Energy Proceedings
Vol 33, 2023
ISSN 2004-2965

Study on the temperament of CCUS-EOR supercritical/dense phase pipeline in Daqing Oilfield

Zhao Xuefeng[1], Li Yuchun[1] , Meng Lan[1*], Ji Xianjing[1], Wu Wei[1], Liu Yong[2], Han Chonglian[3]

1. Daqing Oilfield Design Institute Co. LTD

2. Exploration and Development Research Institute of Daqing Oilfield

3. Daqing Oilfield Production Technology Institute

(*Corresponding Author: Email: menglan@petrochina.com.cn)

ABSTRACT

The best way to connect CCUS-EOR carbon source and carbon sink is Supercritical long-haul pipeline containing impurities of carbon dioxide. Due to the variety of source of carbon and capture technologies, the combination of carbon source impurities has diversity. Carbon sink also has certain requirements on carbon source components owing to the specificity of reservoir and the requirements of oil displacement and storage injection system facilities. To sum up, it is necessary to study the limit of carbon source temperament composition which can not only satisfy the matching of carbon source and carbon sink, but also ensure the safe long-distance transport of carbon dioxide containing impurities in the supercritical phase [10]. This article obtains from the source of carbon source and capture process analysis of carbon source, and the content limits of various impurities are studied according to the requirements of carbon sink injection engineering and oil reservoir enhanced oil recovery, which in all at the same time in the process of research and analysis through the impurities in supercritical carbon dioxide/dense-phase long-distance pipeline safety transportation technology requirements and characteristics of Daqing area meteorological environment, in the end, the suitable source - sink matching temperament is given. Impurities in supercritical carbon dioxide long-distance pipeline temperament limit mainly include carbon dioxide, water, total quantity of non-condensable gas and hydrogen, hydrogen sulfide, nitrogen oxides, carbon monoxide, sulfur oxide content limit value, whether its value is scientific or not is not only crucial to the safe operation of the pipeline, but also have a huge impact on the benefit and effect of CCUS-EOR as well as the investment and cost of capture construction. This study will provide technical support for the construction and operation of the whole industrial chain of CCUS-EOR in Daqing Oilfield.

Keywords: CCUS-EOR, carbon dioxide pipeline, supercritical phase transport, impurity component limit

1. INTRODUCTION

Long-distance CO_2 pipeline transportation is a key link in the whole industrial chain of CCUS-EOR. The development of large-scale CO_2 long-distance pipeline transportation technology is a strong support for the low-cost and large-scale development of CCUS-EOR. Existing CCUS demonstration projects in China are small in scale and mostly use tank trucks for delivery. Domestic CO_2 pipeline transportation started late, in the industrial demonstration stage, mainly gas phase transportation. Compared with gas-phase CO_2 pipeline transportation, supercritical CO_2 has higher density with smaller diameter and higher wall thickness pipeline, and slightly lower overall construction investment. Compared with liquid phase CO_2 pipeline transportation, supercritical CO_2 has lower viscosity, smaller pressure drop and

Fund Project: China National Petroleum Corporation's Major Science and Technology Special Project "Research and Demonstration of Key Technologies for the Whole Industry Chain of Carbon Dioxide Scale Capture, Oil Displacement and Burial and Storage (2021ZZ01)" (202110-202512)

Author's profile: Zhao Xuefeng, male, born in 1972, is a senior engineer. He graduated from China University of Petroleum (East China), majoring in oil and gas storage and transportation, and now works in Daqing Oil Field Design Institute Co., Ltd., mainly engaged in the research and planning design of oil and gas field surface engineering technology. Address: No. 46, Xiyuan Street, Ranghulu District, Daqing City, Heilongjiang Province, 163712. Email: zhaoxuefeng@petrochina.com.cn.

This is a paper for International CCUS Conference 2023 (ICCUSC2023), April 14-15, 2023, Beijing, China.

slightly lower overall operating cost. Therefore, supercritical CO_2 pipeline transportation is the first choice for long-distance large-scale pipeline transportation [2]. Due to the small scale of domestic CCUS projects, there is no long-distance supercritical CO_2 transmission pipeline with a transport distance of more than 100km. Daqing oilfield "Difference" to undertake major r&d projects, China national petroleum group co., LTD. The scale of the carbon dioxide capture and storage and oil displacement are industrial chain key technology research and demonstration zz01 (2021) ", expand the scale of capture project demonstration and make breakthrough in key technologies of supercritical pipeline, enhance oil displacement engineering system, the research of carbon asset development methodology, Building a demonstration zone for the whole industrial chain. In the process of pipeline transportation technology research, the combination of carbon source impurities is diversified due to various source of carbon and capture technologies, and carbon sinks also have certain requirements on carbon source components due to the specificity of reservoir and the requirements of oil displacement and storage injection system facilities. Therefore, it is necessary to study the limit of carbon source temperament composition which can not only satisfy the matching of carbon source and carbon sink, but also ensure the safe long-distance transport of carbon dioxide containing impurities in the supercritical phase. This article obtains from the source of carbon source and capture process analysis of carbon source, according to carbon sink injection engineering and reservoir enhanced oil recovery requirements, which in all at the same time in the process of research and analysis through the impurities in supercritical carbon dioxide/dense-phase long-distance pipeline safety transportation technology requirements and characteristics of Daqing area meteorological environment, Finally, the suitable source - sink matching temperament is given.

2. CCUS-EOR CARBON SOURCE

As there are many types of CCUS-EOR carbon sources and capture technologies, different gas sources and capture technologies will produce different impurity combinations. At present, the carbon sources of CCUS projects have come from carbon-containing natural gas, refineries, coal chemical industry, coal-fired power plants, etc. In the future, the carbon sources of potential industries will be more diverse and the temperament components will be more complex.

The carbon source components are mainly divided into two parts: the main component (CO_2) and the impurity component (H_2S, H_2O, total hydrocarbon, N_2, O_2, H_2, CO, NO_X, SO_2, fluoride, hydrocarbons, Ar, etc.).

