GEOTHERMAL WATERS: A SOURCE OF ENERGY AND METALS

Rainwater that percolates down major faults and fractures, and is retained in suitably porous and permeable rocks, can be heated by molten rocks at great depths in the crust. Rather dilute brines are formed as a result of fluids and gases from the molten rocks being mixed with the rainwater, and also because of reactions that occur between the water and the rocks at these high temperatures (~250^{o}C) and pressures (~12 bar).

The energy in this hot water can be extracted for industrial processes and electricity generation, but the once-dissolved gases and heavy metals in the water need to be appropriately disposed of to minimise adverse environmental effects of the exploitation of geothermal fields. Extraction usually proceeds at a faster rate than natural replenishment, thus geothermal resources cannot be sustainably managed.

Geothermal waters are the present-day analogues of epithermal ore deposits (e.g., Coromandel Peninsula), mined particularly for gold and silver.

INTRODUCTION

Geothermal waters are associated with active (or recently active) areas of volcanic activity (**Figure 1**). With the exception of Ngawha Springs the most significant fields are in the Taupo Volcanic Zone, associated with the magmatism consequent on the subduction of the Pacific plate beneath New Zealand. Small hot water fields may also be associated with tectonism, rather than magmatism (e.g., those on North Island's east coast and the foothills of the Southern Alps). Last century, these warm waters were believed to be able to cure numerous ailments, and Rotorua and Te Aroha seemed destined to become spa towns, modelled on those in Europe. Although the curative properties of the waters are no longer in medical favour, interest in geothermal waters as a tourist resource and as a source of energy and minerals continues. Not only this, but gold mines in New Zealand, particularly Coromandel, are a reminder that similar processes and activity to those in present-day geothermal fields operated in the geologic past.

Origins

Although a small amount of geothermal water may be derived from gases that were originally dissolved in magmas (molten rocks that are the source of volcanic eruptions and intrusive rocks), most is recycled rainwater. The water descends through faults to considerable depths, and the water is stored in suitably porous and permeable rocks called aquifers. For most of the New Zealand geothermal waters, these aquifiers are in older volcanic rocks (typically the silica-rich ignimbrites and rhyolites). These rocks are overlain by less porous mudstones and other sediments to inhibit the 'escape' of the water. This water is heated by the magma and ultimately attains high temperatures (>250^{o}C) and pressures. Some of this hot water reaches the surface naturally to form hot pools and springs, but most remains in the aquifer, to be exploited by drilling, often to depths of 1-2 km. **Figure 2** gives a schematic cross section of

