Spontaneous inhibition phenomena of corrosion in CCUS system and their mechanisms

Prof. Yong Xiang

China University of Petroleum, Beijing

Report Outline

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Research Group

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1. Research Group Laboratory

- **Laboratory for Low Carbon Energy Equipment and Materials Protection** dedicated to equipment material failure and protection **in the field of low carbon energy production and utilization.**
- Our researches aim at improving the safety and economics of low-carbon energy equipment and process.
- Our lab is mainly involved in the areas of **Carbon Capture Utilization and Storage (CCUS), Enhanced Oil Recovery, Gas Turbines, and Hydrogen Utilization.**

CO_2 capture device in CCUS

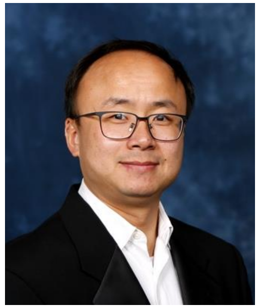
Hydrogen enriched natural gas transportation

Downhole tubing corrosion failure

1. Research Group

Team Members

We have three professors, three associate professors and one lecturer.



Yong Xiang

Professor/Doctoral Supervisor

CCUS, Material Protection

Wei Yan

Researcher/Doctoral Supervisor

Wellbore Integrity

Jiangyun Wang

Researcher/Doctoral Supervisor

Multiphase flow and erosive corrosion

Erdong Yao

Associate Researcher

Oilfield Chemistry and Applications

Zitao Jiang

Associate Professor

Cathodic Protection

NACE CP4

Yanfang Fan

Associate Professor/Master Supervisor

CO_2 capture technologies

Zehui Zhao

Lecturer/Doctor

Biomimetic Nano-coating Materials

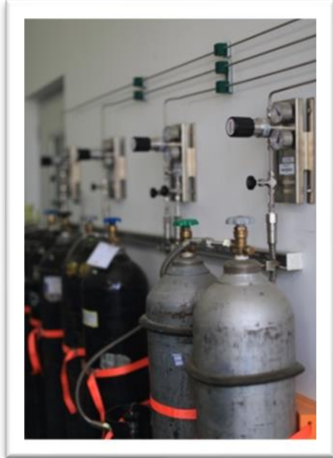
Yong Xiang **China University of Petroleum, Beijing**

- **Ocean Engineering Research Institute**, Vice President
- College of Mechanical and Transportation Engineering, Professor/Doctoral Supervisor
- **Ohio University**, Institute of Corrosion and Multiphase Flow Technology, Postdoctoral Fellow, Co-Supervisor: Srdjan Nesic.
- **Tsinghua University**, Power Engineering and Engineering Thermophysics, Ph.D.
- **Tsinghua University**, Thermal and Power Engineering, B.S.

Yong Xiang is mainly engaged in the research of carbon capture and sequestration technology, corrosion and protection of oil and gas equipment, and high temperature failure of power plant equipment materials. He is in charge of the surface/youth projects of National Natural Science Foundation of China, the surface project of Beijing Natural Science Foundation, the project of Open Fund for State Key Laboratory, and a number of enterprise projects, and participates in the sub-projects of the National Key Research and Development Program of China. He has published more than 50 academic papers, including more than 30 SCI papers and more than 500 citations.

