figure 6 :
C02 in dry gas vs. time at six Aidlin project wells, 1989 - 1993
(line styles the same as on figure 2)

There is much less data scatter on figure 7 than on figure 6, which suggests that the carbon dioxide - methane reaction is significant. For example, note the well which entered production in early 1991. From start-up until early 1992 CO$_2$ in dry gas increased from **64%** to 68%, then until late 1993 the concentration declined back to **64%** (figure *6)*. Concentrations of CH$_4$ (not shown here) show the reverse trend. and the mole fraction C remained essentially constant at 90% ±1% throughout the period (figurr 7).

C, N and S are combined on figure 8. showing all Aidlin steam samples collected from 1989 through 1992. Compositions trend straight away from the total C apex along line L1, then diverge slightly along line L2. The deep steam is particularly high in total C. due both to the high CO, shown on figure 6 and to somewhat higher CH, (0.5 to 2% higher in dry gas of deep steam than shallow steam). High CO, in **HTR** steam of the CCPA area has previously been reported (Walters *et al.*, 1988).

Trends L1 and L2 on figure 8 are the results of two separate processes which are further illustrated by considering mole fraction C in relation to total moles C, S and N in steam (figure 9). Samples along L2 have all been affected by boiling of reservoir liquid, principally during the first 1-1/2 years of production. This boiling dilutes the gases in primary reservoir steam and releases the relatively water-soluble species NH, and H$_2$S, causing both a dilution of the less soluble carbon species (*i.e.*, a shift away from the C apex) and a shift towards the N apex because ammonia is more soluble than hydrogen sulfide.

The intersection of trends L1 and L2 represents shallow steam unaffected by the early boiling process, and unaffected by mixing with deep steam. Most of the samples plotting at this point were collected after 1-112years of production, and have 14,000 - 16,000 ppm-wt gases in steam, as observed at the two southeastern wells.

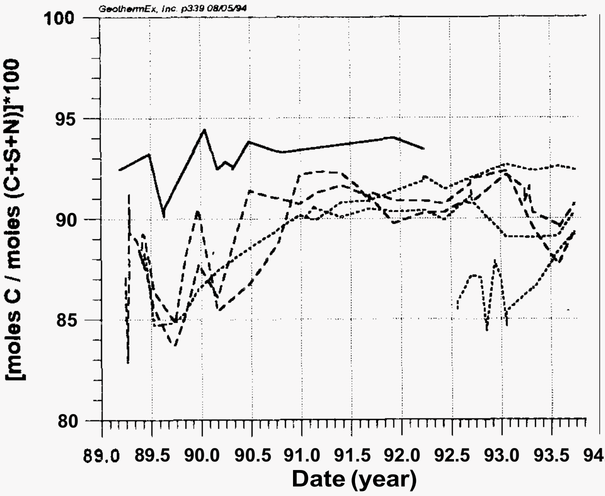

Figure 7 : Carbon as fraction of (carbon + sulfur + nitrogen) vs. time at six Aidlin project wells, 1989 - 1993
(line styles the same as on figure 2)

Samples along L1 show a wide range of total gases in steam (figure 9) which is due to mixing between shallow and deep steam and/or to varying dilution of deep steam by boiling of reservoir liquid and/or wellbore condensation (which may affect only the samples with moles (C+S+N) above c.50). Since the composition of the deep steam changes very little over a wide range of total gases, and since dilution by boiling would seem likely to cause some shift at lower concentrations towards the L2 trend, it seems likely that the dominant process along trend L1 is shallow-deep mixing. This might be confirmed by numerical modeling, which should also consider other processes such as effects of Rayleigh condensation. Mixing with injection-derived steam could also be occurring along L1, but experience with reactions of production wells to more recent injection into the deep well indicates that this could cause a shift towards the N apex, not observed on figure 8.

