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Research on the Hydrate Formation in the process of Gas Phase CO_2 Pipeline Transportation

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ABSTRACT

With the development of the third oil recovery in oil fields and CO_2 capture, utilization and storage (CCUS) technology, CO_2 injection has become an effective means to enhance oil recovery (EOR) and relieve the greenhouse gas effect. The CO_2 pipeline transportation technology started relatively late in China, where the gas phase and liquid phase transportation are widely used methods. The CO_2 hydrate formation in the process of transportation may reduce the valve, destroy the equipment and even cause pipeline ice blockage, but research in China on CO_2 hydrate is not very extensive. In this paper, the CO_2 hydrate formation conditions were simulated using HYSYS, and the simulation results were compared with the experimental results to verify the feasibility of the simulation method. Based on this, factors in the influence of gas impurities on CO_2 hydrate formation are simulated, and the pipeline transportation process of CO_2 hydrate formation are predicted. The results show that when there is a low amount of impurity content, the gaseous impurities such as CH_4, N_2, H_2, O_2, have little effect on CO_2 hydrate formation in gaseous CO_2 pipeline transport. Furthermore, environmental temperature has little effect on the changes in pipeline pressure along the transport route. However, with a change in environment temperature, temperature along the pipeline changes greatly. CO_2 will change from a gas state to a liquid state in the pipeline when the ambient temperature is low. In the case of low ambient temperature, a thick insulation layer should be used, and heating of the pipeline may also be required. When the ambient temperature is higher than about 10℃, there will be no hydrates formed in the pipeline.

Keywords: Gaseous CO_2, Pipeline Transportation, Hydrate, HYSYS Simulation.

1. INTRODUCTION

The greenhouse effect and global warming are the focus of current energy and environmental issues, and great emphasis has been attached on the problem of reducing CO_2 emissions. Recently, research has strenghtened on CO_2 carbon capture, utilization and storage (CCUS), transportation and enhanced oil recovery technology in various countries globally [1-3]. For example, the Jiangsu FuMing area has applied natural carbon dioxide gas to oil exploitation and achieved great economic benefits and has improved the efficiency of oil recovery in the process [4]. China began to build the CO_2 long distance pipeline in the beginning of the 1970s, and the CO_2 was transported from the CO_2 gas fields and other gas sources (such as natural gas purification plants) to the corresponding oil field for the third exploitation to improve the oil recovery. It has been proved that there are abundant CO_2 resources and very large CO_2 consumption potential in China, but there is no practical experience of construction in China on a large-scale industrial CO_2 pipeline system. Furthermore, there is still a long way to go in the study of design, construction and operation of CO_2 in the long distance pipeline transportation system, and the related technology involved during the management are only in the initial stages compared with other countries [5]. The main delivery methods are the gas phase and the liquid phase in the process of CO_2 transportation in our country. Currently, there is much research globally on the hydrate experimental test, formation conditions and inhibiting methods of thermodynamics, and formation and decomposition dynamics of hydrate, but they are all mainly concentrated on the conventional natural gas hydrate research, eith little research results on CO_2 gas hydrate formation conditions. Therefore, it is necessary to carry out related research.

2. THE PHYSICAL PROPERTIES OF CO_2

CO_2 is a colorless and odorless gas which is soluble in water in normal conditions, and because it has a higher density air, the diffusion rate is slow, and it is in the form of a gas in normal temperature and pressure [6]. The phase state is divided into the following five regions: gas, general liquid, solid, dense phase and supercritical fluid. The triple point of CO_2 appears at -56℃ and 0.52 Mpa and the critical point appears at 31.4℃ and 7.38 MPa, as shown in Figure 1.

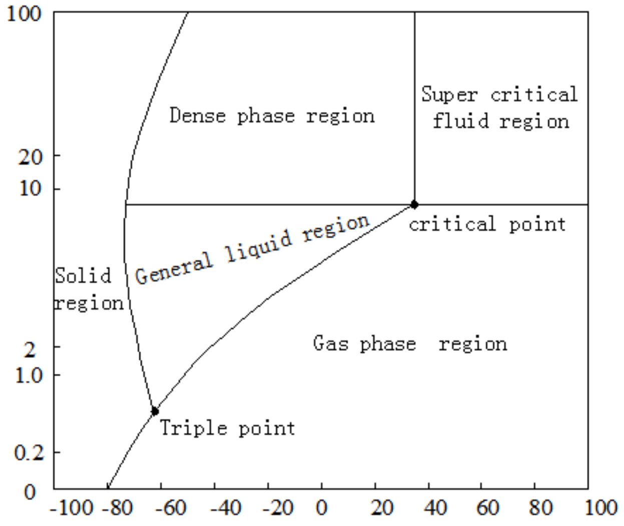

Figure 1. CO_2 phase diagram

CO_2 hydrate is a non-stoichiometric cage-type crystal compound produced by CO_2 gas and water under a certain temperature and pressure conditions. The density of hydrate is about 0.88-0.929/cm³.

