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Key Techniques of Super-critical CO_2 Pipeline Transportation

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Abstract

Carbon capture, utilization and storage (CCUS) has been globally recognized as an important technology for the large-scale reduction of CO_2 and pipeline transportation is the basis of this technology. For all the pipeline transportation technology, super-critical CO_2 pipeline is developing rapidly with its best economy and transporting efficiency and successfully applied in the actual operation in many countries. CO_2 pipeline transportation system is similar to the natural gas transportation system, but due to the particularity of CO_2, there are some special requirements on the pipeline design and operation.

Keywords: *CO_2, Pipeline, Super-critical, Transportation*

1. Introduction

With the propulsion work of CO_2 reduction in China, pipeline transportation has been the inevitable trend of long-term development using CO_2 and CCUS technology. Super-critical CO_2 has both the characteristics of gas phase and liquid phase, that is: liquid phase has large solubility for solutes and gas phase is easy to diffuse and movement, so in the process of pipeline transportation, its mass transfer rate is better than that of liquid phase transportation; because the CO_2 phase is susceptible to temperature and pressure, it's easy to appear the multiphase flow in the transportation process to cause erosion and super-critical transportation can avoid two-phase flow; at high pressure, CO_2 has large density and small viscosity, controlling pressure at 8.8~18.6MPa can keep a higher transportation efficiency, thereby reducing the diameter and improving the throughput. Therefore, in the large-scale, long-distance CO_2 transportation, super-critical CO_2 pipeline transportation is superior to other transportation mode on the economy and efficiency.

Combined with the special properties of CO_2 and the current pipeline construction environment in China, the super-critical CO2 pipeline construction in China needs to pay attention to the following key issues: the requirements of gas source components, the selection of routing, the special requirements of equipment and materials, *etc*.

2. The Impact of Gas Quality on Super-critical CO_2 Pipeline Transportation

Pipeline systems play an important role in transporting captured CO_2 to distant storage fields. Unfortunately, hydraulic and mechanical designs are very sensitive to the level of impurities contained in the CO_2 product stream. This will affect the limits in which the CO_2 pipeline can be operated safely [1].

2.1. The Influence of Impurities

Generally, CO_2 unavoidably contains CH_4, H_2O, N_2, H_2S and other impurities after

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purification treatment. These impurities will affect the phase behavior, the thermodynamics performance, viscosity of CO_2 and pipeline corrosion; some impurities may generate hydrates to block pipes and valves, destroy the equipment and even in some extreme cases, it may block the whole pipes; the impurities also have some effects on the pipeline fracture and fracture extension performance. As a result, it will affect the pipeline transportation ability [2]. Table 1 lists the influences of impurities in CO_2 on the pipeline transportation ability.

Table 1. The Influence of Impurities in CO_2 Pipeline Transportation

The impurities in CO_2	The pipeline transportation ability
CO_2	1.000
CO_2+5%CH_4	0.906
CO_2+10% CH_4	0.837
CO_2+5%N_2	0.874
CO_2+5%H_2	0.817

It can be seen from Table 1, with the increasing of the impurities in CO_2, the pipeline transportation capacity will be reduced. So the following introduces the influence of various impurities in super-critical CO_2 pipeline transportation:

1) The influences of CH_4. The presence of CH_4 will have various impacts. The CH_4 in CO_2 can add additional compression work. When pressure is high, it will also increase the pressure of CO_2 to form hydrate and the saturation vapor pressure of CO_2 to affect the selection of materials. At present, for the aquifer, the concentration of CH_4 limit is 4% and for EOR project, the concentration of CH_4 limit is 2%.

2) The influences of H_2S. H_2S has strong toxicity and even when exposed to a very small concentration, it also can produce huge harm to human body. So it is necessary to limit the H_2S in CO_2. The recommended use of CO_2 pipeline concentration is below 0.02%, but 0.02% can also change based on the differences of the construction environment, the population density and the technical requirements. For example, a CO2 pipeline in Weyburn containing 0.9% H2S is still running well [3]. H2S can form weak acid when dissolved in water causing corrosion to pipes and other equipment. It will make the structure of the material thickness and reduce the intensity and it will also reduce the critical tensile stress in the hydrogen induced cracking of the metal material, high strength steel is prone to SSC and low strength steel is prone to HTC or HB. In order to avoid corrosion caused by H2S and considering its economy, stainless steel pipes can be used in some key parts such as the compressor inlet section [4].

