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An Integrated Survey of the Geochemical Study at the Blawan-Ijen Area, East Java

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Article History: A	Abstract	
Received: July 12, 2020GeReceive in Revised Form: December 10,th2020fieAccepted: December 22, 2020Bl	Geothermal energy is a renewable alternative energy source. One of the analyses used to determine the characteristics of a geothermal field is water geochemical analysis. The target of this research is the Blawan-Ijen geothermal prospect area, Bondowoso. The geochemical	
Keywords:	base titration. This survey shows the characteristics of the	
Geochemical, bicarbonate, chloride, ge sulphate, upflow. ge Bl dc Ad in ge sy cc pe lo po in in id cc W W el ar ne CC CC	geothermal system and geothermal fluid in the Blawan area, Ijen. From the chemical analysis of hot water, we found that the types of geothermal water fluids in the Blawan Ijen area vary. In samples BL1, BL2 and BL5 included in the type of Sulphate Water with the dominant elemental Sulphate (SO4) content is also known as Sulfuric Acid Water (Acid-Sulphate Water). Then for the BL4 sample included n the type of chloride water. This type of water is a type of geothermal fluid found in most areas with high-temperature systems. Areas with large-scale hot springs flowing with high Cl concentrations originate from deep reservoirs and indicate permeable zones in those areas. However, this area may not be ocated above the main upflow zone. There are several other possibilities, such as topographic influences, which can significantly mpact hydrological control. The presence of chlorine gas can also dentify high zones' permeable areas (e.g., faults, breccia eruptions or conduit). In contrast, BL3 samples are included in the Bicarbonate Water-type. The element HCO3 (bicarbonate) is the most dominant element (main anion) and contains CO2 gas from the chemical analysis results. HCO3 water is generally formed in marginal and near-surface areas in systems dominated by volcanic rocks, where CO2 gas and condensed water vapour into groundwater. The vapour condensation can either heat the groundwater or be heated by steam	

INTRODUCTION

Geothermal is an environmentally friendly energy source because it uses repeated fluid injection under the earth's surface. Reinjection of geothermal fluid after the fluid is used for electricity generation and the recharge (seepage) of surface water, making geothermal energy sustainable (Nasional, 1998). Emissions from geothermal power plants are very low when compared to oil and coal. Because of its low emissions, geothermal energy has the criteria according to the Kyoto Protocol Clean Development Mechanism (CDM) product. This mechanism stipulates that developed countries must reduce greenhouse gas (GHG) emissions by 5.2% below the 1990 level. It should be done by purchasing clean energy from developing countries whose projects were built above 2000 (Kementrian ESDM, 2005). Clean energy includes geothermal. The development of geothermal energy can be one solution to increase Indonesia's energy reserves aside from fossil fuels. According to existing research, Indonesia is known as the country with enormous geothermal energy potential globally, with around 40% of its geothermal potential. However, in its use, Indonesia is still lagging behind other countries such as New Zealand and the Philippines (Badan Standarisasi Nasional,

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1999). Indonesia has about 265 existing geothermal areas with 138 locations (52.07%) of those existing geothermal areas still at the initial preliminary stage. Simultaneously, 24 other locations (9.05%) are still at the introduction investigation stage to the resource class hypothetical potential (Maryanto et al., 2017).

The Ministry of Research and Technology of the Republic of Indonesia (Kemenristekdikti), as one of the state institutions responsible for technology development in Indonesia, has established a roadmap for research, development and application of science and technology in the field of new and renewable energy sources to support the security of energy availability in the year 2025. In this roadmap, geothermal/geothermal energy is one of the focuses. In line with the roadmap of the Ministry of Research and Technology of the Republic of Indonesia, UNEJ (Universitas Jember) is building its capacity in the field of geothermal science and technology development. The ability of UNEJ in the geothermal field is directed primarily to process geothermal potential in East Java. East Java has a geothermal potential of 774 MWe, spread in 11 locations, one of which is in Blawan-Ijen, Bondowoso Regency. The Ijen caldera was formed more than 50,000 years ago due to the Ijen stratovolcano collapse (van Hinsberg et al., 2010). The Blawan-Ijen volcano complex also has a high potential for agriculture for primary commodities such as coffee, timber, and fruits. Furthermore, lush natural conditions in the caldera of old Ijen are home to residents with the Sempol district's establishment in Bondowoso (Konstantinou et al., 2013).