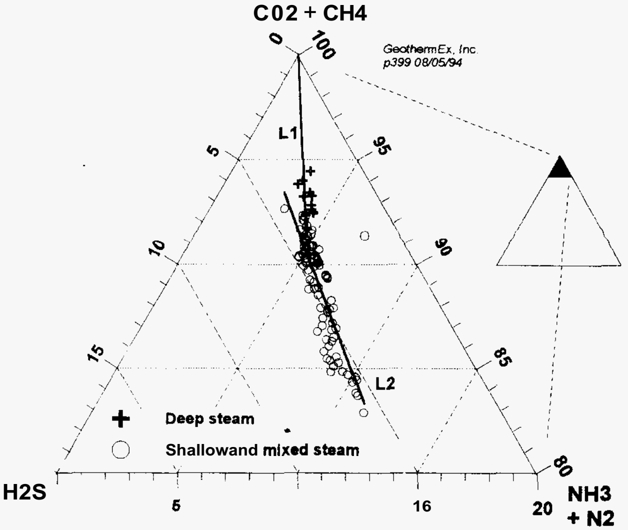

Figure 8 Ternary diagram showing relative moles of C, S and N in gases at Aidlin project wells, 1989 - 1992

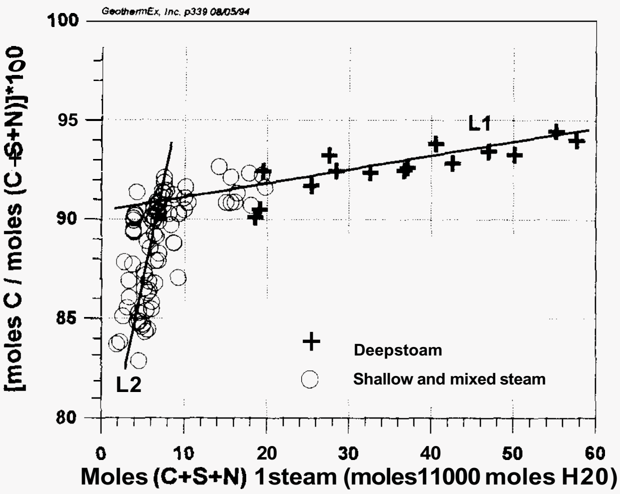

Figure 9 Carbon as fraction of (carbon + sulfur + nitrogen) vs (carbon + sulfur + nitrogen) in steam at Aidlin project wells, 1989 - 1992 (Lines L1 and L2 correspond to L1 and L2 on figure 8)

5. COMPOSITION VERSUS TEMPERATURE

Geysers gas compositions have been shown to conform well to predictions of the H_2S/CO_2 geothermometer of D'Amore and Truesdell (1980, eqn.12), presented here in graphical form as figure 10. For example, Klein and Enedy (1989) showed that steam from the southern tip of the reservoir clusters along the 240°C line, in good agreement with reservoir temperature in that area. The samples on figure 10 represent the three Aidlin wells for which reliable downhole temperature surveys are available. One well has produced only shallow steam. one has produced both shallow and mixed shallow-deep steam, and the third is the deep well. There is a good differentiation of shallow, mixed and deep steam along temperature lines at about 255°C, 265°C and 275°C, respectively, and comparison with a small set of downhole temperature measurements, listed on figure 10, indicates that the geothermometer is 5°C to 10°C low. Among the deep steam samples, the temperature appears to be uniform and equilibrium conditions are implied except perhaps when log (liters CO_2) is lower than about 1.5 (total gases in steam below 65,000 ppm-wt). This may be an effect of shallow-deep mixing on the lower gas concentrations.

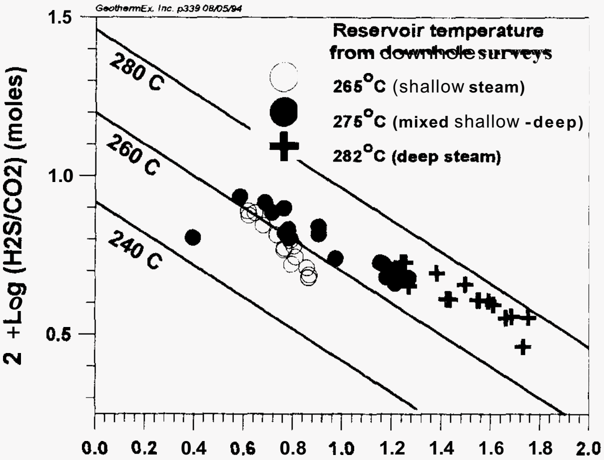

Figure 10 : Gases at three Aidlin project wells with respect to D'Amore Truesdell H2S/CO2 geothermometer, samples collected 1989 - 1992 (reference lines given by D'Amore and Truesdell, 1980, eqn.12)