1. Research Group Experimental Equipment

High-temperature and high-pressure autoclave



Gas distribution system

Potentiostat

Glass Reactor

High Temperature Thermal Cycling Test Furnace

High temperature tube furnace

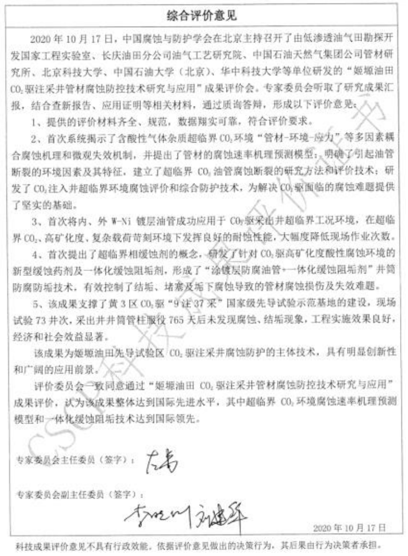
Sterilizer

Constant temperature mold incubator

1. Research Group Supercritical CO_2 Corrosion Prediction Software

- Currently, **SuperCCorp** software **has been applied to thirteen units** in Changqing, Daqing, Jilin, Zhongyuan and Yanchang oilfields.
- The appraisal opinion of the Chinese Society of Corrosion and Protection (Prof. Xiaogang Li, Chairman of the Board of Directors, and Prof. Yu Zuo, an expert in materials protection, were members of the appraisal committee)
  - ✓ The team established a mechanistic supercritical CO_2 corrosion rate prediction model, **which has reached the international leading level.**
  - ✓ The team's scientific achievements have created an overall economic benefit of **32.357 million RMB**.
- In this field, we successfully applied for one national and one Beijing Municipal surface funding and successfully published several academic papers

Evaluation Opinions



综合评价意见

2020 年 10 月 17 日，中国腐蚀与防护学会在北京主持召开了由低渗透油气田勘探开发国家工程实验室、长庆油田分公司油气工艺研究院、中国石油天然气集团公司管材研究所、北京科技大学、中国石油大学（北京）、华中科技大学等单位研发的“姬塬油田 CO_2 驱注采井管材腐蚀防控技术研究与应用”成果评价会。专家委员会听取了研究成果汇报，结合查新报告、应用证明等相关材料，通过质询答辩，形成以下评价意见：

1、提供的评价材料齐全、规范，数据翔实可靠，符合评价要求。

2、首次系统揭示了含酸性气体杂质超临界 CO_2 环境“管材-环境-应力”等多因素耦合腐蚀机理和微观失效机制，并提出了管材的腐蚀速率机理预测模型；明确了引起油管断裂的环境因素及其特征，建立了超临界 CO_2 油管腐蚀断裂的研究方法和评价技术；研发了 CO_2 注入井超临界环境腐蚀评价和综合防护技术，为解决 CO_2 驱面临的腐蚀难题提供了坚实的基础。

3、首次将内、外 W-Ni 镀层油管成功应用于 CO_2 驱采出井超临界工况环境，在超临界 CO_2、高矿化度、复杂载荷苛刻环境下发挥良好的耐蚀性能，大幅度降低现场作业次数。

4、首次提出了超临界相缓蚀剂的概念，研发了针对 CO_2 驱高矿化度酸性腐蚀环境的新型缓蚀药剂及一体化缓蚀阻垢剂，形成了“涂镀层防腐油管+一体化缓蚀阻垢剂”井筒防腐防垢技术，有效控制了结垢、堵塞及垢下腐蚀导致的管材腐蚀损伤及失效难题。

5、该成果支撑了黄 3 区 CO_2 驱“9 注 37 采”国家级先导试验示范基地的建设，现场试验 73 井次，采出井井筒管柱服役 765 天后未发现腐蚀、结垢现象，工程实施效果良好，经济和社会效益显著。

该成果为姬塬油田先导试验区 CO_2 驱注采井腐蚀防护的主体技术，具有明显创新性和广阔的应用前景。

评价委员会一致同意通过“姬塬油田 CO_2 驱注采井管材腐蚀防控技术研究与应用”成果评价，认为该成果整体达到国际先进水平，其中超临界 CO_2 环境腐蚀速率机理预测模型和一体化缓蚀阻垢技术达到国际领先。

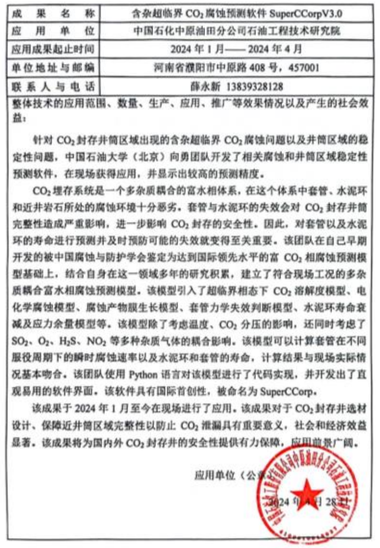
专家委员会主任委员（签字）：

专家委员会副主任委员（签字）：

2020 年 10 月 17 日

科技成果评价意见不具有行政效能，依据评价意见做出的决策行为，其后果由行为决策者承担。

Application Proof



成 果 名 称	含杂超临界 CO_2 腐蚀预测软件 SuperCCorpV3.0
应 用 单 位	中国石化中原油田分公司石油工程技术研究院
应用成果起止时间	2024 年 1 月—— 2024 年 4 月
单位地址与邮编	河南省濮阳市中原路 408 号，457001
联 系 人 与 电 话	薛永新 13839328128