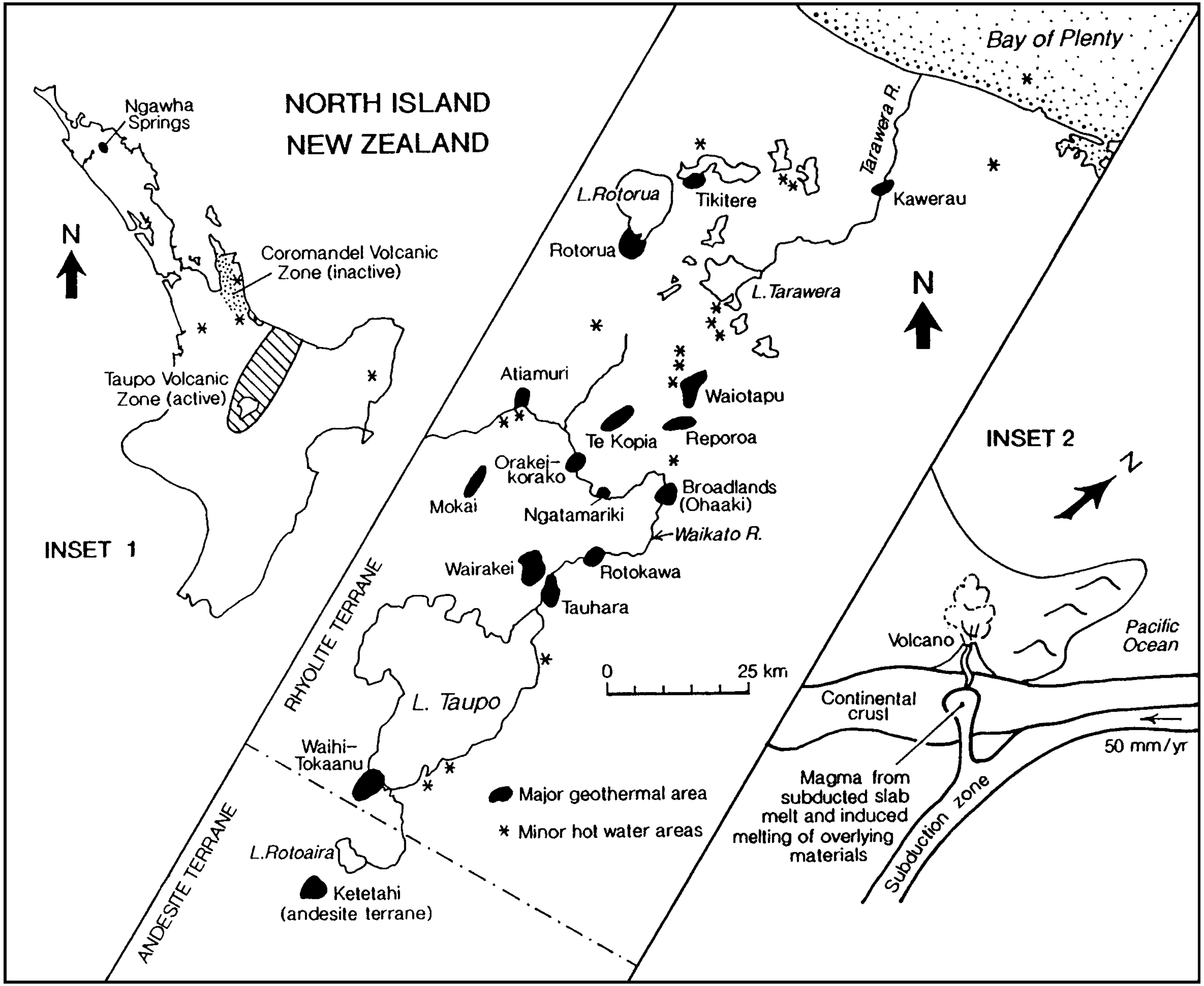

Figure 1 - Location of geothermal fields in New Zealand

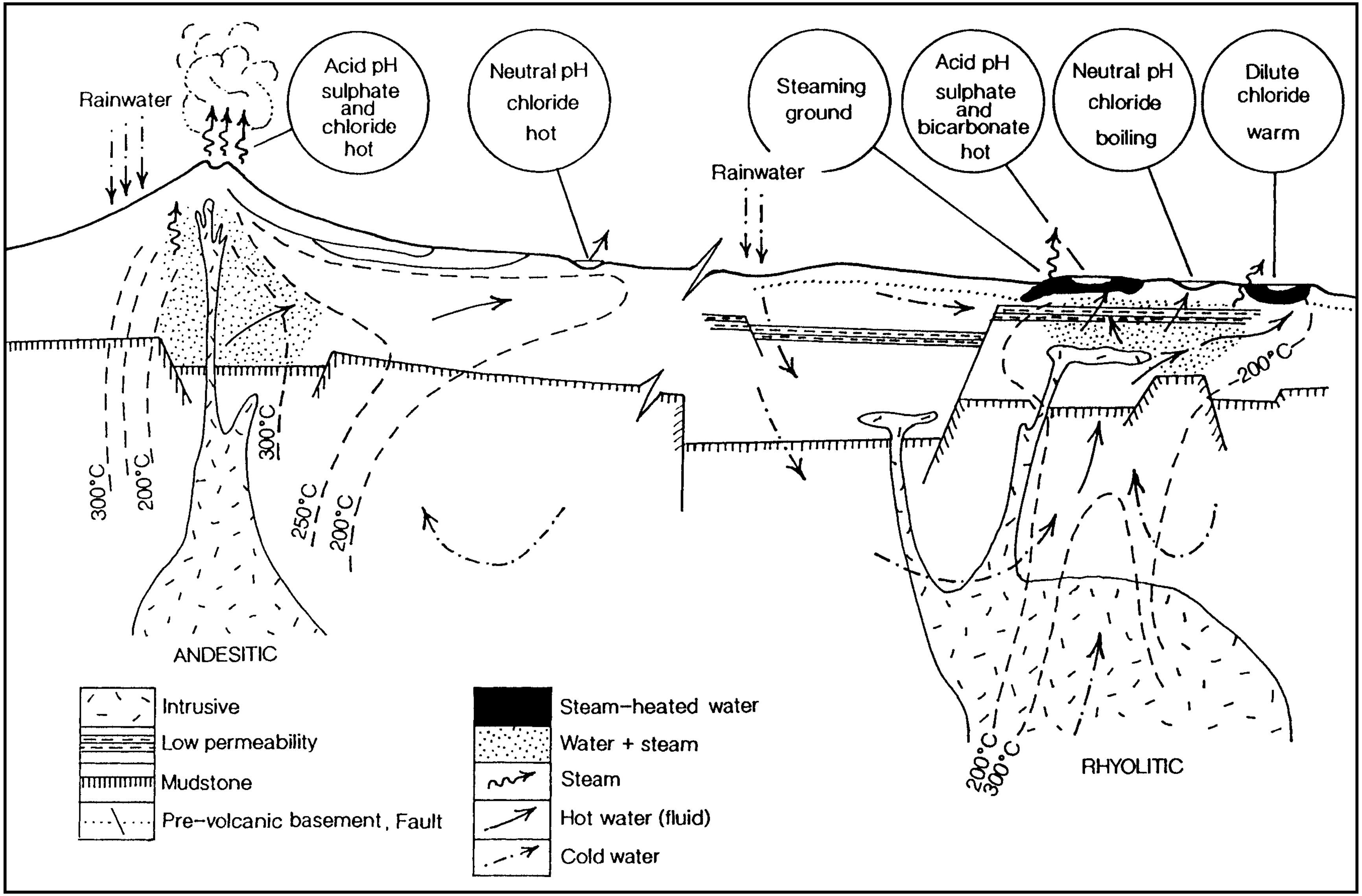

Figure 2

[Based on Henly, R.W.; Hedenquist, J.W., 1986. Introduction to geochemistry of active and fossil geothermal systems. Monograph Series on Mineral Deposits, 26: 1-22] the geothermal systems associated with andesitic terranes (left), which yield crater lakes (like Ruapehu) and hot springs on the volcano flanks (e.g., Ketetahi on Tongariro); and rhyolitic terranes (right), which yield high chloride waters as boiling springs and geysers (e.g., Waiotapu and formerly Wairakei) and more oxidised (e.g., Lake Rotokawa) and diluted springs (e.g, Lake Rotoma) as well.

THE CHEMISTRY OF GEOTHERMAL WATERS

A variety of chemical reactions occur within geothermal waters. These are mostly associated with interactions between the water and the rock of the chambers in which it is located. Within the waters many other reactions occur, and these typically involve sulfur and / or metal cations.

