



GEOCHEMICAL SIMULATION OF LAKE WATER INJECTION INTO THE GEOTHERMAL RESERVOIR IN TIANJIN, CHINA

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ABSTRACT

With the development of geothermal resources in Tianjin, geothermal energy plays an important role in socio-economic development. Large scale production has already resulted in a rapid drawdown of the water level. Increasing the quantity of injection water may be a good method to supplement the natural recharge to geothermal systems. This report focuses on the geochemical feasibility of lake water injection into the bedrock geothermal reservoir in Tianjin Dongli Lake area. PHREEQC is used to simulate the geochemical effects of lake water injection. The results show that if the lake water is injected on its own into the reservoir in winter, it is more likely to cause significant precipitation than injection of geothermal water only. Precipitation dominates if the mixture contains 50% lake water. The amount of dolomite precipitated exceeds that of dissolved calcite. The dolomite precipitated is 0.55 g/kg, six times more than from spent geothermal water. Precipitation dominates if lake water only is used as has been the custom in summer. Then the dolomite precipitated is 0.97 g/kg, eleven times more than from spent geothermal water. In order to reduce scaling in the reservoir during lake water injection, the injection water is acidified with hydrochloric acid. Adding 0.529 ml of 30% industrial hydrochloric acid to 1 kg of a mixture containing 50% lake water can remove the precipitation effectively. When the pH of the mixture is 6.054, it is calculated that no deposition takes place. If a higher proportion of lake water is injected into the reservoir, more acid is needed.

1. INTRODUCTION

In recent years injection has become an integral part of sustainable and environmentally friendly geothermal utilisation projects. Injection provides an additional recharge to geothermal reservoirs and, as such, counteracts pressure drawdown due to production, thus causing more of the thermal energy from reservoir rocks to be extracted than through conventional utilisation. In some cases, injection will increase the production capacity of geothermal reservoirs.

To meet the rapid increase in demand for geothermal resources in Tianjin, it is necessary to increase research on injection into the reservoir, especially to its basement. In Tianjin, all geothermal production from the basement of the reservoir has been balanced by injection, employing a doublet

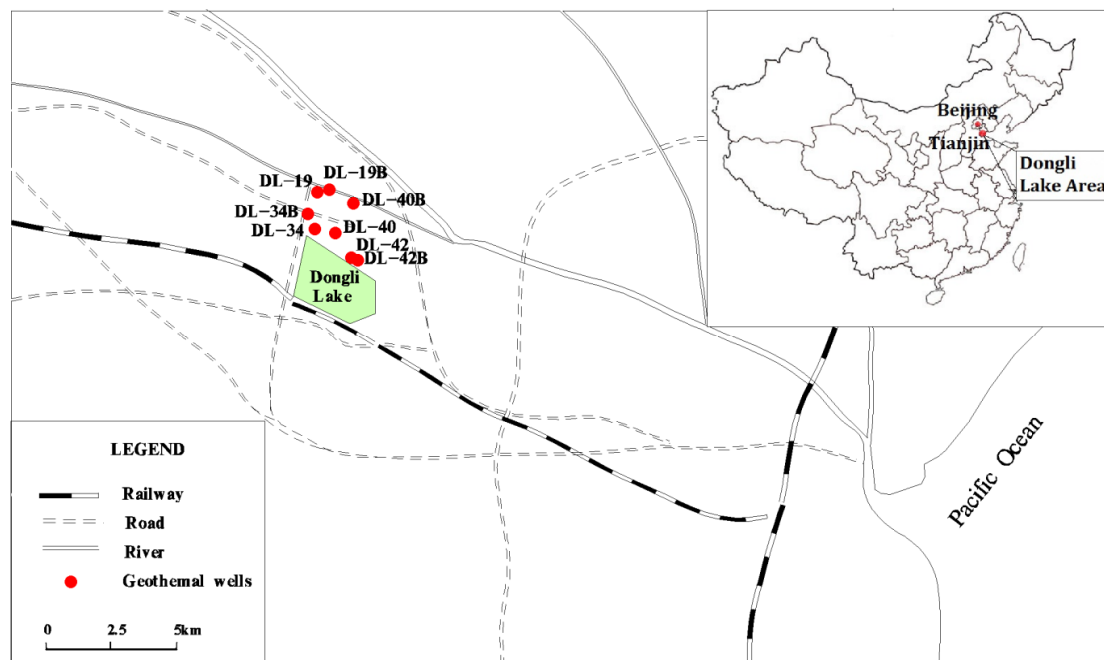


FIGURE 1: Location of the Dongli Lake area

well system since 1996. At present there are about 60 doublet production and injection systems in Tianjin. The annual injection rate reaches 6,930,000 m³ but, even so, the rate of the injection is small compared to the rate of production. Many single production wells drilled before 1996 are still in use. Meanwhile, most single well production is located in the urban area and, in many cases there is not enough space available to drill injection wells. The large scale production has already resulted in a rapid drawdown of the water level. It is necessary to find a new way to increase the quantity of injection water in the urban area. Additional recharge to geothermal systems in the suburbs of Tianjin is a good method of increasing the quantity of injection water into the urban area system. An attractive way to achieve that is to use lake water from the Dongli Lake area.

The Dongli Lake area is located between the Tianjin Binhai New District and the urban area of Tianjin city, about 24 km from the urban area. The area of this district is 85.51 km² (Figure 1) and includes a lake named Dongli Lake. With its surface area of 8 km², a shoreline perimeter of 12 km and total water capacity of 2200 × 10⁴ m³, it is known as the "fresh small sea." This lake is a good water resource. The water comes from the Xindi River. Geothermal resources there are abundant, with geothermal water temperatures reaching 102°C.

Although additional injection is a good method to increase the pressure of reservoirs, some operational risks and problems are associated with it. These include possible cooling of production wells, often because of short-circuiting and cold-front breakthrough, and scaling in surface equipment and injection wells because of the precipitation of chemicals from the water (Axelsson, 2008).

Various chemical processes take place during injection, including the movement of chemical fronts in the reservoir and chemical deposition in the surface pipeline, the injection well, or in the reservoir itself. Chemical deposition from the injected fluid may block the well and damage formation permeability close to the injection well (Arnórsson, 1995). Therefore, it is necessary to predict specific mineral deposition from water of a known composition to estimate its suitability for injection.

This report starts by briefly reviewing the geological characteristics of the geothermal system to provide the reader with some idea of the nature of the area. Then some results from the current study obtained from the geochemistry of the geothermal fluids are presented. Subsequently, the characteristics of the lake water and injection water are analysed. Finally, different approaches to simulate the geochemical effects of lake water injection are applied.

2. GEOLOGICAL AND HYDROLOGICAL SETTING

2.1 Structural features

The Dongli geothermal area is located in the area common to the Panzhuang uplift and the Beitang depression (Figure 2). The Cangdong fracture, the Tianjin fracture and the Haihe fracture faults are all situated in this region. The Cangdong fracture is a major fracture which can conduct heat from the bottom of the reservoir to the shallow reservoir by heat convection. The effect of heat convection becomes weaker with distance from the fracture. The geothermal water recharge in natural conditions is from northwest to southeast. The overall storage and transport of water are obviously influenced and controlled by the Cangdong fault zone, indicating that the geological structure provides favourable conditions for the Dongli Lake area geothermal resources. Due to the features of the Cangdong fracture, additional recharge to the geothermal systems in the Dongli Lake area is a good method of increasing the quantity of injection water for the urban area.