整体技术的应用范围、数量、生产、应用、推广等效果情况以及产生的社会效益：

针对 CO_2 封存井筒区域出现的含杂超临界 CO_2 腐蚀问题以及井筒区域的稳定性问题，中国石油大学（北京）向勇团队开发了相关腐蚀和井筒区域稳定性预测软件，在现场获得应用，并显示出较高的预测精度。

CO_2 埋存系统是一个多杂质耦合的富水相体系，在这个体系中套管、水泥环和近井岩石所处的腐蚀环境十分恶劣。套管与水泥环的失效会对 CO_2 封存井筒完整性造成严重影响，进一步影响 CO_2 封存的安全性。因此，对套管以及水泥环的寿命进行预测并及时预防可能的失效就变得至关重要。该团队在自己早期开发的被中国腐蚀与防护学会鉴定为达到国际领先水平的富 CO_2 相腐蚀预测模型基础上，结合自身在这一领域多年的研究积累，建立了符合现场工况的多杂质耦合富水相腐蚀预测模型。该模型引入了超临界相态下 CO_2 溶解度模型、电化学腐蚀模型、腐蚀产物膜生长模型、套管力学失效判断模型、水泥环寿命衰减及应力余量模型等。该模型除了考虑温度、CO_2 分压的影响，还同时考虑了 SO_2、O_2、H_2S、NO_2 等多种杂质气体的耦合影响。该模型可以计算套管在不同服役周期下的瞬时腐蚀速率以及水泥环和套管的寿命，计算结果与现场实际情况基本吻合。该团队使用 Python 语言对该模型进行了代码实现，并开发出了直观易用的软件界面。该软件具有国际首创性，被命名为 SuperCCorp。

该成果于 2024 年 1 月至今在现场进行了应用。该成果对于 CO_2 封存井选材设计、保障近井筒区域完整性以防止 CO_2 泄漏具有重要意义，社会和经济效益显著。该成果将为国内外 CO_2 封存井的安全性提供有力保障，应用前景广阔。

应用单位（公章）

2024 年[illegible]月 28 日

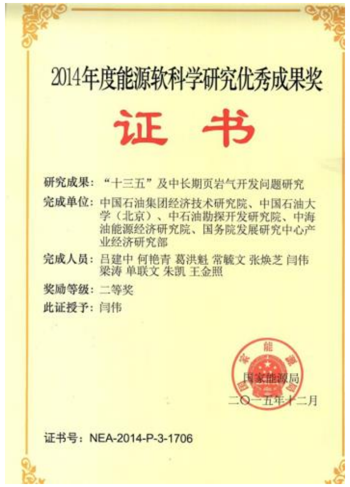
1. Research Group Science and Technology Awards

- **Won the second prize of Shaanxi Provincial Scientific and Technological Progress in 2023.**
- **Accumulated 6 provincial and ministerial level awards.**

中国腐蚀与防护学会
科学技术奖励
证 书
为表彰中国腐蚀与防护学会科学技术奖获得者，特颁发此证书。
项目名称：姬塬油田 CO_2 驱注采井管材腐蚀防控技术研究与应用
奖励等级：一等奖
获 奖 者：向 勇
2021年1月20日
证书编号：2020-KJ-1-005-W04

陕西省科学技术进步奖
证 书
为表彰陕西省科学技术进步奖获得者，特颁发此证书。
项目名称：CO2 驱注采环境管材腐蚀防控技术研究与应用
奖励等级：二等
获 奖 者：向勇
2024年3月22日
证 书 号：2023-J-234142-2-R03

