Determination of reaction rate constant for increasing pH level in geothermal hot spring

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Abstract. Geothermal hot spring can be used as source of hot bath. It contains mineral elements such as Cl\(^-\), K\(^+\), Na\(^+\), and SO\(_4\)^2\(^-\). One of geothermal hot springs in Leilem, Sulawesi Utara, is categorized as Acid Sulfate Water. Leilem geothermal hot spring contains high acid sulfate and causing the pH level reach to 1. Leilem hot bath is categorized into acidic type. In order to reach mildly acidic type, the pH level should be up to 4. The method research to increase the pH level is to flow the hot water to the stack of CaCO\(_3\). To design the system, the reaction rate constant should be known. These constants are assumed to follow the Arrhenius’ equation, \(k = A e^{(-E_a/RT)}\). The value of frequency factor \((A)\) and activation energy \((E_a)\) are collected through a laboratory scale experiment of H\(_2\)SO\(_4\) with CaCO\(_3\) (powder) by using variant variables of the temperature of water and the mass of CaCO\(_3\). Based on the result of the experiment, the value of \(A\) is 1.8 and \(E_a\) 18.515 J(gmol\(^-1\)) and the research successfully increases the pH up to 4 or even higher.

1. Introduction

Geothermal is heat which is generated in earth’s interior. Indonesia is located on the ring of fire, so Indonesia has many potentials of geothermal. There are 251 locations of geothermal potential in Indonesia [1]. Indonesia has 40% of world wide of geothermal energy, however only 4% of these potentials has been utilized recently. Therefore, it is needed to increase the utilization of geothermal.

Utilization of geothermal that has been applied in Indonesia is electric generation and tourism. Manifestations of geothermal can be used for tourism, such as sightseeing mud pool, geyser, and fumarole. In addition, the geothermal hot spring can be applied for hot bath. This research refers to Leilem hot bath which is located in Lahendong geothermal field.

Leilem geothermal hot spring is estimated derived from Lokon Mountain, a volcanic mountain near Tomohon city in North Sulawesi. The heat source from Lokon Mountain cannot flow up to the surface due to its high density. Fracture in the rock above the heat source enables surface water entering down to the heat source. The surface water which enters has chemical reaction with the magma from the heat source. The reaction fluid flows up to the surface and creates geothermal manifestations [2]. Leilem hot spring is located near the hot bath. This hot spring contains high acid sulfate (H\(_2\)SO\(_4\)) and is categorized as Acid Sulfate Water [3], therefore the potential of Hydrogen (pH) level reaches to 1, while Leilem hot bath has pH level 2. According to the pH level, the hot spring and the hot bath are categorized as acidic [4]. Strong acid can cause skin damage, such as irritation in long term especially for skin disease’s patient Leilem and its surrounding society using the hot bath daily and the duration of bathing is quite long (20-30 minutes).
To overcome this problem, the research is aiming to increase hot spring’s pH level. The increase of pH level should be suitable with pH standard level for mildly acid category, which is 4. This research uses limestone (CaCO$_3$) in the form of powder as the main element in increase pH level. The assumption of the research is by using water that contains acid sulfate and pH level 1. Then, the water is heated until its temperature reaches the same temperature as in Leilem hot bath, which is 41.2 °C. The experiment reacts CaCO$_3$ and the water due to calculating the reaction rate constant from the reaction. The value of reaction rate constant needs activation energy value and frequency factor value in the calculation.

2. Theoretical basis

Leilem hot spring’s type is acid sulfate water. This water type formed by the condensation of geothermal gases into near-surface, oxygenated groundwater. This type of fluid is separated from the chloride water due to boiling at depth. This kind of water usually found near surface (≤ 100 m). Sulfate water can penetrate to depth through faults into the geothermal system. This type of water is often found in turbid pools or mud pools and even springs. Sulphate in this case is formed by the oxidation of condensed hydrogen sulphide $[3]$

$$\text{H}_2\text{O}_\text{aq} + \text{H}_2\text{SO}_4\text{aq} \rightarrow \text{H}_2\text{SO}_4\text{aq} + 0.5 \text{O}_2\text{g}$$  \hspace{1cm} (1)

Calcium Carbonate (CaCO$_3$) usually is found in limestone. Limestone formed from by organic shells especially superficial sea organism which lives in place exposed to sunlight. The reason of using of CaCO$_3$ in this research is because it can react with strong acid $[5][6]$. If CaCO$_3$ reacts with H$_2$SO$_4$, H$_2$SO$_4$ will release H$^+$ therefore the equation could be expressed as:

$$\text{H}_2\text{SO}_4\text{aq} + \text{CaCO}_3\text{s} \rightarrow \text{CaSO}_4\text{g} + \text{CO}_2\text{g} + \text{H}_2\text{O}_1\text{l}$$  \hspace{1cm} (2)