3) The influences of non-condensable gas. N_2, H_2 and Ar belong to the non-condensable gas. This gas reduces the available volume of the pipelines, consumes extra compression work in the process of CO_2 compression and also affects the CO_2 injection. Therefore, in the design and operation, their concentration is limited to 4%.

4) The influences of CO. CO is a flammable poisonous gas， it can combine with hemoglobin to make it lose the ability to carry oxygen and causes asphyxia. Therefore, its concentration is limited to 0.2% in the design and operation [5].

The existences of impurities have a great impact on CO_2 pipeline design and safe operation，limiting the impurity content is helpful to improve the transportation efficiency. When determining the super-critical CO_2 pipeline project, it must give full consideration to the effects of impurities and control the content of impurities, so as to eliminate the effects of impurities on the design and operation management of the pipeline system to improve the CO_2 pipelines transportation capacity.

2.2. The Influences of Water Content

The dry CO_2 have no corrosion to carbon steel, but when there is some free water in the pipelines, the corrosion rate of CO_2 would be very large. The reason is that when CO_2 exists in the pipes, it would trigger electrochemical reaction between carbon steel and water， under the same pH, the corrosion of carbon steel is greater than HCl [6]. CO_2 can react with water to form carbonic acid to cause corrosion to pipelines or equipment and it also can form hydrate to jam pipelines even destroy the equipment. So, before CO_2 enters into the pipelines, it must make dehydration processing.

The water solubility in pure CO_2 is shown in Figure 1.

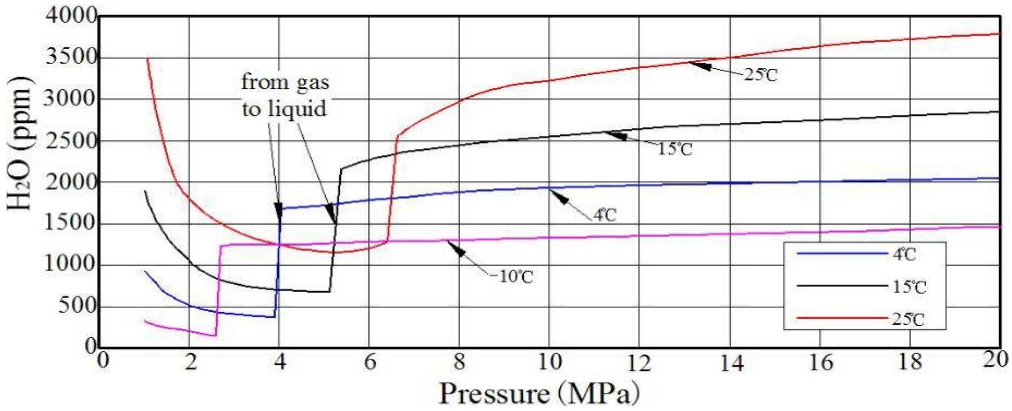

Figure 1. The Water Solubility in Pure CO_2

From Figure 1, it can be seen the range of water solubility in gas CO_2 is much smaller than it in liquid CO_2 and it can be known the trend of water solubility with temperature in CO_2, that is when CO_2 is gas, the water solubility decreases with the pressure increasing and when CO_2 phase state changes, the water solubility would increase significantly; when CO_2 is liquid, the water solubility increases with the pressure increasing [7].

Above all, the impurities and water not only affect the properties of super-critical CO_2 but also cause the pipeline corrosion, blockage and leakage *etc.*, then it would reduce the effective transportation capacity and service life of the pipelines. Therefore, the water content in CO_2 should be strictly controlled during the process of transportation.

3. Key Techniques of Super-critical CO_2 Pipeline Transportation

CO_2 transportation process mainly includes the pipeline frictional pressure drop calculation, choice of the optimal pipeline diameter, the method of inflating and determining the distance. Super-critical CO_2 pipeline transportation process is shown in Figure 2.