国科奖社证字第0191号
2021年中国产学研合作创新与促进奖
产学研合作创新成果奖
获奖证书
为表彰在产学研深度融合中取得的重要科技创新成果，特颁发此证书。
奖项等级：二等奖
完成单位：中国石油大学（北京）
证书号：20216083
中国产学研合作促进会
2022年1月



2014年度能源软科学研究优秀成果奖
证 书
研究成果："十三五"及中长期页岩气开发问题研究
完成单位：中国石油集团经济技术研究院、中国石油大学（北京）、中石油勘探开发研究院、中海油能源经济研究院、国务院发展研究中心产业经济研究部
完成人员：吕建中 何艳青 葛洪魁 常毓文 张焕芝 闫伟 梁涛 单联文 朱凯 王金照
奖励等级：二等奖
此证授予：闫伟
国家能源局
二〇一五年十二月
证书号：NEA-2014-P-3-1706

中国海洋石油集团有限公司科技进步奖
证 书
2018AY03R08
为表彰在促进科学技术进步工作中做出的重大贡献者，特颁发科技进步奖证书。
项目名称：海上油套管防腐及优化技术研究与应用
获奖等级：一等奖
获 奖 人：闫伟
中国海洋石油集团有限公司
二零一九年二月

证 书
为表彰在促进石油和化工科技进步中做出突出贡献者，特颁发此证书，以资鼓励。
奖 种：创新团队奖
团队名称：中国石油大学（北京）非常规油气研究创新团队
带 头 人：宋岩、钮凤林、周福建
奖励日期：2018 年 11 月 30 日
证书编号：2018T002
中国石油和化学工业联合会

1. Research Group

More Than 30 SCI Articles and 500 Citations

1. Chen Li, Yong Xiang[#*], Rongteng Wang, Jun Yuan, Yuhao Xu, Wenguan Li, Zhanguang Zheng. Exploring the influence of flue gas impurities on the electrochemical corrosion mechanism of X80 steel in a supercritical CO_2-saturated aqueous environment, ***Corrosion Science***, 211 (2023) 110899.
2. Kai Yan, Yong Xiang[#*], Haiyuan Yu, Zhenrui Li, Yajing Wu, Jian Sun. Effect of irregular microcracks on the hot corrosion behavior and thermal shock resistance of YSZ thermal barrier coatings. ***Surface and Coatings Technology*** 431 (2022) 128038.
3. Kai Yan, Haiyuan Yu, Yong Xiang[*], Yuwei Guo, Yajing Wu, Zhenrui Li, Jian Sun, Zhanqing Li. Oxidation and interfacial cracking behaviors of TBCs with double-layered bond coat on different substrate materials. ***Corrosion Science*** 209 (2022) 110770.
4. Qingjun Gong, Yong Xiang[#*], Jianquan Zhang, Rongteng Wang, Dahui Qin. Influence of elemental sulfur on the corrosion mechanism of X80 steel in supercritical CO_2-saturated aqueous phase environment. ***The Journal of Supercritical Fluids*** 176 (2021) 105320.
5. Yong Xiang, Weiman Xie, Shiyi Ni, Xihan He. Comparative study of A106 steel corrosion in fresh and dirty MEA solutions during the CO_2 capture process: Effect of NO_3^-. ***Corrosion Science*** 167 (2020) 108521.
6. Yong Xiang, Chicheng Song, Chen Li, Erdong Yao, Wei Yan. Characterization of 13Cr steel corrosion in simulated EOR-CCUS environment with flue gas impurities. ***Process Safety and Environmental Protection*** 140 (2020) 124-136.
7. Yong Xiang, Zhengwei Long, Chen Li, Wei Yan. Neutralization and adsorption effects of various alkanolamines on the corrosion behavior of N80 steel in supercritical CO_2 with impurities. ***Corrosion*** 75 (2019) 999-1011.
8. Chen Li, Yong Xiang[#*], Wenguan Li. Initial corrosion mechanism for API 5L X80 steel in CO_2/SO_2-saturated aqueous solution within a CCUS system: Inhibition effect of SO_2 impurity. ***Electrochimica Acta*** 321 (2019) 134663.
9. Chen Li, Yong Xiang[*], Chicheng Song, Zhongli Ji. Assessing the corrosion product scale formation characteristics of X80 steel in supercritical CO_2-H_2O binary systems with flue gas and NaCl impurities relevant to CCUS technology. ***Journal of Supercritical Fluids*** 146 (2019) 107-119.
10. Yong Xiang. Corrosion issues of carbon capture, utilization, and storage. ***Materials Performance*** 57 (2018) 32-35.
11. Yong Xiang, Chen Li, Wuermanbieke Hesitao, Zhengwei Long, Wei Yan. Understanding the pitting corrosion mechanism of pipeline steel in an impure supercritical CO_2 environment. ***Journal of Supercritical Fluids*** 138 (2018) 132-142.
12. Yong Xiang , Yu Yuan, Pei Zhou et.al . Metal Corrosion in Carbon Capture, Utilization, and Storage: Progress and Challenges. **Engineering Sciences**, 2023, 25(3): 1-12. (In Chinese)

