# Improved Energy Harvest Potential from Highly Corrosive Geothermal Fields: Laboratory Formulation Developments

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## ABSTRACT

To meet the urgent demands of Taiwan's energy diversified governmental policy by 2025, we take on the endeavor of expanding the exploitation operations focusing on screening potential geothermal resources across whole region. Numerous examples of the acidic conditions of geothermal fluid observed exhibit presence of extremely corrosive fluids (pH < 2) at the sites investigated; thus, any attempt of building full-scale power plant and whole project would be cost prohibited under such harsh conditions. To alleviate some of these unique challenges, we explored the potential of developing injective amendments and formulations targeting for the production wells, aiming to effectively neutralize extreme acidity of geothermal fluids in-situ to allow better transport of hot fluid while provide reliable power generation and safe plant operations.

We have successfully developed several potential formulations indicating some unique characteristics as, 1. reasonable chemical dosage (0.5 to 2.3 wt%), 2. rapid reaction rate (between minutes to few hours), 3. elevated temperature activated (reactions occurred only after reach the threshold level), 4. safe chemicals and low cost, 5. minimum or no scaling formation or line plugging concern (unlike simple alkaline case).

Results of this study reveal the newly developed formulations can be easily adapted to a variety of fields inherited with strong to extreme acidic geothermal fluid conditions. And they demonstrated superior performance in modifying acidic geothermal water to weak acid or neutral, and the post treated samples showed no sign of scaling after few weeks or extended period. We anticipated the improved chemicals offer great potential to mitigate the excessive damages caused by acid erosion of the pipelines and generators, while reduce the maintenance costs of pipes and machinery. Further investigations are underway to verify the effectiveness of these formulations for a variety of geothermal fluids retrieved from sites under different site-specific conditions to collect additional engineering data for the planned field pilot test.

## 1. INTRODUCTION

Located at the junction of the Eurasian Plate and the Philippine Sea Plate in western Pacific, Taiwan possesses quite abundant in geothermal resources because the strata are squeezed by these two distinct plates historically. Recently, due to the rapid developments of various industries and sectors, the demands for electricity usage have grown increasingly yearly, and sometimes caused power shortage concern during peak consumption period as extreme weathers occur more frequently. In order to maintain the healthy economic growth and meet the government's sustainable energy policy standards for the coming decades, these geothermal resources become an indispensable source of future energy supply and important piece of the solutions for filling up some of Taiwan's current energy gap.

The territory of Taiwan is comprised of a series of islands rich in different hot spring resources, with more than 100 hot springs locations been identified and recorded previously, yet only two geothermal power plants were successfully built (Lee, 2022) to date; which also indicates that Taiwan's geothermal potential has mostly yet to be fully explored. Based on the latest geothermal related studies in Taiwan, the geothermal systems observed can be mainly categorized into two types: either igneous systems or metamorphic rock systems. Among these, the igneous system resources are derived originally from various volcanic activities, which triggered the intrusion of igneous rocks penetrated upwardly into the earth formation of shallow depth, and then effectively and frequently released significant amount of thermal energy. Thus, the characteristics of the igneous system are largely reflected by their higher formation temperatures. As a result, the retrieved underground fluids near this type of geothermal resource are mainly superheated steam and also possess greater power generation potential. However, a lot of volcanic activities are often accompanied with production of various acidic compounds such as sulfur dioxide and other anionic species present in solution. And some of the adverse operational issues regarding the pipeline acid erosion due to these corrosive compounds should be carefully assessed and resolved prior to proper implementation of energy installation based on this particular type of geothermal resource.

According to the recent reports documented by the Taiwan Institute of Industry and the research resulted from the National Energy Project phase I and II in Taiwan, the site distribution of geothermal resources in Taiwan can be divided into nine main regions (indicated in Figure 1). The power generation potential from these nine major geothermal resource areas is estimated to a total of 32,340 MWe; of which the geothermal potential from the Datun (or also known as Tatun) (or Area I near the northern part of the Island) volcanic area accounts for 6% of the total geothermal power generation potential of Taiwan (about 2075 MWe) (Lee et al., 2022).