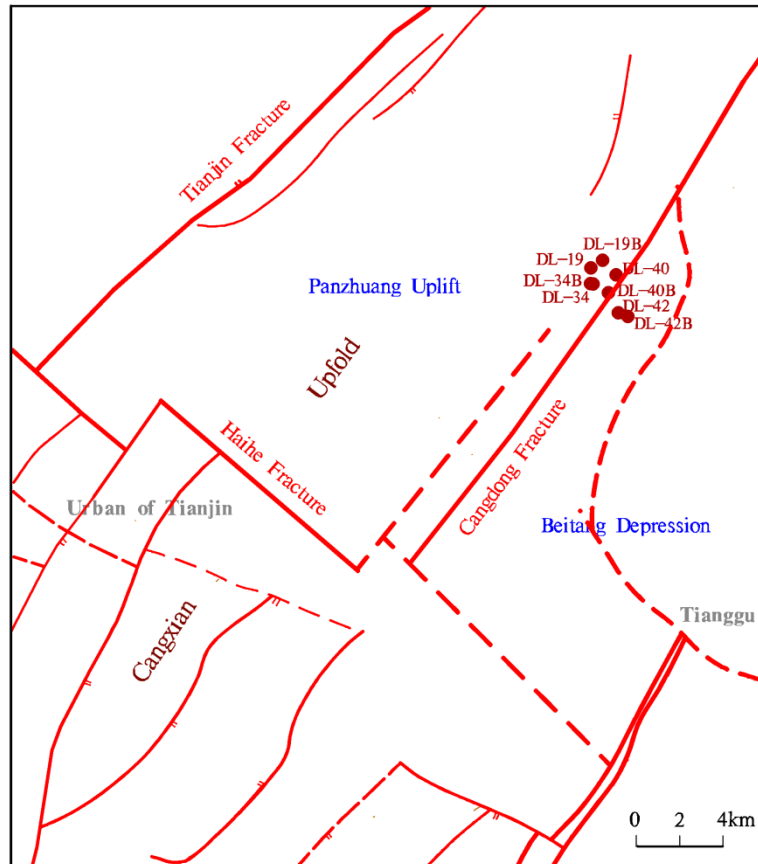


FIGURE 2: The geological structures and tectonics of the Dongli Lake area

2.2 Geothermal reservoir

Drilling data have shown that the exposed strata from the surface to the bottom of the Dongli Lake area are: Quaternary, Neocene, Eocene, Mesozoic, Ordovician, Cambrian, Qingbaikou and Jixian. The Tianjin geothermal reservoir consists of “fractured karst geothermal water in bedrock”, accumulated in the medium Proterozoic Jixiannian Wumishan (Pt2W), lower Paleozoic Cambrian (PzH) and Ordovician (PzO) reservoirs and “porous geothermal water in clastic rock” that exist in Tertiary and Quaternary strata (Wang Kun, 2008).

There are two major productive geothermal reservoirs in the Dongli Lake area geothermal system, with eight geothermal wells; half of them are production wells which are used for space heating and recreation, but the others are injection wells and are just used for spent water injection. One of the reservoirs is the Ordovician reservoir (O), which is mostly composed of limestone and limestone-dolomite, extending to a depth of 2053-2922 m. Some evidence shows that it is connected to the deeper Wumishan reservoir, as the temperature and salinity of the fluid are similar to that of the latter. The temperature is in the range 96-99°C. Wells DL-42 and DL-42B produce geothermal fluids from this reservoir.

Secondly, there is the Wumishan reservoir (Jxw) which is mainly composed of dolomite. This reservoir has a good karst condition and it is a main producer in Tianjin because of its high temperature and high rate of production. At present, six geothermal wells have been drilled into this aquifer with depths of 1805-2356 m (Table 1). The average single well flow rate is 80-120 m³/h. The geothermal water is at temperatures of 96-102°C. The Wumishan reservoir is the key reservoir in this study due to the good geological condition.

TABLE 1: Details of geothermal wells in the Dongli Lake area

No.	Well	Date of well completion	Reservoir	Type of well	Temperature (°C)	Production /injection zone (m)	Max flow rate (m ³ /h)	Production/injection* (10 ⁴ m ³)
1	DL-19	1986	Jxw	Production	96	1805~1842	Artes. well, ~30-40	none
2	DL-19B	11/2008	Jxw	Injection	88	1846~2384.36	117.98	none
3	DL-34	1999	Jxw	Production	100	1655~2327	204	26.5
4	DL-34B	6/2006	Jxw	Injection	96.5	1798~2356.8	140	24.2
5	DL-40	1/2007	Jxw	Production	98.5	1794~2328	126	32.9
6	DL-40B	11/2006	Jxw	Injection	102	1770~2278.99	132	29.2
7	DL-42	8/2008	O	Production	99	2053~2472	128.8	none
8	DL-42B	11/2008	O	Injection	96	2630~2922	112.78	none

*(Zeng et al., 2009)

2.3 Exploration and utilisation of the geothermal resources

The exploration of the Dongli Lake area geothermal resource started in the 1980s; the first geothermal well DL-19 was drilled into the Wumishan reservoir in 1986 to a depth of 1842 m. This geothermal well was an artesian well with hot water spouting up to 40.7 m above the well head. Its initial flow rate was between 35 and 40 m³/h. Thus, the reservoir was over-pressurized during its initial exploration. This geothermal well was used for agriculture, fishing and recreation.

With the addition of more geothermal wells within the same reservoir, the production rate increased and the pressure of the reservoir dropped progressively. DL-19 was no longer an artesian well after 1998. After 2003, the Dongli Lake area was replanned and redeveloped and has gradually developed from an agricultural area to an urban residential area. The demand of geothermal water for agriculture and fishing was reduced at that time, and the wells were gradually phased out; production completely stopped after 2005. The static water level was 95 m below the wellhead in 2007. The rate of lowering has ranged from 8 to 9 m per year.

In 1999, a second geothermal well (DL-34) was drilled and taken into use. From 2001 to 2005, the annual production rate of the geothermal resource was only between 1×10^4 and 5.3×10^4 m³. DL-34 and DL-40 were put into use for space heating and recreation in 2007 and 2008, respectively. Corresponding injection wells were also put into use. In 2008 and 2009, the total heating area was 31×10^4 and 35×10^4 m², respectively. The total annual production and injection were 59.4×10^4 and 53.4×10^4 m³, respectively.

In June 2010, the redevelopment of the Dongli Lake area heating system was completed. Geothermal wells number 1-4 were connected to each other and the other four geothermal wells were also connected to each other. In total, they constitute two separate joint heating systems. Based on the total heat demand, the joint heating systems adjust the amount of geothermal water used automatically. All the geothermal water will be pumped to the joint system, for heating and domestic water supply,

and finally the spent geothermal water is pumped into the injection system through connected pipes. After the redevelopment of the heating system, the heating area of the first joint system was increased to $53.5 \times 10^4 \text{ m}^2$, and the heating area of the second joint system was increased to $51.6 \times 10^4 \text{ m}^2$.

3. CHEMICAL CHARACTERISTICS OF THE THERMAL FLUID AND LAKE WATER

3.1 Sampling and analytical methods

Geochemical studies of geothermal fluids involve three main steps: 1) sample collection, 2) chemical analysis and 3) data interpretation (Arnórsson, 1991). Sample collection and chemical analysis are the basis of data interpretation; therefore, the methods of sampling are very important.

Eight geothermal water samples with temperatures in the range 88-102°C were collected at different times from geothermal wells in the Dongli Lake area for analysis of the total chemical composition. The samples from DL-19, DL-19B, DL-34B, DL-40, DL-40B, DL-42 and DL-42B were collected at the end of a pump test when drilling had completely finished. The sample from DL-34 was collected in 2006 during geochemical monitoring. The geothermal injection water is the water of DL-34 from which geothermal energy has been extracted. The samples of Dongli Lake water were collected in the summer and winter in 2007 in order to analyse them for total chemical composition.

These samples have made it possible to establish a basis for interpreting the chemistry of the thermal water in the Dongli Lake area. Analysis of the chemical composition of the water samples was carried out by the Tianjin Geological Mineral Test Centre. The different methods adopted are listed in Table 2. The results of the chemical analysis of water from the geothermal wells are listed in Table 3.

TABLE 2: Most important chemical analytical methods used for the samples

Composition	Method of analysis	Composition	Method of analysis
K	Atomic absorption spectrometry	SO ₄	Ion chromatography
Na		Cl	
Ca		B	Spectrophotometry
Mg		SiO ₂	
CO ₂	Alkalinity-titration	F	Ion selective electrode
Fe	Atomic absorption spectrometry	pH	Electrometry
H ₂ S	Titration	TDS	Gravimetry

3.2 Results of chemical analysis of the geothermal water and the lake water

3.2.1 Features of the lake water

Two samples from the centre of Dongli Lake were collected at different times. Table 3 shows that the TDS concentration of the lake water is greater than that of the geothermal water. The sodium and magnesium concentrations range from 1023 to 1032 mg/l and 133.5 to 140.1 mg/l, respectively. The concentrations of chloride and sulphate are also greater than those of the geothermal water, 1400.3-1421.5 mg/l and 617.5-631.7 mg/l, respectively. The TDS concentration of the lake water is very high and probably causes extensive precipitation during injection.

