Geochemistry of hot springs in the *Ie Seu'um* hydrothermal areas at Aceh Besar district, Indonesia

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Abstract. Indonesia geothermal resources are the largest in the world, about 40 percent of the total geothermal resources worldwide with a potential energy of 28,617 MW. Geothermal energy is one of the renewable energy in the world that can be developed sustainably. This kind of energy is not only environmentally friendly but also highly prospective compared to fossil energy. One of the potential geothermal energy in Indonesia is *Seulawah Agam* geothermal field with some manifestation areas. The fluid type of *Ie Seu'um* manifestation was chloride (Cl^-) obtained from the ternary diagram Cl^--SO_4^{2-}-HCO_3^-, using UV-Vis spectrophotometry, argentometry and acidimetry method. The reservoir range temperature was $188{,}7 \pm 9{,}3$ ºC calculated using geothermometer Na-K-Ca, Na-K Fournier and Na-K Giggenbach by applying Atomic Absorption Spectroscopy method. This data processing was carried out using liquid chemistry plotting spreadsheet version 3 powell geoscience Ltd.3 September 2012 by Powell & Cumming. The potential in the geothermal manifestation of *Ie Seu'um* was estimated about 50-100 MW (medium enthalpy).

1. Introduction

Geothermal resources in Indonesia have been explored since 1970 with approximately over 200 geothermal systems throughout Indonesia utilizing surface manifestations. Most geothermal systems in Indonesia manifested the high-temperature fluid which exists along the volcanic line area [1].

There are not many countries in the world that have potential geothermal energy reserves, except a few countries which passed by the ring of fire. This Ring of Fire also known as the circum-Pacific belt, it is a significant area in the cavity of the Pacific Ocean where a great number of earthquakes and volcanic eruptions occur. Indonesia as a country that passed by the ring of fire is currently identified to have about 117 active volcanoes as the potential sources of geothermal energy [2].

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The potential resources of Indonesian's geothermal predicted was about 40% of the total share of the world's geothermal reserves or circa 28,617 MW. Whereas, only about 4.5% is being exploited as electrical energy in the country. The power plant comes from a minimum of 10 locations: Darajat (260 MWe), Dieng (60 MWe), Kamojang (200 MWe), Gunung Salak (377 MWe), Sibayak (11 MWe), Lahendong (87 MWe), Wayang Windu (227 MWe), Ulu Belu – South Sumatra (110 MWe), Ulumbu – Flores (5 MWe) and Mataloko (2.5 MWe) [3]. Therefore, it is necessary to explore and exploit other geothermal sources especially in the Aceh province.

Nearly half of Indonesia's geothermal potential is on the island of Sumatera. One of the areas in Sumatera that has a potential geothermal energy is the Seulawah Agam mountain with the discovery of many manifestations around it, such as *Ie seu'um, Ie Jue, Ie Busuk, Alue Ie Suum, Alue Utuen Pineung* and much more. *Ie Seu'um* was the explored manifestation in this study that located circa 20 km from the top of a mountain and about 35 km from the city of Banda Aceh. Until now, the area of *Ie Seu'um* manifestation or hydrothermal area has been utilized by the district government and society as a hot spring and one of tourism objects close to Krueng Raya harbor, Mesjid Raya sub-district, Aceh Besar regency, Aceh province.

Geochemistry studies of geothermal manifestations have been conducted in many countries including the Obock coastal hot springs in the Republic of Djibouti [4], The Sabatini Volcanic District and the Tolfa Mountains, Italy [5], geothermal fields in Salihli [6], Mapamyum Western Tibet, China [7], Tang-Bijar oilfield springs, Zagros region, Iran [8], Southern Saint Lucia, Lesser Antilles island arc [9], Domuyo volcanic complex, Argentina [10], Southern Sula graben, Honduras [11] and Eastern Himalayas, China [12]. Related to Seulawah Agam geothermal field of Ie-Seu'um manifestation area, Aceh Besar district, Indonesia, up to now has never been published particularly concerning the determination of the fluid type and reservoir temperature. This research began with estimating bottom surface reservoir temperatures based on geochemical composition. Several geothermometers were used in this research include Na-K-Ca, Na/K Fournier (1973) and Na/K Truesdell (1973), while geothermal type determination using ternary diagram Cl^--SO_4^{2-}-HCO_3^-.