In addition to CO_2 as a product, impurities can be mainly divided into five categories according to component properties: (1) Corrosive components: H_2S, CO, SO_X, NO_X and O_2; (2) Toxic and harmful components: H_2S, CO, SO_X and NO_X; ③ Non-condensing gas components: N_2, Ar, H_2, CH_4 and O_2, etc. ④ Hydrocarbon components: CH_4, C_2H_6 and C_3^+, etc.; ⑤ Solution components: H_2O, amine and alcohol, etc. Some impurity components belong to more than two categories [3].

In foreign countries, it is usually mandatory to specify part of corrosive components (H_2S and O_2), part of toxic and harmful components (H_2S), part of non condensing gas components (O_2, N_2 and CH_4) and part of solution components (H_2O) for CO_2 pipeline transportation temperament standards [9]. In addition, other components are selective provisions without unified requirements.

3. CARBON DIOXIDE CONTENT REQUIREMENTS

CO_2 is the main body of CCUS-EOR carbon source pipeline transportation. From the comprehensive consideration of investment and operation cost, the CO_2 content of conventional supercritical pipeline should be greater than or equal to 95% [6]. As for CCUS-EOR, the purity of CO_2 directly affects the flooding effect, Daqing oilfield takes Aonan CCUS demonstration area under construction as the research object. Through displacement experiment, reservoir numerical simulation and coupling of pipeline gas and associated gas, it is suggested that the purity of CO_2 for oil flooding should be above 95%, and the purity of CO_2 for pipeline gas carbon source should be above 99%.

3.1 Displacement experiments

In Daqing oilfield, the formation crude oil from well Nan168-deviation 276 in Ao 9 block was selected to measure the minimum miscible pressure of CO_2 flooding by the fine tube method. According to the relationship curve between the recovery degree of CO_2 flooding and the displacement pressure, the minimum miscible pressure of this block was 19.81MPa, while the formation pressure was 16MPa, so it was determined as immiscible displacement. On this basis, the long rock core displacement test was carried out as follows:

（1）90%CO_2 long core flooding experiment: 16MPa water flooding 0.6PV, water flooding recovery degree 47.09%; Then gas flooding 0.4PV, a large amount of gas from gas to gas water injection at the outlet, gas-liquid ratio 2:1, total injection $CO_2$1.9 PV, total recovery degree 63.92%.

（2）95%CO_2 long core flooding experiment: 16MPa water flooding 0.6PV, water flooding recovery degree 46.59%; Then gas flooding 0.4PV, a large amount of gas to gas water injection at the outlet, gas-liquid ratio 2:1, total injection $CO_2$1.9 PV, total recovery degree 68.82%, 4.9 percentage points lower than 90% CO_2.

（3） Pure CO_2 long core flooding experiment: 16MPa water flooding 0.6PV to more than 98% water cut, water flooding recovery degree 46.61%; Then gas flooding 0.4PV, a large number of gas to gas water injection at the exit, gas-liquid ratio 2:1, total injection $CO_2$1.9 PV, total recovery degree 74.75%, gas water injection can increase the oil recovery on the basis of water flooding 28.14 percentage points, 10.83 percentage points higher than 90% CO_2.

It can be seen from the above tests that the recovery efficiency increases by 1 percentage point for every 1 percentage point increase in CO_2 concentration.

3.2 *Numerical reservoir simulation*

Taking the actual geological model of a block in Daqing Aonan Oilfield as an example, the influence of CO_2 concentration on the oil displacement effect was studied. With the increase of N_2 content in CO_2, the EOR points decreased rapidly first and then became smooth. The concentration of CO_2 increased from 90% to 100%, and the EOR increased from 21.57 to 26.13 percentage points, an increase of 4.56 percentage points. According Figure 1 for details. Therefore, it is recommended that the purity of CO_2 for oil displacement be above 95%.

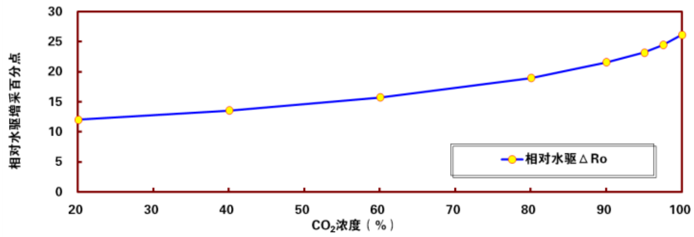

Fig.1. The relationship between the number of points increased in the numerical simulation recovery and the concentration of CO_2

3.3 *Pipeline gas is coupled with associated gas*

When CO_2 is injected into the reservoir to displace the oil, some of the injected gas will be produced along with the oil in the producing well, and this part of the gas will be recycled and injected back. According to the preliminary study, the mixing of carbon source and oil field associated gas is the lowest cost cycle gas injection mode. According to the development plan, the oil field will produce 75.6t/d to 737t/d of associated gas and 64.5% to 94% of CO_2 from 2024 to 2030. After the carbon source is mixed with the associated gas in the oilfield, the CO_2 content needs to be above 95% to ensure the requirements of CO_2 injection and reservoir development in the oilfield. Therefore, the CO_2 content in the pipeline gas carbon source needs to be above 99%.

