

Carbon dioxide: Its role in geothermal systems

W.A.J. MAHON, G.D. McDOWELL, and J.B. FINLAYSON

*Chemistry Division, Department of Scientific and Industrial Research, Wairakei,
New Zealand*

Carbon dioxide is probably the most important constituent, apart from hot water, present in geothermal systems. It influences to a major extent the chemical and physical characteristics and properties of a system. The chemical composition and pH of hot water together with hydrothermal rock alteration and deposition of secondary minerals are strongly influenced by the concentrations of carbon dioxide. Sodium bicarbonate sulphate waters, which are frequently present in large volumes in geothermal systems, are produced by the movement of carbon dioxide and hydrogen sulphide through cold meteoric waters.

The density of fluids and the fluid content of rocks in a geothermal system are influenced by the presence and concentration of carbon dioxide. Gassing and degassing of a system can have a marked effect on the bulk hydrology of the system and the movement of fluids within the system. The thermal gradients and the depths to given temperatures are influenced by carbon dioxide concentrations. Free carbon dioxide gas can effectively decrease the porosity of rocks available to water and allow complete evaporation of water in a very porous medium, when thermal equilibrium between all phases exists.

Carbon dioxide can control the discharge behaviour of wells and is considered by the authors to be a critical component in determining whether a system produces steam or a steam/water mixture. It explains how 'vapour dominated systems' could be formed and the apparent similarity of temperature and pressures within these systems in the early stages of exploitation. It is notable that the well known 'vapour dominated systems' all contain relatively high concentrations of carbon dioxide per unit mass discharge. It is considered that some geothermal systems are controlled more by the presence of carbon dioxide than they are by the presence of free steam.

The thermal contribution from carbon dioxide to a geothermal system is probably considerable. Similarly, the movement of a carbon dioxide rich vapour phase can have a marked influence on shallow fluid temperatures and the formation of temperature inversions within the system.

Keywords Geothermal systems; carbon dioxide; geochemistry; hydrology; geothermal water; geothermal steam; carbon dioxide-water froths.

OCCURRENCE, DISTRIBUTION, AND ORIGIN OF CARBON DIOXIDE IN GEOTHERMAL SYSTEMS

Carbon dioxide, hydrogen sulphide, methane, hydrogen, nitrogen, and ammonia are the gases most frequently present in geothermal systems. In the majority of systems carbon dioxide predominates over the other gases, and frequently contributes over 85% v/v of the total gases present. In a few areas, such as in lower temperature systems of Iceland and

near the Lake Hannington system in Kenya, nitrogen is the predominant gas, while in other areas methane and hydrogen can be present in considerable proportions. Table 1, modified from Ellis & Mahon (1977), shows the percentages of gases present in different geothermal systems throughout the world.

The weight percentage of carbon dioxide relative to water phases (steam, water) in different systems varies widely. Carbon dioxide concentrations in the total discharges from wells drilled in geothermal systems range from below 1% w/w up to 70-80% w/w. Within the same system concentrations in the hot fluids may vary widely with depth and position in the

Table 1 Percentages of gases in geothermal systems.

| Source | Source depth (m) | Temp. (°C) | Pressure for comp-osition (bar abs.) | Steam fraction in discharge at pressure | Total gas in steam (mol %) | Total gas in total discharge (mol %) | Gas composition (mol %) | | | | | | | | Ref. † |
|------------------------------|------------------|------------|--------------------------------------|---|----------------------------|--------------------------------------|-------------------------|------------------|-----------|---|--------------------|----------------|-----------------|--------------------------------|--------|
| | | | | | | | CO ₂ | H ₂ S | HC* | H ₂ | N ₂ + A | O ₂ | NH ₃ | H ₂ BO ₃ | |
| Fumaroles, Larderello | 0 | 100 | 1 | 1.00 | 3.0 | 3.0 | 92.3 | 2.06 | 1.4 | 2.6 | 1.07 | 0.05 | — | 0.5 | a |
| Average well, Larderello | 500 | 200 | 1 | 1.00 | 2.0 | 2.0 | 94.1 | 1.6 | 1.2 | 2.3 | 0.8 | — | 0.8 | 0.33 | b |
| Average well, The Geysers | 200-2000 | 230 | 1 | 1.00 | 0.59 | 0.59 | 55 | 4.8 | 9.5 | 15 | 3 | — | 12.5 | 0.25 | c |
| Well MR-2, Matsukawa | 1080 | 230 | 1 | High | 0.22 | 0.22 | 81.8 | 14.1 | | remainder | 4.1% | | | | d |
| Wells, Reykjavic | 500 | 100 | | Water only | | | — | — | — | — | 1.00 | — | — | — | e |
| Well G-3, Hveragerdi | 400 | 216 | 1 | 0.2 | 0.015 | 0.003 | 73.7 | 7.3 | 0.4 | 5.7 | 12.9 | — | — | — | e |
| Karapiti fumarole | 0 | 115 | 1 | 1.00 | 0.17 | 0.17 | 94.6 | 2.3 | 0.74 | 1.0 | 1.1 | — | 0.26 | — | f |
| Average well, Wairakei, N.Z. | 650 | 260 | 1 | 0.32 | 0.063 | 0.02 | 91.7 | 4.4 | 0.9 | 0.8 | 1.5 | — | 0.6 | 0.05 | f |
| Well 11, Broadlands, N.Z. | 760 | 260 | 1 | 0.355 | 0.61 | 0.22 | 94.8 | 2.1 | 1.2 | 0.2 | 1.5 | — | 0.2 | — | f |
| Well 1, Ngawha, N.Z. | 585 | 228 | 1 | 0.33 | 20.0 | 6.6 | 93.9 | 0.7 | 4.1 | 0.5 | 0.8 | — | 0.04 | — | f |
| Fumarole Matsao, Tatun | 0 | 100 | 1 | 1.00 | 3.2 | 3.2 | 55.0 | 37.2 | | remainder | 7.8% | | | | g |
| Well E.205, Matsao, Tatun | 1500 | 245 | 1 | 0.3 | 0.15 | 0.045 | 92.0 | 5 | 0.7 | 0.8 | 1.5 | — | — | — | f |
| Well 5, Mexicali | 1285 | 340 | 1 | 0.44 | 0.54 | 0.24 | 81.4 | 3.6 | 7.0 | 0.5 | 7.0 | 0.4 | — | — | h |
| Fumarole, El Tatío, Chile | 0 | 86.6 | 0.6 | 1.00 | 0.10 | 0.10 | 75 | 0.6 | 0.1 | 0.0 | 19.4 | 4.9 | — | — | f |
| Well 2, El Tatío, Chile | 650 | 220 | 0.9 | 0.24 | 0.11 | 0.025 | 99 | 0.7 | 0.01 | 0.03 | 0.2 | — | — | — | f |
| Wells, Salton Sea | 1500-1800 | 300-350 | 16 | 0.18 | 0.1-1.0 | 0.02-0.18 | 90 | | remainder | mainly H ₂ S + minor HC and H ₂ | | | | | i |
| Well 1, Ahuachapan | 1195 | 230 | 1 | 0.23 | 0.007 | 0.002 | 50-80 | 4 | — | 10-40 | 2-10 | — | — | — | e |
| Well 7, Otake, Japan | 350 | 230 | 3.0 | 0.215 | 0.10 | 0.021 | 96.7 | 0.65 | | remainder | 2.7% | | | | j |

Table 1 is modified from Ellis & Mahon (1977).

* HC, total hydrocarbon gases.

† References: a, Nasini (1930); b, ENEL (1970); c, Kruger and Otte (1973); d, Nakamura and Sumi (1967); e, Dr G.E. Sigvaldason (pers. comm.); f, Chem. Div. DSIR, N.Z. and Dr R.B. Glover (pers. comm.); g, Y-C Liu (pers. comm.); h, Alonso (1966); i, Helgeson (1968); j, Noguchi (1966).

‡ Area of steam discharges only

Table 2 Carbon dioxide concentrations (% w/w) in volcanic steam from White Island, New Zealand.

| Fumarole no. | Date | Outlet temp.(°C) | H ₂ O | CO ₂ | SO ₂ | H ₂ S | HCl | HF | H ₂ | N ₂ | CH ₄ |
|--------------|----------|------------------|------------------|-----------------|-----------------|------------------|------|-------|----------------|----------------|-----------------|
| 1 | 9.7.72 | 480 | 94.8 | 3.86 | 0.31 | 0.23 | 0.32 | 0.008 | 0.068 | 0.019 | 0.0005 |
| 2 | 30.11.71 | 620 | 86.3 | 9.71 | 2.60 | 0.70 | 0.72 | 0.046 | 0.135 | — | — |
| 3 | 29.7.71 | 380 | 84.6 | 10.00 | 2.91 | 0.71 | 1.92 | 0.010 | — | — | — |
| 4 | 30.11.71 | 430 | 80.8 | 13.21 | 4.21 | 1.61 | 0.17 | 0.019 | 0.095 | — | — |
| 5 | 30.11.71 | 650 | 79.6 | 13.9 | 4.28 | 1.51 | 0.11 | 0.012 | 0.162 | — | — |
| 9 | 30.11.71 | 300 | 97.9 | 1.22 | 0.80 | 0.05 | 0.11 | 0.002 | 0.006 | — | 0.0062 |

Results from Giggenbach (1975).

system although concentrations are frequently highest at shallow depths. Geothermal systems associated with sedimentary rocks — such as The Geysers, U.S.A.; Larderello, Italy; Kizildere, Turkey; and Broadlands and Ngawha, New Zealand — commonly have much higher subsurface carbon dioxide concentrations than systems associated primarily with volcanic rocks as for example, Wairakei, New Zealand (cf. Table 1).

A close association frequently exists between active volcanic centres and geothermal systems. High temperature volcanic steam emissions contain a mixture of gases including carbon dioxide, sulphur dioxide, hydrogen sulphide, hydrochloric and hydrofluoric acids, hydrogen, nitrogen, and methane. Mahon & McDowell (1977) discussed the role of volcanic-magmatic steam in geothermal areas and the possible relationship between volcanic and geothermal gases. The concentration of carbon dioxide in volcanic emissions is frequently high and it generally predominates over other gases. Carbon dioxide invariably makes up over 80% w/w of the total gases present, and the weight percentage of CO₂ in the total vapour frequently ranges from 1 to 20% w/w. Table 2 shows the carbon dioxide concentrations in volcanic steam from White Island, New Zealand, an active andesite volcano (Giggenbach 1975).

Carbon dioxide is an integral part of natural steam discharges (fumaroles, solfataras) and of the gases of hot springs which occur above most geothermal systems. In a large number of areas, hot and cold gas emissions occur above the hot system but more particularly on the boundaries and perimeter of the systems. The predominant gas in the majority of these emissions is carbon dioxide, with nitrogen and methane rivalling hydrogen sulphide as the next most important gaseous constituent.

In many geothermal areas located on top of recently active volcanoes, for example those occurring in Indonesia, cold, warm, and hot water lakes occur in large centres formed by historic eruptions. Large volumes of carbon dioxide and other gases are emitted as vapour bubbles through the waters, giving the appearance of boiling. The waters are nearly always

acid (pH 2–5) and contain high concentrations of iron and aluminium leached from the confining rocks. At lower altitudes on the same volcanic complex, steam emissions and acid waters are common, while at still lower altitudes the discharge of boiling or near boiling neutral sodium-bicarbonate-sulphate waters frequently occurs (Mahon *et al.* 1980).

There is very little difference between the range of carbon dioxide concentrations found in so-called vapour dominated geothermal systems, such as The Geysers and Larderello, and that in the steam formed from water dominated systems, over a range of separating pressures. Thus the carbon dioxide concentrations found at The Geysers ranged from 2 to less than 1% w/w (Bruce 1970), and at Larderello averaged about 4–5% w/w (Corti *et al.* 1970) while at Broadlands, New Zealand, the steam separated from the hot waters at a pressure of 4–5 bar averages about 5–6% w/w (Mahon & Finalyson 1972, Grant 1977).

Pertinent information on the origin of carbon dioxide in geothermal systems has been obtained from isotopic studies. Ellis & Mahon (1977) reviewed much of the available data and concluded that it was possible to correlate the overall carbon isotope composition of the gases in geothermal fluids with mixed carbonate and organic carbon sources in rocks which contact the hot fluids, but an addition of juvenile carbon to the systems could not be ruled out.

In most areas it would be difficult to distinguish the ultimate origin of carbon dioxide. Muffler & White (1969) concluded that the carbon dioxide associated with the Salton Sea geothermal area in southern California, U.S.A., originated from the metamorphism of deep deltaic sediments deposited by the Colorado River. In New Zealand, greywacke rock containing appreciable amounts of carbon in different forms underlies the main volcanic zone. Assimilation of this rock into local magmas produces acid volcanic rocks such as rhyolites, dacites, and ignimbrites. The carbon dioxide associated with the hot waters of geothermal areas in New Zealand's Taupo Volcanic Zone could therefore originate from a number of different sources. At The Geysers, Larderello, and Kizildere, carbon rich sedimentary rocks

could produce plentiful supplies of carbon dioxide. Deep magmatic carbon dioxide would be supplemented by carbon dioxide originating from the sedimentary rocks at shallower levels.

In conclusion the following points are stressed since they form the basis of the discussion in the remainder of the paper.

- 1 Carbon dioxide is an integral constituent (as CO₂ gas, bicarbonate, and carbonate) in geothermal systems, and its emission is widespread in surface discharges.
- 2 In the majority of systems it forms over 80% w/w of the gases present, excluding steam.
- 3 The large and widespread emission of the gas above geothermal systems implies that a continuous flux of the gas occurs through the system in the same manner as the heat flux.
- 4 There are numerous possible sources of the gas in the rocks and magmatic emissions.

SOLUBILITY AND PHYSICAL CHEMISTRY OF CARBON DIOXIDE

The solubility of carbon dioxide in pure solution and in solutions of sodium chloride has been discussed by Ellis (1959) and Ellis & Golding (1963), and an extensive review of the thermodynamics of the CO₂-H₂O system was given by Malinin (1974). Of particular importance in assessing the behaviour of carbon dioxide in geothermal systems is the distribution of the gas between water and vapour phases at various stages of steam separation from high temperature water. A useful indication of this parameter is obtained from the mass distribution coefficient A :

$$A = \frac{n_g^l/n_{H_2O}^l}{n_g^v/n_{H_2O}^v} \quad (1)$$

where n_g is the number of moles of gas and n_{H_2O} the number of moles of water, in the liquid (l) and vapour (v) phases. To relate carbon dioxide concentration and the partial pressure of the gas, the Henry's law coefficient K_g is required, at the temperature of the solution:

$$K_g = f/x \quad (2)$$

where f is the fugacity of the gas, and x is the mole fraction of the gas in solution. In the range of carbon dioxide pressures in many geothermal systems (up to about 20 bar), partial pressure and fugacity of the gas can be equated. At higher pressures small variations occur.