Rock-water interactions

Rocks generally dissolve only slowly in water, but like most reactions their dissolution occurs more readily at higher temperatures. Prolonged water-rock interaction liberates ionic species and produces a saturated silica solution (**Table 1**):

$$2H^+(aq) + \underset{\substack{\text{feldspar} \\ \text{"rock"}}}{2KAlSi_3O_8} + 9H_2O \rightarrow 2K^+(aq) + \underset{\substack{\text{kaolinite} \\ \text{"clay"}}}{Al_2Si_2O_5(OH)_4} + \underset{\substack{\text{dissolved} \\ \text{silica}}}{4H_4SiO_4(aq)}$$

Similar reactions provide $Na^+(aq)$ and $Ca^{2+}(aq)$ to the geothermal water.

Table 1 - Typical composition of geothermal waters[1]

Species	**Wairakei[2]** wells ~ 1.5km	**Rotorua[3]** springs	**Waitoa[4]** springs	**for comparison**	
				seawater[5]	**riverwater**
Cl^-	2156	560	57	19350	5.7
Na^+	1200	485	220	10760	4.8
SiO_2	660	490	175	0.005-0.01	13
K^+	200	58.5	43	399	2
HBO_2^-	115	21.6	1.2	0.004	-
HCO_3^-	32	167	3177	142	23
SO_4^{2-}	25	88	<1	2710	6.7
Ca^{2+}	17.5	1.2	37	411	15
Li^+	13.2	4.7	0.6	0.18	-
F^-	8.1	6.4	0.3	0.0013	-
NH_3	0.15	0.2	-	-	-

[1] figures given in ppm, where ppm = mg kg^{-1}; [2] "neutral chloride" waters; [3] "acid sulphate" waters; [4] "alkali carbonate" waters; [5] seawater has a pH range of 8.1-8.3 and riverwater has a pH range of 5-6.5.

The water remains in the aquifer for a sufficiently long time (hundreds to thousands of years) and the reactions are sufficiently slow for them to be used to calculate the temperature of the water. In effect, the ratios of the concentrations of the liberated cations (Ca^{2+}, Na^+, K^+) are temperature dependent.

The solubility of silica is also temperature dependent, but this equilibrium is attained rather more rapidly than the dissolution of other silicate minerals.

$$\underset{\text{dissolved silica}}{H_4SiO_4(aq)} \rightarrow 2H_2O + \underset{\substack{\text{quartz}\\ \text{siliceous sinter}}}{2SiO_2}$$

This reaction can be used as a geothermometer too. Any difference in temperatures obtained from the two geothermometers is related to the sampling of the water relative to the deep aquifer: waters that have moved away from the aquifer are likely to have lower temperatures derived from silica concentrations than temperatures derived from concentrations of Na, K and Ca.

As the water rises to the surface it cools, and silica and other minerals are precipitated. This may help "cap" the aquifer, and prolong the geothermal system's existence. Water that does reach the surface through faults and fractures will cool further and produce the sinter mounds and terraces that are typical around geysers and hot springs.

Reactions involving sulfur

Geothermal waters generally contain sulfur, initially in the form of hydrogen sulfide. This, along with other dissolved gases like HCl, is probably derived from the magma. As the water rises to the surface, the sulfide may be oxidised, especially if the path to the surface is tortuous or the rise of water is slow - through rock fractures rather than faults. The water becomes more acidic and sulfur, sulfur dioxide, or sulfate may be produced:

$$2H_2S + O_2 \rightarrow 2S + 2H_2O$$
$$2H_2S + 3O_2 \rightarrow 2SO_2 + 2H_2O$$
$$H_2S + 2O_2 \rightarrow SO_4^{2-} + 2H^+$$

Sulfur or sulfur dioxide are produced under comparatively mild oxidising conditions; Rotorua and Lake Rotokawa are examples of such geothermal systems. Where oxidation is more pervasive - and waters are of the "acid sulfate" type - the minerals in rocks may be transformed to weaker clay minerals. Also, iron and manganese ions may be liberated from silicate minerals and ultimately precipitate as their highly coloured oxides. The example below shows the oxidative liberation of iron from a silicate mineral under acid conditions. Iron (II) is oxidised to iron (III).