These stages are mandatory, considering the enormous geothermal investment costs. Stages Preliminary and exploration surveys are the initial stages of geothermal reservoirs' characterisation, which are very important. These stages include the study of geology, geophysics, and geochemistry. If at this stage carried out in detail and correctly, then the investment risk can be minimised (Hutapea F, 2010).

This research's targets are geochemical studies in the Blawan-Ijen geothermal area, a continuation of previous studies (characterisation of rock parameters and remote sensing analysis). This knowledge is essential for potential investors for geothermal developers to reduce their investment risk. Blawan-Ijen was chosen because it is close to the UNEJ campus, which in the future could be developed as a natural laboratory for the earth, not only in the geothermal field. Several field measurements have been carried out by the Center for Geological Resources (PSDG), the National Geological Agency. This study's results can be expected to improve the quality of potential interpretations that have been done before. Thus, investors will be more confident to participate in the Blawan-Ijen WKP auction because trust in the data and models is getting higher. This condition means that the risk of exploration failure can be reduced. Indirectly, these results are essential to be fostered for collaboration with geothermal development investors, including governments that regulate through regulations, in the form of both laws and government regulations.

This research aims to characterise the geological reservoir of Blawan, Ijen, with geochemical analysis.

MATERIAL AND METHOD

Material

The study was conducted in Mount Ijen and its surroundings (Figure 1). The presence of geothermal potential is characterised by hot springs scattered in the north of the area (Zaennudin et al., 2012). The materials used in this study are secondary data, namely the regional geological map of Mount Ijen and the map of geothermal manifestations on Mount Ijen, East Java.

The tools used in this study include:

- a. Roll meter, room blade, permanent marker, a geological hammer, plastic, field book, geological compass, and pH meter.
- b. GPS (Global Positioning System) The use of GPS to determine the coordinates of sampling points in the field.

Method

Research Stages in this study include:

a. Literature Study

This study begins with the literature collection from previous research that discusses Mount Ijen, East Java's geological and geographic conditions.



Figure 1. Location of the study area at Blawan-Ijen area, East Java

b. Collection of field samples

Sample collection is carried out in two stages, namely collecting rock samples, and collecting hot water samples. Collection of rock samples using random map trajectories. Determination of coordinates using Global Positioning System (GPS). The collection of hot water samples is done by taking hot water samples at several different points. Hot water geochemical survey refers to the GNS Science New Zealand Standard

c. Data Processing

Data processing begins with the analysis of hot water content in concentrations of cations and primary element anions. We use F-AAS tools and spectrophotometers. Furthermore, geochemical data is processed and plotted into ternary diagrams (Cl-SO₄-HCO₃, Cl-Li-B, Na-K-Mg). Furthermore, the process of calculating subsurface temperature estimation is carried out using the geothermometer method.

d. Interpretation of Data

After data processing is complete, interpretation is based on the leading element's anion cation content. Based on these results, an interpretation in geological and geochemical geothermal studies in Blawan, Ijen. The geothermal reservoir is where hydrothermal fluids heated by the heat source, which here means hot rock.

e. Data Validation

The interpretation results are then validated with primary and secondary data (geological maps, geological structure distribution and geothermal manifestations). It aims to get an accurate interpretation and following field conditions in the Blawan-Ijen area.

RESULT AND DISCUSSION Measurement of Field Data

Measurement and data collection in the field were carried out in three locations: Blawan hot springs, Wurung Crater, and Kalipahit River, as shown in Figure 2. The first location, the Blawan-Ijen hot spring location, is taken with three points. At this location, hot springs were found with 50.9 °C and pH of 5.8, while air temperatures were 26.6 °C. In the second point, hot springs were found with T 44.4 °C and pH 6.6, while the air temperature was 26.1 °C, there was dense vegetation surrounded by large trees. The third point is the limestone cave on the riverbank and closes to the Blawan waterfall.

In the Wurung Crater, the second location obtained a surface temperature of 22.6 °C. The pick-up location is at five points. The sampling points are BL 1, BL 2, BL 3, BL 4, and BL 5, respectively denoted by STA 04, STA 05, STA 06, STA 07, and STA 08 in Figure 2. The vegetation is dominated by grass. In the Kalipahit river, the third location obtained water with a very acidic pH (<0.01) with a temperature of 22.5 °C. At the same time, the existing rock is volcanic breccia. This river is a stream from the Ijen crater, which crosses the Blawan region. It mixes with neutral pH water in the Blawan waterfall (Suciningtyas et al., 2013).