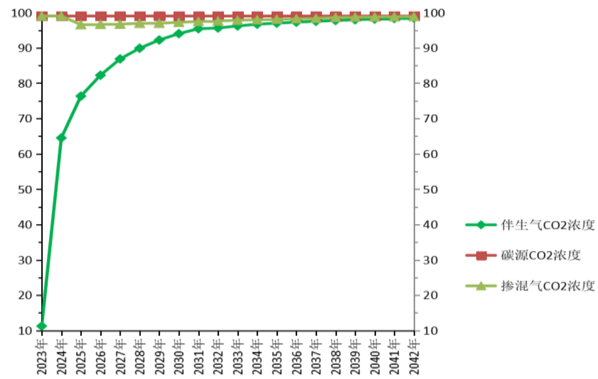

Fig.2. Purity of CO_2 after mixing CCUS-EOR associated gas with carbon source(mol%)

4. WATER CONTENT REQUIREMENT

The water content in CO_2 should be controlled no matter in CO_2 transmission pipeline or oil displacement surface injection system. There are two main reasons: First, from the corrosive point of view, the water content limit should ensure to prevent the corrosion of free water on the pipeline; Second, from the perspective of hydrate generation, the limit of water content should ensure that no hydrate will be formed under the design conditions. The two main reasons are attributed to a control measure, namely: "The water content limit should be considered to prevent the release of free water in the pipeline and injection system"[11]. In engineering design, the limit value of "water dew point" is set to prevent the production of free water. According to "Code for Design of Gas Pipeline Engineering" (GB 50251-2018), the gas temperament standard for pipeline transportation should meet the requirements of Class II in the natural gas standard, that is, the dew point of gas water entering the gas pipeline should be 5℃ lower than the lowest ambient temperature under transportation conditions. Since there are no specific regulations on CO_2 transport and injection, the dew point limit of CO_2 water is intended to be designed as "5℃ lower than the lowest ambient temperature".

In Daqing Oilfield, the proposed CO_2transmission pipeline and demonstration area mainly involve 4 Administrative Districts include Longfeng, Datong, Zhaoyuan and Anda, Suihua City of Daqing City. The temperature conditions of these areas are shown in Table 1.

Table 1. Temperature condition table of the administrative region mainly involved in the proposed CO_2 transport pipeline and demonstration area

No	county	Temperature(℃)				
		Extreme minimum	Mean monthly minimum temperature	Average temperature of the hottest month	Maximum monthly mean maximum temperature	Annual mean temperature
1	Anda	-38	-23.8	23	28	4.2
2	Longfeng	-38	-23.9	23	27.8	4.4
3	Datong	-38	-23.9	23	27.7	4.4
4	Zhaoyuan	-41	-24.8	23	28	5

As can be seen from the above table, in Daqing Oilfield, in order to fully guarantee the safe operation of transportation pipeline and ground injection system, the limit value of water dew point is selected as -30℃.

In order to clarify the water content requirements, the relationship between water content and water dew point under different pressure conditions was simulated, analyzed and calculated, and the results were shown in Table 2.

Table 2. Simulation analysis and calculation table of the relationship between water content and dew point under different pressure conditions

Simulated value of CO_2 water dew point			
water content	water dew point(℃)		
ppm	3.5MPa	6.0MPa	12MPa
10	-38.2	-38.1	-37.8
20	-28	-27.8	-27.5
50	-13.3	-13	-12.6
100	1.3	-0.9	-0.3
500	14.4	23	31.7

As can be seen from the above table, according to the "water dew point limit -30℃", the moisture content limit of 20ppm is appropriate, and according to domestic and foreign research and operation experience, when the water content in the pipeline exceeds 60% of the saturated water content under operation condition, free water will be formed, resulting in serious corrosion [25]. Therefore, from the perspective of safety, the water content limit is finally set at 10ppm.

5. REQUIREMENTS FOR THE TOTAL AMOUNT OF NONCONDENSABLE GAS

What is callednon-condensable gas refers to the chemical substances that exist partly in the gas state under the conditions of CO_2 transport and injection. For example, N_2, Ar, H_2, CH_4, O_2 and so on.

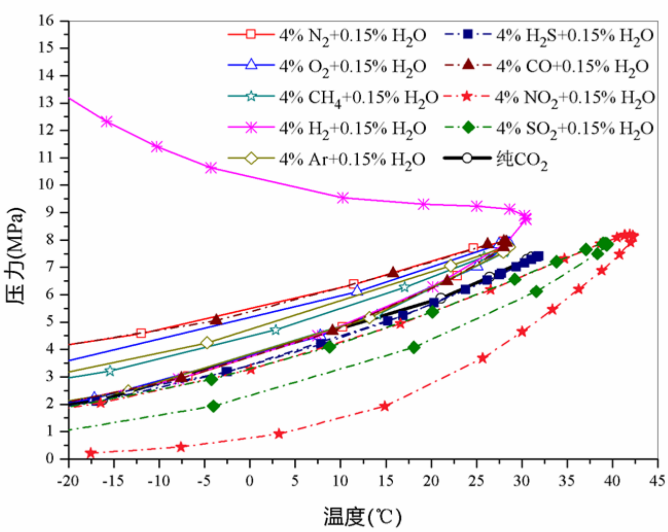

Fig.3. CO_2 fluid phase diagram containing impurities

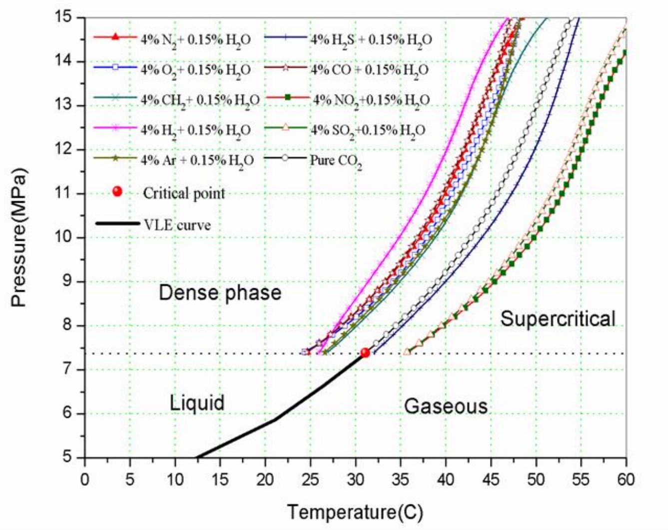

Fig.4. Variation trend of quasi - critical region of impurity CO_2

From the perspective of ground engineering, compared with pure CO_2, the influence of impurities on the CO_2 phase equilibrium is mainly reflected in two aspects: first is to cause the change of critical properties, so that the position of the critical point is shifted; The second is to produce gas-liquid two-phase coexistence zone, which further affects the actual operating boundary conditions of the pipeline. The study found that the degree of influence of impurity components from strong to weak is:H_2＞NO_2＞N_2＞CO＞SO_2＞Ar＞O_2＞CH_4＞H_2S，the effect of H_2S is basically negligible [13]。