If the hydrate forms in the pipeline, it will cause blockage in the pipeline, the transmission capacity to fall, increase the pipeline friction loss, damage the along conveyor equipment, and may even lead to pipeline failure.

Low temperature and high pressure are the two necessary conditions for hydrate formation [7-8]. Certain thermodynamic conditions are needed for the formation of CO_2 in the pipeline and the formation of free water is the necessary condition. The nucleation of hydrate will be continuously increased and form dense CO_2 hydrate, and thus blocking the pipeline.

3. FEASIBILITY ANALYSIS OF SIMULATION METHOD

3.1 The selection of state equation

HYSYS software was used to simulate the hydrate formation conditions of CO_2, and the P-R state equation was selected in the simulation process, which was proposed by Peng-Robinson in 1976.

$$p=\frac{RT}{V-b}-\frac{a(T)}{V(V+b)+b(V-b)} \tag{1}$$

$$a(T)=a(T_c)\alpha(T_r,\omega) \tag{2}$$

$$a(T_c)=0.45724\frac{R^2T_c^2}{p_c} \tag{3}$$

$$b=0.07780\frac{RT_c}{p_c} \tag{4}$$

$$\sqrt{\alpha}=1+m\left[1-\left(\frac{T}{T_c}\right)^{0.5}\right] \tag{5}$$

$$m=0.37464+1.54226\omega-0.26992\omega^2 \tag{6}$$

Type: p - system pressure, kPa.

V - molar volume, m³/mol.

R - universal gas constant, 8.3143kJ/ (kmol/ k).

p_c -critical pressure, kPa.

T - system temperature, K.

T_c - critical temperature, K.

T_r - contrast gas temperature; $T_r = T/T_c$.

ω - eccentric factor (the eccentric factor of CO_2 is 0.225).

3.2 Comparison of simulation results with experimental values

Hui Jian used the hydrate prediction experiment to conduct the hydrate prediction on different gas components. The experiment was conducted at the National Key Laboratory which named “Oil and Gas Reservoir Geology and Development Engineering” of Southwest Petroleum University. Isobaric cooling method was used to study the hydrate formation thermodynamic conditions in the process of the experiment [4]. In this paper, HYSYS software is used to simulate the corresponding working conditions, and the results are compared with the experimental results, as shown in Figure 2 and Table 1.

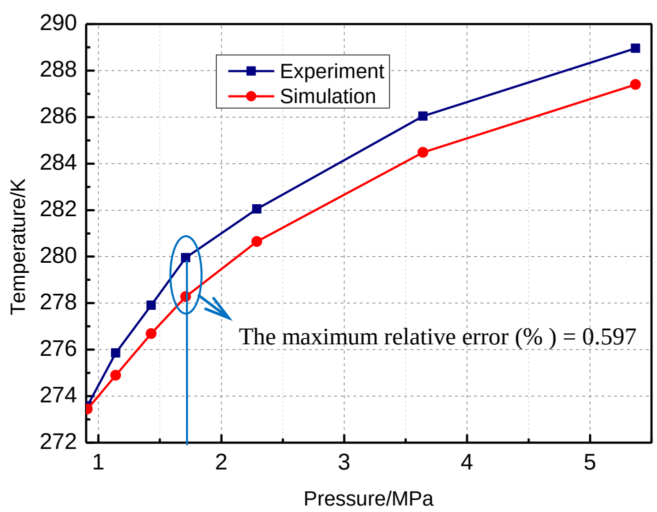

Figure 2. Formation temperature of hydrocarbon gas hydrate without CO_2

The formation temperature of hydrocarbon gas hydrate without CO_2 is shown in Figure 2. When the pressure range is between 0.91Mpa and 5.37Mpa, the maximum relative error rate between the experimental temperature and the simulated temperature is 0.597%.

