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GECHEMICAL ANALYSIS OF HOT SPRINGS IN MASSEPE, TELLU LIMPOE SIDENRENG RAPPANG REGENCY, SOUTH SULAWESI PROVINCE, INDONESIA

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Abstract : Location of the study is administratively located in the District Tellu Limpoe, Sidenreng Rappang Regency in South Sulawesi Province. Geographically located at coordinate 119°47'00" – 119°49'00" east longitude and 04°00'00"– 04°02’00" latitude. This study aims to determine the geological conditions and geochemical, it is hot spring types, and subsurface temperature of the geothermal Massepe area Sidenreng Rappang district of South Sulawesi Province. Methods of research are conducted in the form of data collection methods and methods of geological and geochemical laboratory analysis. The geomorphology of the study area consists of one unit, the unit is flat. The type of developing river is the river periodically with stadia geomorphology including adults. The stratigraphy of the study area is divided into two units of rocks, it is rock units of ignimbrite from Pare – Pare Volcanics Formation of Pliocene age and rock units of basalt from Soppeng Volcanics Formation of Early Miocene – Middle Miocene. The structure that developed in the research area is a joint and strike–slip fault, it is a Massepestrike–slip fault. Geothermal manifestations in the study area consist of 3 stations hotspring. The percentage values of ion content of HCO3-, Cl-, and SO42- in hot water samples were analyzed, indicating that the hot springs area of research, including the chloride water type. Estimation of subsurface temperature by using the geothermometer Na - K in the research area at station 1 – 3 is 162°C - 168°C, using the geothermometer Na - K - Mg are known, that the hot springs in the area of research included in partially equilibrated.

Keywords: *Geothermal, hot spring, chloride water type, subsurface temperature, Massepe*

INTRODUCTION

The increase in fuel consumption and the increasingly limited reserves of existing fuel require humans to develop new energy sources. Along with the scarcity of fossil energy, which is also a non-renewable energy source, efforts to replace the role of fossil fuels with new and renewable energy sources need to be increased again. One of the energy sources with enormous potential that is currently being developed in Indonesia is geothermal energy sources, where this energy source can reduce the role of fossil fuels in generating electricity, and is an energy source that has very low levels of pollution.[1] South Sulawesi has many geothermal manifestations, one of which is the hot springs in the Massepe area, Tellu Limpoe District, and Sidenreng Rappang Regency. Taking into account the potential of this geothermal energy source, the authors researched the geochemical analysis of hot springs in the Massepe area, Tellu Limpoe District, Sidenreng Rappang Regency, South Sulawesi Province.

Regional Geology

According to Rab Sukamto (1982), the western Pangkajene and Watampone sheet stratigraphy, where the oldest rocks are Ultramafic rocks which are generally unknown, while the results of radiometric dating on Sekist rocks are 111 million years old or Late Cretaceous. These old rocks are unconformably overlain by the Balangbaru formation in the form of flysch deposits with a thickness of more than 2000 meters and Late Cretaceous age.

[1] Dickson and Fanelli, 2004; Gupta and Roy, 2007; UU RI no. 27, 2003; Nilandaroe et. al., 2001.

Paleocene volcanic rocks that were deposited in a marine environment overlapped with flysch deposits[2,3].

Waianae Formation is Composed of sandstone interspersed with siltstone, tuff, marl, claystone, conglomerate, and limestone. The lower part of the Walanae Formation is joined by the Camba Formation, while the upper part is surrounded by Gunung Pare–Pare rocks. In this formation, limestone is also found scattered in several places. This limestone is known as the Taccipi limestone, consisting of coral limestone with inserts of marl-coated limestone, claystone, sandstone, and tuff that are white, light gray, and brownish gray, locally containing many Mollusca.

Soppeng Volcano rocks, composed of volcanic breccias and lava, intercalated with tuff grains from sand to lapilli, and claystone; in the north, there is more tuff and breccia, while in the south there is more lava, some of which are composed of pyroxene basalts and leucite basalts; some of the lava has pillow structures and some are brecciated; the breccia has components between 5 – 50 cm, the color is mostly dark gray to greenish gray. These volcanic rocks are generally very strongly altered, amygdaloid with secondary minerals in the form of carbonate and silicate veins. This unit is estimated to be 4,000 m thick, overlapping the Tonasa Formation limestone unconformably and overlain by Camba Formation rocks, estimated to be Lower – Middle Miocene in age.