3.2.2 Features of the geothermal water

The geothermal water is colourless and odourless but contains CO₂ gas. The water is generally of low

mineral content, with TDS about 1.4-1.6 g/l and pH in the range 7.11-7.96; the maximum measured temperature is 102°C and the minimum 88°C. The sodium and potassium concentrations range from 380 to 450 mg/l and 77 to 90 mg/l, respectively. Some components are not listed in the following tables because their concentrations were very low, such as those of NO_3^- , I^- and NO_2^- . Bicarbonate concentrations are between 390.5 and 408.8 mg/l, i.e. similar to Cl^- , which is in the range 351-418 mg/l, but much higher than that of other anions. Calcium concentrations are in the range of 29.6-39 mg/l. The sulphate concentrations range from 273-310 mg/l.

TABLE 3: Chemical composition of geothermal water and lake water samples (mg/l)

Sample	DL-19	DL-19B	DL-34	DL-34B	DL-40	DL-40B	Lake water in winter	Lake water in summer	Spent geothermal water
Date		11.24.08	12.12.06	4.11.06	1.29.07	11.8.06	1.9.07	9.3.07	12.22.06
ST* (°C)	96	88	100	96.5	98.5	102	2	25	35
RT* (°C)	18	18	18	15	18	18	18	27	18
pH	7.11	7.63	7.82	7.65	7.82	7.96	9.02	8.86	7.31
K^+	89	77.1	78	107	87.6	90	41.3	41.5	78.6
Na^+	425.5	449.7	380.4	448	422.7	415.6	1023	1032	387.1
Ca^{2+}	33.1	38.7	35	29.6	33.9	32.9	50.4	36.3	30.7
Mg^{2+}	9.7	13.7	9.3	10.4	10.1	10.6	140.1	133.5	9.2
NH_4^+	0.78	1.66	0.87	1.46	1.57	1.02	0.93	0.65	0.8
Cl^-	351	418.3	352.7	391.7	384.6	349.2	1400.3	1421.5	352.7
SO_4^{2-}	299.7	309.6	273.9	296.3	294.6	308	631.7	617.5	277.1
HCO_3^-	390.5	381.4	408.8	399.7	390.5	390.5	244.1	390.5	396.6
CO_3^{2-}							114	42	
F^-	11	9.5	10.5	10.5	11	10	3.28	2.82	10.5
SiO_2	71.9	69.5	74	73	85	74.2	9	4.6	74
TDS		1564.6	1407.7	1553.6	1513.8	1475.8	3531.8	3524.2	1404.7

*ST = Sampling temperature, *RT = Room temperature

3.2.3 Piper diagram

A Piper diagram is one type of trilinear diagrams. In the Piper diagram, the major ion concentrations are plotted as percentages of milli-equivalents in two base triangles. The total cation and the total anion concentrations are set equal to 100% and the data points in the two triangles are projected onto an adjacent grid. This plot reveals useful properties and relationships for large sample groups. The main purpose of the Piper diagram is to show clustering of data points to group together samples that have similar compositions. All major elements can be displayed in the Piper diagram. However, only relative ratios rather than absolute concentrations are displayed. All samples in an open database or selected sample groups can be plotted in a Piper diagram.

The chemical type of geothermal water and lake water in the Dongli Lake area can be deduced from the diagram in Figure 3. In the geothermal water, the dominant cation is sodium. Sodium is also characteristic of the lake water. The dominant anions in the geothermal water are bicarbonate, chloride, and sulphate. The main chemical types of geothermal water are Na-Cl-HCO₃-SO₄ and Na-Cl-SO₄-HCO₃. There are minor differences in the chemical types of geothermal water in the Dongli Lake area, detectable by a Piper diagram (Figure 3). The lake water can be classified as a Na-Cl-SO₄ water. Table 4 shows the chemical characteristics of the geothermal water and the lake water in the Dongli Lake area.

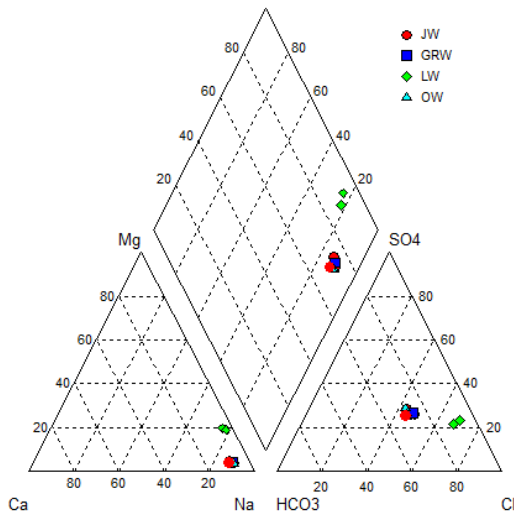


FIGURE 3: Piper diagram showing chemical types of geothermal water and lake water in Dongli Lake area

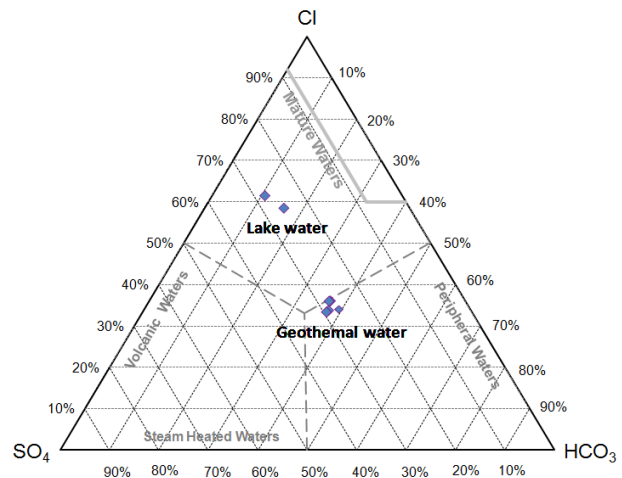


FIGURE 4: Cl-SO₄-HCO₃ ternary diagram used for the classification of water samples from Dongli Lake area

TABLE 4: Chemical characteristics of geothermal water and lake water in the Dongli Lake area

Sample	Type	Sample	Type
DL-19	Na-Cl-HCO ₃ -SO ₄	DL-42	Na-Cl-SO ₄ -HCO ₃
DL-19B	Na-Cl-SO ₄ -HCO ₃	DL-42B	Na-Cl-HCO ₃ -SO ₄
DL-34	Na-Cl-HCO ₃ -SO ₄	Lake water in winter	Na-Cl-SO ₄
DL-34B	Na-Cl-HCO ₃ -SO ₄	Lake water in summer	Na-Cl-SO ₄
DL-40	Na-Cl-HCO ₃ -SO ₄	Geothermal injection water	Na-Cl-SO ₄ -HCO ₃
DL-40B	Na-Cl-SO ₄ -HCO ₃		

3.2.4 Cl-SO₄-HCO₃ triangular diagram

The Cl-SO₄-HCO₃ triangular diagram (Giggenbach, 1991) is often used in order to classify water. It helps to detect immature unstable water and gives an initial indication of mixing relationships or geographical groupings. The diagram (Figure 4) shows several types of thermal water (including peripheral waters, immature waters, volcanic waters and steam-heated waters). It gives a preliminary statistical evaluation of groupings and trends. The position of a sample point is ascertained by obtaining the sum (S) of the concentrations (C) of the three constituents considered (Giggenbach, 1991):

$$S = C Cl + C SO_4 + C HCO_3 \tag{1}$$

and then calculating the percentage of each of the three anions (Cl, SO₄ and HCO₃):

$$Cl (\%) = \frac{100Cl}{S} \tag{2}$$

$$SO_4 (\%) = \frac{100SO_4}{S} \tag{3}$$

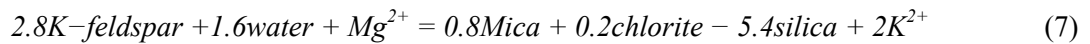
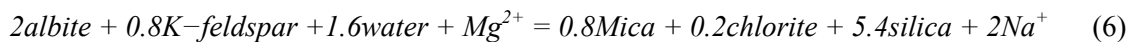
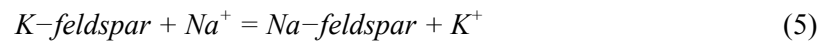
$$HCO_3 (\%) = \frac{100HCO_3}{S} \tag{4}$$

The relative Cl, SO₄ and HCO₃ contents of the water samples are plotted on the triangular Cl-SO₄-HCO₃ diagram.