The release of H$^+$, according to Bronsted-Lowry $[7]$, causing the compound has higher pH level $[8]$. Reaction rate is molarity of solute in a reaction which is measured every second. The molarity of solute is defined as a concentrate of its substance. The equation of reaction rate constant presented as:

$$r = k[X]^m$$  \hspace{1cm} (3)

Where $r$ is reaction rate (mol/liter.s), $k$ is reaction rate constant, $X$ is H$_2$SO$_4$ concentration (mol/liter), and $m$ is reaction order. The section of the limestone placement is shown in Figure 1.

![Figure 1. Cross-section of limestone placement.](image)

Principle of mass conservation states that the reaction can neither be created or destroyed, however it can be moved. According to continuity equation $[9]$, fluid cannot be compressed therefore the flow...
of each point is equal. Reviewing from two points, the water’s flow rate to the system are equal to the water’s flow rate from the system. Based on the Figure 1., this equation can be expressed as:

\[
Q_{in} = Q_{out}
\]  

(4)

\[
\frac{dC}{dz} = -\frac{\pi D^2 \Delta z}{4Q} \phi r
\]  

(5)

Where \( Q \) is flow rate (m\(^3\)/s), \( CH_2SO_4 \) is the concentration of H\(_2\)SO\(_4\), and \( \phi \) is the porosity. Figure 1. shows the scheme of the reaction if the reaction occurs in the tube, so \( D \) is the diameter of the tube (dm), \( z \) and \( \Delta z \) are the barrier in calculation. When the water enters, the flow rate is depended on \( z \), meanwhile after the reaction, the water is followed by \( z + \Delta z \). The output water is defined as the input water added by the reaction, thus the change of the concentration becomes equation (6).

Principle of energy conservation states that the reaction can neither be created or destroyed, however it can be transformed from one form to another [10]. Each reaction will create heat therefore Black’s principle can be applied. This principle happens when two things have different temperature being mixed, the one with higher temperature will give the heat to the other with lower temperature. The equation can be represented as [11]:

\[
q|z = q|_{z+\Delta z}
\]  

(6)

q in equation (11) is heat (J). The principle equation of heat defines that heat is equal as follows:

\[
q = mc_p \Delta T
\]  

(7)

Where \( \dot{m} \) is flow rate mass (kg/s), \( c_p \) is the specific heat capacity, and \( \Delta T \) is the temperature difference (K). From equation (7), can be defines that \( \dot{m} \) can be described in \( Q, \rho \) where \( Q \) is flow rate (m\(^3\)/s) and \( \rho \) is density. The comparison between input and output can be expressed as:

\[
Q_{\rho, c_p, T}|_{z} = Q_{\rho, c_p, T}|_{z+\Delta z}
\]  

(8)

\[
\frac{dT}{dz} = \frac{\pi D^2 \phi r}{4Q_{\rho, c_p}} \Delta h_R
\]  

(9)

The equation of energy balance principle is similar with mass principle where the output water is the addition of the input water and the reaction. The reaction needs the value of porosity of the CaCO\(_3\) and the enthalpy of the reaction between H\(_2\)SO\(_4\) and CaCO\(_3\). The value of \( \rho \), \( c_p \) can be approached with the density and specific heat capacity of the liquid of H\(_2\)SO\(_4\) and limestone (CaCO\(_3\)) as follows:

\[
\rho, c_p \cong \phi \rho_{L, c_p, L} + (1-\phi) \rho_s c_p,
\]  

(10)

From equation (2), the enthalpy of reaction (\( \Delta h \)) can be obtained from the calculation product’s enthalpy and reactant’s enthalpy.

\[
\Delta h_{reaction} = \Delta h_{product} - \Delta h_{reactant}
\]  

(11)

The \( \Delta h_{reactant} \) is the the sum of \( \Delta h \) form of CaSO\(_4\), H\(_2\)O, and CO\(_2\), meanwhile \( \Delta h_{reactant} \) is the sum of the CaCO\(_3\) and H\(_2\)SO\(_4\).