RESEARCH METHODS

The method used in this research is to use field research methods and laboratory analysis methods.

a. Field research methods include collecting geological and geochemical data which includes taking chemical data from hot spring samples, and measuring pH, temperature, color, taste, and smell of hot water.
b. Laboratory analysis methods include chemical analysis methods of hot water chemical elements and microbiological analysis of hot water samples. The

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[2] R W van Van Bemmelen, *The Geology of Indonesia. Vol. IA: General Geology of Indonesia and Adjacent Archipelagoes* (US Government Printing Office, 1949).

[3] R Sukamto and S Supriatna, "Geologic Map of the Ujung Pandang, Benteng and Sinjai Quadrangles, Sulawesi," *Geological Research and Development Centre, Bandung, Indonesia* (1982).

chemical analysis consists of AAS for Potassium (K) and Sodium (Na) parameters, a titrimetric method for Bicarbonate (HCO_3), Chloride (Cl) parameters, and Calcium (Ca) and Magnesium (Mg) hardness), DREL 2800 Spectrophotometer for Sulfate parameters (SO_4).

From a sample of hot springs taken from the research location and then analyzed in the laboratory, chemical element analysis was carried out at the Chemical Oceanography Laboratory, Department of Marine Science, Hasanuddin University. The procedures for determining some of the chemical content of the hot springs are, :

a. Procedure for Determining Ca2+ Hardness
b. Sulfate Determination Procedure

RESEARCH RESULT

Ca2+ Hardness

In determining the hardness of $Ca2^+$ the procedures carried out for the analysis are[4,5] ; Ellis and Mahon, 1997; Bottrell et al., 2008; Nilando) :

1) Take a 100 ml water sample using a dropper and put it in the Erlemmeyer,
2) Add 2 ml of buffer solution and stir it,
3) Add 0.1 – 0.2 grams of murexide indicator and stir it,
4) Titrate with Na-EDTA until the color changes from pink to purple,
5) Perform the following calculations:

$$\text{Kesadahan } (Ca^{2+}) = \frac{ml\,titran\,x\,M\,titran\,x\,100{,}1\,x\,1000}{ml\,sampel}$$

(For laboratory analysis of $Mg2^+$, Cl-, and HCO_3, the procedure is the same as above).

[4] Keith Nicholson, *Geothermal Fluids: Chemistry and Exploration Techniques* (Springer Science & Business Media, 2012).
[5] W F Giggenbach, "Chemical Techniques in Geothermal Exploration," *Application of geochemistry in geothermal reservoir development* (1991): 119–144.

Sulphate Determination

In determining the sulfate content in a hot water sample, the procedures carried out for the analysis are[6,7,8]:

1) Prepare a standard solution with a concentration of 1000 mg/liter of sulfate, then dilute it with 0.1 M HCl to the mark on a 1-liter measuring flask,
2) Prepare a calibration solution with a concentration of 5, 10, 15, 20, 30, 40, and 50 mg/liter using a standard solution, then add 2.5 ml (conditioning x-ray) and 1 small spoonful of BaCl2 crystals (capacity (0, 2 – 0.3 ml) and dilute it to the mark in a 100 ml measuring flask,
3) Prepare the tool (spectrophotometer) and calibrate it according to the tool manual. Measure the wavelength of 420 nm with a 4 or 5-cm measuring tube (the length of the liquid through which the light will pass),
4) Rinse the measuring tube with distilled water several times, then fill it with distilled water and use it to set the tool at 0.001 mm.
5) Enter the calibration solution one by one and measure the absorbance (don't forget to rinse with a blank after each measurement),
6) Enter the sample solution and measure the absorbance,
7) Take measurements on the tool every 30 seconds for 4 minutes. If there are several samples to be checked, check the calibration with one of the standard solutions in every 3 or 4 samples measured,
8) Record constant measurement values and use these values in the calibration curve or regression equation which will later be used in calculating the sulfate content in the sample. (For laboratory analysis of elements NH3, K, and Na, the procedure is the same as above).

[6] Clive Oppenheimer, "KN Nicholson, 1993. Geothermal Fluids. Chemistry and Exploration Techniques. Xv+ 263 Pp. Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong: Springer-Verlag. Price DM 138.00, Ös 1076.40, SFr 138.00 (Hard Covers). ISBN 3 540 56017 3.," *Geological Magazine* 132, no. 1 (1995): 125–126.

