Application of geothermal temperature scale method in temperature estimation of underground heat storage in Rizhao coastal area

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Abstract. Rizhao coastal area is located in the southeast of Shandong Province. The development and utilization of geothermal resources are relatively low, and there are few geothermal wells. The research on the deep thermal storage temperature is not high in general. Therefore, this paper attempts to use the geothermal temperature scale method to evaluate the deep thermal storage temperature in this area. Geothermal temperature scale is an economic and effective means to evaluate the temperature of deep thermal reservoir. At present, the commonly used geothermal temperature scales can be divided into four categories: silica geothermal scale, cationic geothermal thermometer, isotopic geothermal thermometer and gas geothermal thermometer. Silica geothermal thermometer and cationic geothermal thermometer are the most studied ones in China and abroad. The empirical formulas of various temperature scales are established by using the relationship between equilibrium reaction of corresponding components in aqueous solution and temperature. Therefore, it is necessary to carefully study the equilibrium state of hot water and minerals and select a reliable geothermal temperature scale. In this paper, the mineral fluid equilibrium of geothermal water in Rizhao coastal camel rock (LTS) and platform (PT) is determined by using Na-K-Mg trigonometry method and multi mineral equilibrium graphic method established by watch program. It is considered that the geothermal water is unbalanced water, which proves that chalcedony temperature scale is more suitable for estimating the heat storage temperature of geothermal system in this area.

1. Introduction
Rizhao coastal area is located in the southeast of Shandong Province, to the east of Yishu Fault Zone and to the south of Jiaolai depression. Rizhao coastal area is located in the southeast of Shandong Province, to the east of Yishu Fault Zone and to the south of Jiaolai depression. No natural hot spring has been found in the area, and there is no obvious geothermal anomaly on the surface. Therefore, the geothermal geological exploration started relatively late. Since 2015, luotuoshi geothermal single wells have been constructed successively. It is revealed that the heat storage type is zonal heat reservoir, distributed at the intersection of two groups of faults, and the thermal reservoir rock is monzogranite. In the research, development and utilization of geothermal water, the temperature of deep thermal reservoir is an important parameter to reasonably evaluate the potential of geothermal resources in geothermal fields in the area and to divide the genesis of geothermal system. However, it is difficult to measure directly under normal conditions. The geothermal temperature scale method is an economic and effective means to provide this parameter [1]. At present, the commonly used geothermal chemical temperature scales can be divided into four categories, namely silica geotherm
scale, cationic geotherm scale, isotopic geotherm scale and gas temperature scale. Based on the example of camel stone hot water, this paper studies the equilibrium state of geothermal fluid by using multi mineral equilibrium diagram method and na-k-mg triangle diagram method, and discusses the application effect of different geothermal temperature scales.

2. Investigation area overview

Rizhao coastal area is located in the southeast of Shandong Province, to the east of Yishu Fault Zone and to the south of Jiaolai depression. The upper Archean Jiaodong Group and the Lower Proterozoic Jingshan group constitute the regional base strata. Their island like and lenticular remnants are scattered in the Proterozoic intrusive rocks. The Cretaceous clastic rocks and volcanic rocks of the Mesozoic are mainly distributed in the western part of the region. The Quaternary loose deposits of the Cenozoic are widely distributed in the coastal areas and rivers On both sides, gullies and hillsides.

Brittle fault structures are well developed in the area, mainly in NE direction, followed by NW direction. Among them, the NE trending fault structure is the most prominent linear structure in the area, and it is a relatively large-scale regional fault. The strike of the fault is 10° to 30° and the dip angle is 60° to 70° and the width of the fault zone is more than 10 meters to 100 meters. In the zone, cataelastic rocks, structural breccia and fault gouge are developed. The development degree of NW trending faults is far less than that of NE trending faults, and the sizes of faults are quite different, and they appear intermittently. Most of the fracture zones are narrow, with strike of 310° to 330° and dip angle of 60° to 70° with a steep dip angle of 60°to 70°. Fault breccia and cataelastic rocks are developed in the fracture zone, and most of them are tension torsional faults.

The intrusive rocks are well developed and widely distributed in the area, and the exposed area accounts for more than 90% of the whole uplift area. The intrusive age is from early Proterozoic to Mesozoic, and the rock types are complex. The ultrabasic rocks, basic rocks and neutral rocks are mainly medium acid rocks, and the ultrabasic rocks, basic rocks and neutral rocks are mainly in the form of rock stocks, dikes and dikes. The scale is small, and the acid rocks are mostly in batholith and stock Large scale.