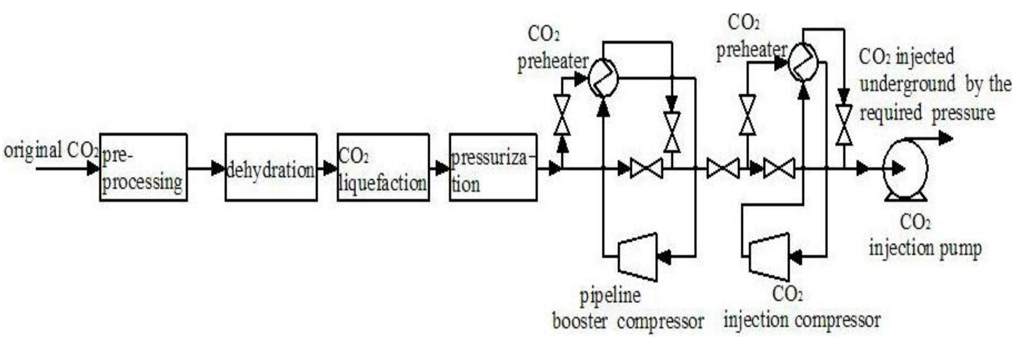

Figure 2. Super-critical CO_2 Pipeline Transportation Process

3.1. Dehydration and Purification Treatment

Under normal circumstances, as long as the water content is less than its solubility in super-critical CO_2, the corrosion rate of carbon steel is very small, but when the water in the super-critical CO_2 is more than its solubility in super-critical CO_2, the corrosion rate of carbon steel will increase rapidly. At present, in terms of CO_2 pipeline transportation, there is still no unified conclusion about the water content in the CO_2. But there is a general requirement of water content, that is: in the CO_2 transportation process, the concentration of water must meet there is no free water during the pipeline pressure and temperature range [8-9].

At present, there is no unified standard for the impurities in super-critical CO_2 in the international community. The requirements of mixed gases composition depend largely on the design of assessment, including the flow safety, pipeline integrity and security. Table 2 lists the Kinder Morgan used pipe specification [10].

Table 2. The Kinder Morgan used Pipe Specification

components	reference values	Limiting conditions
CO_2	95.000%	the minimum miscible pressure
N_2	4.000%	the minimum miscible pressure
hydrocarbons	5.000%	the minimum miscible pressure
H_20	0.0257%	corrosion
O_2	0.001%	corrosion
H_2S	0.001%~0.02%	health and safety
temperature	50℃	material limit

3.2. Key Techniques of Super-critical CO_2 Pipeline Transportation

In order to ensure the safety of CO_2 pipelines and reduce the operation cost, first of all it needs to maintain the stable and single super-critical phase during the transportation. However, the special properties of super-critical CO_2 and the impurities in CO_2 determine its pipeline transportation and the general oil and gas pipelines have larger differences, mainly for its special corrosion, leakage risk and the special requirements of pipe sealing material.

1) The super-critical CO_2 pipeline corrosion. The researches from Ohio State University show that: during the temperature and pressure of super-critical CO_2 pipeline operation, when there is some water in the pipelines and its pH can be 3 ~ 4, it will have very strong corrosion. Super-critical CO_2 is only 1/5 of the saturated water content and exists traces of O_2 and SO_2, the corrosion rate is 4 mm/a. When there are traces of NO_2 in super-critical CO_2, the corrosion rate is 12 mm/a. The CO in super-critical CO_2 will also accelerate the corrosion of carbon steel. So, further study of corrosion mechanism and control technology for super-critical CO_2 corrosion in the pipeline system is one of the important measures to reduce the pipeline leak risk [11-13].

2) The special requirements for sealing material. Super-critical CO_2 is excellent industrial solvent and its solvent increases with pressure and temperature. When pressure decreases and the CO_2 solubility decreases, it may precipitate out any substances that dissolved in the high pressure CO_2 pipelines. So super-critical CO_2 can destroy the artificial rubber sealing material and damage the pipe seat and then cause leaks. Therefore, the nonmetal sealing material for high pressure CO_2 pipelines shall have low permeability of CO_2, swelling resistance and degradation resistance; it can maintain flexibility in the process of operation at the same time. So, high hardness (hardness> 90) synthetic rubber is used to seal. In order to control the leak amount of pipeline burst accidents and

maintain conveniently, it usually arranges the line block valve chambers in the pipeline at intervals.