[7] Giggenbach, "Chemical Techniques in Geothermal Exploration."

[8] A H Truesdell, "Calculation of Deep Temperatures in Geothermal Systems from the Chemistry of Boiling Spring Waters of Mixed Origin," *Proceedings 2nd UN Syposium on development and use of geothermal resources* 1 (1975): 837–844.

Geology of Research Area Geomorphology

An explanation of the geomorphology of the study area includes the division of geomorphological units, river classification, and stadia of the study area. The grouping of landscapes into geomorphological units is carried out through orthographic and genetic approaches. An orthographic approach is an approach based on the shape of the earth's surface found in the field, namely in the form of undulating topography and swampy wavy topography. A genetic approach is an approach based on the processes that shape the landscape on the earth's surface, which are controlled by either exogenous or endogenous processes. The study area has undulating topography with a height between 15 – 30 meters above sea level. Based on the orthographic and genetic approach associated with the physical characteristics found in the study area, the landscape unit of the study area is the undulating landscape unit (Figure.1) and the wavy swamp (Figure. 2).

Figure.1 The undulating geomorphological unit in the study area. Photographed towards N 1750E.

Figure.2 Hot mud swamp on a wavy swamp landscape unit in the study area. Photographed towards N 400 E.

Stratigraphy

The naming of rock units in the study area is based on unofficial lithostratigraphy, which is based on physical characteristics that can be observed in the field[9], so the rock units encountered in the study area are limestone units. The basis for naming limestone units megascopic ally uses, while the petrographical names use Dunham's classification[10]. Limestone units found in the study area (Figure.3), megascopic ally limestone in a fresh state is white, weathered black, bioclastic texture, material components in the form of large forams, material size 2 – 8 mm, non-layered structure, carbonate chemical composition, the name of the rock of Bioclastic Limestone[11]. Locally, tridacna and other Mollusca fossils were also found (Figure.4).

[9] Komisi Sandi Stratigrafi Indonesia, "Sandi Stratigrafi Indonesia," *Ikatan Ahli Geologi Indonesia* 14 (1996).

[10] Stephen W Lokier and Mariam Al Junaibi, "The Petrographic Description of Carbonate Facies: Are We All Speaking the Same Language?," *Sedimentology* 63, no. 7 (2016): 1843–1885.

[11] Richard C Selley, "Subsurface Environmental Analysis of North Sea Sediments," *AAPG Bulletin* 60, no. 2 (1976): 184–195.

Figure 3. Reef limestone outcrop at St.1, photographed towards N 22°E

Figure 4. Tridakna fossil on research area, photograped N 30oE

Microscopic appearance obtained from petrographic observations of thin slices of JP/BG/ST1 limestone (Figure 4.5) shows white color on parallel Nicols, blackish gray on cross nicols, bioclastic rock texture, layered structure, a material composition consisting of grains (skeletal grains) and mud (carbonate mud). The grains are in the form of large Discocyclinidae forams (70%) and mud (30%). Based on these physical characteristics, the name of this rock is Grainstone[12].

[12] Jacques Cohen et al., "Gamete and Embryo Micromanipulation for Infertility Treatment," in *Seminars in Reproductive Endocrinology*, vol. 8 (Copyright© 1990 by Thieme Medical Publishers, Inc., 1990), 290–295.

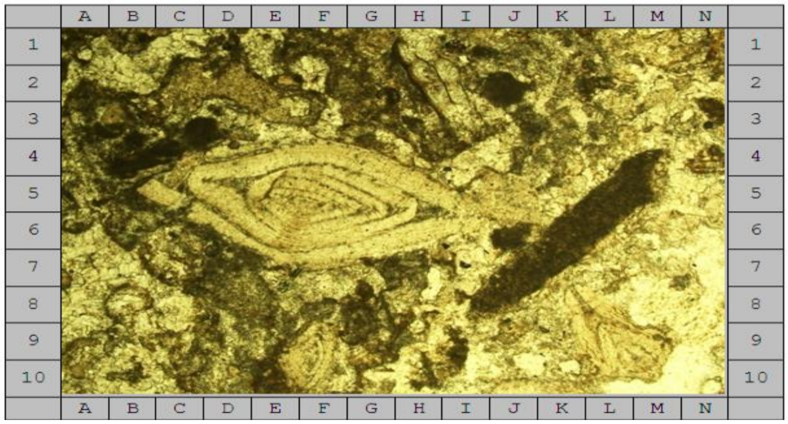

Foto.5 Microphotograph Limestone with section number JP/BG/ST1 composing several materials such as large foram Discocyclinidae (5F) and mud (2C) on the parallel nicols appearance with 50x zoom