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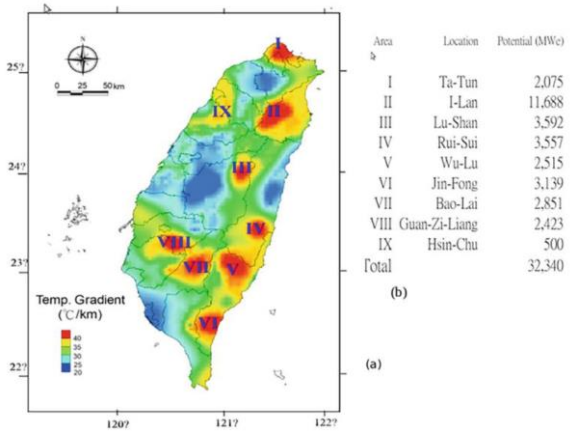


**Figure 1: Distribution map of major geothermal potential Field in Taiwan (Lee et al., 2022)**

Due to the unique location of the Datun Mountain geothermal field situated at close proximity to the Capital, city of Taipei, a densely populated metropolitan area, the future development of a highly efficient geothermal-based power plant site will be of great beneficial to the power supply and crucial needs in northern region of Taiwan. Since the Datun Mountain geothermal field belongs to a classical volcanic and igneous geothermal resource, data indicated that acid erosion from the hot fluid would be severe and is one of the foremost challenges that must be overcome when executing the developing plan of geothermal resources near this region.

For example, based on the results of surface fluid samples collected from the Datun Mountain thermal area recorded in the literatures (Liu, et al., 2011; Liao, 2019), the range of pH values of geothermal water in this area is between -0.7 to 7.4. Among those sampling locations, the extreme strong acidic, pH <1, fluid samples retrieved from the Da-You-Keng (DYK) site is speculated to be originated from the cooling and mixing of different volcanic fluids and sources.

According to the classification of geothermal fluid sources, the geothermal fluids of Datun Mountain can be conveniently divided into three groups: 1. Acidic sulfate springs ($SO_4^{2-}$ >>$Cl^-$); 2. Neutral bicarbonate spring (increased pH due to neutralization of Andesite during volcanic geothermal acidic fluid migration); and 3. Acidic sulfate chloride spring ($Cl^-$ >>$SO_4^{2-}$) (Liu et al., 2011).

In addressing the corrosive issues of acid geothermal fluids at the target Datun site, in addition to replacing with the acid resistance of pipeline materials (an expensive option), proper use of reagents to adjust the pH of acid geothermal fluids may also be a viable approach that has been discussed and considered in the literatures (Akazawa and Itoi, 2009; Magaly et al., 2010; Díez et al., 2015). Among these prior investigations, sodium carbonate is an example of reagent frequently suggested for acid-base neutralization. When sodium bicarbonate is applied to geothermal wells, it tends to precipitate the divalent cations and cause problems such as pipeline blockage.

For oil and gas industry, others had suggested various alternatives of alkali (a pH-elevation amendment) for improved oil recovery operations (Rudin and Wasan , 1993; Sharma et al, 2015; Southwick et al, 2016). To overcome the scaling issues while raising the solution pH, some have reported ammonium (or aqueous $NH_4OH$) is a much better and safe alternative (than NaOH and $Na_2CO_3$) to mitigate the scaling and permeability damages due to the occurrence of precipitates (Southwick et al, 2016). As compared to mature and larger oil industry community, much less efforts were specifically focused on use of alkalis for geothermal resources and applications previously.

In addition, when oil extraction is carried out in highly complex oil sands field, Flury's research notes that addition of ammonium hydroxide is more effective at improving quality and increasing production than sodium hydroxide (Flury et al., 2013).

The primary aim of this study is to develop viable formulations to solve the common problem of precipitation of existing compositions in acid geothermal fluids while proper executing pH adjustment operations. Specifically, this study will target the acidic sulfate springs site and conditions near the potential geothermal field of Datun Mountain and hopefully offer the viable alternative chemical for further testing and investigation of the future plan of building the geothermal power plant at this region.