Table 1. Mixed gas hydrate of CO_2 and CH_4 formation conditions

Experimental pressure/MPa	CO_2/%	Experimental temperature of hydrate/K	Simulated hydrate formation temperature /K	Relative error %
3.10	9	275.8	275.65	0.054
2.52	10	273.7	272.59	0.406
2.59	14	274.6	273.96	0.232
2.12	25	273.8	273.79	0.005
2.08	70	276.4	274.52	0.682
1.45	79	273.7	272.70	0.365
2.25	100	278.5	277.85	0.233

The conditions for the formation of mixed gas hydrate of CO_2 and CH_4 is shown in Table 1. When the pressure range is between 1.45 Mpa and 3.10 Mpa for different content of CO_2, the maximum relative error rate between the experimental temperature and the simulated temperature is 0.682%.

By analysis and comparison of the experimental data and simulation data above, it is shown that using the P-R state equation in HYSYS to simulate the formation of CO_2 hydrate is very feasible.

4. EFFECTS OF IMPURITIES ON THE HYDRATE FORMATION IN CO_2 GASEOUS TRANSPORTATION

The formation of hydrate in the CO_2 pipeline is similar to natural gas. CO_2 has some impurities such as CH_4, H_2S, N_2, Ar, O_2, H_2, and heavier hydrocarbons (C_2H_6 and C_3H_8, etc.) can also form hydrates [9-11]. Because the pressure in the process of CO_2 gas conveying is under 4.8 MPa, it therefore selects 4.5 MPa as the maximum pressure of the CO_2 hydrate formation conditions simulation. HYSYS software is used to simulate CO_2 hydrate formation conditions when several impurities are present such as CH_4, N_2, H_2, O_2 in the molar percentage of 0%, 5%, 10%, 15%, 20%. The simulation results are shown in Figures 3 to 6.