The two solubility coefficients can be related by the expression:

$$K_g = P_w/AZ_w \quad (3)$$

where P_w is the water vapour pressure, and Z_w is the compressibility factor for steam:

$$Z_w = \frac{P_w V}{RT} \quad (4)$$

The solubility of carbon dioxide expressed as a Henry's law coefficient passes through a minimum with rising temperature, then increases to infinite solubility at the critical point temperature for the system. In contrast A the mass distribution coefficient has a continuous trend with rising temperature (Ellis 1967). In solubility calculations, only the un-ionised fraction of carbon dioxide in the liquid phase is used. The mass distribution of carbon dioxide lies heavily in favour of the vapour phase at temperatures in the range of 200–300°C. The presence of dissolved salts lowers the solubility of the gas, the salting-out effect being greatest at higher temperatures. In the concentration range of dissolved constituents frequently found in geothermal waters the salting-out effect is small.

The distribution of carbon dioxide between liquid and vapour, and the proportions of free carbon dioxide and carbon dioxide dissolved in hot water, have a very marked influence on the physical characteristics of a geothermal system. The temperature gradient, hydrology, densities of fluids, type of rock mineral alteration, fluid pressures, and heat distribution can be influenced to a great extent by the modes of occurrence and concentrations of the gas at any particular depth. These physical parameters are discussed in some detail in the following sections.

PRESSURES AND TEMPERATURES IN GEOTHERMAL SYSTEMS

Pressures measured at shallow levels (0–300 m) in geothermal systems are often close to hydrostatic pressure, allowing for water density at the measured temperature. In a few cases pressures have exceeded hydrostatic and have been intermediate between hydrostatic and lithostatic (White *et al.* 1970). In other, and more numerous, cases (perhaps because more measurements have been made in systems where this occurs) pressures have been lower than hot hydrostatic pressure, and a fluid density less than that of pure water at similar temperature is indicated.

At deeper levels (> 300 m) pressures frequently follow hydrostatic pressure or fall below hydrostatic pressure for the depth. When pressures fall below hydrostatic two types of situation occur. In many cases the pressures appear to be generated by fluids of somewhat lower density (0.2–0.7 g/cm³) than that of pure water. In several systems, most notably The Geysers and Larderello, pressures become almost constant with depth, the small pressure increase cor-

responding approximately to the weight of a column of steam or other gaseous constituent. Pressures measured at the top of the slowly increasing pressure zones vary from 30 to 40 bar. Table 3, from White et al. (1971), illustrates this behaviour.

Pressures in a geothermal system are related to the quantities of carbon dioxide and other gases present in the fluids. The contribution to the total pressure at any particular depth, by the pressure of carbon dioxide is dependent on whether the gas is dissolved or present as vapour. Tables 4 and 5 show the partial pressures of carbon dioxide for solution in water and pressures in saturated steam at different temperatures.

Sutton (1976) calculated *P-T* curves for the system H₂O-CO₂, and Mahon & Finlayson (1975) and Grant (1977) carried out similar estimates for the Broadlands geothermal system in New Zealand. Pressures exerted by dissolved carbon dioxide are considerable, and for example a 6% w/w solution has a CO₂ partial pressure greater than saturated vapour pressure of water at 300°C. Where accurate downhole measurements are available in geothermal systems, a direct correlation is frequently found between the measured pressure and the combined vapour pressures (water plus the dissolved gas) (James 1975). In these

Table 3 Pressures and temperatures in a two phase reservoir in which steam is the continuous phase. Top of reservoir is assumed to be 236°C, 31.8 kg cm⁻², and 360m deep (from hydrostatic boiling-point curve).

| Depth (m) | Pressure (kg cm ⁻²) bottom hole | Temperature (°C) |
|-----------|--|------------------|
| 360 | 31.8 | 236 |
| 500 | 32.0 | 236.1 |
| 1000 | 33.5 | 239.0 |
| 1500 | 34.3 | 240.3 |
| 2000 | 35.1 | 241.6 |

From White et al. (1971).

cases a quasi-boiling point for depth relationship exists, where gas acts as steam.

A small decrease in hydrostatic pressure where a balance exists between hydrostatic pressure and total steam plus gas pressure can result in a very rapid decompression of the system. Ellis (1962) produced curves showing the distribution of CO₂ between a liquid and steam phase for given amounts of steam separation. Table 6 shows the distribution of carbon dioxide between a steam and water phase when boiling of 260°C water occurs. At 260°C a CO₂ con-

Table 4 Partial pressures (bar) of CO₂ dissolved in water.

| T (°C) | CO ₂ (% w/w) CO ₂ (mol/100 mol H ₂ O (water)) | | | | | | | | |
|--------|---|---------------|--------------|--------------|------------|-------------|--------------|--------------|------------|
| | 0.024 0.01 | 0.122 0.05 | 0.24 0.10 | 1.22 0.50 | 2.4 1.0 | 10.9 5.0 | 19.6 10.0 | 32.8 20.0 | 55 50.0 |
| 50 | 0.28 | 1.4 | 2.85 | 14.3 | 28.5 | 143 | 285 | 570 | 1426 |
| 100 | 0.51 | 2.6 | 5.2 | 25.9 | 51.7 | 259 | 518 | 1035 | 2588 |
| 150 | 0.67 | 3.3 | 6.7 | 33.4 | 66.7 | 334 | 667 | 1335 | 3338 |
| 200 | 0.65 | 3.2 | 6.45 | 32.2 | 64.5 | 322 | 645 | 1290 | 3226 |
| 250 | 0.53 | 2.6 | 5.2 | 26.1 | 52.2 | 261 | 522 | 1043 | 2608 |
| 300 | 0.39 | 1.95 | 3.95 | 19.65 | 39.4 | 196 | 394 | 788 | 1970 |
| 350 | 0.21 | 1.05 | 2.09 | 10.5 | 20.95 | 105 | 210 | 420 | 1051 |

Table 5 Pressures generated by CO₂ (gas) in steam (bar).

| T (°C) | CO ₂ (% w/w) CO ₂ (mol/100 mol H ₂ O (steam)) | | | | | | | | |
|--------|---|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|------------------------|
| | 0.024 0.01 | 0.122 0.05 | 0.24 0.10 | 1.22 0.50 | 2.4 1.0 | 10.9 5.0 | 19.6 10.0 | 32.8 20.0 | 55.0 50.0 |
| 50 | 1.2 × 10 ⁻⁴ | 6.2 × 10 ⁻³ | 1.2 × 10 ⁻² | 6.2 × 10 ⁻² | 1.2 × 10 ⁻¹ | 6.2 × 10 ⁻¹ | 1.2 × 10 ⁻¹ | 2.5 × 10 ⁻¹ | 6.2 × 10 ⁻¹ |
| 100 | 1.0 × 10 ⁻⁴ | 5.1 × 10 ⁻³ | 1.0 × 10 ⁻² | 5.1 × 10 ⁻² | 1.0 × 10 ⁻¹ | 5.1 × 10 ⁻¹ | 0.1 | 0.2 | 0.51 |
| 150 | 5.0 × 10 ⁻⁵ | 2.5 × 10 ⁻³ | 5.0 × 10 ⁻³ | 2.5 × 10 ⁻² | 5.0 × 10 ⁻² | 0.25 | 0.5 | 0.99 | 2.58 |
| 200 | 1.7 × 10 ⁻⁵ | 8.6 × 10 ⁻³ | 1.7 × 10 ⁻² | 8.6 × 10 ⁻² | 0.17 | 0.8 | 1.7 | 3.4 | 8.6 |
| 250 | 4.8 × 10 ⁻⁵ | 2.4 × 10 ⁻² | 4.8 × 10 ⁻² | 0.24 | 0.48 | 2.4 | 4.8 | 9.6 | 24.1 |
| 300 | 1.2 × 10 ⁻⁵ | 6.1 × 10 ⁻² | 0.12 | 0.6 | 1.2 | 6.1 | 12.9 | 24.4 | 61.0 |
| 350 | 3.3 × 10 ⁻⁵ | 0.16 | 0.33 | 1.6 | 3.3 | 16.0 | 32.6 | 65.3 | 163 |

Table 6 Distribution of CO₂ between the liquid and vapour phases when water at 260°C boils.

| Steam separation (%) | Temperature of residual water (°C) | Gas in steam (as fraction of gas concentration in original system) | Gas in residual liquid (as fraction of original concentration) |
|----------------------|------------------------------------|--|--|
| 1 | 256.5 | 4.8 | 0.53 |
| 2 | 253.0 | 33.5 | 0.33 |
| 3 | 249.5 | 26 | 0.23 |
| 4 | 245.8 | 21 | 0.17 |
| 5 | 242.0 | 17.5 | 0.13 |
| 6 | 238.2 | 15.5 | 0.10 |
| 7 | 234.1 | 13.0 | 0.08 |
| 8 | 230.0 | 12.0 | 0.06 |
| 10 | 221.0 | 10.0 | <0.05 |
| 12 | 212.0 | 8.5 | <0.05 |
| 14 | 202.5 | 7.0 | <0.05 |

centration 0.25% w/w has a partial pressure of 5.15 bar. After a 1% steam separation, corresponding to a drop in water temperature of 3.5°C, the gas pressure falls to 2.4 bar — a 50% decrease. Another comparison can be obtained from Tables 4 and 5; for example, the CO₂ partial pressure for a solution of 1.25% w/w is 25.8 bar whereas the same concentration of gas in a saturated 250°C vapour phase contributes only 0.24 bar to the total pressure.

The effects of carbon dioxide on the pressures in a geothermal system are obviously related to the quantities of the gas present. In systems such as Wairakei, where carbon dioxide concentrations of about 0.05% w/w are present ($P_{CO_2} \cong 1$ bar), the gas has little influence on the deep pressure or temperature conditions. In areas such as Broadlands and Ngawha, The Geysers, and Larderello, where gas concentrations lie in the range 0.5–5% w/w, the effects can be appreciable.

In assessing the effect of carbon dioxide on the deep physical conditions in a geothermal system most investigators have considered a situation where the gas is in a dissolved or static gas pocket form. Thus Haas (1971) in developing thermal gradients in hydrothermal systems at hydrostatic pressures commented, 'a gas phase coexisting with the liquid in a channel is consistent with the arguments presented here provided the gas is contained in pockets and not suspended in the liquid of the channel'. Sutton's (1976) pressure-temperature data in comparison assume that continual equilibrium exists between the three phases, carbon dioxide, steam, and liquid water, after the point that boiling first commences. In areas of low carbon dioxide concentrations Haas's assumptions are likely to approximate the natural

conditions, but with carbon dioxide concentrations greater than approximately 0.1–0.2% w/w Sutton's values are closer. The liberation of carbon dioxide from solution by small changes in the system, or a continuous gas flux which occurs in many systems, may result in the presence of much free gaseous CO₂ dispersed in the liquid and upward movement of gas bubbles through the system (air bubbles rising in a column of liquid water have a velocity of around 0.3 m/s; R. James pers. comm.).

A mixture of steam and carbon dioxide rising towards the surface can experience considerable steam condensation, producing an increasingly gas rich vapour phase. The effect of the gaseous carbon dioxide and other low solubility gases (H₂, N₂, H₂S) on the density of the surrounding composite fluid could be appreciable. In a later section the effects of the density of coexisting liquid water-carbon dioxide gas on the behaviour of the system are considered in more detail.

Temperatures within a geothermal system are primarily controlled by pressure when boiling conditions prevail, at least at depths up to approximately 5 km. In a number of well-studied systems, such as Wairakei, temperature increases occur very close to the two-phase boundary, liquid water-steam. In most wells at Wairakei, before extensive exploitation, temperatures fell slightly below the boiling point for depth boundary owing to a small amount of dissolved carbon dioxide present.

Fig. 1 shows the minimum depths to the points of first boiling (bubble point depth) for systems containing different amounts of dissolved carbon dioxide. The curves have been constructed given the conditions that gas plus steam pressure must just balance the hydrostatic pressure exerted by the hot water column. Water densities have been integrated to obtain the depth to the various temperatures, and it is assumed that the density of water is not influenced to a major extent by the dissolved gas (*cf.* comments below on gas/water froth densities). The depth-temperature relationship for pure water is taken from Haas (1971). The conditions at the top of the hot water column are taken as 100°C (boiling point) temperature and 1 bar pressure. In many geothermal systems boiling point conditions do not occur at the surface, and for these cases the curves must be depressed to deeper levels.

It is apparent from Fig. 1 that the bubble point for water of a given temperature is found at deeper depths as carbon dioxide concentrations in the water increase. For example, 250°C water containing no carbon dioxide commences to degas and boil at a depth of around 460 m. The same temperature water containing 0.12, 0.24, 1.2, 2.4, and 10.9% w/w CO₂ in water commences to degas and boil at 490, 520, 760, 1070, and 4000 m respectively. The maximum ef-

fect of carbon dioxide on the depth to first boiling in a geothermal system occurs over the temperature range 150–200°C when the solubility of carbon dioxide, expressed as Henry's law coefficient, passes through a minimum.

It was assumed when developing Fig.1 that the effect of free carbon dioxide in the system above the point of first boiling was small. In actual fact the presence of free carbon dioxide in waters above the bubble point could have a marked influence on the fluid densities. There is considerable evidence from some systems, such as Kamojang in Indonesia, that mixed carbon dioxide and water solutions exist as a type of froth.

Fig.2 shows the densities of carbon dioxide–water froths at various temperatures. At the gas concentrations listed maximum density variations occur at lower temperatures. At higher temperatures (350°C) and higher gas contents (2.44% w/w CO₂–H₂O froth) there are still appreciable differences between the densities of gas–water froths and pure water. At intermediate temperatures of 150–250°C and higher carbon dioxide concentrations (1% w/w), densities vary from less than 0.1 to around 0.6 g/cm³.

The major influence of lower density carbon dioxide–water froths in geothermal systems is to depress the bubble points to lower levels than those indicated in Fig.1. Thus two major physical parameters, both involving the presence of carbon dioxide, can influence the temperature regime and temperature gradient in geothermal systems. Since both have the effect of increasing the depth to a given temperature, the temperature gradients within systems containing carbon dioxide are generally much lower than those in low gas or gas free systems.

It is apparent from the foregoing discussion that temperature versus depth relationships in a geothermal system must be interpreted with considerable care if the gas concentration in the deep water is unknown. Conversely, assessment of deep carbon dioxide concentrations, from analysis of hot springs and fumarole discharges (Ellis 1970), should enable some prediction to be made of the geothermal gradient present. In the past close to zero temperature gradients in a relatively hot system (> 150°C) have been interpreted as indicating that widespread convection occurs in these zones. This is not necessarily true, and a low gradient may simply result from the presence of dissolved carbon dioxide and other gases in the system. Extrapolation of shallow temperature gradients to obtain deep temperatures may also give fallacious results under these conditions.