Determination of the formation environment and the age of the limestone units are based on observing the physical characteristics of the rocks found in the study area. The limestone units found in the study area are megascopic ally fresh, grayish white, weathered black, clastic texture with a grain size of 1/4 - 1 /16 mm, poor sorting, closed packing, and non-layered structure. Coral limestone (Ql) originating from the Fufa Formation (TQf) which is in the Masohi Sheet has similar physical characteristics to the limestones found in the study area and from its geographical distribution, the limestone units in the study area are comparable to limestones from the Fufa Formation (TQf). The limestone units in the study area were formed in a shallow marine environment and are Upper Pleistocene - Holocene in age.

Geological Structure

The geological structure that develops in the study area is closely related to the existence of regional structures. The existence of this structure can also be seen by the lineages found on the SRTM Image Map of the study area (Fig. 3).

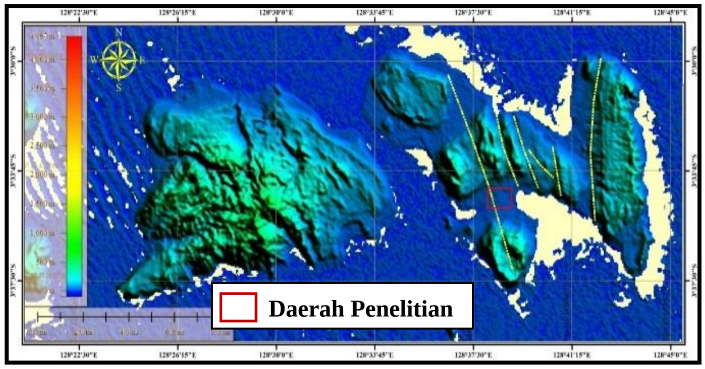

Figure 3. Structure geology interpretation using SRTM

The geological structures found in the study area are correlated with regional geological structures in the form of shear faults. This fault is trending north-southeast. The identifier for the existence of this fault structure is the juxtaposition of hot springs found in the Tiouw area (Figure.6).

Figure 6. Hot springs in Tiwou Area photographed at N 30°E.

This fault is named according to the geographical area through which this fault passes, hence the name of this fault is the Tiouw Fault. Determination of the age of this fault is determined by the age of the younger rock unit through which it passes, the Limestone Unit. The age of the limestone in the study area is Upper Pleistocene - Holocene, so the age of the Tiouw shear fault is Post-Pleistocene.

Geothermal Manifestation

Geothermal manifestations in the study area are hot springs, which are in the Tiouw area. These springs are found along fault zones that appear in Limestone

Unit. This location is reached by walking ± 30 minutes from the settlement with relatively flat terrain and sunny weather conditions with temperatures ranging from 29° – 31°C. Around the location of the hot springs, the soil and plant conditions are very arid, this is caused by the heating that comes from the hot springs. The hot water that comes out of this hot spring all flows and becomes a hot pool. At this location, there are three (3) hot springs with different temperatures, namely:

a. Spring I

   This hot spring is found with a temperature of 52°C, a pH of 8, and a water discharge of between 5.4 l/s (Figure.7).

b. Springs II

   These hot springs are found south of Ma.1. The hot water temperature is 72°C, pH is 8 and the water discharge is between 5.6 l/s. (Figure.8).

c. Springs III

   These hot springs are found towards the south-southwest. The hot water temperature is 67°C, the pH is 8, and the water discharge is between 5.4 l/s (Figure.9).

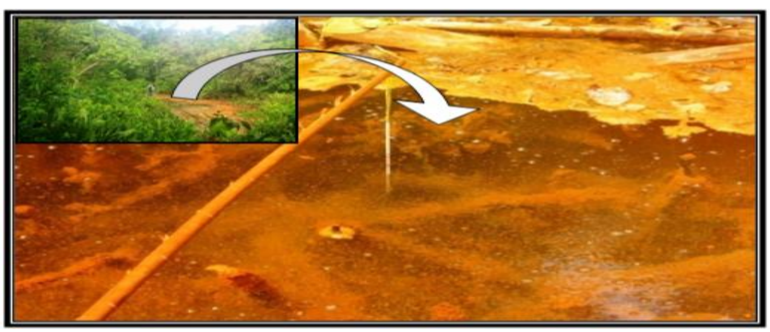

Figure 7. Tiouw Hot Spring, Photographed at N 5°E (Station Ma.1).