Figure 4 shows that the lake water plots close to the mature waters area and is classified as a Cl-rich water. Meanwhile, most of the geothermal water in the Dongli Lake area is close to the centre of the diagram, trending towards the HCO_3 corner, being bicarbonate-rich waters with a neutral pH, possibly suggesting a peripheral nature of the thermal water. The reservoir rocks in the Dongli Lake area are composed of dolomite. Waters emerging from such reservoirs are naturally rich in calcium and bicarbonate ions. The concentration of sulphate in the thermal water is also rather high. Such sources explain the relative abundance of SO_4 , HCO_3 , Cl in the geothermal water. In the Dongli Lake area, the thermal water originally came from the old sedimentary formations, and they may reach the deep reservoir because of the faults and fissures that result from repeated tectonic activity. A high Cl concentration is a prominent characteristic of sea water, consistent with the location of the Dongli Lake area which is not very far away from the sea. Maybe the geothermal water is a mixture of sea water and peripheral water in the process of forming mature geothermal water.

3.2.5 Na-K-Mg triangular diagram

The Na-K-Mg triangular diagram (Giggenbach et al., 1983) can be used to classify waters into full equilibrium, partial equilibrium and immature waters (dissolution of rock with little or no chemical equilibrium). The diagram can be used to better clarify the origins of water, and then determine whether the fluid has equilibrated with hydrothermal minerals and predict the equilibration temperatures, $T_{\text{Na-K}}$ and $T_{\text{K-Mg}}$. The diagram is based on the temperature dependence of the three reactions:



A large number of samples can be plotted simultaneously on this diagram, and mixing trends and groupings predicted. The sum is calculated as:

$$S = \frac{C_{\text{Na}}}{1000} + \frac{C_{\text{K}}}{100} + \sqrt{C_{\text{Mg}}} \quad (8)$$

Then the “%Na”, “%K” and “%Mg” can be calculated as:

$$\%Na = \frac{C_{\text{Na}}}{10S} \quad (9)$$

$$\%K = \frac{C_{\text{K}}}{S} \quad (10)$$

$$\%Mg = 100 \frac{\sqrt{C_{\text{Mg}}}}{S} \quad (11)$$

where C is in mg/l.

Figure 5 shows that a clear distinction can be made between waters suitable or unsuitable for the application of ionic solute geothermometers. Because of the low temperature and the high Mg concentration, all the water sample points plot very close to the Mg corner in this diagram. It suggests that the geothermal water in the Dongli Lake area may be mixed with cold groundwater. Data points

in this area may then be taken to generally correspond to those of “partially equilibrated and mixed water”, waters unsuitable for the evaluation of Na/K-equilibration temperatures. Therefore, cation geothermometry is not likely to yield valid equilibration temperatures.

4. EQUILIBRIUM CALCULATIONS

4.1 General

The chemical equilibrium composition of a chemical system permits one to calculate theoretical thermodynamic properties for the system. These properties can be applied to a wide variety of problems in chemistry and chemical engineering (Gordon and McBride, 1994). Two kinds of applications for geothermometers based on chemical equilibrium are used.

Chemical geothermometry is used to evaluate the temperature in geothermal reservoirs. The composition of geothermal solutions is commonly, to a large extent, controlled by local and partial chemical equilibria between the fluid and the host rock. These chemical equilibria are temperature dependent. Chemical geothermometry makes use of this by inferring subsurface temperatures from observed fluid composition (Fridriksson and Ármannsson, 2008). One of the fundamental assumptions in the use of chemical geothermometers is that chemical equilibrium is attained in the geothermal reservoir. The concentrations (or more correctly the activities) of the reactive components are controlled by equilibria between the fluid and secondary minerals in the rock that it is in contact with. The state of equilibrium between the fluid and the minerals is very important in deciding which geothermometer to use.

The use of multiple mineral equilibria is another method for estimating subsurface temperature in geothermal systems. Reed and Spycher (1984) have suggested that the best estimate of reservoir temperature using geothermometers can be attained by simultaneously considering the state of equilibrium between specific water and many hydrothermal minerals as a function of temperature. Equilibrium is evaluated by computing $\log(Q/K)$, where Q is the calculated ion activity product corresponding to different minerals in the geothermal water and K is the theoretical solubility constant for the respective minerals at a certain temperature. If the calculated value of Q for a mineral is equal to its theoretical solubility constant (K), $\log(Q/K) = 0$. This means that the deep water in the reservoir has reached equilibrium with this mineral. If the value is above zero, it shows supersaturation but, below zero, it indicates undersaturation. If some minerals are close to equilibrium at a certain temperature, it means that these minerals have equilibrated with the water at that temperature, and the temperature represents the reservoir temperature.

Software programs like WATCH (Arnórsson and Bjarnason, 1993) and SOLVEQ (Reed et al., 2010) are generally used to calculate aqueous speciation of geothermal fluids using chemical analyses of samples collected at the surface as input. These programs are used to calculate the equilibrium constant, the reaction quotient and the saturation index for a given reaction at any given temperature. Other parameters include pH, redox potentials, and partial pressures of gases. The state of saturation of many minerals as a function of temperature can be shown by $\log(Q/K)$ diagrams.

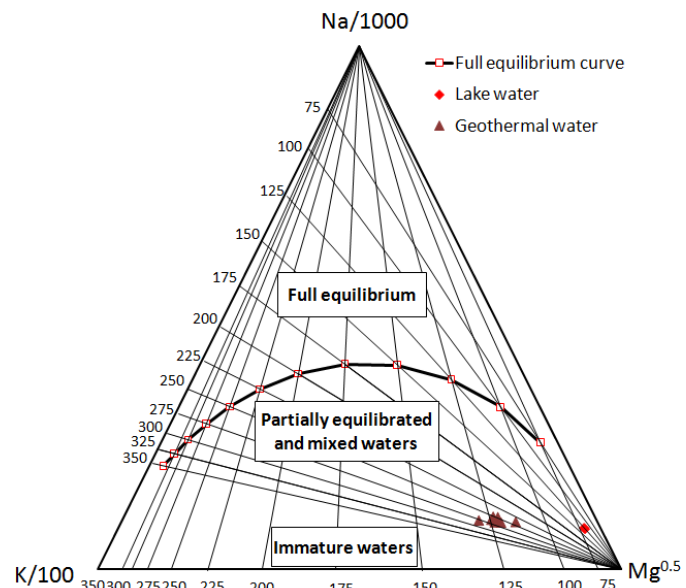


FIGURE 5: Na-K-Mg ternary plot

4.2 Geothermometers

Geothermometers have been widely used for the estimation of reservoir temperature. Two basic assumptions for geothermometers are that a temperature dependent equilibrium is attained in the reservoir and that the specific solute concentrations are not affected by chemical reactions during upflow. The use of different geothermometers depends on data quality, temperature range, and rock type.

The program WATCH (Arnórsson et al., 1982, 1983; Bjarnason, 1994) was used to calculate the relationship between the chemistry of the deep circulating water and the solubility of minerals and to evaluate the state of calcite and amorphous silica saturation of the aquifer water at selected temperatures.

4.2.1 Silica and cation geothermometers

Fournier (1991) reported various silica geothermometer equations based on equilibria for different crystalline forms of silica, and discussed the properties of dissolved silica in thermal water including equilibrium, mixing models, salinity and pH effects. It is thought that chalcedony often controls dissolved silica concentrations at temperatures below about 180°C because its small crystals dissolve quickly. But as Fournier (1991) pointed out, in some places where water has been in contact with rock at a given temperature for a long time, such as in deep sedimentary basins, quartz may control the dissolved silica at temperature down to 100°C.

The silica that crystallizes at the Earth's surface is a finely intergrown mixture of quartz and moganite. Gíslason et al. (1997) pointed out that there is a scarcity of moganite in rocks older than 100 m.y. As the isotopic age of the rocks in the Wumishan reservoir in Tianjin is 1400 Ma., quartz might be the major mineral of silica but, even though the rocks are very old, chalcedony is likely to control silica solubility as the temperature is about 100°C and quartz is not likely to be in control at such a low temperature.