At Broadlands in New Zealand and Kamojang in Indonesia the bubble points occur at depths of 2.3–2.7 and 1 km respectively (Grant 1977, Mahon & Finlayson 1977, Mahon unpub.), and the presence of the gas at higher levels in the system has a marked in-

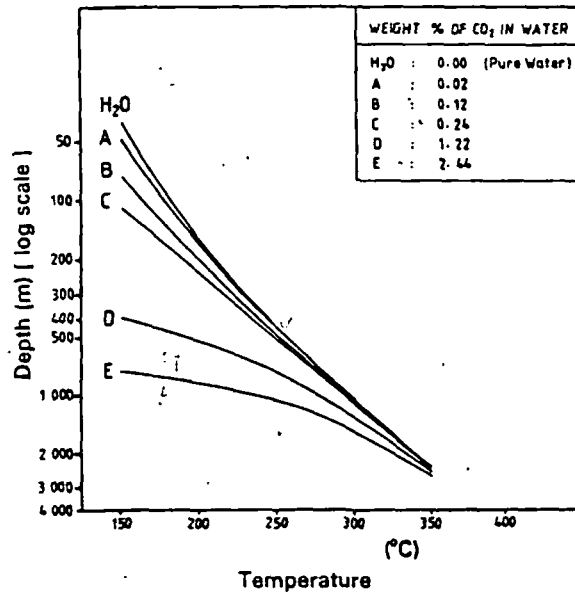


Fig.1 Minimum depth to point of first boiling for waters of given temperatures and CO₂ concentrations.

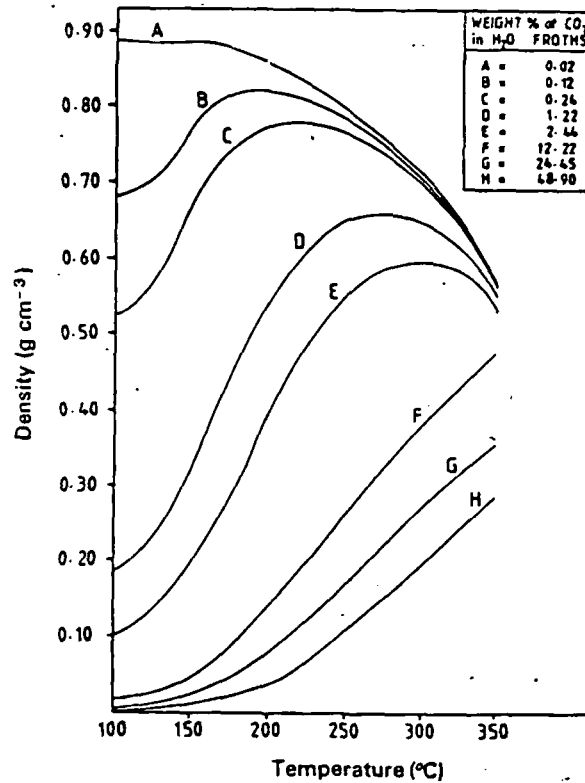


Fig.2 Densities of CO₂–H₂O froths.

fluence on the density of the hot fluids. There are well-defined zones at Broadlands and Kamojang where carbon dioxide, as both hot and cold gas, escapes at the surface. Many downhole pressure and temperature measurements made in different geothermal systems have indicated the presence of low density fluids. This has frequently been interpreted as the presence of a two phase (steam-water) mixture, but in the authors' opinion this could as easily and more likely result when a non-condensable gas, such as carbon dioxide, is entrained as a type of froth in a liquid phase.

HYDROLOGY

The hydrology of a geothermal system is frequently discussed in terms of the shallow surface waters (<100m) and the deep waters (>100m). In many ways the shallow hydrology of geothermal systems follows the normal types of patterns present in cold water systems. The physical parameters controlling the deep hydrology, however, are frequently unique. In its simplest form the hydrology of a geothermal system can be described as the movement of cold water into a hot zone; heating and lowering of fluid density by a combination of conduction and convection; and migration of the less dense fluids towards the surface and lower pressure zones in the system. If the hot water level reaches the surface, hot springs occur, and the volumes of fluid discharged are determined by the supply of cold water and the permeability of the rocks in the system.

The pressures in the columns of hot and cold fluid are partly controlled by the density of the fluids. The height to which the hot column rises is determined by the respective levels of the columns to a reference level (frequently the height of the cold water column above sea level) and the density of the fluids. As a simple example, water heated to 350°C and flowing towards the surface maintaining temperatures along the two phase boundary (liquid water-steam) has an approximate average density from the point of boiling of 0.57 g/cm³. If the hot water is balanced against cold water of density 0.998 g/cm³ the level of the hot water surface would appear some 1000m higher than the top of the cold water surface if a connection between the two occurred 2.35 km below the reference level and the hot column was sufficiently confined to prevent horizontal dispersion. Whether the hot water discharges at the surface will depend on the topography, the lateral and vertical movement of cold ground water, and the respective surface elevations of hot and cold water.

Reducing or increasing the density of the fluid in the hot column can have a marked influence on the level of the hot fluid, the movement of the fluid

within the system, and the general hydrology of the system. Fig.2 shows the variation in densities of froths containing various concentrations of carbon dioxide in a gas phase. For the gas concentrations and temperatures that exist in many geothermal systems fluid densities are appreciably lowered by the presence of the gas. For example, within the temperature range 150–250°C and a gas concentration of approximately 2% w/w densities of the froth fall to approximately 50% of that of non-gaseous water at similar temperatures.

Carbon dioxide movement through the hot zones as a froth can thus have a very marked effect on the hydrology of a geothermal system. It is well known that variations occur in the gas flux through geothermal systems. This could produce changes in the level of the hot system leading to intermittent periods of surface flow.

Vertical movement, or belling, of the hot fluid, produced by this mechanism is extremely important in geothermal systems formed in the interiors of recently active volcanoes, e.g., Kamojang in Indonesia, where fluids are confined to well-defined zones by the local geological structure and hydrothermal alteration of the rocks. Hot water surfaces in these systems can be located hundreds of metres above the local cold water levels on the flanks of the volcanoes. The high levels that the hot water surfaces occur above the cold ground water surface are difficult to explain on a simple non-gaseous hot-cold column pressure relationship.

CHEMISTRY OF GEOTHERMAL SOLUTIONS

Although many different chemical types of hot water occur in geothermal systems, two predominate in abundance and volume. These are most commonly defined as near-neutral pH sodium chloride waters and near-neutral pH sodium-sulphate-bicarbonate waters. The former waters have been discussed in great detail in a large number of publications (cf. White *et al.* 1971), while the chemistry and location of the latter waters are the subject of a recent paper (Mahon *et al.* 1980). Carbon dioxide plays a major role in the chemistry of both types of water.

Carbon dioxide is a relatively reactive gas and in high temperature natural hot waters, reaction of the gas with aluminosilicate rock minerals produces solutions containing varying amounts of bicarbonate and carbonate. The proportions of CO₂, HCO₃⁻, and CO₃²⁻ present are basically dependent on temperature and solution pH. At deep levels in a hot system, solution pH is controlled by reactions involving the aluminosilicate phases in the rocks and the salinity of the solution. As hot waters rise to the surface and boil, carbon dioxide and other acidic gases, for example

hydrogen sulphide, are lost from solution and the various acid-base ionic equilibria present then control solution pH (Ellis 1969). Since the $\text{CO}_2/\text{HCO}_3^-$ buffer is generally the most dominant of the acid base equilibria present, it is the principal relationship controlling the solution pH during the process of boiling.

Calcium carbonate (calcite) solubility in hydrothermal solution is controlled by a number of factors which include the partial pressure of carbon dioxide, solution pH, and temperature (Ellis 1963). As temperatures increase, the solubility of calcite decreases, whereas the solubility increases with increasing pressure of carbon dioxide at constant temperature. Boiling of geothermal waters, with resulting loss of CO_2 from solution, frequently results in calcite precipitation. Geothermal waters of highest carbon dioxide concentration are the most likely to precipitate calcium carbonate (as at Kizildere).

Steam formed by the boiling of neutral pH sodium chloride waters frequently separates from the water phase and migrates into cold water zones above or alongside the main chloride water reservoir. The cold water is heated by condensation of steam and/or the hot gases which are present in the steam. Reaction of the gases with the oxygenated water produces acid solutions containing mainly sulphate, produced from hydrogen sulphide oxidation, and bicarbonate produced from the reaction of CO_2 with the confining rocks. The acidity is neutralised by rock-water reaction which liberates sodium, potassium, calcium, magnesium, and other common rock constituents into solution. The low solubility of calcium carbonates and sulphates at higher temperatures limits the concentrations of calcium in solution by precipitating calcium carbonate (calcite) and calcium sulphate (anhydrite). Magnesium is readily removed as the minerals chlorite and montmorillonite (Ellis 1971). The major cation remaining is sodium which is soluble at all temperatures (Ellis & Mahon 1977, Mahon *et al.* 1980).

HYDROTHERMAL ROCK ALTERATION IN GEOTHERMAL SYSTEMS

The role of carbon dioxide in the alteration of rock minerals in hydrothermal systems was outlined by Ellis (1969) and Browne & Ellis (1971). Two very common minerals found in geothermal systems — calcite and anhydrite — are formed by the processes described in the previous sections. The formation of these minerals results in a lowering of rock permeability and porosity, and together with quartz deposits, they affect the movement and direction of movement of water within the system.

The alteration minerals present in geothermal systems are very dependent on the concentrations of

carbon dioxide present. Using phase diagrams of the various minerals commonly found in these systems Ellis (1969) showed that, as carbon dioxide concentrations increase, certain minerals are prevented from forming due to the formation of calcite. At low carbon dioxide concentrations of 0.55% w/w and at temperatures of around 260°C calcium rich minerals such as wairakite and zoisite are stable; at 0.73% w/w zoisite cannot form; and at 4.4% w/w wairakite would be unstable. The presence or absence of wairakite and epidote in alteration mineral assemblages at temperatures in the range of 260°C can thus be directly related to carbon dioxide concentrations.

DISCHARGE CHARACTERISTICS OF A GEOTHERMAL SYSTEM

Wells drilled into geothermal systems frequently produce a mixture of steam and water. These systems are commonly referred to as water dominated systems, the inference being that the systems are filled with water. Less commonly wells produce a dry steam discharge from depths ranging from a few hundred metres to over 2000m. Systems where this occurs are referred to as 'vapour dominated systems' and are considered to contain large volumes of steam in the more permeable zones associated with pore water in the less permeable rocks (Truesdell & White 1973).

The physical and chemical characteristics, mode of formation, and stability of vapour dominated systems have been discussed by many workers, most notably Facca & Tonani (1964); Elder (1966); James (1968); Sestini (1970); Ferrara *et al.* (1970); White *et al.* (1971); and Truesdell & White (1973). Truesdell & White (1973) correlated and interpreted most of the information and data available from all sources to produce a model of a vapour dominated system. The two physical features which have been used to distinguish vapour dominated systems from water filled systems are: (1) Wells produce mainly dry steam; and (2) Below a certain depth, which can vary from area to area, temperatures and pressures increase very slowly with increasing depth. Temperatures and pressures measured near the top of the minimum gradient zones frequently lie in the range 230–240°C and 31–40 bar respectively. These values approximate to the temperature and pressure of steam at its maximum enthalpy (236°C, 31.2 bar).

The best known and certainly the most studied vapour dominated systems are Larderello, The Geysers, and Matsukawa. Steam production from the first two systems comes basically from sedimentary and metamorphic rocks, while production at Matsukawa is from volcanics (andesites and dacites). The non-condensable gases contained in the steam discharges at Larderello, mainly CO_2 , are present at a

concentration level of 1–5% w/w, at The Geysers from 0.2 to 2% w/w (CH₄ and H₂ are also significant here), and at Matsukawa approximately 0.5% w/w. In all three cases the gas contents per unit mass discharged from wells are relatively high.

As Ellis & Mahon (1977) pointed out it is not uncommon to find geothermal systems where dry steam wells and wells producing steam–water mixtures occur in the same general locality and produce from the same depth. Thus at Wairakei, New Zealand, which is always referred to as a 'water dominated system', well 25 produced a completely dry saturated steam discharge. At Broadlands in New Zealand, well 7 produced a very high enthalpy discharge shortly after opening, while well 19 produced a completely dry discharge several weeks after opening. The majority of wells in the Broadlands system discharge steam–water mixtures with enthalpies considerably higher than the enthalpies of the waters that supply them. The carbon dioxide contents of the waters at Broadlands and Wairakei, to depths of about 700m, are respectively 0.6 and 0.06% w/w.

At Wairakei and Broadlands, where considerable well production has occurred, the trend in temperatures and pressures is towards those which are commonly present in vapour dominated systems. This trend was rapid at Broadlands and less rapid at Wairakei; but on reaching the temperatures and pressures close to those of steam at its maximum enthalpy, the rates of decrease became small for considerable periods of time (years).

Following this brief introduction to the two major modes of production from geothermal systems the role of carbon dioxide in influencing the nature of the discharge from a well is investigated. To help understand the role of carbon dioxide it is necessary to initially consider a system where gas is absent.

The maximum porosities of rock whereby water contained in the pores can completely evaporate to steam at a given pressure (production pressure) for temperatures between 100 and 350°C are shown in Table 8. Calculations were made assuming a heat balance between the combined heat contained in the rock and water and the heat required in the steam. The density of rock was taken as 2.5 g/cm³ and the specific heat as 0.837 J/(g°C). It was assumed that sufficient surface area of rock was available for conductive heat transfer between rock and water, allowing complete evaporation. This is a reasonable assumption for systems where the migration of water towards a geothermal well occurs under a pressure differential of several bars.

At high temperatures (> 300°C) and production pressures (5–7 bar absolute), maximum porosities are relatively high (15–30%) and in the range of rock porosities found in many geothermal systems. At temperatures below 300°C the maximum porosities

decrease to below 12% for the quoted production pressures, although if evaporation is allowed to proceed to lower temperatures and pressures (100°C and 1 bar) the porosities still remain between 12 and 20%.

Table 7, which shows the densities of liquid water–gas mixtures (froth), illustrates the possible effects of carbon dioxide on the maximum possible rock porosities (cf. Table 8) under which complete evaporation of water from rocks can occur. At low carbon dioxide concentrations (0.024% w/w) the effect on the density of the gas–water froth is slight: e.g., at 250°C the density of pure liquid water is 0.799 whereas that of a 0.024% w/w gas in water froth is 0.7955. As gas concentrations increase the effect on froth density becomes appreciable, and at a temperature of 250°C and at gas concentrations of 2.4 and 10.9% w/w, froth densities would be 0.55 and 0.26 respectively. At a given temperature, and assuming that thermal equilibrium is maintained between rock and froth and that the froth is distributed homogeneously through the pores, the maximum porosities of rock for complete water evaporation increase as the gas concentrations increase. At lower temperatures and/or high gas concentrations the porosity increase can be 2–3 times higher than that needed for the complete evaporation of pure water. The higher porosities of 15–40% are in the range found in rocks common to many geothermal systems. Whereas it would be difficult to completely evaporate pure water from rocks of average porosity at lower temperatures (< 250°C), it would not be difficult for water in water–gas froths.