## 2. EXPERIMENTAL DESIGN

Acid sulfate springs contain a large number of sulfate ions, resulting in low pH in water, and as previously mentioned in the literature (Liu et al., 2011; Dobson et al., 2018), the pH value of this type of geothermal water may sometimes even be less than 1.

Since the sulfate ion of the target fluid of this study is the dominant component of geothermal fluid, this study uses concentrated sulfuric acid (95%-97%) and deionized water for preparation of stock solutions, and then adjusts the pH value of the solution to pH =1 as the mimic acidic geothermal fluid for the chemicals tested in this effort.

In this study, three reagent candidates were chosen and studied for acid-base neutralization tests of mimic acidic geothermal fluid. In terms of testing standards and the performance criteria, this study conveniently preset the difference between the pH value between pre- and post-chemical treatments, and the resulted solution should be greater than or equal to pH = 4; as well as no occurrence of sediments or precipitates settled out as meeting the target criteria of success. To streamline and conduct the screening of the optimal chemical concentrations required in the mimic acidic geothermal fluid, we have adopted the experimental flowchart (figure 2) and procedures as briefly listed below:

1. Prepare the stock solution of mimic acidic geothermal fluid using concentrated sulfuric acid (95-97%) and deionized water
2. Measure the pre-determined weights of the chemical used for treatment
3. Mix the chemical and the mimic acidic geothermal fluid with stirring bar in the reactor
4. Detect the pH of the well mixed and pre-heated fluid
5. Placed the mixed solution in an autoclave (a Parr bomb reactor) and maintained in a fixed temperature of 100-degree C oven for at least 24 hours to simulate the pre-set geo-field environment.


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6. Removed and observed the post heated fluid samples for any sign of presence of sediments or precipitates. And recorded the final solution pH value

7. If there appears absence of sediment and the resulted pH value in solution is greater than or equal to 4, the experiment is deemed successful and further testing will be executed; otherwise, repeated and returned to the second step to re-adjust the dose of the chemical added and recorded the test results and decided go-or-no-go for the recipes.

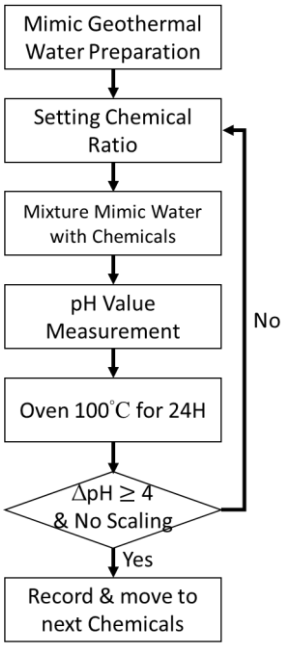


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**Figure 2: Flowchart of the neutralization test of mimic acidic geothermal fluid**

## 3. RESULTS

In this study, three chemicals that are potential alkalis in water were selected for experimental work, namely Ammonium Carbonate, Industrial Grade Ammonium Carbonate (Mixture of Ammonium bicarbonate and Ammonium carbamate) and Urea. Others had suggested use of urea for in-situ EOR applications, but no geothermal application and pH-amendment was referred in those work (for example, Wang et al, 2018; 2019). Since the compositions of these three chemicals are quite simple, and the composition of mimic geothermal fluid is mainly sulfuric acid, the reaction equation formed by these three chemicals and sulfuric acid can be written and briefly described as follows:

A. Ammonium Carbonate + Sulfuric Acid：

$$(NH_4)_2CO_3 + H_2SO_4 + H_2O \leftrightarrow (NH_4)_2SO_4 + CO_2 + 2H_2O$$

B. Industrial Grade Ammonium Carbonate (Mixture of Ammonium bicarbonate and Ammonium carbamate) + Sulfuric Acid：

$$2NH_4HCO_3NH_2COONH_4 + 3H_2SO_4 \leftrightarrow 3(NH_4)_2SO_4 + 4CO_2 + 2H_2$$