The following reliable geothermometers were applied to samples from the Dongli geothermal area:

Na/K (Giggenbach, 1988):

$$t(^{\circ}\text{C}) = \frac{1390}{1.75 - \log\left(\frac{K}{Na}\right)} - 273.15 \quad (12)$$

Quartz (Fournier and Potter, 1982):

$$t(^{\circ}\text{C}) = -42.198 + 0.28831SiO_2 - 3.6686 \times 10^{-4}(SiO_2)^2 + 3.1665 \times 10^{-7}(SiO_2)^3 + 77.034 \log SiO_2 \quad (13)$$

Chalcedony (Arnórsson et al., 1983):

$$t(^{\circ}\text{C}) = \frac{1112}{4.91 - \log(SiO_2)} - 273.15 \quad (14)$$

Eight samples from the Dongli Lake area were used to predict a possible reservoir temperature by means of silica and cation geothermometers (Table 5). The measured temperatures are in the range of 88-102°C. All calculated geothermometer temperatures seem to be reasonable except the Na-K geothermometer temperature which gives too high values, which may be expected as the samples plot as partially equilibrated and mixed water in the Na-K-Mg diagram (Figure 5). The quartz geothermometer temperature is ~20-30°C higher than the measured temperature. The chalcedony temperature is more or less the same as the measured temperature, with differences of only 1-10°C.

TABLE 5: Geothermometer temperatures (°C) for the thermal waters in the Dongli Lake area

Number	Well	Measured temp. (°C)	T _{qtz}	T _{cha}	T _{Na/K}
1	DL-19	96	119	90.2	280.4
2	DL-19B	88	116.7	87.7	280.4
3	DL-34	100	118.6	89.8	278.4
4	DL-34B	96.5	118.6	89.7	294.8
5	DL-40	98.5	125.9	97.8	279.4
6	DL-40B	102	118.2	89.3	284
7	DL-42	99	120.2	91.5	266.6
8	DL-42B	96	122.8	94.4	272.1

4.2.2 Chemical equilibrium

In contrast to using individual geothermometers, Reed and Spycher (1984) presented a different approach to geothermometry. This method is not based on the assumption of predetermined mineral equilibria or the use of empirically calibrated geothermometers. It involves evaluating the saturation state of a specific composition with a large number of minerals as a function of temperature. If a group of minerals is close to equilibrium at a particular temperature, the water has equilibrated with this group of minerals close to this particular temperature, and the temperature represents the reservoir temperature.

The saturation indices for one sample were calculated by WATCH. After considering the occurrence of dolomite and commonly observed secondary minerals, five types of minerals were selected for the calculation of equilibrium with the solutions, i.e. anhydrite, calcite, chalcedony, quartz and fluorite. The saturation indices were calculated and a Log(Q/K) diagram generated (Figure 6). The diagram illustrates that the fluid is close to equilibrium with respect to chalcedony at the measured temperature, supersaturated with respect to calcite, slightly supersaturated with respect to fluorite and quartz but undersaturated with respect to anhydrite. Quartz, chalcedony and fluorite belong to minerals with prograde solubility which means that their solubility increases with increasing temperature. The others, i.e. calcite and anhydrite have retrograde solubility. The diagrams do not show a clear conversion to the zero saturation index by any group of minerals. In other words, the fluid is not in equilibrium with the assumed subsurface mineral assemblage at a particular temperature.

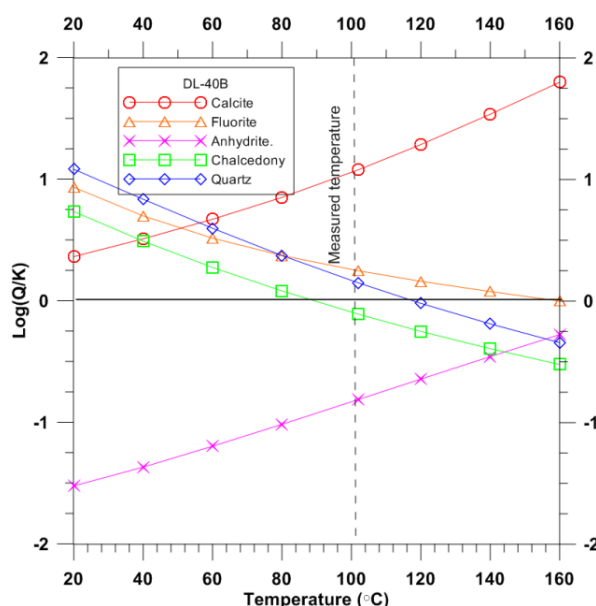


FIGURE 6: Log(Q/K) diagram for thermal water samples

Studies of fluid-mineral equilibria in active geothermal systems, ranging in temperature from 70 to 300°C, show that equilibrium between geothermal fluids and alteration minerals in the host rocks prevails in the vast majority of cases. Apparent departures of the fluids analysed from equilibrium with host rock minerals can be traced to errors in chemical analysis, degassing of CO₂, and dilution of the ascending deep fluids by shallow waters before they emerge.

This raises two additional problems in reconstructing fluid composition. First, there is a significant difference between field and laboratory measurements of pH and alkalinity (Pang and Reed, 1998; Palandri and Reed, 2001) that is caused by degassing of CO₂ from the fluid prior to analysis. It has

been shown that degassing may occur even before the field measurements of pH and alkalinity. The second problem is that organic acid anions are seldom determined, and alkalinity is attributed solely to carbonate and bicarbonate CO₂ degassing and the missing organic anion data results in an apparent supersaturation of carbonate minerals in the formation, which almost certainly is not valid. Given the long residence times of sedimentary fluids in their host rocks, fluid-mineral equilibrium is expected to prevail in sedimentary formation waters.

It is suggested that the water should be in true equilibrium with calcite in the formation, and that the apparent supersaturation is a result of the escape of CO₂ from the sample before carbonate analysis. Thus, CO₂ can be stuffed back in and the correct carbonate concentration calculated.

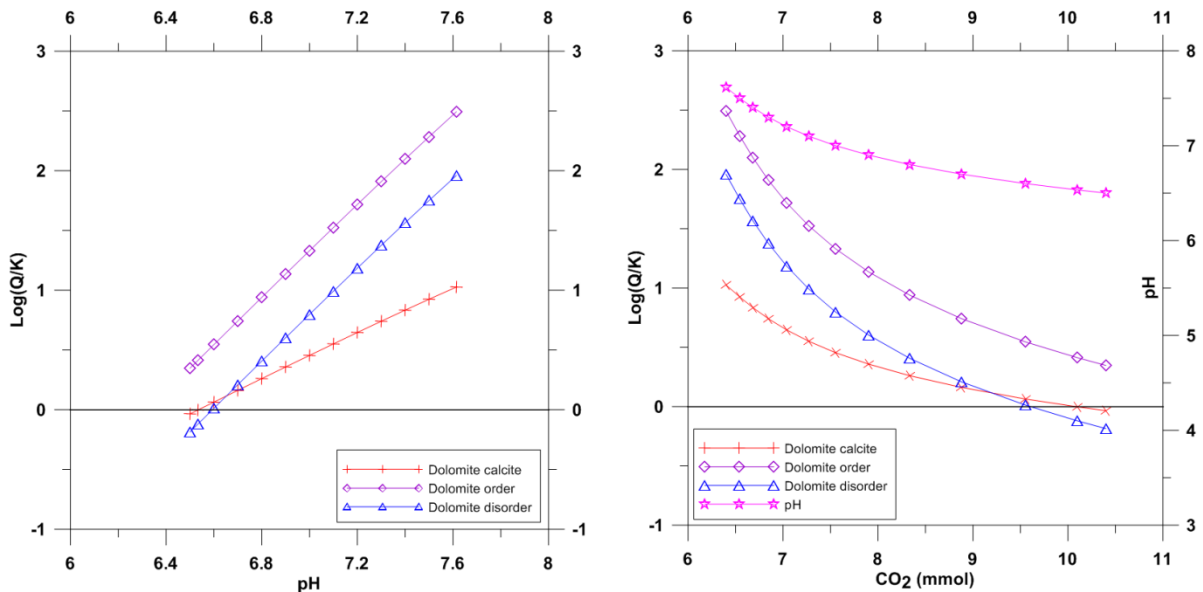


FIGURE 7: Diagrams showing CO₂ loss correction

All calculations for the reconstructions were performed using the computer program SOLVEQ (Reed et al., 2010) with improvements of the technique to account for CO₂ loss from degassing. For calculation purposes, the reservoir temperature was assumed to be 100°C. The addition of CO₂ is accomplished implicitly by fixing the charge balance with HCO₃⁻ while changing the pH until the calcite's saturation index is near zero at 100°C. The amount of escaped CO₂ can then be found from the difference in carbonate concentrations between the measured sample and the fluid at its assumed original composition.