According to the actual operation experience of foreign CO_2 transport pipelines, the non-condensing gas component (N_2, Ar, H_2, CH_4, CO and O_2) has the largest content in the pipeline transport medium besides the product component CO_2. Although these components have no direct impact on the CO_2 pipeline transport process, they will not only occupy a certain amount of additional pipeline transport, but also increase the critical pressure of the pipeline transport medium. More compression work is required at the pipeline entrance to compress the CO_2 fluid into the dense phase/supercritical state, and it becomes more difficult to maintain the dense phase in the subsequent pipeline transport process [26]. Therefore, it is necessary to limit the non-condensing gas component strictly in large scale and long-distance CO_2 fluid pipeline transport to reduce the compression cost. Foreign countries usually limit the total amount of non-condensable gas to below 4%~5%. Considering the size of the pipeline and injection system proposed for the field, the limit of the total amount of non-condensable gas is recommended to be below 4%.

From the perspective of geological utilization, at present, some relevant foreign scientific research institutions have given different recommended values of the quality indexes for CO_2 flooding and salt water reservoir storage and other CO_2 uses, and the differences are mainly reflected in the content of non-condensable gas components (N_2, Ar, H_2, CH_4 and O_2) [18]. These components are not conducive to miscible formation, so the noncondensable gas component in the temperament index used for CO_2 flooding is more stringent than the geological sequestration. For example, both NETL and DYNAMIS projects suggest that the total amount of non-condensed gas should be limited to 4% during geological storage, but NETL suggests that the total amount of non-condensed gas should be limited to 1% during CO_2 flooding, while DYNAMIS project suggests that the total amount of non-condensed gas should be limited to 4%, specifically pointing out that the content of CH_4 should be less than 2%.

To sum up, it is suggested that "the total limit of non-condensed gas is below 4% (40,00ppm)".

6. HYDROGEN CONTENT REQUIREMENTS

According to the current CCUS-EOR "14th Five-Year Plan" development plan of Daqing Oilfield, the main carbon sources are: ammonia synthesis unit of Daqing Petrochemical and Fertilizer plant (400,000 tons/year), power plant boiler of thermal power plant (1 million tons/year), catalytic cracking unit of refinery (1 million tons/year) and power plant boiler of CPC electric thermal power plant (600,000 tons/year). Through sampling analysis and investigation, the carbon source components are preliminarily determined as follows:

①Carbon source of ammonia plant in Daqing Petrochemical and Fertilizer Plant: high concentration carbon source, the capture process is mainly dehydration. According to the sampling analysis conducted by Daqing Petrochemical and "Quality Supervision and Inspection Center of Petroleum Industry Crude Oil and Petroleum Products" commissioned by Daqing Oilfield, the dry base of carbon source (after dehydration) mainly consists of CO_2, H_2, N_2 and CH_4. The analysis results are shown in Table 3. It can be seen from the analysis results that the CO_2 content is up to 99%, and the impurities are mainly H_2, followed by a small amount of N_2 and CH_4.

Table 3. Summary table of sampling analysis results of carbon source components (dry base) in ammonia plant of Daqing Petrochemical and Fertilizer Plant

Component	mole (%)		
	December 2021	January 2022	February 2022
Methane	0.01	0.01	＜0.01
Ethane	＜0.01	＜0.01	＜0.01
Propane	＜0.01	＜0.01	＜0.01
Isobutane	＜0.01	＜0.01	＜0.01
N-butane	＜0.01	＜0.01	＜0.01
New pentane	＜0.01	＜0.01	＜0.01
Isopentane	＜0.01	＜0.01	＜0.01
Is pentane	＜0.01	＜0.01	＜0.01
Hexane and more are divided	＜0.01	＜0.01	＜0.01
Carbon dioxide	99.22	99.16	99.00
Oxygen	＜0.01	0.10	0.10
Nitrogen	0.14	0.13	0.43
Carbon monoxide	＜0.01	＜0.01	＜0.01
Helium	0.01	0.01	＜0.01
Hydrogen	0.61	0.58	0.46
Total	99.99	99.99	99.99

②Carbon source of power plant boiler of Daqing Petrochemical thermal Power Plant and power station boiler of Petro China Electric thermal Power Plant: low concentration carbon source, and the capture process is planned to adopt the process package of Sinopec Nanjing Research Institute of Chemical Industry. Through consultation and data investigation with Nanhua Institute, the impurity of the two carbon sources after capture and dehydration is only N_2, as shown in Table 4. In Table 4, the mole fraction before dehydration was provided by Nanhua Institute.

Table 4. Carbon source component analysis table of CNPC Electric Power Thermoelectric No.1 Company

Component		Before dehydra tion /%	After dehydration/%(10ppm)
Temperature(°C)		40	50
Component(mol%)	CO_2	91.7	99
	O_2	0	0
	N_2	0.9	1
	H_2O	7.4	0
	SO_2(mg /m^3)	0	0
	NO_x(mg/ m^3)	0	0
Total		100	100

③Carbon source of catalytic cracking unit of Daqing Petrochemical Refinery: low concentration carbon source, and the capture process is planned to adopt the process package that Research Institute of Petrochemical Industry of Petro China is working on. After consulting with the Petrochemical Institute, the reply is: "Low and medium concentration carbon source adopts the amine chemical absorption method, which realizes the capture of CO_2 in flue gas through the highly selective absorption and desorption process of amine solvent. During the capture process, N_2 and O_2 components (content > 85%) do not react with solvents and will not enter CO_2 products. Harmful impurities such as SOx and NOx (< 100mg/L) enter the solvent but not the CO_2 product." The gas composition of the captured product is shown in Table 5.