3. Common geothermal temperature scale

3.1. Hydrological information SiO2 geothermal temperature scale

SiO2 temperature scale is the earliest and most commonly used geothermal temperature scale. Its theoretical basis is that the content of SiO2 in geothermal fluid depends on the solubility of quartz in water under different temperatures and pressures [2]. SiO2 is a special component of underground hot water. At higher temperature in the deep underground, SiO2 can dissolve in groundwater and reach water rock equilibrium. The concentration of SiO2 and other ions in water will not be affected by the concentration of SiO2 and other ions at 300 °C in water [3]. Therefore, SiO2 is an ideal geothermal temperature scale, which can well indicate the temperature of underground thermal storage. The results show that quartz controls the content of SiO2 in the solution below 110 °C, quartz controls the content of SiO2 in the solution above 180 °C, and chalcedony and quartz can reach equilibrium with the solution between 110 °C and 180 °C [4].

The commonly used correlation formula of SiO2 geothermal temperature scale is as follows.

Quartz temperature scale (no steam loss):

\[ t(°C) = 1309/(5.19 - \log_{10} C_{SiO2}) - 273.15 \]  

(1)

Chalcedony temperature scale:

\[ t(°C) = 1032/(4.69 - \log_{10} C_{SiO2}) - 273.15 \]

(2)

Where: \( C_{SiO2} \) mass concentration of SiO2 in water, mg / L.

3.2 cation geothermal temperature scale

The cation geothermal temperature scale is based on the relationship between temperature and cation exchange of Na, K, Ca, Mg between hot water and solid materials. The expression of the relationship
between the ratio of some cations in underground hot water and temperature is an approximate algorithm based on experience. The advantage of the cation temperature scale is that it can be used to study the water rock balance and mixing during hot water upwelling [5]. There are Na-K, Na-K-Ca, K-Mg and so on.

3.2.1 Na-K temperature scale

Na-K temperature scale is established based on the equilibrium between albite and Potash Feldspar under certain temperature conditions. That is, in natural water with sodium and potassium feldspar equilibrium environment, the ratio of Na and K mass concentration is a function of temperature, which is not affected by the subsequent temperature reduction. The suitable temperature is 25-250 °C [5].

Na-K temperature scale:

\[ T = \frac{933}{0.993 + \log(Na/K)} - 273.15 \]  

with, \( T \) is the thermal storage temperature, °C. Na and K are the mass concentrations of sodium and potassium in groundwater, mg / L.

3.2.2 Na-K-Ca temperature scale

The establishment of Na-K-Ca temperature scale is based on the ion exchange reaction of alkali feldspar with Na, Ca and K ions. He said that the temperature scale commonly used in medium and low temperature geothermal systems [6] was adopted. The suitable temperature range is 0-250 °C [7].

Na-K-Ca temperature scale:

\[ T = \frac{1647}{\log(Na/K) + \beta(\log(Ca^{1/2}/Na) + 2.06) + 2.47} - 273.15 \]  

where, \( T \) is the thermal storage temperature, °C. Na, K, Ca are the concentrations of sodium, potassium and calcium in groundwater, mg / L. \( \beta \) is the coefficient. when \( (\log(Ca^{1/2}/Na) + 2.06) < 0 \) or \( T > 100 \) °C, \( \beta = 1/3 \), otherwise \( \beta = 4/3 \).

3.2.3 K-Mg temperature scale

The K-Mg temperature scale established by Giggenbach is based on the ion exchange reaction of K-feldspar to Muscovite and clinopyroxene [8]. In the water rock system, the K-Mg solute reaches the equilibrium most quickly, and the relative content of K-Mg is adjusted much faster than that of Na-K, even at low temperature. Therefore, the K-Mg temperature scale is suitable for low-temperature hot water system [9]. The suitable temperature range is 0-250 °C.

K-Mg temperature scale:

\[ T = \frac{4410}{(14.0 - \log(L/Mg^{1/2}))} - 273.15 \]  

Where \( T \) is the thermal storage temperature, °C; K and Mg are the concentrations of potassium and magnesium in groundwater, mg / L.