2. Materials and Methods

2.1. Water Sampling
Hot spring samples were collected on October 4, 2016, from *Ie Seu'um* hot spring at *Ie Seu'um* Village, Mesjid Raya Sub-district, Aceh Besar Regency, Aceh Province by purposive sampling method. Hot spring sampling technique is done by observing the springs debit coming out from hot spring resources. The *Ie Seu'um* manifestation area is categorized in the outflow geothermal zone of Mount Seulawah Agam. The hot spring samples were found from two geothermal sampling site, which is the sampling point 1 (S1) at 06 ° 13'77.8 "E and 07 ° 82'38.2" N and at sampling point 2 (S2) at 06 ° 13 ' 73.9 "E and 07 ° 82'38.7" N coordinates (Figure 1).

2.2. Materials and Instruments
The instruments used among others are Portable Temperature (Fisher Scientific Traceable), pH meter (Schott Instrument) and Conductometer (Schott Instrument), Atomic Absorption Spectroscopy (AAS) instruments (Shimadzu 6200), UV-Vis (DR / 2010), GPS, Spectrophotometer (Garmin 62S), 1000 ml polyethylene bottle, glass mouthpiece, universal pH indicator, glove, dropper, plastic bucket, 50 mL burette, 250 mL Erlenmeyer flask, 100 ml and 1000 mL flask, 100 mL measuring cup, 25 mL measuring pipette, spatula, electric heaters, analytical scales, watch glasses, spray bottles and cool boxes.
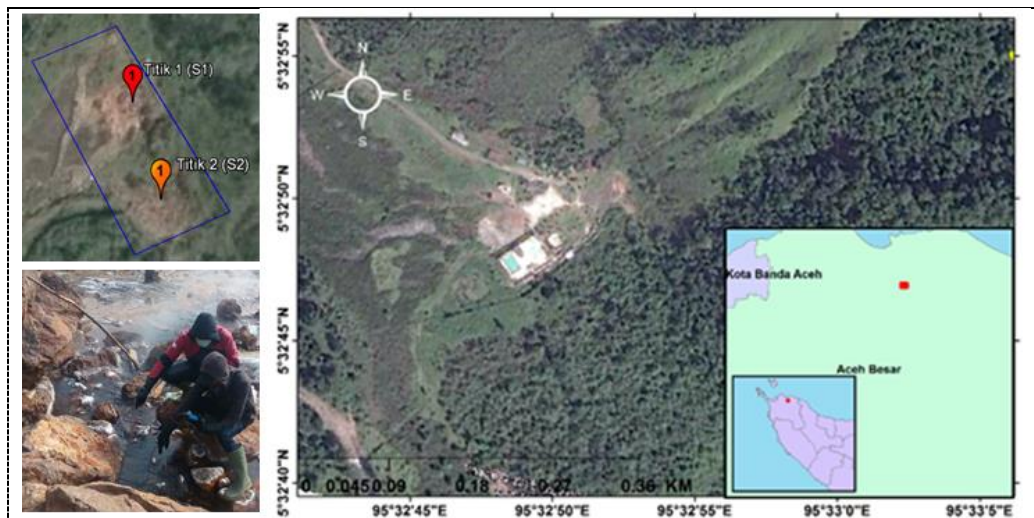
Figure 1. Satellite imagery of google earth of hot spring sampling point location at *Ie Seu'um* hydrothermal areas.