C. Urea + Sulfuric Acid：

$$CO(NH_2)_2 + H_2SO_4 + H_2O \leftrightarrow (NH_4)_2SO_4 + CO_2$$

From the above equations, it can be observed that the dominant products of these three reagents and sulfuric acid are quite similar after various chemical reactions and decompositions. However, the kinetics and the rates of various reactions involved (dissociation, hydrolyses, and neutralization) associated with individual compound could be distinctly different. The carbon dioxide generated after the neutralization and other complex reactions can also be partially channeled to facilitate the gas lifting step and processes while pumping the geothermal fluid to the surface. And the dissolved ammonium sulfate in the produced fluid can further be processed to serve as the source material for other uses such as the manufacture of agricultural fertilizers. Therefore, if the proposed formulations and mechanisms can be verified experimentally, the advance of this modification may offer a viable alternative to effectively solve the corrosion problem of acidic geothermal fluid in the field.

In order to avoid the harm of reaction products to the human body, this study also conducted its safety search on Ammonia and Ammonium Hydroxide, which mainly are created as a result of these chemical reactions, and the product ammonium sulfate. And it was basically shown that Ammonia and Ammonium Hydroxide can be safely used as pH adjusters in cosmetics (Johnson, 2018.). In addition, the report of the Japan Food Safety Commission pointed out that Ammonium sulfates can be applied to the products of food additives (Food Safety Commission of Japan, 2019), so this study considers these chemicals to be extremely harmless toward humans, environment and other ecosystems.

### 3.1 Urea

In the case of urea experiments, we designed and screened a series of 7 different percentage mixtures based on net weight concentrations, including 0.1%, 0.5%, 0.66%, 0.86%, 0.9%, 0.95%, and 1%. The results of post neutralization are listed in the following table:

**Table 1: Neutralization test results of urea with different weight percent concentrations versus mimic acidic geothermal fluid.**

| | 0.1% | 0.5% | 0.66% | 0.86% |
|---|---|---|---|---|
| Initial pH | 1.01 | 1.00 | 0.97 | 1.45 |
| Mixture before heating | 1.1 | 1.04 | 1.06 | 1.65 |
| Mixture after heating | 1.36 | 1.99 | 2.4 | 3.83 |
| ΔpH | 0.35 | 0.99 | 1.43 | 2.38 |
| | 0.9% | 0.95% | 1% | |
| Initial pH | 1.01 | 0.97 | 0.99 | |
| Mixture before heating | 1.07 | 1.03 | 1.12 | |
| Mixture after heating | 6.64 | 7.2 | 7.71 | |


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| | | | |
|---|---|---|---|
| ΔpH | 5.63 | 6.23 | 6.72 |

The results of the experiment using urea for the neutralization of mimic acidic geothermal fluid showed that, there was no obvious pH value change when urea was mixed with mimic acidic geothermal fluid at room temperature. And after uniformly stirring, the mixed solution was transparent and colorless, and there was no precipitation and bubble generation in all samples. After 24 hours of heating and equilibration in the oven, it appeared that there are some bubbles released and detected in the extracted sample solutions, and there is no occurrence of precipitation observed in all cases. Evolution of bubbles in these mixed fluids, presumably are due to gaseous carbon dioxide produced through hydrolysis and other reactions between urea and sulfuric acid. After heating and equilibration with addition of urea, a distinct change in the pH value of the mixed fluid would be realized and detected above certain urea concentrations been added. The results of the experiment showed that in order to achieve the tentative pH value criteria set for this work, the required urea concentration in the mixed solution must be higher than 0.9% (weight percentage).

The resulted graph of the pH difference (ΔpH) against total weight percentage of urea (figure 3) depicts that when the urea concentration is less than 0.86%, the pH value of the mixture of acidic geothermal fluids has no change. When the urea concentration exceeds beyond 0.86% and approaches 0.9%, the final pH value of the mimic acidic geothermal water mixture rises drastically to near neutrality. Therefore, this study reveals that when the concentration of urea used is between 0.86% and 0.9%, there will be a critical threshold concentration value; and this is equal to the minimum amount of urea can be used to accomplish the goal of modifying the mimic acidic geothermal fluid to the target higher pH level.