Figure 7 shows that the calcite saturation index is near zero when the pH is 6.533 and the CO₂ added to the sample is 0.0101 moles. At the same time, the saturation index of dolomite disorder approaches zero. That gives good support for this hypothesis. Much of the 'apparently lost' CO₂ can be numerically added back until the water is saturated with calcite at the measured temperature (Palandri and Reed, 2001).

One Log(Q/K) diagram was generated (Figure 8). Considering that dolomite is the dominant rock in the reservoir and the lack of Al analysis, ten types of non-aluminium minerals were selected to show the equilibrium situation of the system. These are calcite, chalcedony, cristobalite, dolomite, quartz,

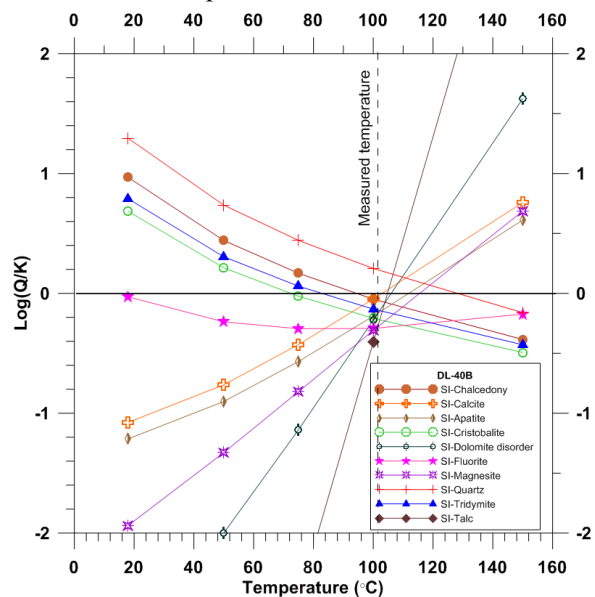


FIGURE 8: Log(Q/K) diagram after CO₂ has been added to DL-40B water

tridymite, anhydrite, apatite, magnesite, and talc.

Chemical equilibrium calculations for the Wumishan reservoir waters show that the water, as analysed, cannot be in equilibrium with diagenetic minerals at their host rock reservoir temperature (100°C). However, if the bicarbonate is corrected for CO₂ loss from the sample, chemical equilibrium between the reservoir water and the host rock diagenetic minerals can be clearly shown for systems in the temperature range 96-104°C.

5. MODELLING THE GEOCHEMISTRY OF LAKE WATER INJECTION

5.1 Modelling approach and processes

The geochemical processes taking place during geothermal injection are very complicated. It is impossible to understand or predict them easily without geochemical modelling. The PHREEQC program was employed to simulate the geochemical processes taking place during injection.

PHREEQC (Parkhurst and Appelo, 1999) is a computer program written in the C programming language that is designed to perform a wide variety of low-temperature aqueous geochemical calculations. It can be used as a speciation program to calculate saturation indices and the distribution of aqueous species. Analytical data for mole balances can be defined for any valence state or combination of valence states for an element. This program is used for the mixing of solutions and processes due to temperature changes. PHREEQC can also allow the concentration of an element to be adjusted to obtain equilibrium (or a specified saturation index or gas partial pressure) with a specified phase. Solution composition can be specified with a variety of concentration units.

Most of the geothermal resources in Tianjin are used for space heating the year round but the extent of the utilisation is season-dependent. The extent of lake water injection also varies with the season. Generally, production is greatest in winter. In order to increase the amount of injection water, additional lake water mixed with spent geothermal water is then injected into the reservoir, thus providing a good way to control the geothermal reservoir pressure drawdown.

Two simulations were performed using two kinds of lake water to elucidate the effects of injection in different seasons. Figure 9 is a sketch of the configuration of the modelling process. One shows modelling injection using a mixture of spent geothermal water and lake water in winter in an attempt to understand the geochemical effectiveness when the water mixture continues to be injected. The other shows modelling the injection using lake water only in summer. These are two extreme conditions. The source of injection water for the whole year is lake water except in winter. These alternatives were simulated by modelling mixtures of different proportions at a fixed temperature, and upon heating, respectively.

The former simulation aimed at modelling injection using a mixture of spent geothermal water and lake water as is normally injected in winter. At each step of the modelling, all information from the previous step was taken into the calculation. First,

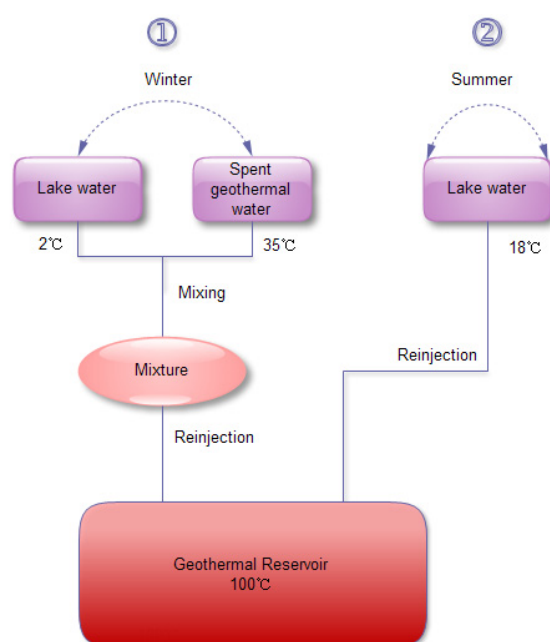


FIGURE 9: Sketch of configuration of the modelling process

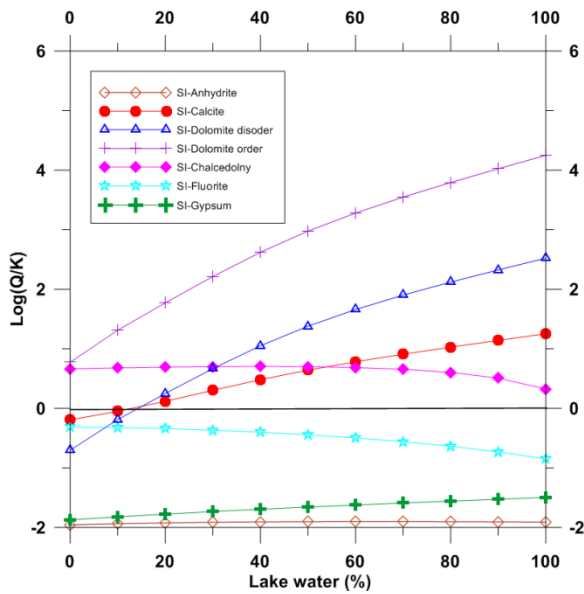


FIGURE 10: Saturation index vs. lake water proportion in winter

the spent geothermal water and the lake water were heated or cooled from room temperature to the sampling temperature. The new compositions were defined as separate new solutions. Secondly, the new solutions were mixed in different proportions and the mineral saturation index was computed for these mixtures. The saturation index vs. lake water proportion diagram (Figure 10) shows the mineral equilibrium condition. The best and worst cases were selected to continue modelling to the next step. Thirdly, the best and worst cases were chosen to define new solutions, which were then heated from the mixing temperature to the reservoir temperature. The saturation index vs. temperature diagram (Figures 11 and 12) shows the mineral equilibrium conditions. Finally, the equilibrium conditions were used to define the amount of an assemblage of pure phases that could react reversibly with the aqueous phase. Each phase dissolved or precipitated to achieve equilibrium or dissolved completely.

Then a qualitative and quantitative estimation of the precipitation and dissolution of minerals was possible.

The latter simulation aimed at modelling injection using lake water in summer. At each step of the modelling, all information from the previous step was taken into the calculation. First the sample was heated directly to reservoir temperature. The saturation index vs. lake water proportion diagram (Figure 10) shows the mineral equilibrium conditions. Finally the equilibrium conditions were used to define the amount of an assemblage of pure phases that could react reversibly with the aqueous phase. Each phase dissolved or precipitated to achieve equilibrium or dissolved completely. Then the precipitation and dissolution of minerals can be estimated, qualitatively and quantitatively.

