Calculation and affection of pH value of different desulfurization and dehydration rates in the filling station based on Aspen Plus

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Abstract. The simulation process of the whole CNG filling station are established using Aspen Plus V7.2. The separator (Sep) was used to simulate the desulfurization and dehydration equipment in the gas station, and the flash module separator Flash 2 was used to simulate the gas storage well with proper temperature and environmental pressure. Furthermore, the sensitivity module was used to analyse the behaviour of the dehydration and desulfurization rate, and the residual pH value of the gas storage wells was between 2.2 and 3.3. The results indicated that the effect of water content on pH value is higher than that of hydrogen sulphide in the environment of gas storage wells, and the calculation process of the pH value is feasible. Additionally, the simulation process provides basic data for the subsequent anticorrosive mechanism and work of gas storage well and has great potential for practical applications.

1. Introduction
Trace amounts of hydrogen sulfide, carbon dioxide and water components in compressed natural gas can dissolve in each other in the process of storing in gas storage well which will form bottom hole liquid loading and causing corrosion of gas storage well, directly related to the safe operation of CNG (compressed natural gas) filling station [1]. As the domestic gas storage wells have are not been used for a long time, there are few studies on the corrosion status of practical use of gas storage wells. In 2010, Cen et al. introduced the corrosion research of abandoned gas storage wells by macrography, scanning electron microscopy (SEM) analysis and energy spectrum (EDX) analysis. But the author only pays attention to the damage and results of internal and external surface which caused by corrosion, and there are few research on the production and composition analysis of etching solution due to the special situation of the gas storage well [2].

Next years, with the increasingly extensive application of chemical simulation technology and the problem caused by hydrogen sulfide stress corrosion cracking (SCC) in the gas storage wells [3, 4], more researches should be done [5]. Thus, in this work, Aspen Plus software was used to establish a simulation process and the sensitivity analysis was utilized to obtain the solubility data of hydrogen sulfide and carbon dioxide with different desulfurization and dehydration conditions in water, and the pH of the mixture was also obtained. This study provides basic data for the corrosion mechanism and anticorrosion work of hydrogen sulfide stress corrosion cracking in gas storage well [3, 4].
2. Establishment of simulation process and material calculation

2.1. Establishment of simulation process

The simulation process of the whole CNG filling station established by Aspen Plus V7.2 is shown in figure 1. Separator (Sep) was used to simulate the desulfurization and dehydration equipment in the gas station, flash module separator Flash 2 was used to simulate the gas storage well with proper temperature of 283K and environmental pressure of 25MPa. As shown in figure 1, firstly, natural gas entered into the separator (B1) for desulfurization and exported to the compressor (B2), then entered the heat exchanger (B3) cooling and exported to the separator (B4) for dewatering, and finally entered the flash module (B5).

![Figure 1. Simulation process of CNG filling station.](image)

2.2. Operating conditions

Aspen Plus V7.2 software operating conditions are as follows: methane as the main component, with a small amount of hydrogen sulfide, carbon dioxide and water [6], feed temperature of 293K, pressure of 0.8MPa, volumetric flow rate of 1000m³/hr, the compressor (B2) output pressure of 25MPa, the heat exchanger output temperature of 293K, flash module operating conditions for 25MPa, 283K.

According to the mandatory national standard GB17820-2012 [6], in the situation of 0.1MPa, 293K, the hydrogen sulfide content in natural gas should be less than or equal to 20mg / m³, the carbon dioxide content should less than or equal to 3% in Mole, water dew point should lower 5K than the lowest atmosphere temperature. All of these are shown in table 1.

Because the gas state equation:

\[ V = nRT \]  \hspace{2cm} \text{(1)}
\[ P = \frac{nRT}{V} \]  \hspace{2cm} \text{(2)}

In the situation of 0.1MPa, 293K, Solution \( \rho \) (H₂S) = 1.1165kg / m³.

It is found that the hydrogen sulfide in the natural gas of 1000 m³ is 20g, that is 0.0143369 m³.

The water content of the natural gas is according to the water dew point 288K and GB/T 22634-2008 [7].