A further observation can be made from data in Table 7. Above 250°C the specific densities of carbon dioxide/water froths increase to a maximum then decrease. The temperatures at which maximum densities occur increase as gas concentrations increase. For carbon dioxide concentrations of 0.024 to approximately 0.25% w/w the maximum densities occur between 190 and 210°C. Between 0.24 and 10.9% w/w the maximum densities occur at temperatures between 210 and 350°C.

As the specific volumes of the froths are inversely related to the densities, the mobility (total mass transfer) of the mixtures is likely to be influenced by temperature and gas concentration. The viscosity of carbon dioxide is very similar to that of steam and decreases with decreasing temperature. At 250°C the viscosity of water is only about 6 times that of carbon dioxide, yet its density is about 40 times that of the gas. The presence of carbon dioxide in a hot water flow therefore lowers mass transfer through the system. Over the temperature range 100–350°C, at saturated water vapour pressure, the viscosity of carbon dioxide increases by a factor of about 4, whereas the viscosity of water at the same pressure decreases by a factor of approximately 9. The density changes

Table 7 Densities of CO₂-H₂O froths.

| Gas concentration | | Temperature (°C) | | | | | | |
|-------------------|---------------|------------------|------|------|------|------|-------|------|
| (% w/w) | (mol/100 mol) | 50 | 100 | 150 | 200 | 250 | 300 | 350 |
| 0.024 | 0.01 | 0.92 | 0.89 | 0.88 | 0.85 | 0.79 | 0.71 | 0.57 |
| 0.122 | 0.05 | 0.72 | 0.68 | 0.78 | 0.82 | 0.78 | 0.70 | 0.57 |
| 0.24 | 0.10 | 0.59 | 0.53 | 0.67 | 0.77 | 0.76 | 0.695 | 0.57 |
| 1.2 | 0.50 | 0.22 | 0.19 | 0.33 | 0.55 | 0.65 | 0.65 | 0.55 |
| 2.4 | 1.00 | 0.12 | 0.11 | 0.20 | 0.40 | 0.55 | 0.60 | 0.53 |
| 10.9 | 5.00 | 0.03 | — | 0.05 | 0.14 | 0.26 | 0.38 | 0.43 |
| 19.6 | 10.00 | — | — | — | 0.08 | 0.17 | 0.22 | 0.36 |
| 32.8 | 20.0 | — | — | — | — | — | 0.10 | 0.29 |

Table 8 Maximum rock porosity limiting total conversion of water into steam. Percentages at given temperatures.

| Initial rock and water temperature | Pressure of steam (bar) | | | | | | | | |
|------------------------------------|-------------------------|------------|-------|------|------|------|------|------|------|
| | (°C) | 1.0(100°C) | 1.4 | 3.5 | 5.0 | 7.0 | 10.5 | 14 | 31.8 |
| 350 | 35.9 | 35.8 | 31.0 | 27.4 | 25.3 | 24.0 | 22.0 | 15.1 | — |
| 300 | 24.2 | 22.8 | 18.75 | 17.1 | 15.3 | 13.2 | 11.6 | 6.9 | — |
| 250 | 16.1 | 14.9 | 11.4 | 9.9 | 8.4 | 6.7 | 5.3 | 1.3 | — |
| 200 | 9.7 | 8.6 | 5.6 | 4.4 | 3.1 | 1.5 | 4.4 | — | — |
| 150 | 4.6 | — | — | — | — | — | — | — | — |

of the two phases are considerable over the same range, and the overall effect is to lower mass transfer as temperatures decrease. Carbon dioxide-hot water froths, with gas concentrations greater than 0.25% w/w are likely to be far more mobile at temperatures in excess of 220°C than at lower temperatures. Similarly the mobility of lower temperature froths, as for example those existing near the surface of a system, would be low and would tend to act as a barrier to upflow and movement towards a well.

Earlier we discussed the effect of dissolved carbon dioxide on the minimum depth to the bubble point and on the temperature gradient in a geothermal system. For gas concentrations less than approximately 0.24% w/w the effect on the depth of first boiling is not great. For example, in 250°C water containing this gas concentration the bubble point would be located some 60m below the bubble point of pure water. At higher gas concentrations and at the same temperature, however, the effect is appreciable, and for example at a gas concentration of 1.0 mol/100 mol H₂O (2.4% w/w) the bubble point is depressed by 600m. One can compare this model with models of vapour dominated systems.

To reach the *240°C bubble point in a system containing a carbon dioxide concentration of 0.5 mol/

100 mol (1.2% w/w) a well would have to be drilled to a minimum depth of 720m (water level at surface). In a system containing 2.44% w/w carbon dioxide the well would have to be drilled to 1020m to reach the same temperature. An extreme case would be for a carbon dioxide concentration of 5 mol/100 mol (10.9% w/w), when the 240°C bubble point would be over 3000m below the surface. Obviously the hot water is not always located at the surface of the system, and thus the depths to the bubble points at 240°C may be considerably greater. A geothermal well deeper than 2000m is not particularly common, and most data and information come from wells considerably shallower than this.

The main point is that in systems where gas concentrations are relatively high drilling to depths of 1000–1500m (common depths of wells at The Geysers and Larderello) are likely to encounter maximum temperatures in the region of 230–250°C.

The likely conditions in a well drilled to 1200m in a geothermal system containing 2.44% w/w of carbon dioxide in a water-gas froth are now considered. It is assumed that the bubble point occurs just below the level of the well. At this gas concentration there is a reasonable possibility that the porosity of the rocks to liquid water-gas mixtures would allow complete evaporation of water or steam as pressures are reduced. At the completion of drilling or when the well

* 240°C was selected since this temperature is commonly found at deeper levels in vapour dominated systems.

is closed in after a short discharge time, the well may fill with a gas-steam mixture with possibly a small amount of water accumulating at the bottom of the well. Water existing close to the well may not have the opportunity of completely evaporating before entering the well. Depending on the extent of evaporation undergone by the liquid phase, the steam-gas mixture in the well will attain certain gas concentrations. These could vary from a minimum of 48.1 mol/100mol for 1% evaporation to less than 7 mol/100mol for evaporation greater than 14%. In any event the gas content of the system is likely to be high. Assuming that the rocks have uniform porosity and permeability throughout the production length of the well, most inflow to the well will virtually take place from the hottest zone (cf. previous comments on mobility of gas-water froths).

After shutdown much of the steam in the well is likely to condense, except perhaps in the bottom section where temperatures are sufficiently high to sustain a steam phase. It is not difficult to show that the volumes of gas required to sustain the necessary pressures in the well can be obtained from close to the well, i.e., it is not necessary to consider the movement of gaseous carbon dioxide at distances greater than 5m from the well. Pressure at the well bottom may correspond to the wellhead pressure plus pressure generated by a column of carbon dioxide. This pressure would be higher than the wellhead pressure plus a column of steam ($2.44 \times$ steam column weight at ambient temperatures).

As far as can be assessed from the literature, very little information is available on the nature of fluids present in a well in a vapour dominated system, in cases where physical measurements have been made. Some interesting and pertinent results were obtained from a steam well at Kamojang in Indonesia (well II) that had been discharged for a short time and then closed. A low density liquid phase (water-gas froth) was present in the bottom 6m of the well where the temperature was approximately 240°C, while the wellhead pressure was equal to that of the vapour pressure of water at 240°C. Samples taken from the vapour column indicated a very much higher ratio of CO₂/steam than in the steam discharged. This ratio increased appreciably from the bottom to the top of the column a short time after the well had been closed. The water, on analysis, proved to be a neutral sodium-bicarbonate-sulphate type and had originated from the adjacent formations. (This was assessed from previous downwell samples that had been collected before the well was discharged.)

On opening a well of this type (2.44% w/w CO₂), notable and measurable changes in the gas concentrations and the isotopic composition (D/H ratio) of the steam discharged should occur. Gas concentrations in the steam discharged should fall to approximately

1.0mol/100mol H₂O (or thereabouts depending on the amount of retention of water in the pores, a presently unknown factor). The ratios of soluble gases to less soluble gases in the discharge should also change during initial discharge (Ellis 1962). In particular the ratio of CO₂/H₂S should decrease. The trends in gas concentrations could be variable since they depend on a large number of factors, and, for example, gas contents may in some cases remain higher and decrease over a longer discharge period than in other cases. Measurements made on well II, Kamojang, (similar to the one hypothesised) gave result very similar to those predicted. Gas concentrations, gas ratios and the isotopic composition of the steam indicated that degassing and evaporation of steam from a water phase was occurring.

Production from the well would then follow predictable trends. The increasing mobility of higher temperatures water-gas mixtures would favour production from higher temperature zones. The expansion of the fluids would create boiling and degassing and steam expansion would produce the temperatures and pressure pattern predicted for steam dominated systems (cf. Truesdell & White 1973). If the entry of higher temperature fluids into the well was prohibited by depth or porosity, the temperature and pressure in the well would be controlled by those fluids present in the most permeable zones. During the migration of steam-gas mixtures, and on the assumption that intimate contact between the gas and water vapour occurred, the temperature of the gas could follow that of the steam. Condensation of steam would then leave a gas of similar temperature to the condensate. The likely heating and thermal effects of gaseous CO₂ on a system are discussed below.

Once a well of this type has been discharged for a number of weeks the temperature and pressure in the zone around the well will relate to, and equilibrate with, the temperature of the fluids entering the well. Rock temperatures near the well would decrease towards that of the steam at the pressure of entry into the well. The original conditions around the well may never be attained again during the production, unless a very lengthy shutdown period occurs. Pressure recovery in the well during shutdown periods would be slow owing to the depletion (decompression) effect produced by degassing.

It is of interest to compare the comments made in the last section with information from vapour dominated systems, particularly the data from Truesdell & White (1973). In both White *et al.* (1971) and Truesdell & White (1973) comment was made on the influence of non-condensable gases on the systems. However, they did not emphasise the important role that these gases could have on the physical conditions present. In the 1971 and 1973 papers a graph showing

- × G1
Maximum temperature at the surface in flowing wells, plotted at drilled depth (Allen & Day 1927)
- + T1
Maximum temperature measured in hole by thermocouple at plotted depth (McNitt 1963)
- ▲ M1
Maximum temperature measured in hole by geothermograph at plotted depth (White 1937a)
- ▽ SB3
Sulfur bank area of The Geysers, saturation temperatures calculated from shut-in well-head pressures corrected for weight of steam, plotted at drilled depths (numbered wells, oral communication, D. McMillian 1964; Q-D, Otte & Dondanville 1968 from generalised pressure of field assumed in-hole absolute, and no effect from other gases.)
- A Reference boiling-point curve for pure water (White 1968; Haas 1970).
- B Predicted temperature in two phase vapour-dominated reservoir (pure water and steam).
- C Approximate temperature below brine water table.
- D Reference boiling point curve for 0.24% w/w CO₂-H₂O froth.
- E Reference boiling point curve for 2.4% w/w CO₂-H₂O froth.
- F Dotted lines represent trends on boiling with loss of CO₂ from 2.4 to 0.24% w/w.

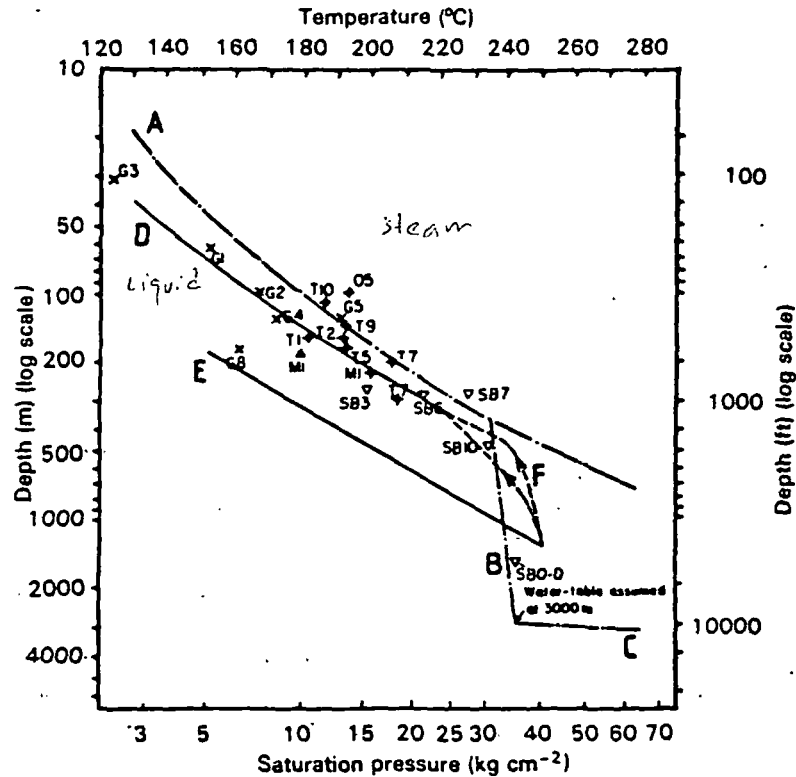


Fig.3 Boiling point curve for pure water and for CO₂-H₂O froths.

the temperature-pressure relations at The Geysers was given (see Fig.3). Similarly, the gas concentration of the steam at The Geysers was quoted as being between 0.2 and 2% (presumably by weight, but no units were quoted). Of the 21 measured and estimated values of temperature versus depth, 14 values fall below the reference boiling point curve for pure water: i.e., the temperatures were less than that of pure water at similar pressure (assuming that the hot water table occurred at the surface and was at boiling point).

The graph of White *et al.* (1971) is reproduced in Fig.3 with the reference boiling point curve for pure water from White (1968) and Haas (1970) drawn in. The boiling point curves for carbon dioxide froths of 0.24 and 2.4% w/w carbon dioxide are superimposed on this diagram. The carbon dioxide-water froth curves have been constructed by graphically integrating the density of the froths through the temperature range indicated. The pressure of carbon dioxide at higher concentration (2.4% w/w) has been included when assessing depths to the various temperatures. The 0.24% w/w CO₂/H₂O boiling curve gives a better fit to the majority of measured and calcu-

lated values than does the standard curve for pure water, particularly at lower temperatures. The higher gas concentration boiling curve goes deep into the hypothetical steam zone part of the curve and falls close to point G8.

The dotted line curves show the possible behaviour of the temperatures and pressures in a solution containing 2.4% w/w CO₂, rising though the system and boiling at 250°C. The solution loses gas to give a final carbon dioxide concentration in a froth of 0.24% w/w. It is interesting to note the similarity between the trends of these curves and the trend of temperatures and pressures in a vapour dominated system.