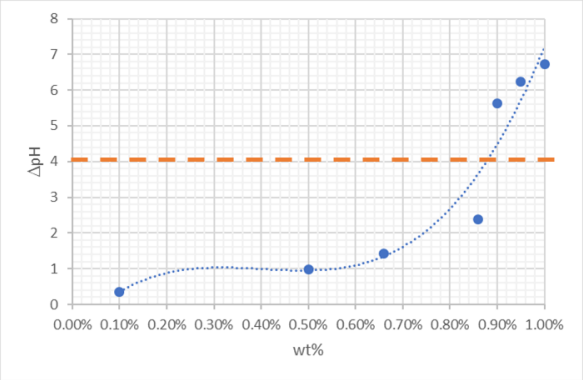


**Figure 3: pH difference varies with the percent concentration of urea by weight in the mixed solution.**

### 3.2 Industrial Grade Ammonium Carbonate (mixture of ammonium bicarbonate and ammonium carbamate)

The results of the experiment using urea in this study show that the neutralization of acid geothermal fluids by amine-based compounds appears quite well. Therefore, we further expand this effort and also looks for other possible candidates of amino compounds for similar testing and function. Among the chemical options of this study, industrial grade ammonium carbonate (mixture of ammonium bicarbonate and ammonium carbamate) is another example of easily available amino-based compound; so, in this section, similar neutralization tests of mimic acidic geothermal fluid will be carried out with industrial ammonium carbonate as another separate group of agents.

**Table 2: Neutralization test results of industrial grade ammonium carbonate with different weight percent concentrations versus mimic acidic geothermal fluid.**

| | 1% | 1.5% | 2% | 2.5% |
|---|---|---|---|---|
| Initial pH | 1.02 | 0.91 | 1.02 | 1.5 |
| Mixture before heating | 1.6 | 1.3 | 1.12 | 6.43 |
| Mixture after heating | 1.88 | 1.81 | 1.78 | 8.42 |
| ΔpH | 0.86 | 0.9 | 0.79 | 6.92 |
| | 3% | 5% | 10% | |
| Initial pH | 1.25 | 1.05 | 1.06 | |
| Mixture before heating | 6.55 | 8.5 | 7.49 | |
| Mixture after heating | 8.52 | 8.5 | 9.16 | |
| ΔpH | 7.27 | 7.45 | 8.1 | |

According to the test results of industrial grade ammonium carbonate and mimic acidic geothermal fluid (Table 2), shortly after mixing industrial grade ammonium carbonate with mimic acidic geothermal fluid, a large number of bubbles were produced in the mixed solution, and no precipitate was detected visually. After mixing at room temperature, the pH value became changing dramatically at certain range of concentration (greater than 2%). Both phenomena detected in (industrial grade) ammonium carbonate were distinctly different as in the case of urea. After heated by the oven and equilibration, there was still no sign of precipitation in the mixed solution, and the pH value of the measured mixed solution would increase further again in some cases.

From the experimental analysis results of industrial grade ammonium carbonate and mimic acidic geothermal fluid (figure 4), it is shown that industrial grade ammonium carbonate might involve two steps of processes, and would trigger a secondary reaction once thermally heated. In Figure 4, the square dot is the change in pH of the mixture before it is placed in the oven (or at room temperature of 22 °C), and the round dot is the change in pH value when it is placed in the oven for 24-hr equilibration. According to these data, heating process will be helpful to further increase the pH value of the mixture of industrial grade ammonium carbonate and acidic geothermal fluid


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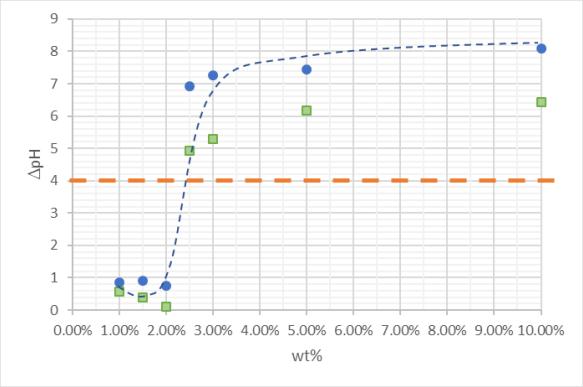


**Figure 4: pH difference varies with the percent concentration of industrial grade ammonium carbonate by weight in the mixed solution before heating (square dot) and after heating (round dot).**

In the experimental result plot (figure 4) of industrial grade ammonium carbonate and acidic geothermal water, it can be expected that there is a critical weight percentage concentration between 2% and 2.5% by weight, and the mimic acidic geothermal water will be modified to the target value.