Table 5. Chemical absorption of amine after combustion trapping product gas composition

Gas composition of trapping product(mol%)	Chemical absorption of flue gas after combustion*
CO_2	99
H_20	0.01
H_2S	<0.01
H_2	<0.01
N_2	0.17
O_2	0.01
CH_4	0.01
Ar	<0.01
SOx	0.001
NOx	0.005
CO	0.001
C_2+	0.01

*： Li H ,ivind Wilhelmsen, Lv Y , et al. Viscosities, thermal conductivities and diffusion coefficients of CO_2 mixtures: Review of experimental data and theoretical models[J]. International Journal of Greenhouse Gas Control, 2011, 5(5):1119-1139.

Through the above analysis, the carbon source impurity in Daqing oilfield is mainly H_2, and H_2 content has the greatest influence on pipeline transportation. Therefore, special requirements are made for H_2 content. Specific requirements are based on the international standard "Carbon Dioxide Capture, Transport and Geological Storage Pipeline Transport System" (ISO 27913:2016), H_2 content limit is 750 PPM.

7. REQUIREMENTS FOR HYDROGEN SULFIDE CONTENT

According to the standard GB/T 20972 (Materials for hydrogen sulfide Environment in Oil and Gas Industry), when the partial pressure of hydrogen sulfide is greater than 0.0003MPa, the stress corrosion cracking resistance of the material should be considered. Therefore, the concentration of hydrogen sulfide calculated by the major of Daqing oilfield production according to different pressures is as follows:

(1) Bottomhole pressure of gas injection Wells in Fuhua Reservoir is 25-30MPa, H_2S content <14ppm in some areas does not meet the requirements, therequiredH_2S concentration should be less than 10ppm.

The hydrogen sulfide concentration under different pressure conditions is calculated according to the partial pressure of hydrogen sulfide of 0.0003MPa. The specific data are shown in Figure 5. If the H_2S content is less than 14ppm, there will be the risk of hydrogen sulfide stress corrosion cracking in some areas within the bottom hole pressure range of Aonan test area, so the H_2S content should be less than 10ppm to avoid such risk.

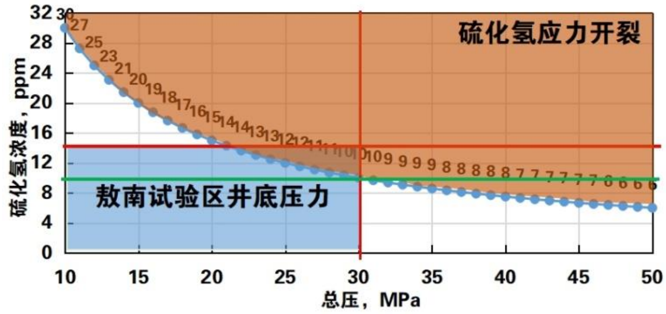

Fig.5.H2S concentration requirements of Putaohua reservoir

(2) The bottom hole pressure of Fuyang reservoir is 44-46MPa, and H_2S content <14ppm in some areas were substandard, while the H_2S content should be less than 6ppmtomeettherequirements.

The hydrogen sulfide concentration under different pressure conditions was calculated according to the hydrogen sulfide partial pressure of 0.0003MPa. The specific data are shown in Figure 6. If the H_2S content is less than 14ppm, some areas will have the risk of hydrogen sulfide stress corrosion cracking within the bottom hole pressure range of Aonan test area. To avoid this risk, H_2S levels need to be less than 6ppm.

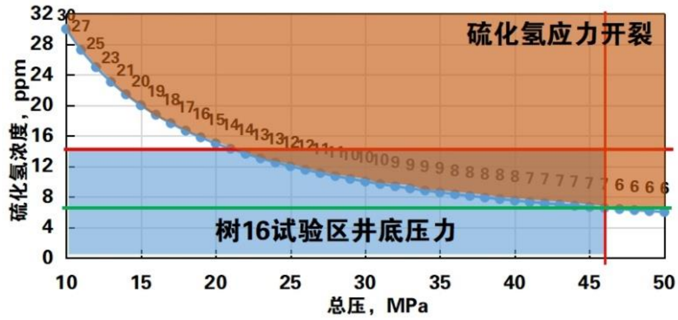

Fig.6. H2S concentration requirements of Fuyang reservoir

To sum up, ordinary carbon steel is used for well casing in CO_2 test area of Daqing oilfield. Casing damage was found in 13 Wells in Yushulin test area in 2015, which was detected and analyzed as H_2S stress corrosion by Xi 'an Pipe Research Institute. Therefore, in order to ensure no H_2S stress corrosion cracking in the wellbore of the test area, H_2S content should be less than 6ppm.

8. OTHER REQUIREMENTS

The CCUS-EOR "14th Five-Year Plan" of Daqing Oilfield involves four carbon sources. The components of high-concentration carbon sources before and after capture have been defined in the ammonia synthesis plant of Daqing Petrochemical and Fertilizer Plant, while the components of the other three low-concentration carbon sources after capture are the predicted components obtained according to the proposed process package. The actual emissions of each carbon source before capture were sampled and analyzed by Daqing Petrochemical and CNPC respectively, and the results of dry base component analysis are shown in Table 6-Table 9.