The materials used were chloride-free and sulphate-free distilled water, HNO_3 solution, 0.045 N NaCl solution, 0.45 μm filter paper, chromate potassium indicator, phenolphthalein indicator, methyl orange indicator, sulfaver®, 0.051 N $AgNO_3$ solution, HCl 0.1 N, standard solution of calcium (1000 mg/L), magnesium (1000 mg/L), potassium (1000 mg/L) and sodium (1000 mg/L).

2.3 *Measurements and Data Processing*
Analysis methods for sodium, magnesium, calcium and potassium cations was carried out using AAS instrument. Analysis of sulphate, chloride and bicarbonate anions was performed by UV-Vis spectrophotometer, argentometry (Mohr) and acidimetry methods respectively. The data processing was done using liquid chemistry plotting spreadsheet version 3 powell geoscience Ltd. 3 September 2012 by Powell & Cumming. The fluid type was determined using the triangular ternary diagram Cl^--SO_4^{2-}-HCO_3^-. The chemical equilibrium of *Ie Seu'um* manifestation reservoir was specified with a ternary diagram Na-K-Mg while geothermometer Na-K-Ca estimated the temperature reservoir manifestation, geothermometer Na/K (Fournier 1979) and geothermometer Na/K Giggenbach (1988), described by equation (1), (2), and (3).

$$T = \frac{1390}{1.750 + \log\left[\frac{Na}{K}\right]} - 273.15 \ (Na - K \ Giggenbach \ 1988) \quad [14] \tag{1}$$

$$T = \frac{1217}{\log\left[\frac{Na}{K}\right] + 1,483} - 273.15 \ (Na - K \ Fournier \ 1979) \quad [15] \tag{2}$$

$$T = \frac{1647}{\log\left[\frac{Na}{K}\right] + \beta(\log[Ca/Na]^{0.5} + 2.06) + 2.47} - 273.15 \ (Na - K - Ca) \ [14] \tag{3}$$

3. Results and Discussion

3.1. Characteristics of Ie Seu'um Surface Manifestation
The measurement of the physicochemical parameter (temperature, pH and conductivity) of *Ie Seu'um* field was conducted with a repetition of five times by insitu analysis. Measurements were made at the manifestation that has the highest debit and temperature. The average results of measurement of the manifestation can be seen in table 1.

Table 1. Locations and manifestations surface characteristic of *Ie Seu'um* carried out on October 4, 2016 at 72-meter elevation.

No	Location	Coordinate		pH	Temperature (^{0}C)	Conductivity (mV)
		E	N			
1	*Ie Seu'um* (S1)	0°61'37.78	0°78'23.82	6,61 ± 0,005	84,20 ± 0,06	27,65 ± 0,46
2	*Ie Seu'um* (S2)	0°61'37.39	0°78'23.87	6,65 ± 0,003	82,55 ± 0,01	26,43 ± 0,13

The condition around *Ie Seu'um* manifestation showed the clear water and deposits on the soil and rocks were reddish brown.
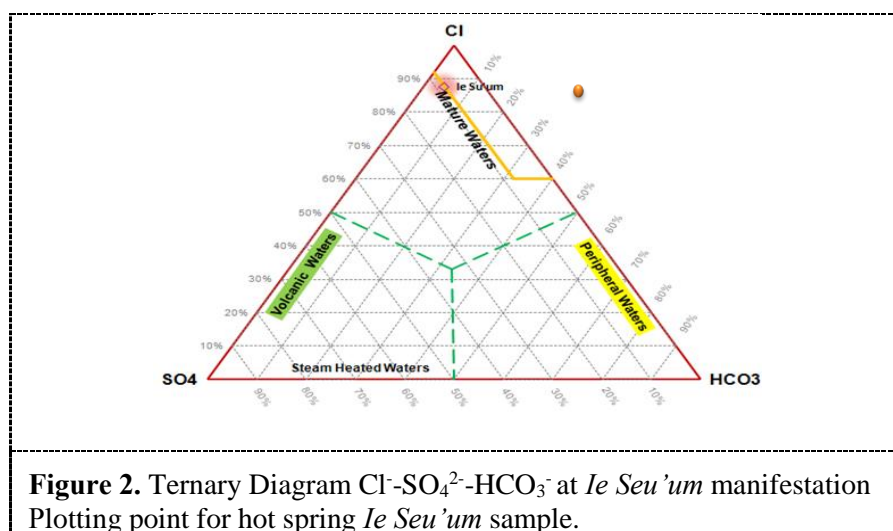
3.2. The Manifestation Fluid Type of Ie Seu'um