### 3.3 Ammonium carbonate

In addition to using industrial-grade ammonium carbonate, similar experiments were performed using pure ammonium carbonate (reagent grade). Results from the previous case of industrial-grade ammonium carbonate show that the percentage concentration of effective drug by weight ranges from 2-2.5%. Therefore, we designed three different concentrations of pure ammonium carbonate experiments, namely 1%, 2.3% and 2.5%, and the experimental results are shown in the following table:

**Table 3: Neutralization test results of carbonate with different weight percent concentrations versus mimic acidic geothermal fluid.**

| | 1% | 2.3% | 2.5% |
|---|---|---|---|
| Initial pH | 1.01 | 0.98 | 0.95 |
| Mixture before heating | 1.38 | 5.85 | 6.33 |
| Mixture after heating | 1.63 | 7.87 | 8.15 |
| ΔpH | 0.62 | 6.89 | 7.20 |

According to the experimental results, the applicable concentration range of pure ammonium carbonate and industrial grade ammonium carbonate for mimic acidic geothermal fluid is similar. The scope of application of industrial grade ammonium carbonate is between 2% and 2.5%, and pure ammonium carbonate is slightly lower, between 1 and 2.3%.

In addition to the similar range of applicable concentrations of chemicals, another similarity between pure ammonium carbonate and industrial grade ammonium carbonate is the two-stage neutralization reaction. When mixing ammonium carbonate with mimic geothermal fluid, the distinct formation of bubbles in the mixed solution rapidly can be clearly observed, and this study speculates that significant amounts of carbon dioxide produced shortly after the neutralization reaction is initiated. When the pH value of the mixed solution is measured using a pH meter, a large change in pH value can be observed at a specific concentration. After the mixed solution is placed in the oven for heating, the same as industrial grade ammonium carbonate, there will be a second change (jump) in the pH levels.

It should be noted that one common reaction product of using these three reagents is ammonium ion ($NH_4^+$). The safety of this ion in solution (or produced fluid) is quite reasonable (see ammonium ion safety 2 articles listed). Though it is claimed to be quite safe, further investigations will be needed to validate this claim for re-injection or other industrial application while considering the spent geothermal fluids and their disposal and handling.

## 4. DISCUSSION

In addition to analyzing the effects of chemical concentration on mimic acidic geothermal fluid based on experimental results, this study also assesses the stoichiometry ratios theoretically to better analyze and discuss mathematical calculations.

In the discussion section, we will further use stoichiometry to perform acid-base neutralization calculations to compare the difference between the theoretical concentrations of various chemicals when performing experiments and their results, and to explore other possible sources of error.

### 4.1 Mimic Acidic Geothermal Fluid

In the preparation of mimic acidic geothermal fluids, we mixed and formulated with deionized water using experimental grade concentrated sulfuric acid (molecular formula is $H_2SO_4$ (98.08), concentrations between 95-97%).

In the experiments of this study, we first used titration to mix concentrated sulfuric acid with deionized water to prepare the mimic acidic geothermal water used in the study.

In the preparation of mimic acidic geothermal water, a total of 262.31 grams of deionized water and 2.85 grams of concentrated sulfuric acid are contained, and the pH value of the prepared mimic acid geothermal fluid is 1.

If the concentration of experimental grade concentrated sulfuric acid is assumed to be 96%, the sulfuric acid molecule of 2.79E-2 mole coexists in the 265.16 grams of mimic acidic geothermal fluid prepared.

### 4.2 Urea Stoichiometry Calculation

In order to use urea to neutralize the mimic acidic geothermal fluid prepared in section 4.1 using urea until the pH value is 5, the required urea dose is calculated as follows:

1. Assuming that the mixed fluid density is 1 and the volume after mixing is 30 ml, the $H^+$=3.0E-7mole present in the mixing fluid.