In the gas storage wells, the chemical reaction of \( H_2O-H_2S-CO_2 \) solution system is:

\[ H_2O + CO_2 \rightarrow H^+ + HCO_3^- \]  \hspace{2cm} \text{(3)}
\[ H_2S \rightarrow H^+ + HS^- \]  \hspace{2cm} \text{(4)}
\[ HCO_3^- \rightarrow H^+ + HS^- \]  \hspace{2cm} \text{(5)}
\[ HS^- \rightarrow H^+ + S^{2-} \]  \hspace{2cm} \text{(6)}
\[ CO_2 + OH^- \rightarrow HCO_3^- \]  \hspace{2cm} \text{(7)}

3. Results and discussion

The desulfurization rate and dewatering rate of the two separators are important parameters in this simulation, and they have a decisive correlation in the pH value of the residual solution.

At present, post-dewatering is usually used in the filling station, but due to the powdery caused by high pressure and the entrance of natural gas after the gasification of the lubricating oil in the compressor, the adhesion of adsorbent to the oil will lead to the decrease of the dehydration capacity. So, there is a replacement for about half a year and the performance of dehydration will gradually
deteriorate over time. As for more solid desulfurizing agent was used in the desulfurization equipment, the desulfurization agent will lose activity in the process of application. Therefore, different desulfurization rate and dehydration rate was used in this process to simulate the actual application process, which demonstrated that efficiency of desulfurization and dehydration equipment was reduced, so as to examine its impact on the gas storage equipment. In order to obtain different effects of desulfurization and dewatering rates for the pH value of the residual solution, the sensitivity module of Aspen Plus was used to analyze the sensitivity of these two parameters.

The pH values at different desulfurization rates and dehydration rates calculated from Aspen Plus are shown in Table 1. Corresponding to table 1, we can see that although the pH values at different dehydration and desulfurization rates are different, the overall pH value of the solution is in the range of 2.2 to 3.3. Moreover, analyzed by samples of the residual solution extracted from the gas storage well, the simulation value will be more accurate. As the dehydration rate remains constant, the desulfurization rate increases and the pH keeps rising. Accordingly, the desulfurization rate remains constant while, the rate of dehydration increases and the pH keeps rising with high speed.

Table 1. The pH values at different desulfurization rates and dehydration rates.

| Dehydration | 20%  | 30%  | 40%  | 50%  | 60%  | 70%  | 80%  |
|-------------|------|------|------|------|------|------|------|
| 20%         | 2.257| 2.416| 2.451| 2.661| 2.843| 3.082| 3.296|
| 30%         | 2.264| 2.423| 2.463| 2.676| 2.854| 3.089| 3.289|
| 40%         | 2.274| 2.431| 2.469| 2.685| 2.866| 3.071| 3.281|
| 50%         | 2.285| 2.440| 2.478| 2.698| 2.873| 3.064| 3.277|
| 60%         | 2.290| 2.451| 2.484| 2.706| 2.886| 3.075| 3.265|
| 70%         | 2.298| 2.456| 2.491| 2.711| 2.895| 3.079| 3.269|
| 80%         | 2.306| 2.461| 2.496| 2.724| 2.902| 3.086| 3.279|

Figure 2. The PH values at different desulfurization rates.
Figure 3. The pH values at different dehydration rates.

The pH values at different desulfurization rates and dehydration rates were shown in figure 2 and figure 3. As shown in figure 2, in the same desulfurization rate, with the increase of the dehydration rate, the pH value increases rapidly. According to figure 3, in the condition of different dehydration rates, the pH values of residual liquid with different desulfurization rates are similar and have minimal distinction. Comparing figure 2 with figure 3, it can be seen that the dehydration rate has a much greater effect on the pH value of the residual liquid than the desulfurization rate.

4. Conclusion
In this study, the simulation process of CNG filling station was established by Aspen Plus software, sensitivity function was used to analyze the sensitivity of pH value of residual liquid under different dehydration rate and desulfurization rate conditions. It concluded that the pH value of residual liquid in the gas storage well is as small as 2.2. Furthermore, by comparing the pH value of the residual solution in different desulfurization rate and different dehydration rate, it can be seen that the effect of the dehydration rate on the pH value in the gas storage as well as environment is much greater than the desulfurization rate. Therefore, in the actual production process of the gas station, the solid desulfurizer and dehydrating adsorbent in the desulfurization and dewatering equipment should be frequently regenerated and the interval of replacement should be reduced.

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