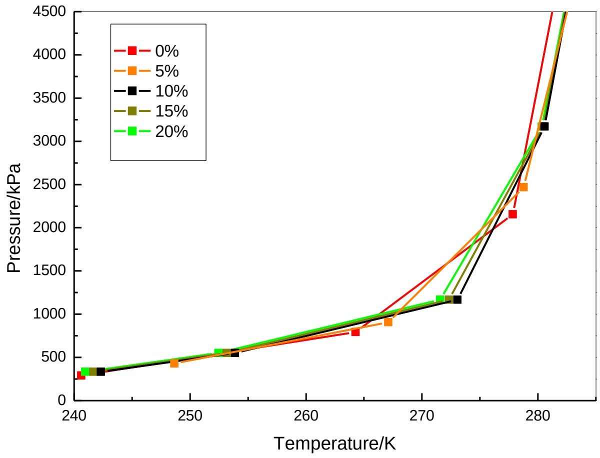

Figure 3. Effect of CH_4 content on the hydrate formation

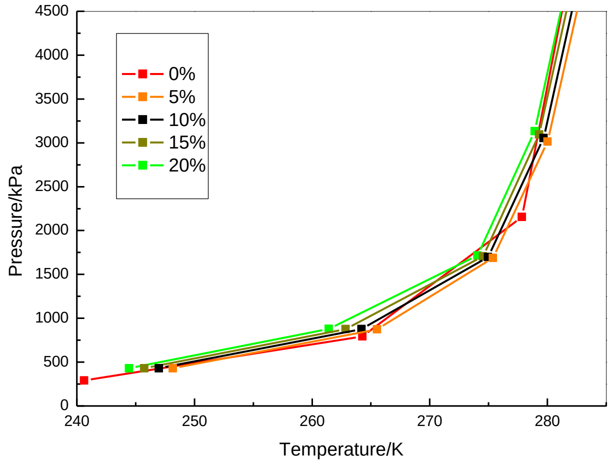

Figure 4. Effect of N_2 content on the hydrate formation

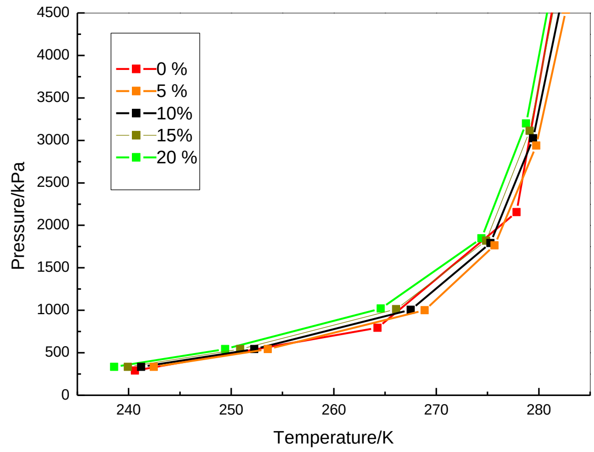

Figure 5. Effect of H_2 content on the hydrate formation

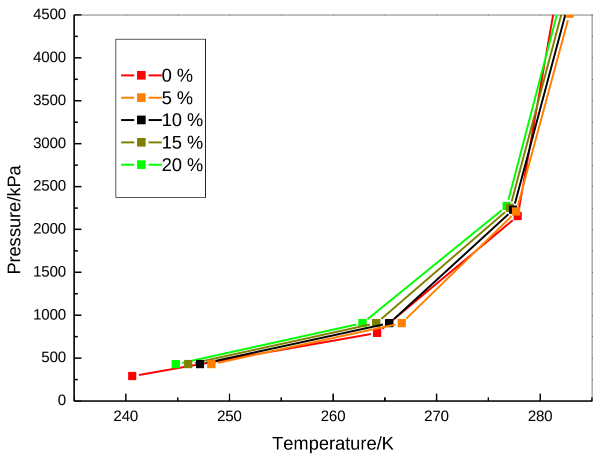

Figure 6. Effect of O_2 content on the hydrate formation

The above figures show that small amounts of impurities have little effect on the CO_2 hydrate formation. When the pipeline transport pressure is between 3.5Mpa and 4.5Mpa, a small amount of impurities will slightly increase the temperature at which CO_2 hydrate forms, and the CO_2 hydrate formation temperature is about 10℃.

5. SIMULATION OF GAS HYDRATE FORMATION IN GASEOUS CO_2 PIPELINE

Generally, there are three methods for transporting CO_2: tanker transportation, ship transportation, and pipeline transportation. The quantity of tanker transportation is small and the cost is the highest among the three kinds of transportation. It is suitable for short distances, small volumes and is commonly used in CO_2 flooding field experiments in small oil field. Ship transportation is applicable to the areas of the seas and rivers, and the CO_2 storage equipment must be able to bear high pressure and/or low temperature. Pipeline transportation is suitable for long distances, with a large capacity and stable flow of directional transmission with a low cost for the average unit of transportation. However, its initial investment is large and the pipeline operation and maintenance requires that the operators must have much experience. According to previous research and practical application, pipeline transportation is the best choice for large scale and long distance CO_2 transportation in both inland and offshore.

Pipeline transportation is the main way for transporting CO_2 and natural gas containing CO_2. The ways of pipeline transportation can be divided into gas phase, liquid phase and super critical transportation according to the phase of the medium. According to statistics, there are about 3100km CO_2 pipeline in the world, its total throughput reaches 44Mt/a, and super critical transmission technology is mainly used. The majority of CO_2 pipelines in the world are built in the western United States, and the total length is more than 2500km. Additionally, there is a total length of nearly 200km CO_2 pipelines in Canada, Norway and Turkey. The CO_2 pipeline transportation technology of China started relatively late and there is no mature long-distance transport pipeline. Only individual oil fields use the advantage of being close to CO_2 gas source point to transport CO_2. It uses gas or liquid pipeline to transport CO_2 into the injection well to improve the oil recovery, such as the Jiangsu oilfield and Jilin oilfield, etc.

Gas CO_2 pipeline transportation technology is shown in Figure. 7. CO_2 maintains the gas phase during the transportation, and its transmission pressure is increased by the compressor. Thermodynamic calculation is used to determine whether thick insulation is needed to be installed in pipeline. For CO2 gas wells, the extraction of gas is mainly in supercritical state. In order to meet the requirements of pipeline transportation, the gas must be throttled to reduce the pressure before entering the pipeline. In order to avoid getting into the supercritical state, the pressure cannot be too high when pressurizing CO_2 gas. Although the higher the initial pressure of the gas phase transportation, the lower the energy consumption, there are potential risks of phase transition when the gas transmission pressure is too high. For example, the maximum operating pressure for a low pressure gas pipeline should not exceed 4.8MPa in the alternative plans for SACROC carbon dioxide pipeline transportation in the United States [12].