$$\underbrace{1\tfrac{1}{2}O_2(aq) + 7H_2O + 2H^+}_{\text{geothermal water}} + \underset{\text{Fe-bearing silicate}}{2KFe_3AlSi_3O_{10}(OH)_2} \rightarrow$$

$$\underset{\text{clay (kaolinite)}}{Al_2Si_2O_5(OH)_4} + \underset{\substack{\text{haematite}\\ \text{(ferric oxide)}}}{3Fe_2O_3} + \underbrace{2K^+ + 4H_4SiO_4}_{\substack{\text{geothermal}\\ \text{water}}}$$

Reactions involving metal cations

As well as hydrogen sulfide the gases dissolved in geothermal water that originate in the magma include hydrogen chloride. Thus, chloride ion in geothermal waters can be at high concentrations. Both hydgrogen sulfide ions (HS^-) and chloride ions (Cl^-) can form complexes with metal cations, e.g.,

$$M^{2+}(aq) + nX^-(aq) \rightarrow M(X)_n^{2-n}(aq)$$

where X is Cl^- or HS^- and M is any transition metal cation (e.g., Cu, Zn, Fe(II) ....) or other less common metal cations like those of gold, silver, antimony, arsenic, mercury and lead. Some of these cations may have been expelled from the magmas as gaseous sulfides and halides; others may have entered the geothermal water by their reactions with aquifer rocks.

These complexes are stable at high temperatures and high concentrations of X. When the temperature falls and/or the fluid boils, the complexes may precipitate metal sulfides, e.g.,

$$PbCl_3^-(aq) + H_2S(aq) \rightarrow PbS(s) + 2H^+(aq) + 3Cl^-(aq)$$

$$Pb(HS)_3^-(aq) + H^+(aq) \rightarrow PbS(s) + H_2S(g)$$

These solids may be precipitated along with silica in sinters around hot springs and may also be deposited in fractures where the fluid boil as it rises to the surface. Gold and silver can be precipitated also from complex ions.

THE USES OF GEOTHERMAL WATERS

Geothermal waters are primarily used in the production of energy and minerals.

Energy

The geothermal fluid that reaches the surface after drilling in New Zealand geothermal fields is a mixture of water and steam at high pressure. By reducing the pressure, the water "flashes" to steam. The steam is led to the turbines that generate electricity (**Figure 3**). The maximum installed capacity at the Wairakei geothermal power station, commissioned during the 1950s, was 192 MW, representing about 12% of the New Zealand's electricity supply in 1965. As fluid has continued to be withdrawn for electricity generation, the pressure in the field has declined. A consequence of this is the reduction of the generating capacity to 157 MW (~4% of New Zealand's increased electricity supply as at 1990). However, there has been a programme of further drilling in the area and improved efficiency in extracting steam from the hot water to compensate somewhat for the declining pressure.

In 1988 a second geothermal power station (Ohaaki) was commissioned, generating electricity from fluid extracted from the Broadlands field. The principle of flashing water to steam is essentially the same as at Wairakei, but the new station differs in two respects:

- the waste water from the extraction process is re-injected back into the ground rather than being added to the Waikato River;
- the cooling of the fluid after electricity generation is achieved by a natural draught
- cooling tower - rather than taking river water from the Waikato River and returning it there (as at Wairakei).