Figure 8. Tiouw Hot Spring, Photographed at N 21°E (Station Ma.2).

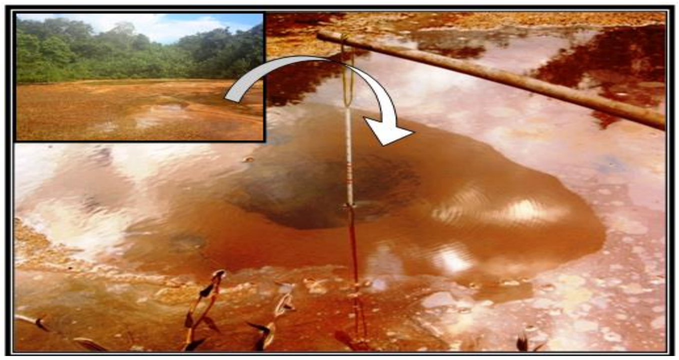

Figure 9. Tiouw Hot Spring, Photographed at N 42°E (Station Ma.3).

The physical and chemical characteristics of the 3 hot springs in the study area are described below (Tabel 1):

Tabel.1 Physical and Chemical characteristic of hot springs

No	Parameters	Hot Springs		
		I	II	III
1	Colour	Transparent	Transparent	Transparent
2	Scent	Sulphur	Sulphur	Sulphur
3	Flavour	Salty	Salty	Salty
4	Temperature	52°C	72°C	67°C
5	pH	8	8	8

Hot Springs Geochemical Analysis

Discussion on the geochemical analysis of hot springs in the study area which consists of 3 (three) springs, including determining the type of hot spring, determining the subsurface temperature of hot springs using a geothermometer, where the determination is determined from the content of chemical elements in the sample of the spring water heat (Table.1).

In the geochemical process of the hot springs in the study area, it is known that there is heat transfer accompanied by chemical reactions from the magma chamber as a heat source with the medium through which (reservoir and overburden) heat flows to the surface[13]. Indications of the presence of heat transfer and chemical reactions can be seen from the content of parameter levels (Ca, Mg, K, Na, Cl, NH_3, SO_4, and HCO_3) which are not constant in the hot water samples (Table.2) for the three (3) eyes water (Nicholson, 1993; [14].

Tabel 2. Analysis of the hot springs elements in the study area.

No	Parameter	Units	Hot Springs		
			I	II	III
1	Salinitas	$^0/_{00}$	18	23	25
2	Natrium(Na)	mg/L	9220.100	9918.300	10231.250
3	Kalium(K)	mg/L	176.400	108.150	228.600
4	Sulfat(SO_4)	mg/L	109	110	113
5	Klorida(Cl)	mg/L	8186.300	12616.700	11928.000
6	Kalsium(Ca)	mg/L	832.832	1154.154	1029.028
7	Magnesium(Mg)	mg/L	491.293	607.102	778.009
8	Amoniak(NH3)	mg/L	1.61	1.71	1.44
9	Bikarbonat(HCO_3)	mg/L	396.396	400.400	364.300

Manifestation Fluid Types

Determination of the type of hot water based on geochemical analysis of hot springs in the study area using the Trilinear diagram classification [15] based on the relative content of chloride (Cl^-), sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) anions plotted on the diagram triangle. This plot aims to find out which geothermal water samples have a chemical composition representative of the geothermal water in the reservoir[16,17].

[13] Giggenbach, "Chemical Techniques in Geothermal Exploration."

[14] Ibid.

[15] Sari Bahagiarti Kusumayudha, *Hidrogeologi Karst Dan Geometri Fraktal Di Daerah Gunungsewu* (Adicita, 2005).

[16] Giggenbach, "Chemical Techniques in Geothermal Exploration."

[17] Tom Powell and William Cumming, "Spreadsheets for Geothermal Water and Gas Geochemistry," in *Proceedings*, 2010, 4–6.