Table 6. Summary table of sampling and analysis results of carbon source components before flue gas capture in Daqing petrochemical thermal power plant

Component		unit	parameter	note
Carbon source gas temperature		℃	30-55	
Carbon source gas pressure		Pa	0	manometer pressure
O_2	1#chimney	%	9.4	On May 2, 2022, the temperature was 15-7 ℃, and the samples were collected and analyzed in the laboratory
	2#chimney	%	8.5	
	3#chimney	%	8.6	
	4#chimney	%	7.2	
CO_2	1#chimney	%	6.87	On May 2, 2022, the temperature was 15-7 ℃, and the samples were collected and analyzed in the laboratory
	2#chimney	%	7.45	
	3#chimney	%	7.48	
	4#chimney	%	8.15	
humidity		%	10	
NO_x		mg/Nm^3	≤50	
SO_2		mg/Nm^3	≤35	
soot		mg/Nm^3	≤6	

Table 7.Carbon Source Components (dry base) before flue gas capture in 1.4Mt/a Heavy oil Catalytic Cracking Unit of Daqing Petrochemical Refinery

Stable operating condition at present	
Diameter of desulfurization tower mouth(mm)	2600
Flue gas flow(Nm^3/h)	233422
Main components of flue gas(v%)	-
CO_2	14.57
H_2	0.08
N_2	70.88
CO	0.01
O_2	2.55

Table 8. Carbon Source Components (dry base) before flue gas capture in 2Mt/a Heavy oil Catalytic Cracking Unit of Daqing Petrochemical Refinery

Calibration condition in 2021	
Diameter of desulfurization tower mouth(mm)	2800
Flue gas flow(Nm^3/h)	303000
Main components of flue gas(v%)	-
CO_2	14.53
N_2	81.54
O_2	3.93

Table 9. Summary of sample analysis results of carbon source components (dry base) before flue gas capture of CNPC Electric Power Thermoelectric No.1 Company

Monitoring points	Waste gas pollutant	Monthly average concentration(mg/Nm^3)										exhaust gas temperature(℃)	percentage concentration of CO_2
		Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.		
1# chimney	SO_2	12.56	12.73	18.31	21.94	28.43	18.15	17.96	12.52	12.61	12.04	60	14.77 %
	NO_x	98.78	96.04	101.25	103.45	110.25	91.75	36.22	29.04	25.29	18.11		
	soot	10.59	10.49	10.25	10.64	11.05	15.55	2.86	2.6	5.83	6.11		
	O_2	7.95	7.69	7.86	8.25	8.85	9.56	5.78	5.92	5.85	6.78		
2# chimney	SO_2	5	6	8	11	11	11	11	10	10	10	55	14.01 %
	NO_x	27	20	25	32	28	24	24	21	29	30		
	soot	2	2	4	3	2	1	1	2	7	4		
	O_2	6	7	8	8	8	7	7	7	6	7		
3# chimney	SO_2	5.4	5.95	6.07	7.57	10.23	9.14	11.54	7.6	5.34	9.76	60	13.88 %
	NO_x	24.58	26.29	28.48	29.73	30.65	31.24	28.92	28.94	30.91	25.22		
	soot	3.19	2.51	2.88	3.26	2.54	1.85	1.58	3.1	4.3	2.54		
	O_2	6.47	6.51	6.1	5.95	6.85	6.53	6.32	6.91	7.19	6.59		

According to the above sampling analysis results before capture of low-concentration carbon sources, it can be seen that in addition to CO_2 and H_2, there are NOx, N_2, CO, SO_2 and O_2. Therefore, when the trapping effect of low-concentration trapping process package is different from the previous investigation results, there will still be NOx, N_2, CO, SO_2 and O_2 impurities after the capture of low-concentration carbon source. This time, the content limits of these 5 impurity components are also required.

After reviewing a large number of domestic and foreign standards and literature, N_2 and O_2 are only regulated as non-condensable gases, which have no toxicity or other hazards except for the influence on pipeline transport volume [27], and their content can be limited according to the requirements of non-condensable gas content.

Due to the presence of NOx, CO, SO_2 with water and O_2 may occur many cross chemical reactions, it is possible to form sulfuric acid, sulfite, nitric acid and elemental sulfur. Therefore, in addition to the non-condensable gas content requirement limit, some countries on its content limit provisions [29]. In the relevant specifications in Europe, the risk of accidental release of pipeline transport medium under special working conditions such as pipeline cavitation or leakage is taken into account, and the content limit of H_2S, CO, SO_X and NO_X is generally set at 100ppm, 400ppm, 100ppm and 100ppm. The Australian Carbon Net specification mainly refers to the DYNAMIS specification of the European Union, and then limits H_2S content to 100ppm, CO to 900ppm, SO_2 to 200ppm and NO_X to 250ppm based on its domestic Occupational Health and Safety short-term Exposure Limit (STEL). Based on the investigation results, the limit of NOx content is 100ppm, the limit of CO content is 400ppm and the limit of SO_2 content is 100ppm.

9. COCLUSION

To sum up, according to the temperament requirements of carbon sink reservoir flooding, combined with the flooding injection process, the pre-capture components of four carbon sources and the capture process, Daqing Oilfield investigated the relevant foreign projects and proposed specific requirements for the temperament of CCUS-EOR supercritical/dense phase pipeline transportation through comprehensive analysis. See Table 10 for details.

Table 10. emperament requirements for CCUS-EOR supercritical/dense phase pipeline transport

Component	CO_2 (%)	H_2O (ppm)	noncondensable gas(ppm)	H_2 (ppm)	H_2S (ppm)	NOx (ppm)	CO (ppm)	SO_X (ppm)
content	⩾99	⩽10	⩽10000	⩽7500	⩽6	⩽100	⩽400	⩽100

REFERENCE

[1] National Development and Reform Commission. Circular of the National Development and Reform Commission on Promoting Experimental Demonstration of Carbon Capture, Utilisation and Storage [EB/OL]. (2013-05-09) [2022-03-24]. http://www.gov.cn/zwgk/2013-05/09/content_2398995.htm.

[2] YE Yunyun, LIAO Haiyan, WANG Peng, et al. Research on the direction of CCS/CCUS technology development and development roadmap for coal-fired power generation in China[J]. China Engineering Science, 2018, 20(3):80-89.