The main point of this discussion is that one does not necessarily have to postulate a steam zone in these systems during initial exploitation and perhaps even after exploitation where pressures and temperatures are relatively constant with depth.

At Larderello and other vapour dominated systems in Italy gas concentrations appear to be considerably higher than at The Geysers (5% w/w CO₂ and higher), and the temperature-depth relationship in the two areas could be quite different. For example,

to reach 240°C in a system containing a carbon dioxide concentration of 5% w/w would require a well to be drilled to greater than 1500 m if a boiling point for depth relationship exists.

The physical characteristics of individual wells in the same system and between different systems in Italy show a range of variations in temperature and pressure when the wells are initially drilled and first opened. Temperatures in excess of 240°C have been recorded in a number of wells, and, for example, in Travale 22, a temperature of 260°C with an accompanying pressure of 62 bar was recorded, (it would appear that a gas pressure of around 15 bar was contributing to the total pressure in this well).

There is little doubt that exploitation of a system containing relatively high gas contents will in time produce the temperatures and pressures characteristic of a steam dominated system, initially in parts of the system and eventually in the exploited parts of the system as a whole. Before exploitation temperatures and pressures in these systems are probably controlled by carbon dioxide rather than steam. It is of particular interest that recent wells drilled at both The Geysers and Larderello have recorded temperatures of 255°C and higher, suggesting that the presence of steam at these depths is unlikely. Unfortunately, the depths of these wells are unknown to the authors, but it would be of interest to plot the temperature-depth data from them on the temperatures and pressure gradients characteristic of 2 and 5% w/w CO₂-water froths.

The authors do not dispute the presently held theories on the behaviour of steam systems after production has commenced and the reasoning that is followed by Truesdell & White in their 1973 paper. However, it is now becoming apparent that some water systems are controlled by the same parameters. Wairakei, for example, was buffered at about 230-240°C and 31-33 bar for long periods after an initial rapid decline in both temperatures and pressures. In the authors' opinion the so-called vapour dominated systems, previous to extensive exploitation, start off with gas-water filled reservoirs, the concentrations of carbon dioxide present controlling the temperatures and pressures at different depths. It is easier to predict from thermodynamic reasoning that non-condensable gases could exist in zones of high permeability than could a condensable steam phase.

THERMAL EFFECTS OF CARBON DIOXIDE ON A GEOTHERMAL SYSTEM

In the past the thermal effects of non-condensable gases, and in particular carbon dioxide, on a geothermal system have been somewhat neglected. This is probably because the mass of carbon dioxide is small compared to the mass of rock and water. The

following section briefly investigates the possible contribution that carbon dioxide makes to the heating of a geothermal system.

The enthalpy of carbon dioxide varies with both temperature and pressure, the variation being considerably less than that of water over the same temperature and pressure range. For the following discussion values for the enthalpy of superheated carbon dioxide are taken from Sweigart *et al.* (1946).

In assessing heat transfer processes occurring in carbon dioxide-liquid water solutions it is necessary to balance the enthalpy of gaseous CO₂, with the enthalpy of solution (or ex-solution) of the gas in water and the enthalpy of the combined gas-water solution (i.e., $H_{\text{total}} = H_{\text{gas}} + H_{\text{soln}}$). Ellis & Golding (1963) summarised values for the heat of solution of CO₂, up to 350°C, and their values are used in this work. Considering the flux of CO₂ that is likely to occur through a given volume of water, particularly in geothermal areas which have high gas contents, the water is likely to become saturated with carbon dioxide, for the prevailing physical conditions, relatively rapidly. Subsequent movement of gas and heat will result in a complex degassing-regassing process. During the formation of CO₂ gas bubbles in a near boiling situation some water vapour (steam) is included in the bubble so that the heat content of the bubble is greater than that of pure CO₂ gas. There is considerable evidence for this both from well measurements (R. James pers. comm. (Turkey)) and from samples obtained from fumaroles and surface discharges of hot gases. The steam is removed from the bubbles when sufficient cooling is available, particularly when the gas passes through near surface water to reach the surface. As examples of the thermal contribution that CO₂ makes to a gas-liquid water system and a gas-vapour water system the following cases are given.

Water containing a carbon dioxide concentration of 2.4% w/w at 235°C has an enthalpy of 1014 J/g ($H_{\text{water}} + H_{\text{gas}} + H_{\text{soln}}$). The gas contributes 2.5% of the total heat — slightly more than its percentage weight. At 370°C and at the same gas concentration, the percentage of the total heat contributed by the gas is 3.4. For a similar concentration of carbon dioxide in a steam phase at the same temperatures, the percentages of the total heat contained in the gas phase are 0.82 and 1.1 respectively.

It was mentioned earlier that a flux of carbon dioxide generally occurs in a geothermal system. The extent of this flux, however, is difficult to assess for any particular system. A case is considered where the heat source of a geothermal system is a molten intrusion of volume similar to that of the magma discharged from a volcano. The quantities and heat content of the volatiles discharged are considered to be similar to those discharged from the fumaroles on

an active volcano. As argued by Mahon & McDowell (1977) the more volatile constituents discharged from the magma are removed relatively rapidly, leaving steam and the less soluble gases including CO_2 , at temperatures just below the critical point temperature, to migrate upwards into the system.

Averiev (1966) estimated that the heat flows from fumaroles on Mutnovsky and Avachinsky, two volcanoes in Russia, were 1.88×10^9 and 0.8×10^9 W respectively, and were of the same order as the natural heat flow from the Uzon-Geysernaya and Semyachinsky geothermal systems (5.6×10^9 and 3.14×10^9 W). The New Zealand geothermal systems also have natural heat flows of this order; for example, Wairakei has a natural heat flow of the order of 4.19×10^9 W.

The carbon dioxide concentration in volcanic steam is taken as 10 mol % or 21% w/w. Values close to this were measured in fumarolic steam discharged from vents on White Island, an active andesitic volcano in New Zealand. The temperature of these fumaroles was around 370°C (Giggenbach 1975). The quantity of volcanic steam entering the system at 370°C is assumed equivalent to that of the total heat output of a volcano of 2×10^9 W (2×10^9 J/s).

For a combined carbon dioxide-steam flow of 2×10^9 J/s at a temperature of 370°C , the quantities of carbon dioxide and steam are respectively 2.03×10^4 and 7.64×10^4 g/s. Approximately 12.2% of the heat discharged is contained in the CO_2 gas. If this vapour mixture heats a body of rock and water, and all the CO_2 and steam dissolves and condenses, the contribution of CO_2 to the heating of the system is approximately 21%. This contribution includes the heat contained in the gas and the heat of solution of the gas. At between 4 and 5 km below the surface, assuming water level outcrops at the surface, all the carbon dioxide would pass into solution, and all the steam would condense.

Consider the heating of 1 km^3 of the aquifer at 4–5 km depth by the vapour emissions. The rock is assumed to have a density of 2.5 g/cm^3 and a porosity of 20%. To heat the saturated block of rock to 370°C requires 130y for steam and gas, and 620y if the heating is carried out by the gas alone. It is apparent that the thermal contribution from carbon dioxide in the formation of a geothermal system could be appreciable.

In a second example, consider carbon dioxide gas which is liberated from water at 235°C , the original concentration of CO_2 being 6% w/w. If the gas is completely separated from the water phase, the temperature of the residual water will fall to 222°C . There are many examples in different geothermal systems where an apparent reversal of temperature has been measured in wells. These lower temperatures, which are often explained as resulting from an inflow

of colder water into the system, could result from a degassing process.

As a final point convection of heat at shallow levels is possibly more readily carried out by carbon dioxide than steam. Hot spots found at relatively shallow levels (0–300 m), where temperatures exceed boiling point for depth conditions, are very likely produced by gaseous carbon dioxide.

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Neutral Sodium/Bicarbonate/Sulphate Hot Waters in Geothermal Systems

W.A.J. Mahon*, L.E. Klyen* & M. Rhode**

Abstract: Of all the chemical types of hot water found in geothermal system perhaps the least understood is a near neutral water which contains varying amounts of bicarbonate and sulphate as the major anions, low concentrations of chloride (<30 ppm) and sodium as the major cation. In the past this water has been referred to as a sodium bicarbonate water but present studies suggest that the quantities of bicarbonate and sulphate in this water type are frequently of the same order. Recent studies in the Broadlands Geothermal System in New Zealand and the Kamojang System in Indonesia, particularly the investigation of the shallow and perimeter areas of the systems, has presented more information on the sodium/bicarbonate/sulphate type water.

Of particular interest is the distribution and position of the sodium/bicarbonate/sulphate water in the same and different systems. Many hot springs in Indonesia, for example, discharge water of this composition. In the past, and perhaps most unfortunately, many workers have suggested that the water supplying this type of spring originates from relatively low temperature (<150°C) reservoirs. This interpretation is frequently fallacious. Present studies indicate that this water type can originate from high temperature reservoirs which form the secondary steam heated part of a normal high temperature geothermal systems.

The hydrological conditions producing these waters in geothermal systems are investigated and the relationship between the water type and vapour dominated systems is discussed. It is suggested that the major water type occurring in the so called vapour dominated parts of geothermal systems is this water. The water does not simply represent steam condensate rather it consists essentially of meteoric water which has been steam heated. The water composition results from the interaction of carbon dioxide and hydrogen sulphide with meteoric water and the rocks confining this water in the aquifer.

Introduction

Little information has been available on the chemical processes operating in the shallow or perimeter parts of geothermal systems. Exploration wells in the Kawah Kamojang system in Java Indonesia, and in the Broadlands systems in New Zealand have allowed these particular parts of the system to be extensively investigated. This has been helpful in clarifying the models of both water-dominated and vapour-dominated geothermal systems.

Geochemical surveys of geothermal areas in Indonesia have shown that many hot springs discharge near-neutral pH sodium/bicarbonate/sulphate waters low in chloride and with bicarbonate and sulphate at similar concentration levels. Comparable waters have been found in near-surface and peripheral zones of several geothermal areas in New Zealand.

The widespread occurrence of acid sulphate springs, frequently in association with a smaller number of neutral-pH bicarbonate/sulphate springs, in a geothermal area in which chloride springs are absent, has been used to indicate the presence of a system dominated by steam at deeper levels (White, 1970). However, shallow vapour-dominated systems may sometimes be associated with

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* Chemistry Division, D.S.I.R., Wairakei, N.Z.

** Chemistry Division, D.S.I.R., Wellington, N.Z.

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chloride water springs, or seepages in rivers, at topographical lows within 2 to 5 kilometres from the major zone of surface acid activity. For example, at Te Kopia, a shallow vapour-dominated system in New Zealand, chloride water springs outcrop in a small stream at Waikite some 4 km away. The Broadlands geothermal system, although mainly water dominated, has shallow steam horizons. Waters within the system and spring discharges exhibit chemical characteristics ranging from bicarbonate low-chloride waters, to high-chloride low-bicarbonate waters.

At The Geysers in California, and at Larderello Italy, which are both deep vapour-dominated systems, no chloride water occurs within many kilometres of the surface activity. Although surface hot waters have been described (White et al., 1971; Truesdell and White, 1973), there is little information on the composition of deeper waters in these systems. However, for the Kamojang system, which in many respects is similar to the systems at The Geysers and Larderello, the chemical compositions of waters are known to depths of 1500 m.

This paper describes the occurrence and nature of the specialised bicarbonate/sulphate types of water that are developed in certain localities within geothermal areas, and their relationships to the high temperature alkali chloride waters that predominate in the deeper parts of most explored hot water geothermal systems (Ellis and Mahon, 1977). The chemical information presented is mainly from the analysis of well discharges and down-hole samples from the Broadlands and Kamojang systems.

Broadlands

Thirty-three geothermal wells have been drilled in the Broadlands geothermal system, the majority within a 10 ohm-m surface resistivity boundary (Schlumberger AB/2 = 500 to 1000 m, with probing depths of 300-1000 m). Well 6 is just inside the boundary while Well 32 is between this boundary and an outer 20 ohm-m boundary (Figure 1).

The water, gas and isotope chemistry of

the wells discharges was discussed in detail by Mahon and Finlayson (1972) and by Giggenbach (1971). Table I shows the analysis of a Broadlands water taken from the centre of the geothermal system at a depth of about 800 m. It is a typical near-neutral pH sodium chloride water common to many water-dominated geothermal systems throughout the world. The chloride concentrations within the 10 ohm-m boundary at deeper levels in the system range from 800 to 1200 ppm.

WELL 6:

Well 6 in the south west of the Broadlands system (Figure 1) is drilled to 1082 m, has solid casing to 656 m and slotted casing from 645 m to the well bottom. Figure 2 shows the temperature profile in the well. The water level reaches the surface and in the closed well generates a pressure of 4.4 b absolute. The maximum temperature in the well standing closed is 186°C at 120 m, and with increasing depth the temperature passes through two inversions. Temperatures fall to 64°C at 240 m, increase to 180°C at 395 m, fall again to 57°C at 675 m and then increase to 130°C at the bottom of the well. The two major heating zones within the well (at 120 m and 395 m) both occur in the solid casing.

The temperature of the water discharged into the atmosphere from well 6 is 56°C, suggesting that the water enters the well at a depth of between 600 and 700 m. The water deposits aragonite in the surface discharge pipe and on the ground. A gas-rich vapour phase associated with the water contains mainly carbon dioxide with minor amounts of hydrogen sulphide. Table I shows the analysis of water discharged from the well on 4. 12. 67, taken from Mahon and Finlayson (1972). Also shown in Table 1 are the partial analysis of nine water samples collected at different depths in the well below the solid liner, using a downhole sampling bottle (Klyen, 1972). With this sampling technique the water does not evaporate during collection and transfer, and the concentrations of non-volatile constituents listed are those in the well at the different depths.