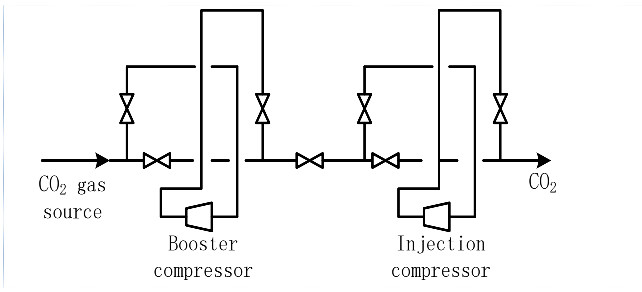

Figure 7. Gas CO_2 pipeline transportation technology

5.1 The simulation of parameters for CO_2 pipeline transportation in HYSYS

Selecting the parameters as shown in Tables 2 and 3 for pipeline transportation simulation.

Table 2. Physical parameters of gas

Component	CO_2	CH_4	N_2
Mole fraction/%	96.1%	3.5%	0.4%

Table 3. Transportation conditions of pipelines

Internal diameter/ mm	Wall thickness/m m	External diameter/m m	Total heat transfer coefficient/ $W/(m^2 \cdot ℃)$
365	6	377	1

The pipeline transportation of the HYSYS model is shown in Figure 8.

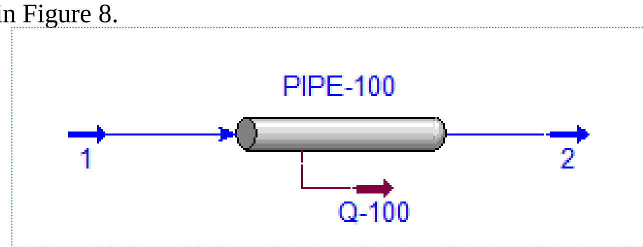

Figure 8. HYSYS model of pipeline transportation

5.2 Effect of ambient temperature on the formation of hydrate

In the process of transporting CO_2 through a pipeline, the environment temperature directly affects the temperature, pressure and the formation of CO_2 hydrate along the pipeline. By using HYSYS software, the change of each parameter in the process of CO_2 pipeline transmission under different operation conditions is simulated, as shown in Figures 9 to 12.

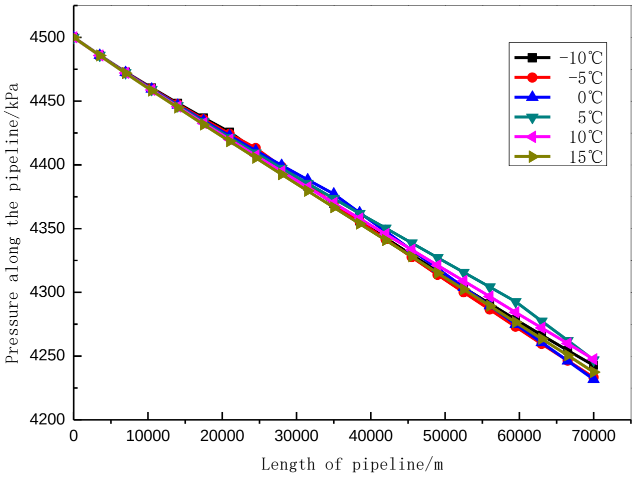

Figure 9. Pressure graph aong the length of the pipeline

From Figure 9, we can see that in the CO_2 gas transmission pipeline under the initial pressure of 4500MPa, without considering the influence of the elevation, the trend of the pressure along the pipeline is basically the same for different ambient temperatures. For a length of 70 km pipeline, outlet pressure is 4250Mpa.

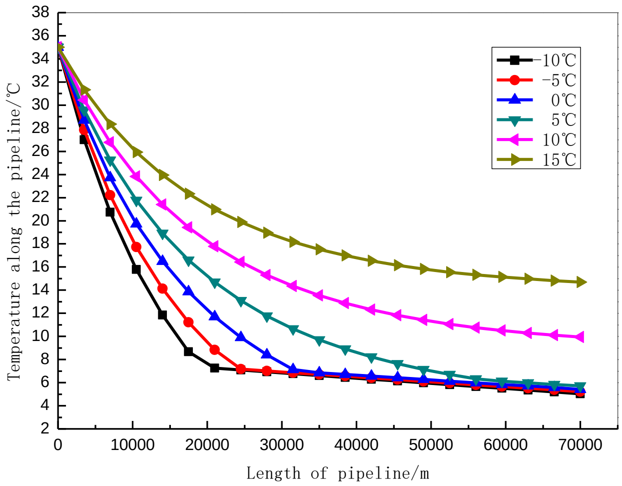

Figure 10. Temperature graph along the length of the pipeline

From Figure 10, we can see that in the CO_2 gas transmission pipeline at the initial temperature of 35 ℃, without considering the influence of heat level, temperature drops along the pipeline are strongly influenced by the ambient temperature. The lower the ambient temperature is, the greater the temperature drops along the pipeline. And when the ambient temperature is low, the phase change will occur in the pipeline; CO_2 changes from the gas state to the liquid state. Phase transition will increase the energy consumption during the process, and also will cause security risks. Therefore, in the case of low ambient temperature, the thickness of the insulation layer should be increased or heating equipment is required.