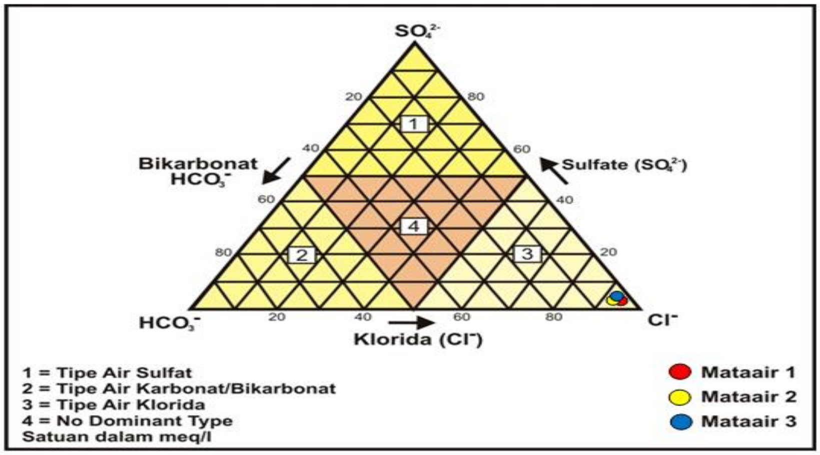

Figure 10. Cl-SO4-HCO3 diagrams (Back, 1966 in Kusumayudha, 2005).

Tabel 3. The percentage levels of chloride, sulfate and bicarbonate.

No	Parameter	Hot Springs		
		I	II	III
1	% Cl	96.337 %	97.569 %	97.582 %
2	% SO_4	0.949 %	0.629 %	0.684 %
3	% HCO_3	2.715 %	1.802 %	1.734 %
Hot Springs Types		*Klorida*	*Klorida*	*Klorida*

Based on the ion content percentage in the hot water samples, the content of chemical elements, especially the content of the anions HCO_3^-, Cl^- and SO_4^{2-}, showed that the dominant hot springs in the study area in springs I, II, and III contained chloride ions (Table. 3). From this percentage, the type of hot water in the study area (Tiouw) is included in the type of chloride water. The type of chlorine water in the study area is associated with low water temperature and has not yet experienced a reaction to surface water.

Geothermometer Na – K – Mg

Na-K-Mg ternary diagrams, are methods used for estimating the origin of geothermal fluids and for determining the water that reaches equilibrium in lithology. From the data and the calculation of the percentage content of the three elements, plotting was carried out on the Na/1000-K/100- triangle diagram for each hot spring sample[18,19]

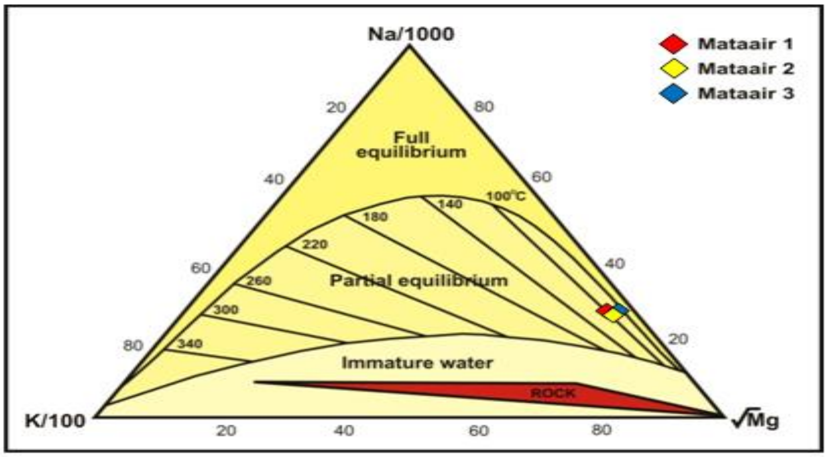

Figure 11. Ternary Diagrams to predict the origin of geothermal fluids (Nicholson,1993).

Based on the calculation of relative content Na-K-Mg and after plotting the results of the values on the Na-K-Mg triangle the Tiouw hot springs are located at partial equilibrium, showing that the hot fluid that appears on the surface has experienced interaction with the rocks it is traversing and then mixed with surface water (meteoric water). By looking at the chemical composition of the water, the effect of seawater intrusion needs to be taken into account.