In order to find the value of reaction rate, this research approaches Arrhenius Law which is an equation of reaction rate that depends on the temperature. Arrhenius Law expressed as:

\[
k = A \exp\left[-\frac{E_a}{(RT)}\right]
\]  

(12)
Where $k$ is reaction rate constant, $A$ is frequency factor, $E_a$ is activation energy (J/gmol), $T$ is the temperature (K), and $R$ is gas constant number (8.314 J/gmol). Reaction rate equation can be stated in linear function equation [12]. Based on linear equation, the reaction rate constant can be simplified as:

$$y = E_a x + \ln(A)$$

Which

$$x = \frac{1}{RT}$$

3. Methods

This research uses jar test method in laboratory scale. Firstly, the experiment creates $\text{H}_2\text{SO}_4$ solvent to mimic the water from Leilem’s hot spring. The pH level is known as 1 so the first step is to prepare the ingredients to make $\text{H}_2\text{SO}_4$ solvent. The water is reacted with $\text{CaCO}_3$, in this research, the $\text{CaCO}_3$ is considered as the powder. The method is expressed by Figure 2.

3.1. Preparing equipment and ingredients

The equipment and ingredients for the experiments is shown in Table 1.

| Equipment          | Ingredients          |
|--------------------|----------------------|
| Glass beaker       | $\text{CaCO}_3$ powder |
| Pipette            | $\text{H}_2\text{SO}_4$ 98% |
| Thermometer        | Water                |
| Spatula            |                      |
| Stove              |                      |
| Petri dish         |                      |
| Wash basin         |                      |
| pH meter           |                      |
| Analytical balance |                      |
3.2. Making $H_2SO_4$ solvent
To approach the Leilem hot spring which has pH level 1, this research uses pH 1 $H_2SO_4$ solvent. The neutral water is mixed with $H_2SO_4$ 98% until it reaches pH 1 using dilution method. The volume of water for dilution method is 350 ml. The variation of temperature is given to $H_2SO_4$, such as 28 °C, 35 °C, 43 °C, and 50 °C.

3.3. Preparing of CaCO$_3$
CaCO$_3$ is usually found in limestone, however in these experiments use CaCO$_3$ in form of powder. The form of the CaCO$_3$ effects the output of the reaction, both the output pH and the time of the reaction. The experiments use four mass variables in order to obtain the difference in a range temperature, it is expressed in Table 2.

| Table 2. CaCO$_3$ variables. |
|-----------------------------|
| Temperature (°C) | Mass (g) |
| 28 | 5, 8, 10 |
| 35 | 5, 8, 10 |
| 43 | 8, 10, 12 |
| 50 | 8, 10, 12 |

3.4. Reacting $H_2SO_4$ and CaCO$_3$
The $H_2SO_4$ solvent and CaCO$_3$ powder are reacted in variants of temperature while being stirred. The temperatures that the research used are 28°C, 35°C, 43°C, and 50°C. These temperatures are chosen because they are the range temperature of Leilem’s hot bath water which is 41.2°C.

3.5. Observing the result
The pH levels are gained in each experiment and measured in specified time using pH meter, hence the changing result of pH level in each variable is obtained. The result is measured until it is constant.

4. Results and discussions
Reaction rate constant determined by doing an experiment which has already been previously described in Method. In the experiment, the initial pH is 2 for all the 12 reactions. First experiment, the temperature is 28 °C and mass of CaCO$_3$ are 5 g, 8 g, and 10 g. Second experiment, the temperature is 35°C and mass of CaCO$_3$ are 5 g, 8 g, and 10 g. Third experiment, the temperature is 43 °C and mass of CaCO$_3$ are 5 g, 8 g, 10 g, and 12 g. The last experiment, the temperature is 50 °C and mass of CaCO$_3$ are 8 g, 10 g, and 12 g.

$H_2SO_4$ is defined as strong acid, C value is calculated with the following equation:

$$pH = -\log[H^+]$$  \hspace{1cm} (15)

$$[H^+] = 10^{-pH}$$  \hspace{1cm} (16)

$$C = 10^{-pH}$$  \hspace{1cm} (17)

Where the ionization reaction is

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$  \hspace{1cm} (18)

Since the $H^+$ in $H_2SO_4$ has reaction coefficient 2, the calculation of $C$ becomes:
Theoretically, reaction rate constant can be affected by temperature and the amount of CaCO$_3$ in reaction. Moreover, the form of CaCO$_3$ in the reaction affects the rate constant. When the temperature is raised, reaction rate raises as well. Temperature in reaction effects in increasing reaction energy. The increasing energy determined as kinetic energy which is a required energy to collision. Collision can happen if every particle has enough energy to collide each other until it creates reaction. Powder has bigger surface area because the form of the particle is small and in big scale, particle will be arranged closely so the collision happens faster. The graphs of the results in each temperature are shown in these following figures. The result graph at 24°C is shown in Figure 3.