Fig. 1 The Broadlands Geothermal Field

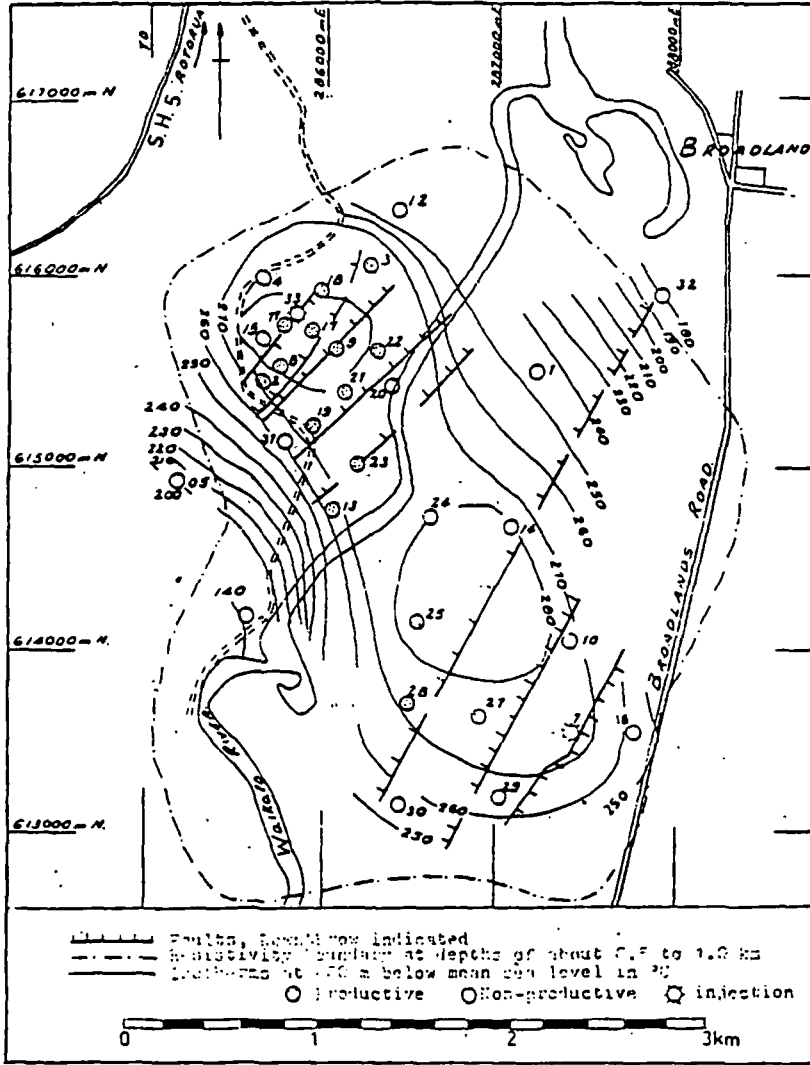
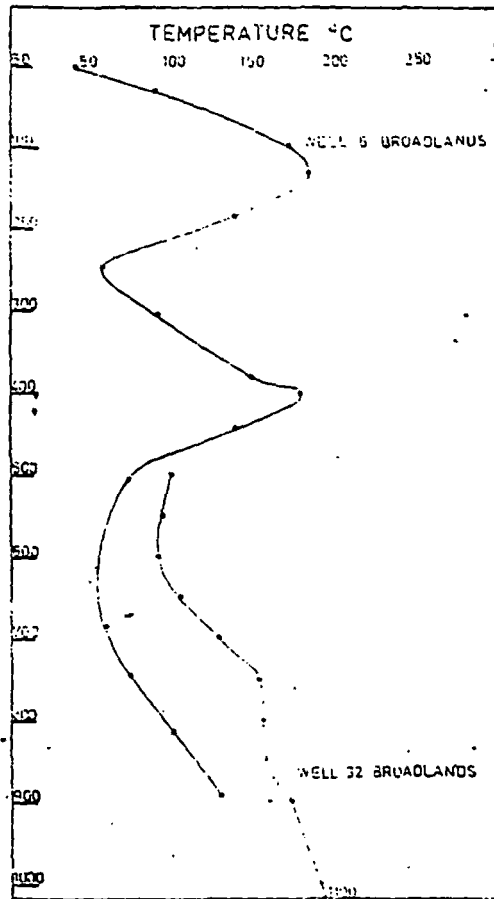


Table 1 Analysis of waters from Well 6, 19 and 32 Broadlands
Concentrations in ppm

| Well | Depth of sampling (20°C) | pH | Li | Na | K | Cs (ppb) | Ca | Mg | Cl | CO ₂ | T | SO ₄ | HCO ₃ |
|------|--------------------------|------|------|------|-----|----------|------|------|------|-----------------|-----|-----------------|------------------|
| 19 | 800 | 8.25 | 7.9 | 655 | 135 | 1115 | 1.7 | 0.05 | 1150 | 5 | 52 | 545 | 417 |
| 6 | surface | 7.4 | 1.2 | 425 | 59 | - | 180 | 90 | 28 | 15 | 1.2 | 180 | 2284 |
| 6 | 646 | 7.2 | 0.9 | 107 | 16 | 3 | 28 | 10 | 28 | 43 | - | 91 | 290 |
| 6 | 655 | 8.0 | 1.3 | 423 | 40 | - | 92 | 70 | 28 | 19 | - | 146 | - |
| 6 | 777 | 7.9 | 1.3 | 480 | 48 | 5 | 139 | 91 | 28 | 17.5 | 0.6 | 146 | 1790 |
| 6 | 768 | 8.2 | 1.3 | 495 | 49 | - | 159 | 91 | 28 | 16 | - | 133 | 2000 |
| 6 | 772 | 8.5 | 1.7 | 417 | 39 | - | 47 | 55 | 28 | 68 | - | 148 | - |
| 6 | 770 | 8.6 | 2.0 | 495 | 48 | - | 67 | 62 | 28 | 58 | 1.3 | 149 | - |
| 6 | 800 | 8.4 | 1.4 | 231 | 23 | - | 59 | 38 | 28 | 12 | - | 114 | 1500 |
| 6 | 831 | 7.8 | 2.2 | 432 | 42 | - | 86 | 65 | 28 | 8.5 | - | 170 | - |
| 6 | 861 | 7.8 | 2.1 | 477 | 46 | - | 55 | 67 | 28 | 10 | 0.1 | 132 | 1680 |
| 32 | surface | 8.0 | 0.18 | 140 | 24 | 4 | 6.6 | 1.7 | 40 | 8 | 0.7 | 380 | 390 |
| 32 | 505 | 8.7 | 0.6 | 131 | 17 | 12 | 6.7 | 1.7 | 35 | 8 | 0.9 | 360 | 367 |
| 32 | 605 | 7.5 | 0.7 | 198 | 15 | 22 | 13.3 | 3 | 40 | 11 | - | 315 | 542 |
| 32 | 700 | 7.9 | 1.2 | 790 | 35 | 125 | 9.6 | 1.2 | 212 | 56 | - | 326 | 1830 |
| 32 | 735 | 8.4 | 2.9 | 2670 | 87 | 340 | 6.4 | 1.0 | 793 | 175 | - | 375 | 6003 |
| 32 | 1000 | 7.8 | 4.3 | 1568 | 119 | 400 | 21.4 | 1.2 | 1053 | 490 | 32 | 242 | 2257 |

Fig. 2 Temperatures, wells 6 and 32 Broadlands



The chloride concentration in the hot water below the solid casing in well 6 remains constant with depth at 28 ppm. This content can be compared with that of approximately 1000 ppm present in deep waters in the more central and higher temperature parts of the system. The major water constituent is sodium bicarbonate, with smaller amounts of calcium and magnesium bicarbonate. Sulphate concentrations range from approximately 10 to 70 ppm and are considerably higher than the average value of about 5 ppm in the high temperature Broadlands waters. Silica concentrations of 90 to 170 ppm lie in the range expected from the solubility of amorphous silica at the measured downhole temperatures. Boron concentrations are very low (0.1 to 0.2 ppm) and together with the low chloride concentration show that there is no high temperature sodium chloride water in the immediate

vicinity of the well. The lithium concentrations are appreciable (1 to 2.2 ppm) but lithium is known to be readily leachable from the rhyolite rocks at Broadlands at relatively low temperatures.

A brief petrological description of the rocks penetrated by well 6 below 525 m was given by Browne (1967). The major rock type is rhyolite occurring as a tuff or breccia. Most of the cores from 625 to 1080 m were either unaltered or the hydrothermal alteration was of low rank. The major hydrothermal minerals present were calcite, albite, illite, pyrite, ptilolite and pyrrhotite.

WELL 32:

Well 32, located on the north eastern boundary of the system is drilled to 1269 m and solid cased to 465 m. Figure 2 shows the temperature profile in the well. The temperature at the bottom of the solid casing is around 100°C but it falls to 90°C at 600 m. Temperatures then increase with increasing depth, reaching a maximum of 205°C at the well bottom. On discharge, some 250 litres per minute of hot water at 90°C were emitted, apparently from a depth of around 600 m. The well stands closed with a wellhead pressure of 1.14 bar absolute.

Table 1 shows the analysis of water discharged into the atmosphere from well 32 and also the water present in the well at different depths. The compositions listed are those present in the waters at the various depths.

The water discharged from the well contains mainly sodium bicarbonate, with little chloride (≈ 40 ppm) and low sulphate (10 ppm). This water is present to a depth of at least 600 m in the vicinity of the well. Between 600 and 700 m there is a compositional change from a sodium bicarbonate/sulphate water into a sodium chloride/bicarbonate/sulphate water. At the deepest level in the well, 1000 m, the chloride concentration is 1050 ppm and similar to that found at equivalent levels in the centre of the Broadlands system. Both sulphate and bicarbonate concentrations are high at the 1000 m level, values of approximately 500

and 2250 ppm, respectively, being present. The waters are saturated with respect to anhydrite, CaSO_4 , for the physical and chemical conditions present.

The Cl/B atomic ratio in the deep water in this well is very similar to that found in higher temperature chloride waters in the northern parts of the system and illustrates the chemical homogeneity which exists in the chloride waters in this zone. Silica concentrations in water at shallow levels in the well are close to equilibrium with an amorphous silica phase in the rocks. At the highest temperature, at the base of the well (1000 m), the silica concentration is lower and in equilibrium with quartz in the rocks at the measured temperature. Lithium concentrations are highest in the chloride water at deeper levels.

A detailed petrological description of the rocks penetrated by well 32 is available from Elders (1976). The rocks at deeper levels are mainly rhyolitic and are overlain by a series of claystones, siltstones and mudstones (Huka Formation). A greywacke conglomerate is present below 1240 m. There is no high rank hydrothermal mineral alteration in the rocks penetrated but extensive silicification of the rocks has occurred between 750 and 870 m. These rocks appear to have been permeable originally but rendered impermeable by silicification. Hot water transmission appears to have occurred in the lower greywacke conglomerate. At deeper levels quartz is the predominant silica phase present in the rocks. The zone of major silicification coincides with the level where the transition occurs from a non-chloride to a chloride water. The silica deposits present appear to be amorphous and the zone also contains major deposits of calcite and pyrite.

A number of other Broadlands wells, such as 5, 12 and 16, also occur close to the perimeter of the system as defined by the resistivity boundaries. Although the hot waters associated with these wells are normal sodium chloride waters they differ from the water chemistry of other wells. The major difference is the presence of relatively

high bicarbonate and sulphate concentrations. The chemistry of well 16 is particularly interesting as the chloride concentration in the water at the bottom of the well has increased under static conditions. This indicates a seepage of higher chloride water from deeper levels into the well.

Kawah Kamojang

The geothermal development work in Indonesia was described by Radja (1975) and the preliminary geochemistry of the Kawah Kamojang geothermal system by Kartokusumo et. al. (1975). Five shallow wells were drilled by Dutch engineers at Kamojang during the period 1926-1928 and a further ten exploration and production wells have been drilled by Geothermal Energy New Zealand Ltd. over the last five years.

The surface thermal activity at Kamojang essentially consists of fumaroles, steam-heated groundwater and steaming ground. Although most of the steam-heated ground water in springs, lakes and seepages is acid a few large springs discharge a neutral-pH sodium/bicarbonate/sulphate water at boiling temperature. A typical analysis of one of these springs is shown in Table 2. Geochemical survey work over a wide area surrounding the prospect failed to locate any warm or hot chloride waters. The average chloride concentration in local cold surface waters is about 5 ppm.

Table 2 shows the analysis of downhole water samples collected from the exploration wells 6, 7, 8, 9 and 10. The wells are drilled to depths ranging from 600 to 750 m and encounter temperatures of 160 to 240°C. The maximum chloride concentration in the well waters is around 30 ppm (well 7) but the average concentration is considerably lower than this value (7 ppm). The major constituents in the waters are sodium sulphate and bicarbonate with sulphate frequently predominating. Calcium and magnesium concentrations in the lower temperature well waters (140-180°C), are appreciable but are considerably lower in the higher temperature waters (200-240°C). This is to be expected as calcium and magnesium sulphates and

Table 2 Analysis of waters from Kawah Kamojang, Indonesia
Concentrations in ppm in waters as particular levels

| Well or Spring | Depth of Sampling m | pH (20°C) | Li | Na | K | Ca | Mg | Fe | Cl | SO ₄ | SiO ₂ | HCO ₃ | B | NH ₃ |
|-----------------------|----------------------------------|--------------|------|------|------|------|------|------|------|-----------------|------------------|------------------|-----|-----------------|
| South Kamojang Spring | surface | 7.0 | <0.1 | 47 | 16 | 73 | 27 | 0.6 | 5 | 74 | 200 | 936 | 1.4 | 0.2 |
| 5 | 160 | 3.6 | - | 155 | 24 | <1.0 | <0.1 | - | <2 | 430 | 240 | 70 | - | - |
| 6 | 500 | 6.8 | 0.75 | 100 | 10 | <1.0 | <0.1 | - | <2 | 290 | 415 | 60 | - | - |
| 6 | 600 | 7.0 | - | 92 | 13 | <1.0 | <0.1 | - | <2 | 300 | 425 | - | - | - |
| 7 | 500 | 8.0 | 0.35 | 148 | 6.7 | 11.6 | 0.1 | 0.15 | 10 | 120 | 375 | 207 | 10 | 0.2 |
| 8 | 350 | 8.2 | - | 630 | 27 | 8.1 | 29 | 2.0 | 26 | 1175 | 75 | 455 | 4.2 | - |
| 8 | 550 | 8.6 | 2.2 | 606 | 30 | 16.1 | 14.5 | 6.0 | 30 | 1425 | 105 | - | 5.3 | - |
| 8 | 600 | 7.1 | 0.7 | 622 | 15 | 32.0 | 4.8 | 6.0 | 13 | 1400 | 195 | 342 | 4.7 | - |
| 9 | 320 | 7.1 | 1.1 | 217 | 45 | 24 | 35 | 0 | 6 | 42 | 190 | 606 | 1.6 | - |
| 9 | 550 | 6.4 | 0.25 | 347 | 8 | 1.3 | 4.8 | 1.5 | 5 | 109 | 390 | 590 | 7.1 | - |
| 9 | 700 | 8.0 | 0.2 | 218 | 39 | 1.8 | 0.2 | 0.6 | 6 | 101 | 385 | 630 | 7.0 | 0.3 |
| 10 | 400 | 7.2 | 0.3 | 89 | 17 | 143 | 3 | 3 | 12 | 432 | 150 | 155 | 0.4 | - |
| 10 | 550 | 8.0 | 1.3 | 81 | 16 | 99 | 6.5 | 4 | 12 | 332 | 190 | 140 | 0.4 | - |
| 10 | 730 | 6.7 | 0.3 | 79 | 16.5 | 67 | 8.1 | 0 | 14 | 260 | 225 | 109 | 0.2 | - |
| 11 | surface discharge interface zone | 7.3 | 0.3 | 44 | 6 | 0.8 | 0.05 | - | 85 | 15 | 300 | 24 | 5 | - |
| 11 | surface discharge | 6.8 | 1.2 | 154 | 42 | 13 | - | - | 428 | 53 | 2400 | 70 | 41 | - |
| 13 | surface discharge | 7.9 | 5 | 1150 | 139 | 25 | <1.0 | - | 1305 | 479 | >400 | 195 | 74 | - |

bicarbonates decrease in solubility with increasing temperature and at high temperatures magnesium is maintained at very low levels by equilibrium with minerals such as chlorite and montmorillonite. In the highest temperature waters sodium should predominate as the major cation in bicarbonate/sulphate waters.