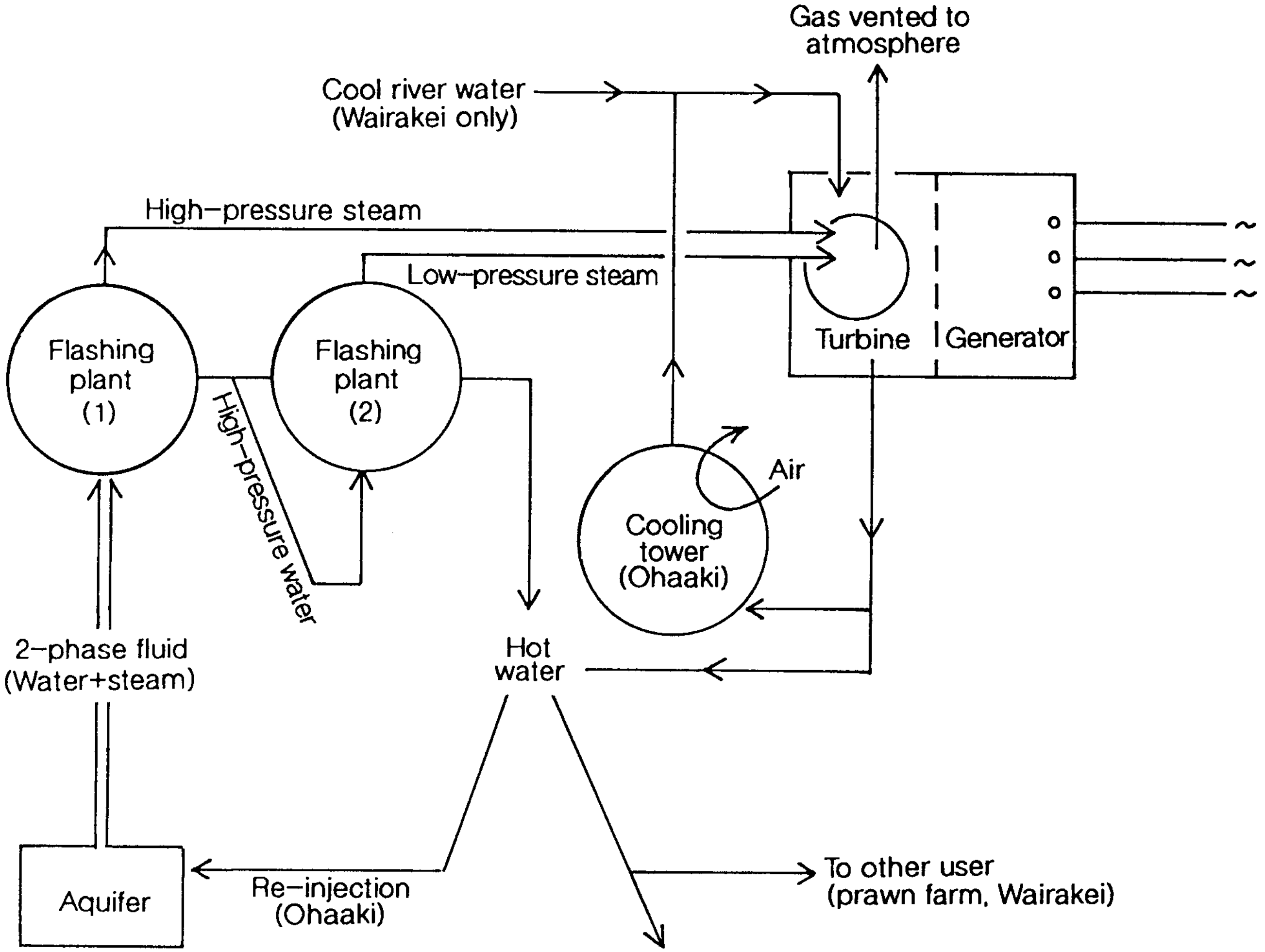

Figure 3 - Schematic diagram of the use of geothermal fluid for electricity generation as at Wairakei and Ohaaki (Broadlands)
(Note that there may be multi-stage "flashing points" which increase the amount of steam extracted from the water-steam fluid but at a lower pressure. Note also that the cooling and 'waste' water disposal technologies differ for the two installations.) [Adapted from: Water Right Applications and Impact assesment, Wairakei Geothermal Power Station. Electrocorp Production, 1990]

Geothermal fluid is also used in the paper mills at Kawerau, both for process heating within the plant and for electricity generation. Heat extracted from geothermal fluid by heat exchangers is used by the prawn farm at Wairakei and on a rather larger scale in Rotorua, principally for domestic use.