In addition, super-critical CO_2 pipeline pressure drop is larger, CO_2 is cooling rapidly in the process of decompression and to maintain the pipeline's pressure and temperature, it needs to design the insulation or heating along the pipelines to prevent phase behavior change in the process of transportation. The pipeline crack extension will be exacerbated when transports CO_2 by super-critical phase. It must take some corresponding measures to protect the pipelines, such as increasing the material notch toughness, reducing the operating pressure or using the mechanical control of crack extension [14-15].

4. The Requirements of Materials, Equipment and Routing Choice

4.1. The Requirements of Materials and Equipment

According to the operation experience of the CO_2 land pipelines in North America, it can be known the internal corrosion of pipelines failure mechanism was not found obviously. Analysis shows that this is mainly due to the water content is strictly controlled before CO_2 entering into the pipelines and strictly abide by the eliminating water system, thus, it is effective to avoid the internal corrosion of CO_2 pipeline. The main scheme to control corrosion is dehydrating CO_2 enough at the entrance of the pipeline, so for the better dehydration CO_2, it can choose carbon steel pipelines. At present, many countries have developed X80 steel, it's very suitable for CO_2 transportation. In addition, from an economic perspective, this steel is reasonable. However, when choosing carbon steel as CO_2 pipeline material, it needs to consider how to stop the ductile crack extension [16-17].

In the process of CO_2 transportation, the pressure may decrease, so some places need to increase the pressure, if so, there will need to set pressure equipment in the transportation. In general, for super-critical CO_2 transportation, it needs to use compressor to improve transportation pressure.

4.2. The Choice of Transportation Routing

The experiences of pipeline construction are rich and generally， CO_2 has low risk to humans, so the construction of CO_2 pipeline is very safe. However, CO_2's leakage had larger harm before; one of the most famous is the disaster of Lake Nyos in Cameroon. The *design and operation of the CO_2 pipelines* published by "DET NORSKE VERITAS" in April 2010 promotes the lethal concentrations of CO_2 level to a higher order of magnitude according to the requirements of the GHS "toxic substances”. So when choosing the transportation routing, it must conform to the local government planning and avoid the environmental sensitive spots, cultural relic protection zone and geological hazards zone. It also must consider the relative relationship between the pipelines and the surrounding villages, towns, factories and the key animal protection zone. Wind direction, topography, and ventilation also must be considered. When choosing the transportation routing, it must make the corresponding protection and warning measures. In the huge storage and high concentration of CO_2 (inhaled CO_2 concentration is higher than 7%), CO_2 pipeline will exist serious hidden danger, so in the densely populated areas, it should classify the hazard levels strictly [18].

In addition, the regional levels are divided according to the population density by consulting the references GB50251-2003 *standard for design gas pipeline transportation engineering* or ISO 13623-2009 *petroleum and natural gas industries-pipeline transportation systems*.

5. Other Security Issues

In order to ensure the safety to avoid major accidents, the pipelines design should take the following measures [19-20].

1) Using SCADA control system achieves the full automation control; Setting up pipeline leak monitoring system based on the technology of thermal imaging technology or infrasonic wave realizes the automatic detection of leakage; setting CO_2 concentration alarm device in the station and the valve chamber.

2) The chromatographic analyzer and water dew point meter should be set in the first station to ensure the qualified gas into the pipelines and avoid internal corrosion. At the same time, the design of internal corrosion detection device and intelligent pigging device can evaluate the corrosion in the pipeline periodically.

3) If it permitted, injecting mercaptan to increase the smell can make the surrounding person to alert the leak more; along the pipeline, warning signs must be set up in the CO_2 gathered sites and it must detect the concentration of CO_2 to ensure security before it enters.

6. The Conclusions

As the CCUS technology being large-scale and commercial applications, CO_2 pipeline construction is becoming an inevitable choice. Though many countries have used super-critical CO_2 pipeline transportation for a long time, there is still no major breakthrough in China. It has less experience than hydrocarbon gases transportation, and there is no unified standard for CO_2 pipeline design and operation. Super-critical CO_2 pipeline transportation in China must combine with its own region, environment, population and other various aspects. It shall consider the differences between China and other countries. Chinese can refer to the foreign experience and then according to China's actual conditions, formulates the standard and specification about CO_2 pipeline design, construction and operation. Thus make a breakthrough in the CO_2 pipeline transportation.

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