4. Selection and calculation of geothermal temperature scale

4.1 calculation of heat storage temperature with different temperature scales

Because there are few geothermal wells in the area, only two groups of water samples were collected for comparative analysis, numbered as LTS and PT respectively. Among them, the camel stone water sample (LTS) is the hot water of drilling hole, the field temperature measurement is 38.5 °C, the platform water sample (PT) collects the self temperature measuring hole, and the field temperature measurement is 20.5 °C. The analysis results of water chemical composition are shown in table 1.

| Table 1. Chemical composition of the hot water samples |
|-----------------------------------------------|
| Hydrochemical Composition mg/L                 |
| K⁺       | Na⁺       | Ca²⁺      | Mg²⁺      | Cl⁻       | SO₄²⁻    | HCO₃⁻    | SiO₂      | TDS       | pH  |
| LTS      | 0.58      | 82.30     | 3.41      | 1.03      | 18.37    | 47.26    | 77.98     | 20.67     | 235.25   | 9.26 |
| PT       | 2.42      | 599.5     | 174       | 37.01     | 1030.05  | 366.08   | 97.91     | 15.93     | 2282.235 | 7.8  |
The above methods are used to estimate the thermal storage temperature of these water samples. The estimated results are shown in table 2.

|                | Quartz °C | Chalcedony °C | Na-K °C | K-Mg °C | Na-K-Ca °C |
|----------------|-----------|---------------|---------|---------|------------|
| LTS            | 64.69     | 32.66         | 23.51   | 45.42   | 36.47      |
| PT             | 55.10     | 22.74         | 2.31    | 33.09   | 31.81      |

It can be seen from table 2 that the thermal storage temperatures of the same water sample calculated by different geothermal temperature scale methods are quite different. This is because the use of geothermal temperature scale method is based on the premise that both minerals and geothermal fluid reach chemical equilibrium at a certain heat storage temperature. If the premise conditions are not met, the geothermal temperature scale method cannot give the correct heat storage temperature. Therefore, it is necessary to further analyze the mineral fluid equilibrium state and select the appropriate temperature scale to determine the temperature range of the underground thermal reservoir.

4.2 Judgment of mineral fluid balance

4.2.1 Na-K-Mg triangulation method

The Na-K-Mg trigonometry method should be used to determine the equilibrium state of geothermal water and whether the geothermal water is mature before using the cation geothermal temperature scale method to calculate the thermal storage temperature. The Na-K-Mg trigonometric diagram was proposed by Giggenbach in 1988. It is commonly used to evaluate the water-rock equilibrium and distinguish different types of water samples. According to the distribution of hot water points, the underground hot water can be divided into fully balanced water, partially balanced water (mature water) and unbalanced water (immature water). The application principle is that the balance adjustment of sodium and potassium is slow, but the balance adjustment of potassium and magnesium content is very fast, even when the temperature is low. Therefore, it is more favorable for the calculation of heat storage temperature of medium low temperature geothermal field. Generally, when the water sample point is in the fully balanced area, the thermal storage temperature can be calculated by using the cation temperature scale. If the water sample point is in the unbalanced area, the thermal storage temperature calculated by the cation temperature scale will have a large error, so other geothermal temperature scale methods should be used to calculate.

The coordinates in the triangle can be calculated as follows [10]:

\[ S = C(Na^+ / 1000) + C(K^+ / 100) + C(Mg^{2+})^{1/2} \]
\[ Na\% = Na^+ / 10S \]
\[ Mg\% = 100(Mg^{2+} / S)^{1/2} \]

The advantage of this method is that the equilibrium state of a large number of water samples can be judged at the same time on the same map, and the mixed water and the equilibrium water can be well separated. Two groups of water samples, LTS and PT, are brought into the Na-K-Mg trigonometry method, and the result is shown in figure 1.
Figure 1. Diagram of Na-K-Mg of the water samples in PT and LTS geothermal well

It can be seen from Figure 1 that the two water sample points fall within the scope of the imbalance zone, close to the Mg end member at the top of the lower right corner, which reflects that the equilibrium temperature of water rock reaction is low and the water sample can not reach complete equilibrium. It also indicates that the underground hot water may be mixed and diluted by the shallow cold water in the rising process, which makes the element content in the hot water lower and turns into immature water. Therefore, it is unreasonable to calculate the thermal storage temperature of camel stone and platform by cation temperature scale method.