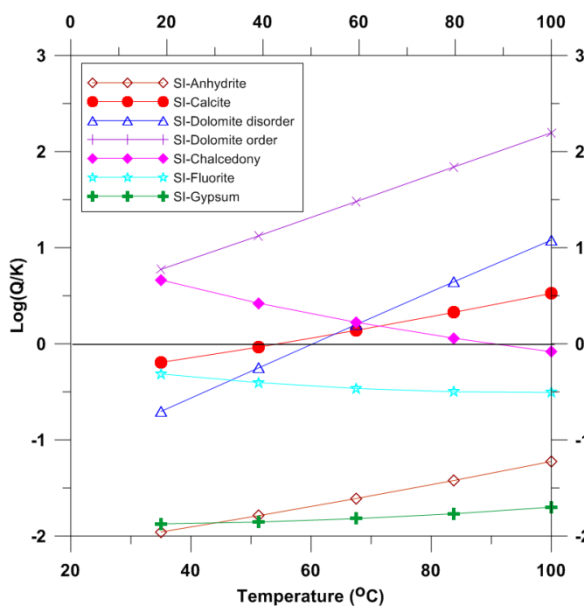


FIGURE 11: Log(Q/K) vs. temperature diagram for spent geothermal water from ambient temperature to 100°C

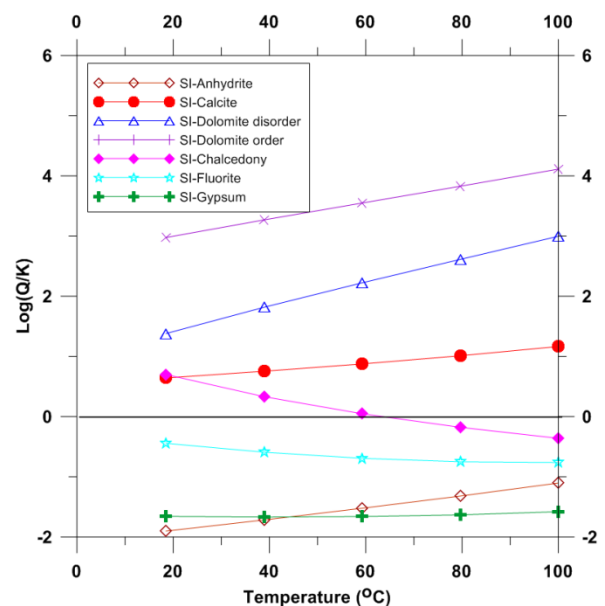


FIGURE 12: Log(Q/K) vs. temperature diagram for a mixture containing 50% lake water from ambient temperature to 100°C

5.2 Modelling injection in winter

5.2.1 Mixing

As mentioned previously, the method of geothermal utilisation in the Dongli Lake area involves pumping water directly into the pipeline for space heating. At the end of energy extraction, the spent water temperature is about 35°C. The temperature of the lake water in winter is 2°C. First the two kinds of water were mixed in different proportions. The PHREEQC program solution-solution mixing option was used to simulate the composition of the lake water and the spent geothermal water at different temperatures and in different proportions. The purpose was to find the best proportions of lake water and spent geothermal water and simultaneously predict the tendency for mineral precipitation. The saturation index was computed using PHREEQC. The saturation index vs. lake water proportion diagram is in Figure 10 and shows that the mixtures are supersaturated with respect to carbonate minerals such as the dolomite-order, no matter which proportion was chosen. Mixtures were supersaturated with respect to dolomite-disorder and calcite except at 0 to 10%, and with respect to dolomite-order and dolomite-disorder at 100% geothermal water at 35°C. These minerals may be the major precipitates that should be focused on from beginning to end. The mixtures were undersaturated with respect to anhydrite, gypsum and fluorite.

The objective is to keep up the reservoir pressure using lake water injection and thus the advantages and disadvantages of such injection should be compared. If the lake water is injected directly into the reservoir, it may be more likely to cause a lot of precipitation than by injection of geothermal water only. In order to reduce the risk of precipitation from lake water injection, it is considered prudent to choose 0~50% of lake water to model the precipitation conditions.

5.2.2 Temperature changes

As mentioned earlier, injected water that contains 0~50% lake water was chosen for modelling the process of injection into the reservoir. In the process of modelling, all the mixtures which contained 0~50% lake water were heated to the reservoir temperature (100°C). Figure 11 is a Log(Q/K) vs. temperature diagram for the spent water heated to reservoir temperature. It shows that at all temperatures, the water was supersaturated with respect to dolomite order but that the calcite saturation index changed signs when the temperature was raised to 50°C. The water is undersaturated with respect to chalcedony at 100°C and undersaturated with respect to fluorite, anhydrite, and gypsum at all temperatures.

Figure 12 shows a saturation index vs. temperature diagram for a mixture containing 50% lake water. It shows that as temperature increases, the water becomes increasingly supersaturated with respect to the minerals calcite, dolomite order and dolomite disorder because the solubility of carbonate minerals decreases with temperature. It, however, becomes undersaturated with respect to chalcedony and SI=0 is intersected at a temperature of 60°C. The water is undersaturated with respect to fluorite, gypsum and anhydrite at all temperatures. Carbonate minerals are a major source of precipitation.

From these two diagrams, we can see that the water is supersaturated with respect to dolomite order at all temperatures, and with respect to calcite and dolomite disorder at 100°C. As a result, these minerals are the most likely to be precipitated in the reservoir when lake water mixed with spent geothermal water is injected.

5.2.3 Mineral-water equilibrium

As mentioned before, all the mixtures which contained 0-50% of lake water were supersaturated with respect to calcite and dolomite. The next step is to know which is the major mineral precipitated and how much precipitate the mixtures deposit.

PHREEQC includes a data base which is used to define the amounts of an assemblage of pure phases that can react reversibly with an aqueous phase. When the phases included in this keyword data base are brought into contact with an aqueous solution, each phase will dissolve or precipitate to achieve equilibrium, or will dissolve completely. Pure phases include minerals with fixed compositions and gases with fixed partial pressures. Two types of input are available: in one type, the phase itself reacts to equilibrium (or a specified saturation index or gas partial pressure); in the other type, an alternative reaction occurs to the extent necessary to reach equilibrium (or a specified saturation index or gas partial pressure) with the specified pure phase (Parkhurst and Appelo, 1999).

PHREEQC was used to force the solutions into an equilibrium condition. Figure 13 shows dolomite precipitated and calcite dissolved. When spent geothermal water only is injected, mineral dissolution is dominant. The amount of calcite dissolved exceeds that of dolomite precipitated. The dolomite precipitated is 0.087g/kg, and the increased volume of the reservoir is -0.103 cm³/kg, leading to increased porosity. However, precipitation dominates if the mixture contains 50% lake water. The amount of dolomite precipitated exceeds that of calcite dissolved. The dolomite precipitated is 0.55 g/kg, which is six times more than from the spent geothermal water. Table 6 contains specific data on equilibrium conditions.

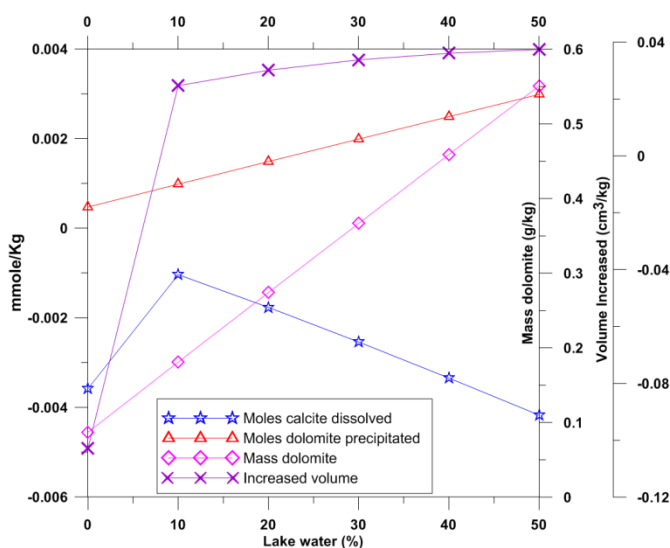


FIGURE 13: Precipitate results for different mixing proportions

TABLE 6: Specific data on solution equilibrium conditions

Number	Lake water proportion (%)	Calcite (mmole)	Dolomite (mmole)	Mass dolomite (g/kg)	Increased volume (cm ³ /kg)
1	50	-4.174	2.987	0.551	0.037
2	40	-3.346	2.489	0.459	0.036
3	30	-2.541	1.989	0.367	0.034
4	20	-1.769	1.487	0.274	0.030
5	10	-1.038	0.9816	0.181	0.025
6	0	-3.582	0.4717	0.087	-0.103

5.3 Modelling injection in summer

Injected geothermal water is not used all year, only in winter. During the other seasons, lake water is used for injection into the reservoir. Figure 14 shows lake water used in summer heated to reservoir temperature (100°C). The water is supersaturated with respect to the minerals calcite, dolomite disorder, and dolomite order. The same method as before was used to force the solution to equilibrium. Calcite and dolomite precipitated in the reservoir. The result of this calculation is shown in Table 7.