[3] MOHITPOUR M, SEEVAM P, BOTROS K K, et al. Pipeline Transportation of Carbon Dioxide Containing Impurities[M]. New York: ASME Press,2012.

[4] MCCOY S T, RUBIN E S. An Engineering-economic model of Pipeline Transport of Application to Carbon Capture and Storage[J]. International Journal of Greenhouse Gas Control, 2008, 2(2): 219-229.

[5] HAUGEN H A, ELDRUP N, BERNSTONE C, et al. Options for Transporting CO_2 from Coal Fired Power Plants Case Denmark[J]. Energy Procedia, 2009, 1(1): 1665-1672.

[6] LIU Jianwu. Key issues of carbon dioxide transmission pipeline engineering design[J]. Oil and gas storage and transportation,2014,33(4):369-373.

[7] HUANG Hui, ZHOU Jing, SU Kehua. Discussion on the design standard of CO2 transmission pipeline engineering[J]. Natural Gas Industry, 2014, 34(12): 131-134.

[8] Chen Lin. CO2 pipeline transport technology and engineering practice in Sinopec [EB/OL]. (2016-03-16) [2022-03-24]. http://chinaccus.org/attachs/2016-4-7_0-37-10-638-0.493770047786538.pdf.

[9] ANHEDEN M, ANDERSSON A, BERNSTONE C, et al. CO_2 Quality Requirement for A System with CO_2 Capture, Transport and Storage[C]// Greenhouse Gas Control Technologies: Proceedings of the 7th International Conference on Greenhouse Gas. Volume II. Oxford: Elsevier Science Ltd., 2005: 2559-2564.

[10] ZHANG Lei, ZHANG Zhe, BA Xili, et al. Development direction of carbon capture technology in oil and gas fields under the background of "carbon

neutrality"[J]. Oil and Gas and New Energy, 2022, 34(1):80-86.

[11] DE VISSER E, HENDRIKS C, BARRIO M, et al. Dynamis CO_2 Quality Recommendations[J].International Journal of Greenhouse Gas Control,2008,2(4): 478-484.

[12] MURUGAN A, BROWN R J C, WILMOT R, et al. Performing Quality Assurance of Carbon Dioxide for Carbon Capture and Storage[J]. Journal of Carbon Research,2020,6(76):1-15.

[13] SNC-Lavalin Inc. Impact of Impurities on CO_2 Capture, Transport and Storage[R/OL]. (2004-08) [2022-03-24]. https://ieaghg.org/docs/General_Docs/Reports/Ph4-32%20Impurities.pdf.

[14] METZ B, DAVIDSON O, DE CONICK H, et al. Carbon Dioxide Capture and Storage[M]. Cambridge: Cambridge University Press, 2005.

[15] WHITE V, TORRENTE-MURCIANO L, STURGEONC D, et al. Purification of Oxyfuel-derived CO_2[J]. International Journal of Greenhouse Gas Control, 2010, 4(2):137-142.

[16] Dynamis Consortium. Near-zero Emissions from Electricity and Hydrogen Production with CO_2 Capture and Storage(CCS)[EB/OL]. (2014-11-17) [2022-03-24]. https://www.sintef.no/globalassets/project/dynamishypogen/publications/brosjyre_web_okt091.pdf.

[17] DE VISSER E, HENDRIKS C, DE KOEIJER G, et al. Towards Hydrogen and Electricity Production with Carbon Capture and Storage-DYNAMIS Quality Recommendation[R/OL]. (2007-06-21) [2022-03-24]. https://www.sintef.no/globalassets/project/dynamis-hypogen/publications/d3-1-3-dynamis-co2-quality-recommendations1.pdf.

[18] World Resources Institute. Guidelines for Carbon Dioxide Capture, Transport, and Storage[R/OL]. (2008-10-27) [2022-03-24]. https://www.wri.org/research/guidelines-carbon-dioxide-capture-transport-and-storage.

[19] Det Norske Veritas. Design and Operation of CO_2 Pipelines: Recommended Practice DNV-RP-J202 [R]. Veritasveien, orway: NV,2010.

[20] Det Norske Veritas Germanischer Lloyd . Design and Operation of Carbon Dioxide Pipelines: DNVGL-RP-F104[R]. Veritasveien, Norway:DNV,2017.

[21] Det Norske Veritas. Design and operation of Carbon Dioxide Pipelines: DNV-RP-F104[R]. Veritasveien, Norway: DNV, 2021.

[22] The IEA Greenhouse Gas R&D Programme. Effects of Impurities on Geological Storage of CO_2[R/OL]. (2011-04) [2022-03-24]. https://ieaghg.org/docs/General_Docs/Reports/2011-04.pdf.

[23] National Energy Technology Laboratory. Quality Guidelines for Energy System Studies: CO_2 Impurity Design Parameters[R]. Pittsburgh:2012.

[24] National Energy Technology Laboratory. Quality Guidelines for Energy System Studies: CO_2 Impurity Design Parameters[R/OL]. (2013-08-23) [022-03-24]. https://www.netl.doe.gov/projects/files/QGESSCO2ImpurityDesignParameters__092713.pdf.

[25] National Energy Technology Laboratory. Quality Guidelines for Energy System Studies: CO_2 Impurity Design Parameters[R/OL]. (2019-01-01) [2022-03-24]. https://www.netl.doe.gov/projects/files/QGESSCO2ImpurityDesignParameters_010119.pdf.

[26] WETENHALL B, AGHAJANI H, CHALMERS H, etal. Impact of CO_2 Impurity on CO_2 Compression, Liquefaction and Transportation[J]. Energy Procedia, 2014, 63:2764-2778.

[27] ISO/TC 265(Carbon Dioxide Capture, Transportation, and Geological Storage). Carbon Dioxide Capture, Transportation and Geological Storage-Pipeline Transportation Systems: ISO 27913:2016[S/OL]. (2016-11-01) [2022-03-24]. https://www.iso.org/standard/64235.html.