Water Geochemical Test

The test aims to know the type of hot water fluid and find out the reservoir temperature using the element geothermometer calculation.

The test uses various spectrophotometer, AAS (Atomic Absorption Spectroscopy) and acid-base titration. Na, Ca, K, and Mg contents were tested using AAS. The SO₄, Cl and B contents were tested using a spectrophotometer. As for HCO₃, it is carried out using acid-base titration. Water samples were tested on five samples stabilised from 5 points. The results of sample testing with the AAS method and the spectrophotometer are shown in Table 1. While testing for HCO³ using the acid-base titration method is being carried out in the lab. MIPA analytical chemistry.



Figure 2. Location of data retrieval in the field

To determine the levels of HCO^{3-} in hot spring samples, the acid-base titration method was used. The sample is put into the beaker as much as 100 ml. The pH meter is put into the beaker, then titrated with H_2SO_4 solution up to pH 4.5. The volume of H_2SO_4 used in the titration process is recorded. The volume of H_2SO_4 used in the titration process is recorded. The volume of H_2SO_4 used in the titration process is recorded. The volume of H_2SO_4 used in the titration process is recorded.

$$HCO_3^- = \frac{A \cdot N \cdot 50000}{V} \tag{1}$$

A is the volume of the H2SO4 solution used in the titration process. N is the normality of H_2SO_4 , and V is the sample volume.

Sample	Ion	Unit	Value	Analysis Method
BL1	Sodium (Na)	ppm	104	F-AAS
	Calcium (Ca)	ppm	72	F-AAS
	Kalium (K)	ppm	32	F-AAS
	Magnesium (Mg)	ppm	107	F-AAS
	Sulphate (SO ₄)	ppm	297	Spectrophotometer
	Chloride (Cl)	ppm	138	Spectrophotometer
	Boron (B)	ppm	4	Spectrophotometer
	HCO ₃	ppm	737	Acid-Base Titration
BL2	Sodium (Na)	ppm	47	F-AAS
	Calcium (Ca)	ppm	14	F-AAS
	Kalium (K)	ppm	32	F-AAS
	Magnesium (Mg)	ppm	42	F-AAS
	Sulphate (SO ₄)	ppm	47	Spectrophotometer

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	Chloride (Cl)	ppm	38	Spectrophotometer
	Boron (B)	ppm	3	Spectrophotometer
	HCO ₃	ppm	421	Acid-Base Titration
BL3	Sodium (Na)	ppm	94	F-AAS
	Calcium (Ca)	ppm	63	F-AAS
	Kalium (K)	ppm	34	F-AAS
	Magnesium (Mg)	ppm	63	F-AAS
	Sulphate (SO ₄)	ppm	165	Spectrophotometer
	Chloride (Cl)	ppm	80	Spectrophotometer
	Boron (B)	ppm	4	Spectrophotometer
	HCO ₃	ppm	620	Acid-Base Titration
BL4	Sodium (Na)	ppm	83	F-AAS
	Calcium (Ca)	ppm	71	F-AAS
	Kalium (K)	ppm	28	F-AAS
	Magnesium (Mg)	ppm	57	F-AAS
	Sulphate (SO ₄)	ppm	147	Spectrophotometer
	Chloride (Cl)	ppm	76	Spectrophotometer
	Boron (B)	ppm	4	Spectrophotometer
	HCO ₃	ppm	532	Acid-Base Titration
BL5	Sodium (Na)	ppm	527	F-AAS
	Calcium (Ca)	ppm	13	F-AAS
	Kalium (K)	ppm	735	F-AAS
	Magnesium (Mg)	ppm	382	F-AAS
	Sulphate (SO ₄)	ppm	40595	Spectrophotometer
	Chloride (Cl)	ppm	19430	Spectrophotometer
	Boron (B)	ppm	33	Spectrophotometer
	HCO ₃	ppm	-	Acid-Base Titration

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Type of Hot Water

Chemical data needed in determining the type of reservoir fluid is the relative content of chloride (Cl), bicarbonate (HCO₃) and Sulphate (SO₄). Data processing is done by calculating the percentage of elements of chloride (Cl), bicarbonate (HCO₃) and Sulphate (SO₄). Then the data is plotted in the Giggenbach triangle diagram (Figure 3). This diagram is used to indicate the characteristic type of geothermal water and subsurface geothermal conditions. The dissolved ions in the surface ascending thermal fluids originate (Sukhyar et al., 2014).