2. Assuming that the desired urea in the experiment is $x$ g, the urea in the solution is $\frac{x}{60.6}$ mole and the sulfuric acid is $\frac{1.03\times10^{-2}(30-x)}{98.08}$ mole

3. After combining the neutralization reaction equation of urea and sulfuric acid from the above


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equation, $x = 0.19$ g can be calculated (The urea weight percent concentration of the mixed solution is about 0.63%).

Comparing theoretical calculations with experimental results, it can be seen that the experimental results show that the weight percentage concentration of urea needs to be between 0.86-0.9%, while the theoretical calculation value is 0.63%.

This study speculates that the reasons for the error between experiment and theory include 1. the accuracy of experimental measuring instruments, 2. density assumption of the mix solution, 3. purity assumptions for chemicals, 4. Temperature vs. reaction kinetics when pH is measured.

### 4.3 Industrial Grade Ammonium Carbonate Stoichiometry Calculation

When performing stoichiometric calculations of industrial-grade ammonium carbonate, we use the calculation process established in section 4.2 for calculations. However, the molecular weight of industrial grade ammonium carbonate is 157.1, so it must be replaced with this value when calculating the mole number.

After theoretical calculations, it can be learned that when experimenting with industrial grade ammonium carbonate, the theoretically required industrial grade ammonium carbonate has a weight of 0.327 grams, that is, the weight percentage concentration of the mixed solution is 1%. However, the actual required percentage weight concentration obtained at the time of performing the experiment is between 2% -2.5%. This study speculates that the cause of this error is similar to that of urea experiments.

### 4.4 Ammonium Carbonate Stoichiometry Calculation

The same process was used in this study for the stoichiometric calculation of pure ammonium carbonate, but since the molecular weight of ammonium carbonate is 96.9, it is necessary to replace this molecular weight when calculating the mole number.

After theoretical calculations, it can be learned that the required weight of ammonium carbonate is 0.3 grams (theoretical weight concentration of 1%), and the result is similar to that of industrial grade ammonium carbonate.

The experimental results show that the concentration of ammonium carbonate (between 1% and 2.3%) required to perform the experiment is larger than the theoretical value, and this study also speculates that the reason for this error is the same as that of the urea experiment.

### 4.5 Comprehensive Discussion

The theoretical and experimental results of the three experimental chemicals used in this study indicate that the experimental measurement results are greater than the theoretical calculations. In the experiment of urea, the error is about 0.23-0.27%, and the error in the ammonium carbonate series (industrial grade and pure ammonium carbonate) is about 1-1.5%.

Exploring the causes of errors that may occur during experiments include 1. measurement errors caused by the instrument being measured; 2. error in the assumption of theoretical purity caused by the purity of the purchased chemical itself; 3. since the pH value is a volume-related measurement, the density must be used to correct the experimental calculation, and in the theoretical calculation, the density of this study is assumed to be 1, which may also cause theoretical calculation errors; 4. since the pH measurement will vary slightly due to the influence of temperature, when measuring, the pH may be incorrect due to the difference in room temperature.

From theoretical calculations and experimental results, the three chemicals found in this study can effectively adjust the pH value of mimic acidic geothermal fluid reaching the target value of this study in the state of no precipitation.

## 5. CONCLUSION

The following findings and conclusions could be drawn based on the experiments and reagents tested:

1. A total of three formulations (Urea, Industrial Grade Ammonium Carbonate, Ammonium Carbonate) were found to be capable to neutralize the acidic geothermal water without precipitation and to meet the expected targets set by the study (pH=5).

2. The results of the study show that addition of urea proceeds a significant neutralization reaction only reaching at elevated temperature, while ammonium carbonate series chemicals can have positive reactions and pH-adjustment even under room temperature.

3. Ammonium carbonate series chemicals will have a two-stage reaction when neutralization occurred, the first stage of neutralization reaction at room temperature, and the second stage is neutralized after heating step.

4. In this study, the comparison of experiments with theories using stoichiometry calculations shows that the experiments are distinctly greater than the theoretical values, and the reasons are speculated to be as follows: 1. the accuracy of experimental measuring instruments, 2. density assumption of the mix solution, 3. purity assumptions for chemicals, 4. Temperature vs. reaction kinetics when pH is measured.

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