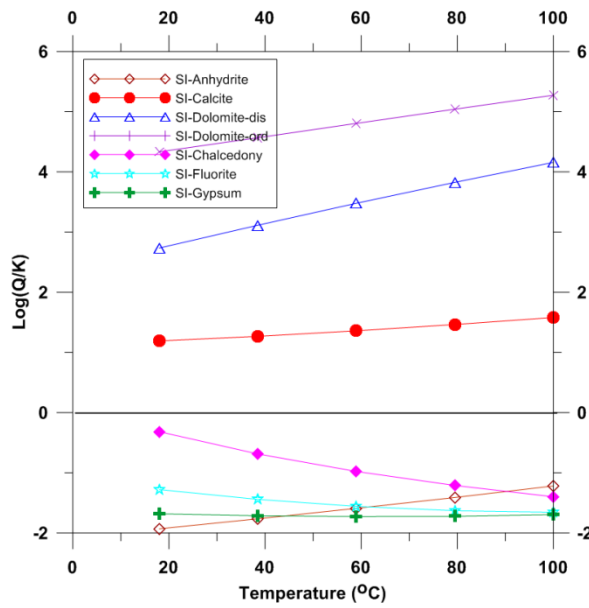


FIGURE 14: Log(Q/K) vs. temperature diagram for lake water only from ambient temperature to 100°C

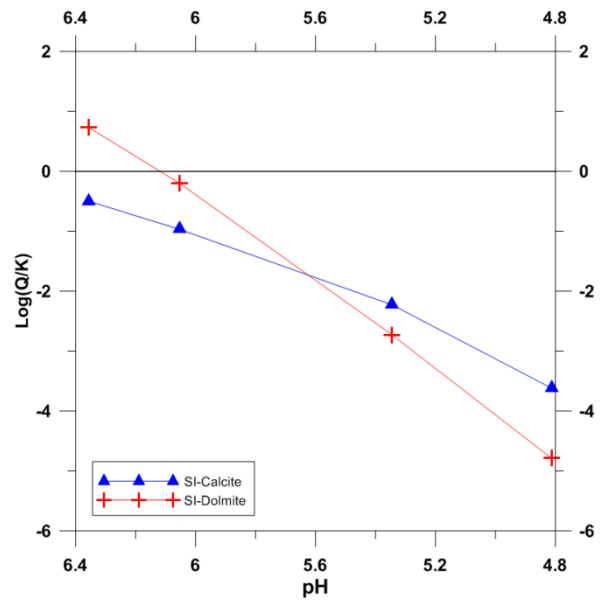


FIGURE 15: Log(Q/K) of minerals vs. pH value

TABLE 7: Specific data on solution equilibrium conditions of lake water used in summer

Lake water proportion (%)	Calcite (mmole)	Dolomite (mmole)	Mass dolomite (g/kg)	Increased volume (cm ³ /kg)
100%	-7.7390	5.26	0.970	0.0513

5.4 Method to deal with deposition

The effect of pH is important in calcite and dolomite precipitation. Therefore, in order to reduce scaling in the reservoir during lake water injection, the injection water is acidified with hydrochloric acid. The quantity added to the mixture containing 50% lake water is 0.1 mole per litre. The aim of this is to decrease the pH value of the injection water to minimize precipitation. Figure 15 shows the mineral saturation indices vs. pH. The detailed data is shown in Table 8. When the pH value is 6.054, the saturation index for both calcite and dolomite is below zero, indicating that 0.529 ml of 30% industrial hydrochloric acid mixture added to 1 kg of the injection water can prevent the precipitation effectively. When the pH of the mixture is 6.054, it seems that no deposition takes place. If a higher proportion of lake water is injected into the reservoir, more acid would be needed.

TABLE 8: Detailed data on acid addition

*V _{HCl} (ml)	*M _{HCl} (mg)	pH	SI calcite	SI dolomite
0.635	0.730	4.813	-3.62	-4.79
0.529	0.608	5.345	-2.23	-2.73
0.423	0.487	6.054	-0.97	-0.2
0.317	0.365	6.357	-0.5	0.73

*30% (mass/mass) industrial hydrochloric acid

6. CONCLUSIONS

1. Studies of the chemistry of the geothermal water in the Dongli Lake area show that the geothermal fluid is classified as Na-Cl-HCO₃-SO₄ or Na-Cl-SO₄-HCO₃ water in a Piper diagram. There are minor differences in the chemical type of geothermal water in the Dongli Lake area. The thermal fluid plots as peripheral water and immature water. The subsurface temperature is in the range 94-106°C, according to the fluid-mineral equilibrium if the bicarbonate is corrected for CO₂ loss from the sample, which is consistent with measured temperatures.
2. Two simulations were performed using lake water to elucidate the effects of injection in different seasons. One models injection using a mixture of spent geothermal water and lake water in winter in an attempt to effectively understand the geochemistry when the water mixture continues to be injected. The other models the injection using lake water only in summer. The modelling yielded the following results:
 - If the lake water is injected on its own into the reservoir in winter, it is more likely to cause a lot of precipitation than injection of geothermal water only. When spent geothermal water only is injected, mineral dissolution is dominant; the amount of calcite dissolved exceeds that of the dolomite precipitated. Porosity will increase. However, precipitation dominates if the mixture contains 50% lake water. The amount of dolomite precipitated exceeds that of calcite dissolved. In the model, the dolomite precipitated was 0.55 g/kg, six times more than from the spent geothermal water.
 - The results of injection using lake water only in summer show that the amount of dolomite precipitated exceeds that of the calcite dissolved. In the model, the dolomite precipitated is 0.97 g/kg, eleven times more than from the spent geothermal water.
 - In order to reduce scaling in the reservoir during lake water injection, the injection water should be acidified with hydrochloric acid. A quantity of 0.529 ml of 30% industrial hydrochloric acid added to a 1 kg mixture containing 50% lake water would prevent the precipitation effectively. When the pH of the mixture is 6.054, it seems that no deposition occurs. If a higher proportion of lake water is injected into the reservoir, more acid is needed.

To increase the quantity of injection water may be a good method to supplement the natural recharge to geothermal systems. As this is the aim of the project, the following recommendations are made:

1. In order to reduce deposition in the reservoir during lake water injection, the injection water should be acidified with hydrochloric acid to solve the scaling problem.
2. A detailed, quantitative understanding of processes and mechanisms based on geochemistry should be conducted, and should involve water-rock interaction, geothermal reservoir engineering and mechanical engineering. It is also necessary to do some experimental studies on possible reservoir damage caused by deposition. The reaction kinetics of mineral alteration and the relationship between porosity and permeability changes are uncertain. Experimental studies in these fields should be performed in the future.
3. Rating experiments with lake water and different amounts of acid should be carried out to find out whether a smaller amount of acid would be sufficient.
4. Modifying the injection water could prevent mineral scaling and enhance injectivity. Mitigating injection water chemistry could be an efficient way to achieve this objective. Alkalis are added to the mixture to maintain a higher pH and let minerals (mainly calcite and quartz) precipitate. Using this modified injection water would result in the injection rate gradually increasing because of continual calcite and quartz dissolution (Xu and Pruess, 2004).
5. The possibility of other inhibitors than acid may be considered and experiments carried out.
6. Most of the problems encountered in the reconstruction can be minimised in the future. The pH value should be measured as soon as possible after sampling to capture it before possible degassing of CO₂. The pH value should also be measured in a laboratory to show changes in sample composition (especially carbonate) between field and laboratory (Pang and Reed, 1998).

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