Figure 3. Ternary Diagram of Cl-SO₄-HCO₃ elemental content of hot water in Blawan, Ijen

The types of geothermal water fluids found in the Blawan Ijen area vary from the chemical analysis results. In the BL 1 and BL5 samples included in Sulphate Water's type with the dominant content of Sulphate (SO₄). This type of geothermal water, also known as Sulfuric Acid, is a fluid that forms at shallow depths and is formed due to the condensation of geothermal gas goes near the surface. Geothermal gas, with its gas and volatile content, is practically soluble in fluid content, which is located in a deep zone but is separated from chloride water. Sulphate water is usually found at the boundary and not far from the main upflow area. When viewed from the topography, the exact location is far above the water table and around the boiling zone. However, most are often found near the surface (at depths <100 m). Sulphate water can flow through faults to the geothermal system. Sulphate water is heated at this location, then takes part in rock alterations and mixes with chlorine water.

Then for the BL 4 sample included in the type of chloride water. This type of water is a type of geothermal fluid found in most areas with high-temperature systems. Areas with large-scale hot springs flowing with high Cl concentrations originate from deep reservoirs and indicate permeable zones in those areas. However, this area may not be located above the main upflow zone because there are several other possibilities, such as topographic influences, which can significantly impact hydrological control. The eyes of chloride can also identify high zones' permeable areas (e.g., faults, breccia eruptions or conduit).

Meanwhile, BL3 samples are included in the Bicarbonate Water-type. The element HCO3 (bicarbonate) is the most dominant element (primary anion) and contains CO2 gas from the chemical analysis results. HCO3 water is generally formed in marginal and near-surface areas in systems dominated by volcanic rocks, where CO_2 gas and condensed water vapour into groundwater. The vapour condensation can either heat the groundwater or be heated by steam (steam heated) to form an HCO₃ solution. HCO₃ water is formed below the groundwater level. It is generally weak acidic, but with dissolved CO_2 , this water's degree of acidity can increase to neutral or slightly alkaline (van Hinsberg et al., 2010). The alterations found are generally argillic (kaolinite, montmorillonite) and mordenite. The high levels of HCO₃ found in Blawan springs probably resulted from the mixing of surface groundwater with CO_2 rich steam, which boiled off the hydrothermal system (Delmelle et al., 2000).

Na-K – Mg Geoindicator

The triangular diagram of Na / 1000 - K / 100 shown by Giggenbach (1988) is used to estimate reservoir temperatures and calculate the water that reaches equilibrium in lithology. The plotting is done on the Na / 1000 - K / 100 - Mg1 / 2 triangle diagram (Figure 4) for each hot spring sample from the data and the percentage calculation of the three elements' contents.



Figure 4. Ternary Diagram of Na, K, Mg elements in hot water in Blawan, Ijen

Based on the calculation of the relative content of Na / 1000-K / 100-Mg¹/₂, the value of the Na hot springs triangle lies in showing that the manifestation temperature that appears on the surface tends to be low. It also influenced by the interaction between hydrothermal fluid and elements in rocks through which silica passes. The condition of immature water is that the reservoir rock is located at a high temperature and pressure condition. Before it reaches the surface, it has also been diluted by surface water (meteoric water).

Na-K-Ca Geothermometer

A good temperature range for use with Na-K-Ca geothermometer is 120°C to 200°C, and the rest is not very good. This geothermometer is useful when applied to water that has a high Ca concentration. For calculating the temperature of Na-K-Ca, the following equation is used:

$$T^{\circ}C = \frac{1647}{\log(Na/K) + \beta(\log\sqrt{Ca/Na} + 2,06) + 2,47} - 273,15$$
(2)

Table 2. Temperature Na–K-Ca ($p = 4/3$)			
No	Sample	T ⁰C	
1	BL1	98.84	
2	BL2	185.08	
3	BL3	106.47	
4	BL4	92.03	
5	BL 5 (Kalipahit)	621.80	

Based on Na-K-Ca temperature calculation using $\beta = 4/3$, the temperature values obtained for samples BL2, BL3, and BL4 > 100 °C while BL4 samples temperature <100 °C and BL5 (Kalipahit) values are very high, the results not acceptable (See Table 2). For this reason, a recalculation is performed using $\beta = 1/3$ and the results obtained in Table 3.