[28] HARKIN T, FILBY I, SICK H, et al. Development of A CO_2 Specification for A CCS Hub Network[J]. Energy Procedia,2017,114:6708-6720.

[29] Health and Safety Executive.EH40/2005 Workplace Exposure Limits[M/OL]. 4th ed.2005[2022-03-24]. https://www.hse.gov.uk/pubns/priced/eh40.pdf.

[30] ISO/TC 265(Carbon Dioxide Capture, Transportation, and Geological Storage). Carbon Dioxide Capture, Transportation, and Geological Storage-Cross Cutting Issues-CO_2 Stream Composition: ISO/TR 2792:2020[S/OL]. (2016-11-01)[2022-03-24]. https://www.iso.org/standard/67273.html.

[31] MELZER L S. The History and Development of CO_2 EOR in the Permian Basin with An Emphasis on Pipelines[EB/OL].(2007-06-26)[2022-03-24]. https://www.uwyo.edu/eori/_files/co2conference07/steve_melzer_ historyofpbco2eor.pdf.

[32] GLASS J.CO_2 Pipelines New Technologies & Economics for Carbon Capture/Sequestration [EB/OL]. (2019-03-29)[2022-03-24]. https://energyatkenanflagler.unc.edu/wp-content/uploads/2019/04/Glass-CO2-Pipelines.pdf.

[33] OOSTERKAMP A, RAMSEN J. State-of-the-Art Overview of CO_2 Pipeline Transport with Relevance to Offshore pipelines[R/OL]. (2008-01-08)

[2022-03-24]. https://www.researchgate.net/publication/228688545_State-of-the-Art_Overview_of_CO_2_Pipeline_Transport_with_Relevance_to_Offhore_Pipelines.

[34] DUGSTAD A, HALSEID M, MORLAND B. Testing of CO_2 Specifications with Respect to Corrosion and Bulk Phase Reactions[J]. Energy Procedia, 2014, 63:2547-2556.

[35] HENDRIKS C, HAGEDOORN S, WARMENHOVEN H. Transportation of Carbon Dioxide and Organisational Issues of CCS in the Netherlands[R]. [S.l.:s.n.],2007.

[36] JOHNSEN K, HELLE K, RØNEID S, et al. DNV Recommended practice: Design and Operation of CO_2 Pipelines[J]. Energy Procedia, 2011, 4: 3032-3039.

[37] Ministry of Industry and Information Technology of the People's Republic of China. Carbon dioxide transmission pipeline engineering design standard: SH/T 3202-2018[S]. Beijing: Sinopec Press,2018.

[38] National Energy Administration. Natural gas: GB 17820-2018[S]. Beijing: China Standard Press, 2018.

[39] ONYEBUCHI V E, KOLIOS A, HANAK D P, et al. A Systematic Review of Key Challenges of CO_2 Transport via Pipelines[J]. Renewable and Sustainable Energy Reviews, 2018, 81(2): 2563-2583.

[40] METZ B, DAVIDSON O, CONINCK H D, et al. IPCC Special Report on Carbon Dioxide Capture and Storage[R/OL]. (2005-11-04) [2022-03-24]. https://www.osti.gov/biblio/20740954-ipcc-special-report-carbon-dioxide-capture-storage.

[41] ZHANG Lei, ZHANG Zhe, WANG Youyang, et al. Study on the adaptability of upgrading technology for tail gas treatment in established sulphur-containing natural gas purification plants[J]. Petroleum Planning and Design,2020,31(5):22-25.

[42] The National Institute for Occupational Safety and Health. Immediately Dangerous to Life or Health(IDLH) Values-Table of IDLH Values [EB/OL].(2019-10-08)[2022-03-24]. https://www.cdc.gov/niosh/idlh/intridl4.html.

[43] United States Department of Energy. Protective Action Criteria: Chemicals with AEGLS, ERPGs & TEELs[EB/OL].(2018-06-29)[2022-03-24]. https://edms.energy.gov/pac.

[44] BRATFOS H A, LEINUM B H, TORBERGSEN L E, et al. Challenges to the Pipeline Transportation of Dense CO_2[J]. Journal of Pipeline Engineering, 2007, 6(3):161-172.

[45] LUCCI A., DEMOFONTI G, SPINELLI C M.CO_2 Anthropogenic Pipeline Transportation: The Twenty-first International Offshore and Polar Engineering Conference[C/OL]. (2011-06-19)[2022-03-24]. https://onepetro.org/ISOPEIOPEC/proceedings/ISOPE11/All-ISOPE11/ISOPE-I-11-170/3264?searchresult=1.

[46] SVENSSON R ODENBERGER M, JOHNSSON F, et al. Transportation Systems for CO_2-application to Carbon Capture and Storage[J]. Energy Conversion & Management, 2004, 45(15-16):2343-2353.

[47] ZETTLITZER M, MOELLER F, MOROZOVA D, et al. Re-establishment of the proper injectivity of the CO_2-injection Well Ktzi 201 in Ketzin, Germany[J]. International Journal of Greenhouse Gas Control,2010,4(6):952-959.

[48] REY A, GOUEDARD C, LEDIRAC N, et al. Amine Degradation in CO_2 Capture. 2. New Degradation Products of MEA. Pyrazine and Alkyl pyrazines: Analysis, Mechanism of Formation and Toxicity [J]. International Journal of Greenhouse Gas Control,2013,19:576-583.

[49] ODRU P, BROUTIN P, FRADET A, et al. Technical and Economic Assessment of CO_2 Transportation[C]//8th International Conference on Greenhouse Gas Control Technologies(GHGT-8). Trondheim:2006.

[50] Petroleum engineering construction professional standardization committee. Design code for gas pipeline engineering: GB 50251-2015[S]. Beijing: China Standard Press,2015.