**Figure 3.** Line graph of reaction between H$_2$SO$_4$ solvent and CaCO$_3$ at 24 °C.

The result graph at 35°C is shown in Figure 4.

**Figure 4.** Line graph of reaction between H$_2$SO$_4$ solvent and CaCO$_3$ at 35 °C.
The result graph at 43°C is shown in Figure 5.

![Figure 5. Line graph of reaction between H$_2$SO$_4$ solvent and CaCO$_3$ at 43 °C.](image)

The result graph at 50°C is shown in Figure 6.

![Figure 6. Line graph of reaction between H$_2$SO$_4$ solvent and CaCO$_3$ at 50 °C.](image)

From Table 3., the final pH in each experiment can be gained. According to it, the increasing value of temperature and mass effect the pH level. The average gradient in each temperature is shown in Table 4.
Table 3. Final pH and time range in experiments.

| Temperature (°C) | Mass (g) | Final pH | Time Range (s) |
|------------------|----------|----------|----------------|
| 24               | 5        | 4.8      | 70             |
|                  | 8        | 5.3      | 40             |
|                  | 10       | 5.5      | 30             |
| 35               | 5        | 2        | 40             |
|                  | 8        | 5.1      | 20             |
|                  | 10       | 5        | 20             |
| 43               | 5        | 5        | 70             |
|                  | 8        | 4.9      | 30             |
|                  | 10       | 5        | 30             |
|                  | 12       | 5.1      | 20             |
| 50               | 8        | 4.9      | 40             |
|                  | 10       | 5.2      | 20             |
|                  | 12       | 5.5      | 20             |

Table 4. Average gradient in each temperature.

| Temperature (°C) | Average Gradient |
|------------------|------------------|
| 24               | 0.226            |
| 35               | 0.33             |
| 43               | 0.433            |
| 50               | 0.388            |

Gradient in trend line expressed $k$ value. As in equation (13), the average gradient will be modified in form of natural logarithm (ln). The calculation of reaction rate constant can be obtained by finding the linear trendline equation between $\ln k$ and $1/RT$ where the temperature should be changed in form of Kelvin. The trendline between $\ln k$ and $1/RT$ is shown in Figure 7.

**Figure 7.** Line chart of determination of reaction rate from 4 temperatures.
From Figure 7, can be known the constant equation.

\[ y = -18.515x + 6.0692 \]  \hspace{1cm} (20)

From the equation (20), the value of \( E_a \) is 18.515 J/mol and \( A \) is value of \( \ln(6.0692) \) which is 1.8. The calculation becomes:

\[
k = 18.515 \frac{J}{\text{gmol}} \exp\left[-1.8\left(\frac{8.314}{\text{gmol} \cdot T}\right)\right]
\]  \hspace{1cm} (21)

Based on the experiment, the reaction rate constant as in equation (21) is obtained so the value of \( k \) can be determined in any temperature as shown in Table 5.

| Temperature (°C) | Reaction Rate Constant |
|------------------|------------------------|
| 25               | 1.786605378            |
| 30               | 1.786825491            |
| 35               | 1.787038488            |
| 40               | 1.787244706            |
| 45               | 1.787444466            |
| 50               | 1.787638065            |
| 55               | 1.787825785            |
| 60               | 1.788007889            |
| 65               | 1.788184625            |
| 70               | 1.788356227            |
| 75               | 1.788522916            |
| 80               | 1.7886849              |
| 85               | 1.788842376            |
| 90               | 1.788995528            |
| 95               | 1.789144533            |
| 100              | 1.789289556            |

5. Conclusion
Based on the experiment, as the temperature gets higher, the value of \( k \) will increase. As adding higher amount of CaCO₃, the value of \( k \) will increase as well. It is proven in the experiment, while adding 12 grams of CaCO₃ in the reaction, the pH level increases in short period of time. The result of the research is the value of \( E_a \) is 18.515 J/mol and the value of \( A \) is 1.8. Determination of reaction rate constant in a reaction between H₂SO₄ and CaCO₃ powder in various temperature can be obtained.

The value of \( k \) and \( E_a \) in reaction between H₂SO₄ and CaCO₃ is fixed for every kind of form and situation, however the value of \( A \) should be adjusted to the form of the particle that is used. This research uses powder particle so the value of \( A \) in this research is a fixed value for reaction with CaCO₃ powder. In order to know the value of \( A \) in another form, another experiment is needed [13].
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