Based on the calculation results in Table 3, all samples' temperature is obtained, ranging from 63-166 °C. From these results, the Na-K-Ca geothermometer estimation is not very good because it is good to be used in the temperature range of 120-200 °C. The rest is not too good despite the value of water samples analysis with high Ca concentrations.

	-	
No	Sample	T ⁰C
1	BL1	63.78
2	BL2	99.37
3	BL3	69.02
4	BL4	64.42
5	BL 5 (Kalipahit)	166.14

Table 3. Temperature Na–K-Ca ($\beta = 1/3$)

Na-K Geothermometer

Na-K geothermometer can be applied to chloride water reservoirs with T> 180°C. However, this geothermometer is not good when applied to T <100°C (Simmons, 1998). For determining the subsurface temperature using a geothermometer with Na-K content, the following equation is used:

$$Na - K \rightleftharpoons (Fourier)T^{\circ}C = \frac{1217}{(\log N a/K) + 1,483} - 273T > 180^{\circ}C$$
 (3)

$$Na - K \rightleftharpoons (Giggenbach)T^{\circ}C = \frac{1390}{(\log N a/K) + 1,75} - 273T > 120^{\circ}C$$

$$\tag{4}$$

No	Sample	T °C
1	BL1	337,06
2	BL2	464,60
3	BL3	359,32
4	BL4	349,53
5	BL 5 (Kalipahit)	636,21

Table 4. Temperature Na-K (Fournier)

Table 5. Temperature Na-K (Giggenbach)		
No	Sample	T °C
1	BL1	265,05
2	BL2	464,60
3	BL3	359,32
4	BL4	349,53
5	BL 5	636,21

Based on temperature calculations using two equations, high-temperature results are obtained, namely 337-636 °C for the Fournier Equation (Table 4) and 265-636 °C for the Giggenbach Equation (Table 5). This geothermometer is not suitable if the water contains high Ca. From the analysis of water samples with high Ca content, this geothermometer cannot estimate reservoir temperatures. Alternative geothermometers, such as the Na–K, are not suitable for the Blawan hot spring conditions due to their high-Ca content and log ((Ca/Na) +2.06) are positive. The Na–K geothermometer requires a low Ca content and a negative value for log ((Ca $^{0.5}$ /Na) +2.06). Additionally, the Na–K geothermometer is applicable for reservoirs with temperature ranges from 180 to 350 °C (Ellis, 1979).

K-Mg Geothermometer

This geothermometer is applied to situations where dissolved Na and Ca have not been balanced between liquid and rock. To determine subsurface temperature using a geothermometer with Na-K content, we can use equation (5):

$$T^{\circ}C = \frac{4410}{14.0 + \log(K^2/Mg)} - 273$$
(5)

Table 6. Temperature K-Mg (Giggenbach)

No	Sample	T ∘C
1	BL1	66,89
2	BL2	77,88
3	BL3	74,47
4	BL4	71,07
5	BL 5 (Kalipahit)	135,20

Based on the calculation results in Table 6, the temperature is obtained using the K-Mg temperature estimation (Giggenbach, 1991). All hot springs in the range between 66-135 °C. For geothermometers, this is best used when re-equilibrium takes place quickly at low temperatures. The K-Mg geothermometer is generally used in conjunction with the Na-K geothermometer, using a Na-K-Mg triangle diagram.

CONCLUSION

From the results of the chemical analysis, it is known that the types of geothermal water fluids found in the Blawan Ijen area vary. In samples BL1, BL2 and Kalipahit included in Sulphate Water with the dominant elemental Sulphate (SO₄) content. This type of geothermal water is also known as Sulfuric Acid Water (Acid-Sulphate Water). Then for the BL 4 sample included in the type of chloride water. This type of water is a type of geothermal fluid found in most areas with high-temperature systems. Areas with large-scale hot springs flowing with high Cl concentrations originate from deep reservoirs and indicate permeable zones in those areas. However, this area may not be located above the main upflow zone because there are several other possibilities, such as topographic influences, which can significantly impact hydrological control. The eyes of chloride can also identify high zones' permeable areas (e.g., faults, breccia eruptions or conduit). In contrast, BL3 samples are included in the Bicarbonate Water-type. The element HCO3 (bicarbonate) is the most dominant element (main anion) and contains CO2 gas from the results of chemical analysis. HCO3 water is generally formed in marginal and near-surface areas in systems dominated by volcanic rocks, where CO₂ gas and condensed water vapour into groundwater. The vapour condensation can either heat the groundwater or be heated by steam (steam heated) to form an HCO₃ solution.

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