The fluid type determination of *Ie Seu'um* hot springs was done using the triangular ternary diagram equation based on the concentration of sulphate, bicarbonate and chloride anions. The Results of these anions were then plotted into the equation triangular ternary diagram $Cl^- - SO_4^{2-} - HCO_3^-$ (Figure 2). The highest anion concentration was chloride with the value of 2656,99 ± 0,577 mg/L that is shown in table 2.

Table 2. The concentration of the sulphate, bicarbonate and chloride anions of hot spring samples at *Ie Seu'um*.

No	Anion	Concentration (mg/L)
1	Chloride	2656,99 ± 0,577
2	Sulphate	240,67 ± 0,236
3	Bicarbonate	122,81 ± 0,575

Based on the plotting results in the diagram ternary $Cl^- - SO_4^{2-} - HCO_3^-$ it was known that the type of hot fluid indicated was chloride. The fluid from this hot springs area indicated that the water came from the deep reservoir without rocks and other fluids mixing. So, this type reflected the condition of the deep reservoir and suitable for calculating the reservoir temperature using geothermometer equation.

Figure 2. Ternary Diagram $Cl^- - SO_4^{2-} - HCO_3^-$ at *Ie Seu'um* manifestation Plotting point for hot spring *Ie Seu'um* sample.
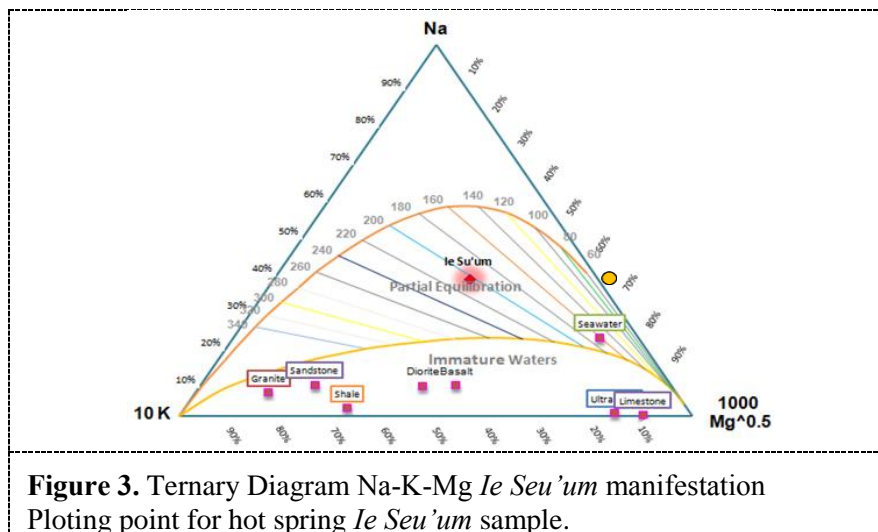
3.3. Ternary Diagram Na–K–Mg

The Na-K-Mg ternary diagram is an equation used to estimate water equilibrium in the lithology. Table 3 showed the laboratory measurements for potassium, calcium, magnesium and sodium ions respectively. The Results of these cations were plotted based on the triangular ternary diagram Na–K–Mg (Figure 3). The highest cation concentration was sodium with the value of 2630.03 ± 0,15mg/L that shown in table 3.