Minerals

The recognition in 1986 that significant quantities of gold and silver were deposited from depressurising geothermal waters in wells highlighted the association between geothermal systems as in the Taupo Volcanic Zone and the epithermal mineral deposits of the Coromandel. These mineral deposits - gold, silver and lesser amounts of base metal sulfides - are now thought to be located at the boiling zones of formerly active geothermal systems (**Figure 2**).

ENVIRONMENTAL IMPLICATIONS

As already described, the extraction of geothermal fluid causes a reduction in pressure: natural surface features like geysers and hot springs are adversely affected. This was an early consequence of exploitation at Wairakei, and more recently became evident at Rotorua. Complete cessation of withdrawal of fluid from the vicinity of Whakarewarewa's world famous geysers and improved efficiency of fluid used elsewhere in Rotorua seems to have resulted in an improvement in Pohutu and other geysers, presumably because the pressure and fluid supply have been at least partially restored. The 'recharge' of geothermal aquifers is a slow process, taking thousands of years. Thus, although geothermal resources are, in principle, renewable, the extraction of the large amounts of fluid for industrial processes or electricity generation occurs at a faster rate than natural replenishment.

Reduction of pressure may also cause boiling and the formation of steam accumulations beneath the ground. Steam heating of local groundwaters is possible (the evidence is hot waters in which there are low concentrations of Na^+, Cl^-, SiO^2, etc.), as are hydrothermal eruptions.

Also, geothermal waters contain significant amounts of toxic metal compounds, including those of arsenic and mercury. Natural discharges of these elements from springs along the Waikato River are enhanced by the wastewater from the Wairakei geothermal field (**Figure 4**). In order to prevent further addition of these substances, the wastewater from the Broadlands field was required to be "reinjected". This involves pumping the wastewater from the wells down wells drilled at the margin of the geothermal field, at a temperature of about 150^{o}C so that the pipes are not clogged up with silica and so that the temperature of the fluid being extracted is not affected. Reinjection may also serve to help sustain the field pressure.

Sulfide minerals deposited around hot springs can be oxidised to liberate metal cations into the environment. Rather more significant is the oxidation of comparable deposits in the former boiling zones of old geothermal systems, when they are exposed to the atmosphere by mining. This process results in acidic metal-enriched waters which, if not contained, can