4.2.2 multi mineral equilibrium graphic method

In 1984, Reed and Spycher proposed a multi-mineral equilibrium graphical method to calculate the equilibrium state of fluid and mineral in geothermal system. The principle of multi-mineral equilibrium graphic method is to take the dissolved state of various minerals in water as a function of temperature. If a group of minerals approaches equilibrium at a certain temperature, it can be judged that the hot water and the group of minerals have reached equilibrium, and the temperature at equilibrium is the temperature of deep thermal storage [11].

The saturation index $SI$ of different minerals in geothermal system under various temperature conditions is calculated by watch program to judge the saturation degree of each mineral [12]. The calculation formula of $SI$ is as follows.

$$SI = \log\frac{Q}{K}$$  \hspace{1cm} (7)

where $K$ is solubility of minerals in underground hot water, mol/L, and $Q$ is ion activity product of minerals actually dissolved in underground hot water, mol/L. $SI > 0$ indicates supersaturation, $SI = 0$ indicates saturation, and $SI < 0$ indicates unsaturation.

Combined with the water quality analysis results of geothermal wells, the log(Q/K)-t curves of minerals in LTS and Pt water samples at different temperatures are calculated by using WATCH program[13]. The log(Q/K)-t curve is drawn with temperature as abscissa and log(Q/K) as ordinate. Five common minerals (anhydrite, amorphous silicon, chalcedony, quartz and chrysotile) are selected to make log(Q/K)-t curves. It can be seen from Fig. 2 that the minerals in the diagram reach equilibrium at a certain temperature, but the temperature when a variety of minerals reach equilibrium is not a certain value, but tends to a certain range. In the log(Q/K)-t curves of LTS and PT water samples, the saturation index of quartz and chalcedony is above the equilibrium line, and quartz is in supersaturation state, only chalcedony is close to equilibrium state. This shows that the chalcedony temperature scale is more suitable to estimate the temperature of geothermal wells in this area, while the temperature given by quartz temperature scale is the highest temperature of deep geothermal reservoir.
4.3 Determination of Thermal Storage Temperature

Generally, when a mineral reaches equilibrium in aqueous solution, the temperature corresponding to the intersection point of the equilibrium curve of the mineral and the SI=0 axis is its theoretical equilibrium temperature, and a small temperature range around the intersection point is the equilibrium temperature of the heat storage. This mineral can be used as the geothermal temperature standard of the heat storage. In the log(Q/K)-t curve of water samples from LTS geothermal wells, the temperature of the intersection point between the equilibrium curve of chalcedony and the axis Si = 0 corresponds to 30 ~ 40°C, which is the equilibrium temperature of the thermal storage in this area. The temperature of the intersection point of the equilibrium curve of quartz and Si = 0 axis corresponds to 60 ~ 70°C, which reflects the highest temperature of deep thermal storage in this area. According to the drilling results, the exposed thermal storage depth of luotuoshi geothermal single well is 1250m ~ 1340m, the actual temperature measurement is about 42.5°C, and the measured temperature of platform temperature measurement hole is 22.3°C, which is not different from the calculation temperature of chalcedony geothermal temperature scale, which indicates that chalcedony is the most suitable geothermal temperature standard to estimate the hot water temperature in this area. In addition, the outlet water temperature of the two wellheads is lower than that of the thermal storage, which indicates that the water with low temperature is mixed in the rising process of deep hot water, which also verifies the conclusion drawn by Na-K-Mg trigonometry method.

5. Conclusion

(1) Geothermal temperature scale method is widely used in geothermal exploration, but water rock balance should be judged before any temperature scale is used. When the water sample is not in equilibrium, the thermal storage temperature cannot be estimated by the cation geotherm scale method.

(2) Using WATCH program to calculate the equilibrium data of mineral solution in geothermal fluid, we can judge the minerals that reach equilibrium, and then select the appropriate mineral temperature scale to estimate the temperature of underground heat storage. In this paper, chalcedony temperature scale is the most suitable to estimate the temperature of thermal storage in this area.

(3) Because there are few geothermal wells in the area, only two groups of water samples are selected for comparative analysis. With the increase of geothermal resources development activities in the area, further research on the geothermal temperature scale in this area can be carried out.
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