6. STEAM SATURATION AND THE HYDROGEN PROBLEM

Ideally, the temporal gas composition shifts at each well would be quantified in light of the reservoir boiling and mixing discussed above, to determine the relative influence of each mechanism. For example, the different solubilities of gas components in water can be expected to cause shifts in component ratios in steam as boiling proceeds. and this is the probable cause of trend L2 on figure 8. Detailed quantitative methods have been developed, *e.g.*, by D'Amore and Celati (1983) and D'Amore and Pruess (1986). but these methods are only approximations, limited by an assumption that reservoir steam and water have equal mobilities and by assumptions regarding the chemical equilibria which control gas composition.

For example, the reactions thought to control H_2S in reservoir vapor are a function of temperature. This means that expected H_2S in steam can be calculated if temperature is known. or H_2S in dry gas can be calculated if temperature and the total gas/steam ratio are known. The method for this is given by D'Amore *et al.* (1982), along with analogous equations for calculating the concentration of H_2 using thermodynamic data for the molecular dissociation of water and oxygen fugacity (improved thermodynamic data are given in D'Amore *et al.* (1983)), and equations for the reaction $CH_4 + 2H_2O = CO_2 + 4H_2$. When these equations are used in a straightforward manner to predict the vapor composition in any two-phase reservoir (including The Geysers), the results do not agree with observed wellhead steam compositions. Improved agreement between theory and observed wellhead steam chemistry is obtained by factoring the reservoir steam saturation. "y", into the equations, to take account of the fact that wellhead gases are a combination of reservoir vapor and vaporized reservoir liquid; the various gas components have different solubilities, so reservoir vapor and vaporized liquid contribute different gas ratios to the wellflow.

Calculations using the methods of D'Amore *et al.* (1982) using 15.000 ppm-wt total gases at 265°C. give a good match to the 4% H_2S in dry gas observed in shallow stabilized Aidlin steam (1-112 years of production) if reservoir steam saturation is about 0.35. Stabilized H_2 is matched at the measured level of 9% if y is about 0.5. Lower values of y cause both species to be underestimated, and higher values cause overestimation.

A test calculation for deep steam using 100,000 ppm-wt total gases at 280°C gives a match to the observed 2.6% H_2S in dry gas if y = 0.9. In contrast, however, the observed 9% H_2 is correctly estimated only if y is about 2.5 (which is impossible), and underestimated by a factor of about 3 if y = 1. D'Amore *et al.* (1982) have shown that the methane + water reaction should give better estimates of y than the water breakdown reaction, but in the case of the Aidlin deep steam (and also among samples of **HTR** steam from the CCPA area), this reaction also gives y values higher than 1. It is possible that this problem is a result of inaccurate thermodynamic data. or that H_2 is being controlled by some mechanism which is not being considered.

McCartney and Haizlip (1989) reported evidence from The Geysers and Larderello that wellhead steam with relatively low total gas content carries "excess" H_2. The basis of their conclusion was that wellhead ratios of H_2 to other gas components (H_2/CH_4, H_2/CO_2, *etc.*) were higher than predicted by a model of simple mixing between vapor and vaporized liquid from a single reservoir source. A key assumption underlying the McCartney and Haizlip (1989) model was that there are no gas-gas or water-rock interactions during or after boiling. This assumption was not examined, yet from a qualitative point of view it may be risky.