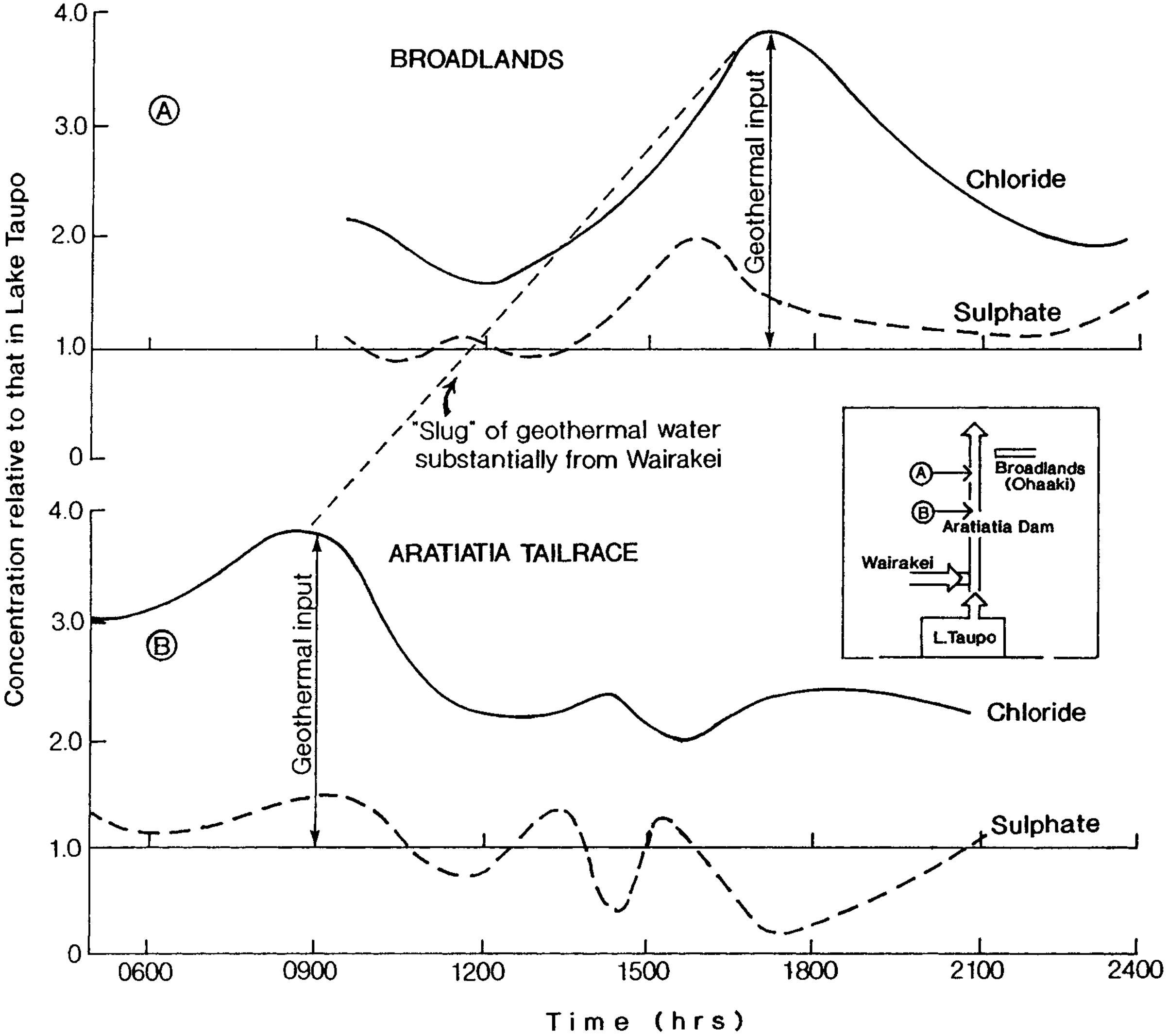

Figure 4 - Concentration variation of selected species in the Waikato River

(The time variation is caused by the build-up of chemical effluent from the Wairakei power station between the daily spillover at the Aratiatia Rapids dam. Although still within acceptable limits for drinking water, the natural backround levels enhanced by the Wairakeiinput wereused to require the newer Ohaaki station on the Broadlands field to reinject its effluent into theground rather than discharge it into the river.)

[Based on Coulter, G.W., 1977. The ecological impact on the Waikato River of untreated effluent from the proposed Broadlands Geothermal Power Station. N.Z. Energy Research and Development Committee, 26: table 3.]

cause serious pollution. Very much simplified, an example of such reactions is:

$$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$$

followed by the hydrolysis of the metal cation:

$$Zn^{2+} + H_2O \rightarrow Zn(OH)^+ + H^+$$

For iron, for which the most well known sulfide is pyrite, the reaction will yield ferric oxide (or a hydrated oxide).

$$2FeS_2 + 7\tfrac{1}{2}O_2 + 4H_2O \rightarrow Fe_2O_3 + 4SO_4^{2-} + 8H^+$$

This hydrated ferric oxide can adsorb other metal cations liberated by the oxidation of sulfide minerals. This scavenging transfers the metal cations from polluted water to polluted sediment!

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