The silica concentrations in the boiling neutral pH sodium bicarbonate sulphate springs are lower than expected for equilibration with amorphous silica. In the deeper waters silica appears to be in equilibrium with the quartz present in the local andesitic rocks, at the measured temperatures.

The compositional differences between the sodium/bicarbonate/sulphate waters at Broadlands and Kamojang basically arise from the temperature difference in the two areas. The rates of equilibrations of various reactions such as the feldspar/clay alteration process and the quartz/amorphous silica solution reactions depend on temperature as does the solubility of minerals such as CaCO₃·MgCO₃, CaSO₄ and CaF₂.

Two of the deeper production wells (11 and 13) at Kamojang, drilled to a maximum depth of 1500 m encountered neutral pH sodium chloride water at depths below 900 m. The interface zone between the upper

bicarbonate/sulphate water and the lower chloride water in each well, has temperatures between 200 and 220°C. Higher temperatures (up to 244 °C) occurred at shallower depths and again below the interface zone. Table 2 shows the analysis of waters discharged by wells 11 and 13 and derived from near the interface zones in both wells.

There is still some uncertainty as to the depth of the hot water surface at Kamojang. Hydrothermal mineral alteration of the mainly andesitic rocks penetrated by the wells suggests that it occurs at a depth of approximately 150-180 m, over a wide area of the system. Below this depth widespread deposits of calcite, anhydrite and more occasionally pyrrhotite occur in the andesitic rocks. Below about 600 to 700m amorphous silica is present as a secondary hydrothermal mineral and widespread secondary quartz occurs below approximately 800 m. The occurrence of a number of hydrothermal minerals such as kaolinite, which generally form under acid conditions at deeper levels (300-400 m), suggests that at some time during the formation of the system the deeper waters were acid. This was presumably a temporary phase as rock/water interaction would neutralise the acidity of solutions.

While wells 6 and 32 at Broadlands pene-

trated water-saturated rocks continuously from the surface down to the drilled depth of the wells, at Kamojang there is evidence suggesting the presence of a steam zone between approximately 700 and 1000 m. Temperatures and pressures in wells after initial discharge tend to support this hypothesis as does the discharge characteristic of some of the wells. Chemical evidence obtained from downhole samples collected before and after discharge of some wells indicates the continuous occurrence of sodium/bicarbonate/sulphate water throughout this steam zone. Mahon et al. (1979) discussed the significance of these physical results in terms of the non condensible gases present in the deeper waters.

Relationship between neutral -pH sodium/bicarbonate/sulphate waters and neutral -pH sodium chloride waters in a hydrothermal system.

As natural hydrothermal systems have been investigated in more detail, particularly the shallow and perimeter parts of the systems, the extent and significance of neutral -pH sodium/bicarbonate/sulphate waters have become more apparent. Although wells from Broadlands and Kamojang have been selected to illustrate the chemical nature of the bicarbonate/sulphate water most other geothermal areas in New Zealand and elsewhere are known to contain these waters. Thus, the northern part of Tauhara, N. Z. system contains this water at shallow levels, as does the Te Kopia system just south of Waiotapu, N.Z. At Orakeikorako, N.Z., the spring waters are a combination of neutral pH system/chloride and neutral pH bicarbonate/sulphate waters. Chloride concentrations of around 300 ppm are accompanied by sulphate and bicarbonate concentrations of about 100; and 150-200 ppm, respectively. The waters are very similar to those found at Broadlands and Kamojang in the interface depth zone.

There is little doubt that neutral -pH sodium/bicarbonate/sulphate waters represent the secondary part of geothermal systems. They are formed by steam and gases con-

densing in or passing through cold meteoric water. It is difficult, if not impossible, to determine whether the major heating component of these waters is steam condensation or long term transfer of heat by convection, and heat of solution, of the gases. The waters always occur above or at the perimeter of large reservoirs of neutral -pH sodium chloride water. The principal heat reservoir of a geothermal system is the sodium chloride water which can and may extend to depths of many kilometres.

The chemical compositions of the bicarbonate/sulphate waters are mainly controlled by the volume and composition of the gases passing through them. The gases contained in the deep neutral pH sodium chloride waters are primarily carbon dioxide, hydrogen sulphide, methane, ammonia, nitrogen, hydrogen and the inert gases. The acidic gases, carbon dioxide and hydrogen sulphide frequently make up over 90-95% by weight of these gases and, together with ammonia, are the most reactive gases present. Reactions between the gases and rock minerals, and with oxygenated meteoric waters finally produce waters rich in sulphate and bicarbonate. Both carbon dioxide and hydrogen sulphide are acidic gases and the initial tendency on reaction with oxygenated solutions is to produce acid solutions. The acidity of the reacting solutions depends on the gas to water ratio, the amount of available oxygen, the neutralizing effect of ammonia, and the rate of neutralization by rock/water interaction. In general the major neutralizing phases are primarily sodium, magnesium and calcium, aluminium and silicate minerals in the rocks (Ellis and Mahon, 1977). The presence of hydrothermal minerals, such as Kaolinite, alunite and anhydrite, which form under acid conditions, in zones containing these waters, indicate that at certain times acid conditions prevail in the system.

The interface or mixing zones between the deep chloride waters and the sodium/bicarbonate/sulphate waters are characterized by heavy rock silicification. The silicification at lower temperatures is amorphous silica,

grading into quartz at higher temperatures. Cold water heated in situ in a rock will dissolve silica from the rock. In laboratory rock/water interaction experiments, (Ellis and Mahon, 1964 and 1967), volcanic rocks were heated with distilled water at temperatures up to 600°C. During the initial reaction large quantities of silica were removed from the rocks and were deposited as an amorphous silica phase on the sides of the reaction vessels and on the rock chips. The initial silica concentrations present were found to be in equilibrium with an amorphous silica phase. With long reaction times at intermediate temperatures (180–220°C) or at high temperatures (>220°C) the silica concentrations in the solutions decreased until equilibrium with a quartz phase occurred. In all cases considerable amorphous silica was left deposited on the rock chips.

Rapid silicification of rocks is likely to occur in zones where hot chloride water comes into contact with cold rocks or cold meteoric water, and similarly in areas where cold meteoric water is heated with steam and gas. The dilution of a high temperature natural water with cold water results in a composite solution which is supersaturated with silica since temperature is a linear factor of dilution whereas silica solubility is roughly logarithmic, (Ellis and Mahon, 1977). Two major effects occur as a result of the rock silicification. The porosity and permeability of the rocks are considerably reduced which causes waters to be diverted or contained within the barrier. This process can effectively seal in a sodium chloride reservoir and prevent its expansion or its appearance at the surface.

The physical conditions in a large proportion of high temperature chloride water systems are such that the hydrostatic pressure at any particular point is close to the combined water vapour pressure and gas pressure. An increase in gas pressure at a particular level, or alternatively a decrease in hydrostatic pressure, can cause boiling to occur and a gas rich steam phase to be liberated from solution. Similarly dilution and cooling of the chloride water can result in de-

gassing of the water. Where a decrease in rock permeability occurs in a system or where rock permeability is influenced by mineral deposition the pressure gradient developed between the permeable and impermeable parts of the system can be considerable and can be increased with time. Water of temperature close to boiling point for the conditions moving through a pressure boundary boils and the throttling effect produced by high specific volume steam and gas reduces total fluid flow. A point can be reached where the permeability is low enough to allow only a steam and gas phase to move through the boundary. Examples of this situation are seen in geothermal wells which are drilled into relatively impermeable but hot rocks. The discharge from these wells are primarily steam and the discharge enthalpies are extremely high. A similar situation is developed in a fissure which is supplied by fluid from a porous medium.

In situations where gas is liberated from the sodium chloride waters, either as the result of boiling or cooling, (this can occur at a depth of 2 km at Broadlands and a somewhat shallower level at Kamojang), high gas pressures build up below or alongside the zone of silicification. Gas and steam, or sometimes gas alone, passes through the relatively impermeable media into the surrounding aquifers. The passage of water is controlled to a low level, or in many cases prevented, by the conditions described earlier. Considerable evidence that this mechanism occurs at Broadlands and Kamojang is available. A continuous gas flux occurs near the surface perimeters of the systems and in zones which have undergone extensive hydrothermal alteration and mineralization, and where rock permeability is extremely low, both hot and cold gas flows occur.

A number of factors determine whether the primary neutral pH hot sodium chloride water reaches the surface of a system. The four most apparent factors are: (a) the depth at which the reservoir forms relative to the original heat source (magma) and the corresponding hydrostatic pressure acting on this reservoir from the surrounding cold

meteoric water; (b) the topography above and around the system, i.e., the position of the water surface relative to ground surface; (c) the extent of silicification and the resulting decrease of rock permeability around the main reservoir; (d) movement and direction of movement of cold meteoric ground water into and around the system. The migration of gases from the chloride water reservoir to the ground surface is only partially controlled, or in some cases not controlled, by these factors.

Of prime importance is that neutral pH sodium bicarbonate sulphate waters occur as secondary features in high temperature chloride water geothermal systems. It is the sodium chloride water which is the prime exploitable energy resource, and the one which should be mined. The depth and position of the sodium chloride reservoir can often be assessed from the distribution of neutral pH sodium bicarbonate sulphate waters.

Distribution of Neutral Sodium, Bicarbonate, Sulphate Waters as a Result of Local Hydrological Conditions

Figures 3, 4 and 5 show three possible

hydrological mechanisms occurring in a hydrothermal system. Figure 3 shows a hydrothermal system which has formed within a recently active strato type volcano or in a volcanic complex made up of several of these volcanoes. This model represents, in most aspects, the Kawah Kamojang geothermal system. The high temperature chloride water reservoir develops at a relatively deep level in the system (A). If unrestricted by rock silicification or a general lack of permeability the upward and lateral migration of the chloride water is controlled by its density and the hydrostatic pressure generated on the reservoir by the surrounding cold meteoric water, (shown in Fig. 3 as pc.). At some stage in the development of the system major upward movement is controlled by silicification of the rocks. Downward percolating ground water in zone C (zones represented by C are frequently cold water recharge areas) meets gas and steam ascending from A. Depending on the relative volumes of cold water and gas and steam interacting Zone B may gradually be heated by steam condensation and heat transferred by the gas (enthalpy of gas plus heat generated by solution of some of the gas) and

Fig. 3 Geothermal system in a strato volcano, or complex. Model I.

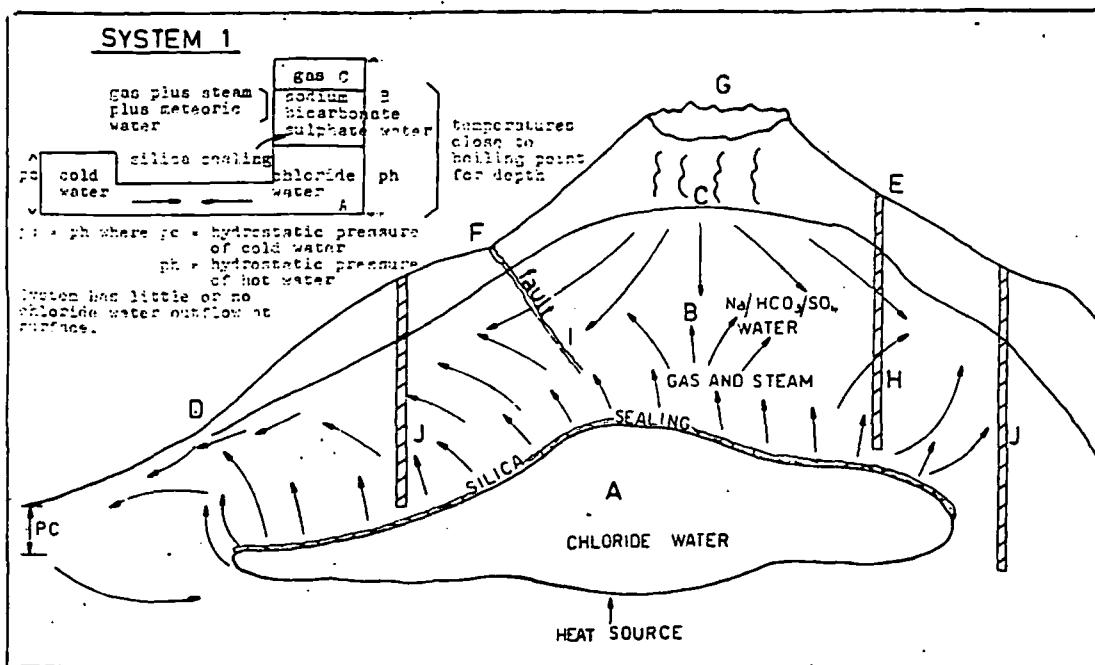


Fig. 4 Geothermal system, model I.