To illustrate this, one may consider the variation of H_2/CH_4 with total gases in steam from the Aidlin wells (figure 11). This case is more complicated than considered by the McCartney and Haizlip (1989) model, because the shallow and deep steam in the Aidlin area constitute two reservoir sources. However, Aidlin stabilized shallow steam (after 1-112 years of production) and Aidlin deep steam both have H_2/CH_4 between about 0.6 and 0.7, so as an approximation the McCartney and Haizlip (1989) model can be assumed to apply. This model indicates that mixing between vapor and vaporized liquid should produce no measurable variation in H_2/CH_4 except when the vaporized liquid fraction is very high. H_2 and CH_4 each have a very high vapor/liquid distribution coefficient, but CH_4 is slightly more soluble than H_2, so below about 15,000 ppm-wt there should occur a decrease of H_2/CH_4. As seen on figure 11, a few samples (from only two wells) may show this rollover, but otherwise there is a distinct increase of H_2/CH_4 as total gases decrease.

The cases of H_2/CH_4 greater than about 0.7 on figure 11 are actually due to a combination of high H, and low CH_4 among samples collected during the first 1-1/2 years of production. Qualitative evidence that the carbon dioxide - methane reaction affects these samples has been discussed above, and a shift of this equilibrium can obviously affect the H_2/CH_4 ratio. Additional H_2 could be contributed by exchange reactions involving the H_2S and NH, which are released by boiling of reservoir liquid.

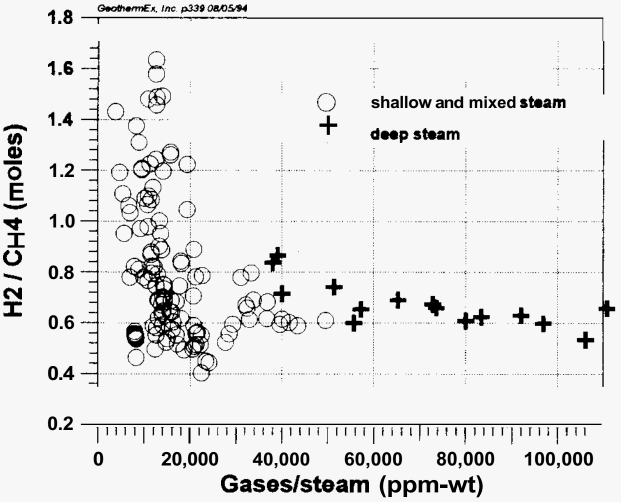

Figure 11 Hydrogen/methane versus total gases in steam at Aidlin project wells, 1989-1992

Considering this. it seems that the concept of "excess" hydrogen should be investigated further, particularly with quantitative modeling of reactions which involve CO,, CH,, H_2S and NH, and which may indeed occur during the boiling process. McCartney and Haizlip (1989) found that the "excess" H_2 could be contributed by reactions between sulfides and silicate minerals during boiling, and by casing corrosion, though mass balance considerations indicated that casing corrosion was at most a minor source. The conclusion of this discussion is that such sources may exist (some corrosion certainly occurs), but the apparent "excess" may also be less than indicated by a simple mixing model which doesn't include hydrogen exchange reactions.

7. CONCLUSIONS

The characteristics of deep and shallow steam zones in the Aidlin area are similar to features of the CCPA production area several miles to the east, and conform to currently held concepts about the history of The Geysers reservoir as discussed by Truesdell *et al.* (1993). However, the isotope composition of shallow steam in the Aidlin area may be affected by Rayleigh condensation, or by mixing with meteoric recharge water, not previously reported from the northern end of The Geysers. Also, the deep steam of the Aidlin area may have a higher deuterium content than HTR steam to the east. Boiling of reservoir liquid dilutes the gases in shallow steam during the first 1-1/2 years of production, and there is evidence that chemical reactions affect the gas composition during this process. In contrast, the deep steam appears to be affected by mixing with shallow steam more than by boiling of liquid. According to chemical equilibria which are believed to control H_2S in the gases, reservoir steam saturation is on the order of 0.3 in the shallow zone and 0.9 in the deep system; *i.e.*, the deeper reservoir is drier than the shallow. There is enough uncertainty in the assumptions and methods of calculating y values that these results should not be over-emphasized. y is very sensitive to total gases in steam, so that higher y values for the deep steam are calculated even if there is a poor match to the observed percent H_2S in dry gas.

8. ACKNOWLEDGEMENTS

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