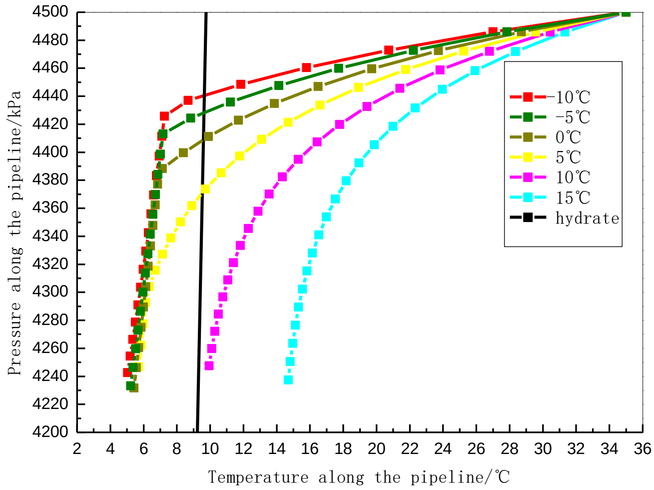

Figure 11. Generating point of hydrate along the pipeline

Figure 11 shows that when the ambient temperature is relatively low, the CO_2 hydrate will be generated in the process of transportation. When the ambient temperature is higher than 10°C, the hydrate will not be formed in the pipeline and the phase shift from gas to liquid will not occur. Therefore, there is no need to heat in the process of transportation when the environment temperature is higher than 10°C.

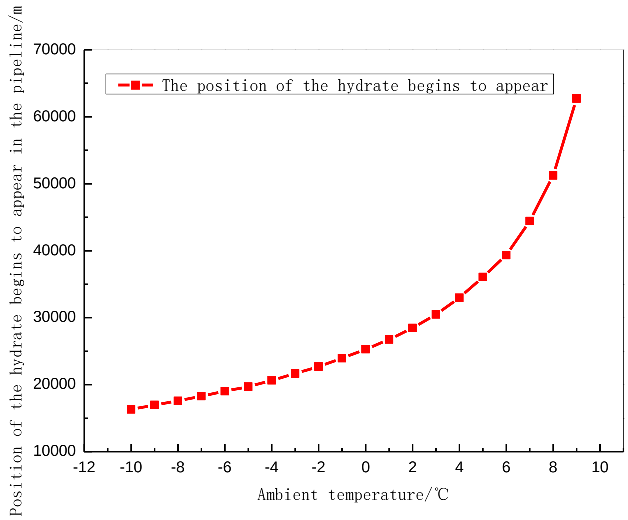

Figure 12. Relationship between ambient temperature and the location of the gas hydrate in the pipeline

Figure 12 shows that when the ambient temperature is relatively low, the hydrates will appear at about 16 km from the start of the pipeline. And when the ambient temperature is low, the position of the hydrates changes slowly with the environment temperature. When the ambient temperature is higher than about 4 °C, the position of the hydrates changes relatively fast with the environmental temperature. When the ambient temperature is higher than about 10°C, there will be no hydrates in the pipeline.

6. CONCLUSION

By comparing the experimental results with the simulation results of HYSYS, the feasibility of the HYSYS simulation has been demonstrated. Based on this, the influence of impurities on the formation of CO_2 hydrates and the various operation conditions in the process of CO_2 pipeline transportation are simulated. The following conclusions can be obtained:

(1) It is feasible to select P-R state equation to predict CO_2 hydrate in HYSYS.

(2) Gas impurities such as CH_4, N_2, H_2, O_2 and other gases have a small influence on the formation of CO_2 hydrates.

(3) In the process of gas CO_2 pipeline transportation, the ambient temperature has a small influence on the pressure of the pipeline. With a change in ambient temperature, the temperature along the pipeline changes greatly. CO_2 will change from a gas state to a liquid state when the ambient temperature is low. In the case of low ambient temperature, a thick layer of insulation should be used and heating of the pipeline may also be required. When the ambient temperature is higher than about 10℃, there will be no hydrates formed in the pipeline.

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