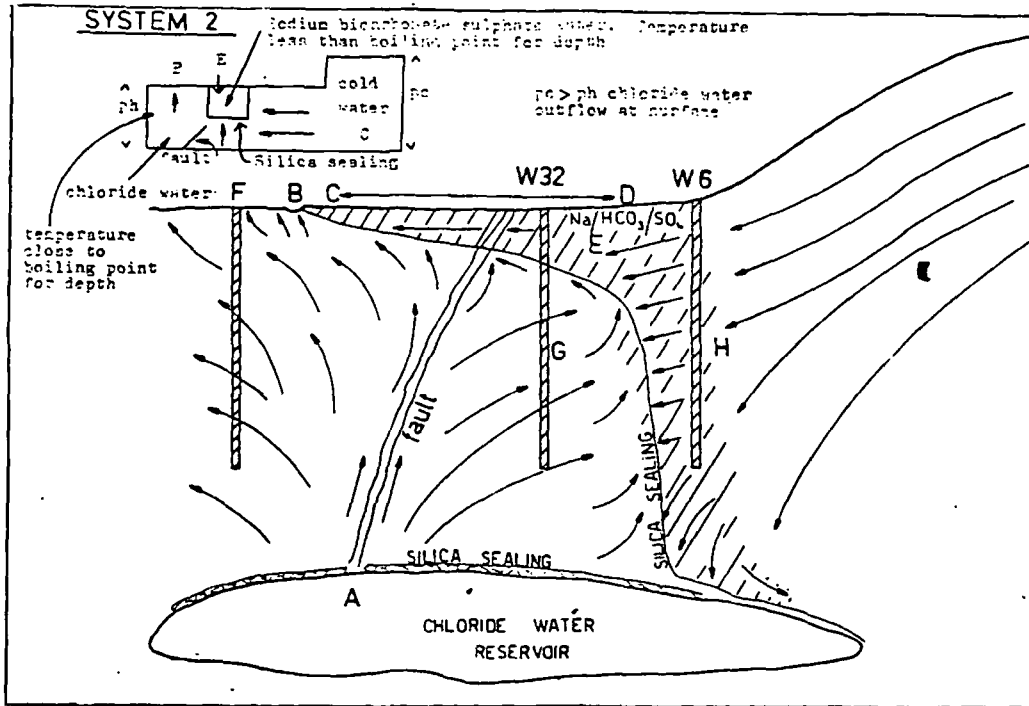
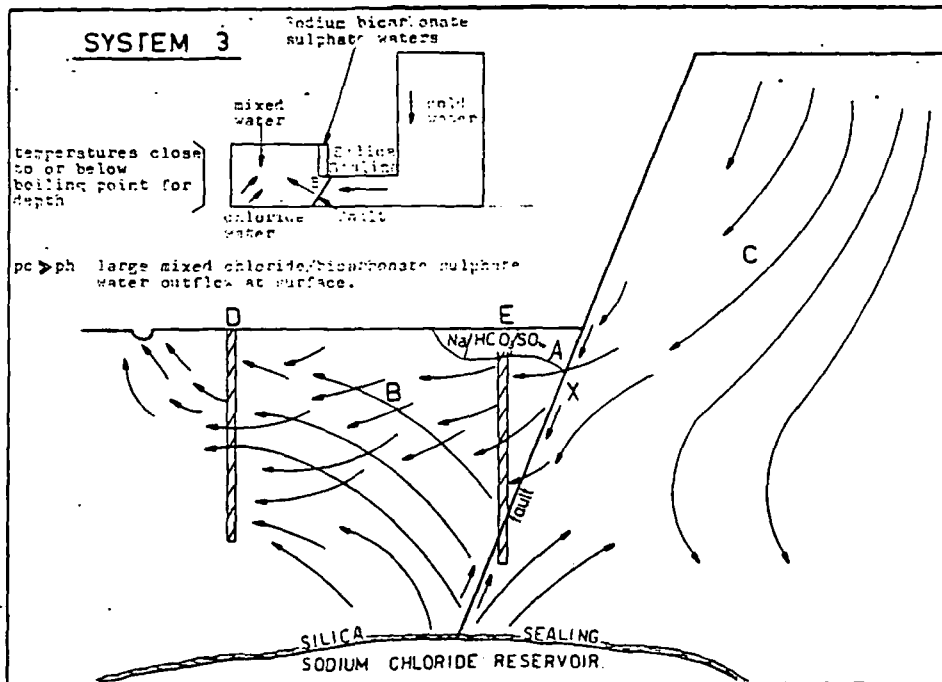


Fig. 5 Geothermal system, model II.



develops into a secondary hydrothermal system. Isotopic evidence from Kamojang suggests that a high proportion of the water in zone B is meteoric and not steam condensate. As long as heat is being transferred into the chloride water reservoir and temperature in the hot part of the system are close to boiling point steam and gas will form within the system. The continuous flow of carbon dioxide through most geothermal systems is evidence of the situation.

The water in zone B is changed into a neutral pH sodium bicarbonate sulphate water in the higher temperature areas at deeper levels and a calcium, magnesium, sodium bicarbonate sulphate water in lower temperature areas at shallow depths. Extensive deposition of calcite, anhydrite, silica (amorphous and quartz), pyrite, illite and montmorillonite occurs as the system develops and reduces the rock porosity and permeability.

Some chloride water may seep from the system at points such as D if the deep chloride water reservoir pressure is sufficient to allow outflow to the ground surface. This is more than likely inhibited by sealing of the system at these points where mixing of cold ground water flowing off the complex and the hot chloride water, may cause silica deposition. Alternatively the chloride water may be diverted into the main cold water table below ground level by the descending cold water. This situation is known to exist in Indonesia. The surface of the sodium, bicarbonate, sulphate water system may intersect the ground surface and hot springs discharging this water could occur at points such as D, E and F. There is considerable evidence from the wells drilled at Kamojang that a water level to this part of the system does exist. Information obtained from the hydrothermal alteration of rocks and down-hole water sampling indicate the surface occurs at a depth of between 150 and 170m. Fumarolic steam activity derived from B may occur at points such as E and F while cold gas emissions could occur at G. Activity is likely to occur along the surface traces of major structural features such as faults or

the sides of calderas which represent areas of deeper rock permeability (I).

The physical conditions in zone B depend to a major extent on the quantities of heat transferred from the chloride water reservoir through this zone and the volume of meteoric water descending down into and through the system. In this type of confined system it is very likely that water temperatures in zone B will be high even when heating occurs mainly through gas convection. As indicated by Mahon et al. (1979) the movement of hot gases through a hydrothermal system is a very effective heat transfer mechanism. Geothermal wells drilled into zone B are likely to produce mainly steam, (Mahon et al., 1979), except when the well penetrates lower temperature (<200°C) conditions. Although only a secondary part of the system, this zone is likely to be a reasonably good geothermal prospect.

In using geochemical data to assess the geothermal potential of a system such as that illustrated by Figure 3, the following points could well be kept in mind. Geothermometry and other geochemical assessment made on waters discharged from neutral pH sodium bicarbonate/sulphate springs at points such as D, E and F are related only to the secondary part of the system. Similar assessments made from gases discharged from fumaroles E or F could also relate mainly to the secondary system. Considerable care must also be taken when interpreting geochemical information from mixed waters which may occur at D. Many geochemists have suggested that spring waters which deposit travertine or aragonite and which contain high bicarbonate, sulphate, calcium and magnesium concentrations are derived from low temperature reservoirs. In the system under discussion this interpretation is incorrect. Many hot springs belonging to the D, E and F category occur in Indonesia and they very likely represent the discharges from the secondary parts of major geothermal systems.

Geothermal drilling into the upper part of the system, in zone B, could produce several results. Wells (H) may not penetrate deep

enough to intersect A, or they may be located alongside A, (J). In neither case will the primary energy source be directly tapped. Wells which do not intersect the sodium chloride system or zones of high rock permeability in B (faults) are likely to produce mainly steam (Mahon et. al., 1979). Although this type of production is useful it may not necessarily be good for long term exploitation of the system. It is therefore important to try and outline the position and depth of the primary heat source, the sodium chloride water, when exploring these systems.

Figures 4 and 5 show possible fluid flow patterns in geothermal systems in which chloride waters reach the surface in areas of low topography. Many systems in the Taupo Volcanic Zone, N.Z., are of this type. In Fig. 4, which relates to the Broadlands system, hot water from the chloride water reservoir flows up faults into near-surface aquifers. Cold ground waters flowing into the system from elevated catchment zones in the east and west move downwards into the system and towards the local cold water sink. At Broadlands the local cold water sink is represented by the Waikato River, which is shown in position B in Figure 4. As mixing of the ascending sodium chloride water with the downward moving cold ground water occurs silica is deposited in the zone of mixing. The resulting sealing of the rocks diverts the mixed flow away from the zones of cold water recharge. The thermoartesian pressure generated in the chloride water system supplies sufficient potential energy to drive some chloride water to the surface, (B).

Although silica deposition and rock sealing limits or prevents the chloride water reaching the surface along the line C D it does not necessarily prevent gas, (CO_2 , H_2S etc.) steam and heat escaping into this zone (cf previous comments on two phase flow through a relatively impermeable medium). A neutral pH sodium bicarbonate sulphate water is formed in zone E. The chloride water is closer to the surface and less confined than in case I and the amount of heat

escaping into zone E is, in most cases, probably less than in zone B of case I. The main consequence of the reduced heat flow is reflected in the lower temperatures present in the sodium bicarbonate sulphate water. Useful exploitation of the sodium bicarbonate sulphate waters is less likely than in case I.

Geothermal wells drilled into the system at F will intersect the chloride water close to the surface and will not encounter any other type of water to a considerable depth. Wells drilled at G will initially penetrate the sodium, bicarbonate, sulphate water before passing into the sodium chloride water (well 32 Broadlands), while wells drilled at H will penetrate only sodium, bicarbonate, sulphate water at intermediate depths (1500 m), (well 6 Broadlands). To obtain production from the main hot chloride water throughout the system it is obviously necessary to drill deeper at points D, G and H than at F. Translating this model to Broadlands it is necessary to drill deeper on the eastern side of the system, possibly also on the north and south, than in the zone of major chloride upflow in the west. It is interesting that temperatures at the bottom of wells 6 and 32 are increasing.

Figure 5 shows a geothermal system where ground water can penetrate down sections of the same fault system in which the chloride water ascends to the surface. The hydrostatic pressure generated by the ground water at X is controlled by the high relief catchment area on the upthrown side of the fault. This type of system is similar to those at Orakeikorako and Te Kopia in New Zealand.

The descending cold meteoric water diverts the ascending chloride water in the direction shown in Figure 5 and a variable mixed water occurs at position B. The pressure generated by the ground water in C is greater than that at E in System 2 and the possibility of greater mixing in zone B in this model is greater than in zone B in system 2. A neutral sodium bicarbonate, sulphate, water could form in zone A.

Wells drilled into the system at point D would penetrate a mixed water at temperatures determined by the amount of mixing,

and the original temperatures of the chloride water and ground water. The rocks in this area will have reduced permeability from the silicification resulting from mixing. The siting of shallow wells (<1500 m) to obtain production from the deeper chloride water system is far more critical and difficult in this case than in system 2. The wells should really be deep (>1500 m) making surface siting less critical.

The presence or absence of chloride and associated heat at the surface is obviously related to the depth at which the chloride reservoir forms, the thermoartesian pressure generated by the chloride water and the near-surface cold water hydrology. Scientific surveys employed for identifying and outlining deep systems are primarily concentrated around vigorous hot spring and fumarole manifestations. It is apparent that potential geothermal areas may frequently go unrecognized where no obvious signs are present at the ground surface.

The self sealing of systems by silicification and other mineral deposition is most likely to occur in zones which border the potentially best producing horizons. For example when hot chloride water ascends through fissures in relatively impermeable rocks and is discharged into a permeable horizon, silicification and sealing are most likely to occur at the contact between permeable and less permeable rocks. The permeable rocks offer a ready access for cold ground water and the contact represents a zone of mixing. This is well illustrated at Broadlands and Kawerau in zones where the basement greywacke has been penetrated by geothermal wells. Considerable silicification is apparent in the contact areas between the less permeable greywacke and the overlying permeable volcanic rocks. Here the silicification probably results from both dilution and boiling.

Silica sealing and the formation of neutral pH sodium bicarbonate sulphate waters are processes that occur most readily at shallow levels (0-1500 m). Drilling within this depth range has a greater probability of encountering non-productive zones than

deeper drilling into the chloride water. A balance is required between drilling deeper and obtaining production directly from the upflowing chloride water, (relatively undiluted), and finding the requisite rock permeability for economic production.

Very little detailed information is yet available about the compositions of liquids present in the so-called "Vapour Dominated Systems". It is likely that the waters present in the upper parts of the systems (0-2000 m) are neutral sodium, bicarbonate, sulphate waters similar to those found at Kawah Kamojang. In the Kamojang system the steam and gas-heated meteoric waters above the deep sodium chloride waters has proven to be a very valuable energy resource. The size of the overlying secondary system perhaps gives some commentary on the huge energy resources available in the deeper sodium chloride water system.

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要 旨

地熱系の中性の Na/HCO₃/SO₄ タイプ熱水

W.A.J. マーホン, L.E. クライエン, M. ロード

地熱系に見出される熱水の化学的タイプのなかで、多分もっとも理解しにくいのは、おもな陰イオンとして HCO₃⁻ や SO₄²⁻ を含み、Cl⁻ は少量 (<30ppm) でおもな陽イオンとして Na⁺ を含む中性に近い水である。過去においては、この水は Na-HCO₃ タイプとして引合に出されたが、現在このタイプの水の HCO₃⁻ や SO₄²⁻ の量は同じ位であることが多いとされている。ニュージーランドの Broadlands 地熱系やインドネシアの Kamojang 系の最近の研究では、特にその系の浅い所や周辺の研究で Na/HCO₃/SO₄ タイプの熱水に関する情報が多い。

特別の興味は、同じ系や違った系での Na/HCO₃/SO₄ 熱水の分布や在りかたである。たとえばインドネシアの多くの温泉はこの組成の水を湧出している。昔

は、多くの研究者達は残念ながら、このタイプの温泉水は比較的低い温度の貯留槽 (<150°C) から来たものであるとってきたが、この説明はしばしば誤っている。最近の研究では、このタイプの水は正常な高温地熱系の 2 次蒸気で加熱された部分を形作っている高温貯留槽から作られることを示している。

地熱系で、これらの熱水を作る水理学的条件が研究され、水質と蒸気卓越系間の関係が議論される。地熱系のいわゆる蒸気卓越部に生ずるおもな熱水タイプはこの水であると思われる。その熱水は単純に蒸気凝縮水とはいえず、むしろ本質的に蒸気加熱されてきた地下水から成っている。水の組成は地下水や熱水だまりにこの水を閉じこめている岩石と CO₂ や H₂S の相互反応から生じたものである。



22-141 50 SHEETS
 22-142 100 SHEETS
 22-144 200 SHEETS

* Forward

| Temp. °C | Well M-26 | Well M-26 | Well M-26 | Well M-26 |
|--------------------------------|-----------|-----------|-----------|-----------|
| 100 | 100 | 100 | 100 | 100 |
| 8.2 | 8.2 | 8.2 | 8.2 | 8.2 |
| PA | PA | PA | PA | PA |
| SiO ₂ | 1156 | 705 | 579 | 490 |
| Ca | 921 | 572 | 1.5 | 308 |
| Mg | 1 | 0.6 | 0.07 | + |
| Al ₂ O ₃ | 10467 | 6382 | 716 | 4530 |
| K | 2549 | 1571 | 143 | 736 |
| HCO ₃ | 46 | 28 | 87 | 21 |
| SO ₄ | < 6 | < 3.5 | 5 | 21 |
| Cl | 19378 | 11918 | 1188 | 8172 |
| F | - | - | 5.0 | - |
| B | 22 | 13.4 | 32.9 | 120 |

* Camp Pardo
 * Broadlands
 * Alwood

Well M-26
 at depth
 100
 Well M-26
 at depth
 292
 Well M-26
 at depth
 260
 Well M-26
 at depth
 232