Table 3. The concentration of the potassium, calcium, magnesium and sodium cations of hot spring samples at *Ie Seu'um* manifestation.

No	Cation	Concentration (mg/L)
1	Potassium	167,91 ± 0,13
2	Calcium	178,61 ± 0,08
3	Magnesium	7,08 ± 0,01
4	Sodium	2630,03 ± 0,15

The content of magnesium ion concentration was minimal, it can indicate that the hot spring *Ie Seu'um* less influenced by surface water (meteoric water). The content of each ion then used to plot the ternary triangular diagram Na-K-Mg.

Based on the plotting results of the ternary diagram Na-K-Mg, the sample *Ie Seu'um* hot springs were in the area of partial equilibration. Equilibration partial area is an area in which the concentration of metal ions is in the chemical equilibrium, it means the dissolved cations in the geothermal water directly comes from the deepwater reservoir (magmatic water).

Figure 3. Ternary Diagram Na-K-Mg *Ie Seu'um* manifestation Ploting point for hot spring *Ie Seu'um* sample.

3.4. Reservoir Temperature of Ie Seu'um Geothermal Manifestation
Geothermometer is an equation that is widely used in predicting the reservoir temperature in the geothermal system. Up to now, the geothermometry has been proposed by many authors with different geothermal fields. Table 4 exhibited the plotting results that used several equations for fluid geothermometer at *Ie Seu'um* manifestations.

Table 4. Plotting result by using the geotermometer Na-K-Ca, Na/K Fournier (1979) and Na/K Giggenbach (1988) equations for *Ie Seu'um* geothermal manifestations.

No	Geothermometer	Temperature Estimation (^{0}C)
1	Na-K-Ca	186
2	Na/K Fournier (1979)	181
3	Na/K Giggenbach (1988)	199

Based on the plotting results on geothermometer Na-K-Ca, the temperature of *Ie Seu'um* manifestation reservoir approximately 186 °C. Na-K-Ca geothermometer is suitable to be applied in water that has high calcium concentration. For *Ie Seu'um* hot spring manifestation, geothermometer Na-K-Ca can be utilized since the result in the temperature range of 120 - 200°C. Based on the equation geothermometer Na/K Fournier (1979) then obtained the estimated reservoir temperature circa 181 °C. From its usefulness, this geothermometer equation also can be applied to estimate the temperature of the reservoir at *Ie Seu'um* manifestations due to exceeding the minimum threshold of 180 °C. By the plotting of geothermometer equation, Na/K Giggenbach (1988) was the estimated reservoir temperature of about 199 °C. This geothermometer Equation Na/K is commonly used to estimate the temperature of the geothermal reservoir system that generated the highest temperature value. According to the results comparison obtained from the three equations of table 4, the average value of geothermal field geothermometer *Ie Seu'um* is 188.7 ± 9.3 (°C).

The reservoir temperature can be classified into three geothermal systems, namely high enthalpy (temperature > 225 °C), medium enthalpy (temperature 125 - 225 °C) and low enthalpy (temperature < 125 °C) Hochstein (1990). Based on the results, the reservoir temperature of *Ie Seu'um* hot spring manifestation is in the *medium enthalpy* area and can be predicted according to reference table [13] then have the potential of geothermal energy range between 50-100 MW.

4. Conclusion

The fluid type of *Ie Seu'um* manifestation is chloride (Cl^-) which was obtained from the ternary diagram Cl^--SO_4^{2-}-HCO_3^-, using spectrophotometry, argentometry and acidimetry method. The reservoir range temperature was 188,7 ± 9,3 °C calculated using geothermometer Na-K-Ca, Na-K Fournier (1979) and Na-K Giggenbach (1988) by Atomic Absorption Spectroscopy method. Finally, the potential in the geothermal manifestation of *Ie Seu'um* was estimated approximately 50-100 MW (medium enthalpy).

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