Subsurface Temperatures of Hot Springs

Hot water samples from the study area show that the water is a type of chloride water. Which is produced by the steam heating process and has dissolved the side rocks during its journey until it comes out as springs, so this type of water does not represent the composition of reservoir water. Consequently, this type of water cannot be used in geothermometric calculations to predict reservoir temperature. This phenomenon can be interpreted as mixing geothermal water in Tiouw, not ordinary surface water, but water with high salt

[18] Giggenbach, "Chemical Techniques in Geothermal Exploration."
[19] Powell and Cumming, "Spreadsheets for Geothermal Water and Gas Geochemistry."

content. The mixing water may be fossilized water or residual seawater that is still stored or trapped in tertiary sedimentary rocks which are the bedrock of volcanic rocks in the area. With the addition or mixing with surface water or fossil water, the water samples taken from the research location are no longer representative of reservoir water conditions. Thus, the hot water sample cannot be used for geothermometric calculations to predict reservoir temperature[20].

Geothermal System

The geothermal system is a geothermal energy system that meets sufficient geological, hydrogeological, and heat transfer criteria, concentrated to form energy resources.

Geothermal systems are formed as a result of heat transfer from surrounding heat sources that occur by conduction and by convection. Heat transfer by conduction occurs through rock, whereas heat transfer by convection occurs due to contact between water and a heat source (Fig. 6).

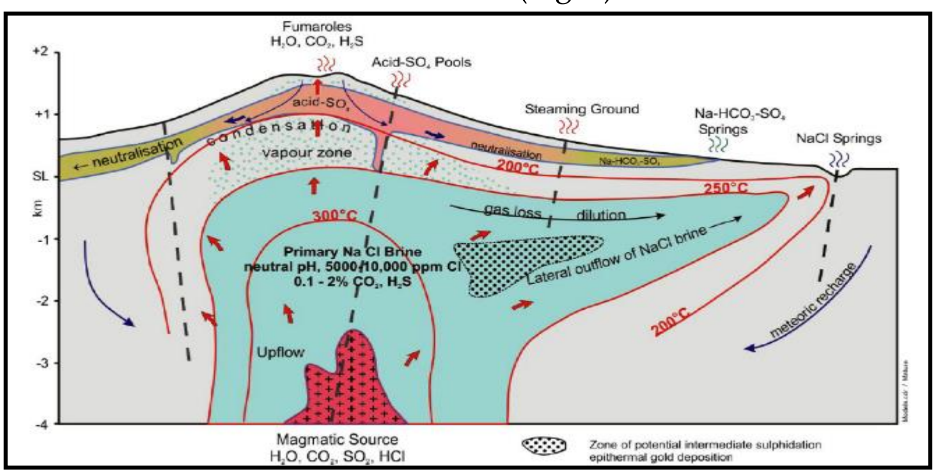

Figure 12. Geothermal System heat transfer (Dickson and Fanelli, 2004).

An important requirement for a geothermal system is the presence of a very broad heat source, the presence of a reservoir to collect heat, and the presence of a barrier to keep the heat that has accumulated. The existence of structural processes that work in the research area causes geothermal energy that is under

[20] Giggenbach, "Chemical Techniques in Geothermal Exploration."

the earth to appear on the surface as geothermal manifestations in the form of hot springs.

Geothermal Utilization

A hot water source can be identified by carrying out a chemical analysis of the value of the pH and temperature of the hot water. Based on the results of field and chemical data analysis carried out on hot water samples, it is known that the temperature of hot water on the surface is between 52^{o}C – 72^{o}C which is included in low temperature (<125^{o}C) with a pH of 8. With the results of this analysis, geothermal utilization in the study area is can be used or functioned as a hot spring (swimming pool) for tourist attraction areas.

CONCLUSION

Based on the results of field research and geochemical analysis of hot springs, reports on geothermal manifestations in the study area:

a. Geothermal potential in the study area is found to have surface manifestations in the form of three (3) hot springs with a temperature of 52^{0}C, 72^{0}C, 67^{0}C, pH 8, clear color, salty taste, there are bubbles of hot steam bubbles, and a mild sulfur smell.
b. On the Cl- - SO_4- - HCO_3 trilinear diagram, hot springs in the study area are of the chloride water type, and on the Na/1000-K/100- trilinear diagram, hot springs in the study area are included in partial equilibrium.
c. Utilization of geothermal energy in the research area based on the results of a chemical analysis study of hot water, geothermal utilization in the research area can be used or function as a hot spring bath (swimming pool) for tourist attraction areas, (Dickson and Fanelli, 2004; Ellis and Mahon, 1997; Hochstein, 1990).

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