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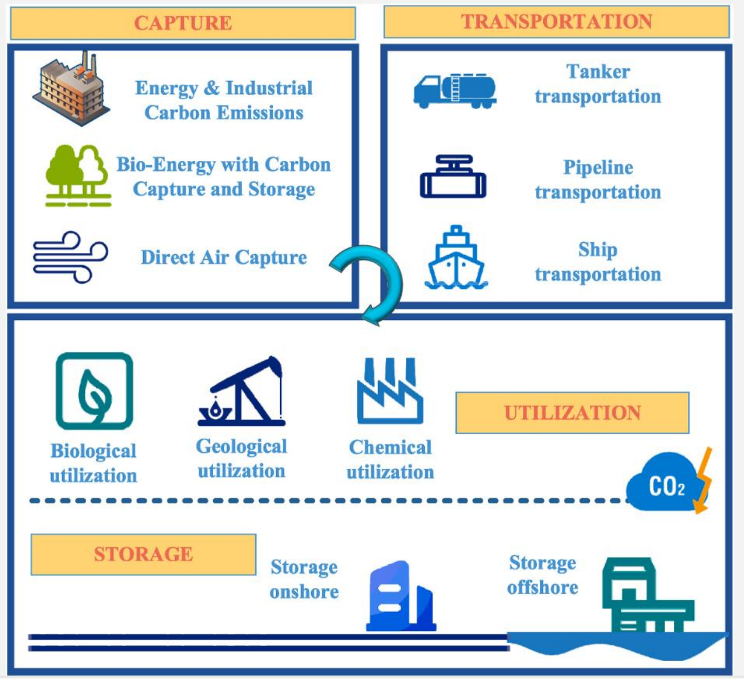
2. Research Background CCUS Background

China CO_2 pipeline facility



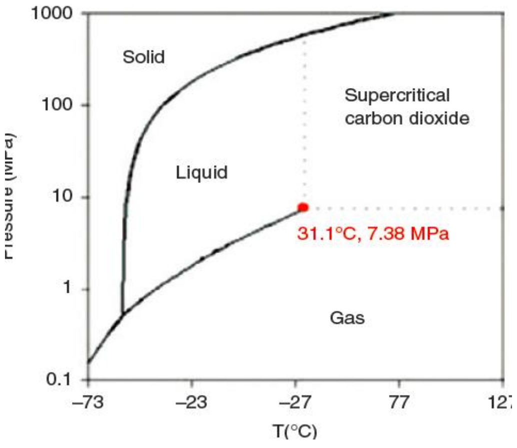
CCUS Process（Zhou, et al. Energy 310 (2024) 133225)

- By 2050, more than 85% of China's fossil energy power generations will use CCUS owing to the carbon peaking and carbon neutrality goals (Dual Carbon Goals). There will be thousands of million-ton CCUS projects.
- CCUS technology currently faces two major challenges: **high energy consumption for capture** and **uncertainty of storage safety.**

2. Research Background CCUS Corrosion Characteristics

CCUS corrosion characteristics:

- Wide range of equipment and materials
- Highly corrosive media
- Multiple phase environments
- **Variety of carbon source impurities**
- Complex cathode and anode reaction mechanisms
- Complex and variable composition of product films
- **Lack of corrosion protection experience**



CO_2 phase diagram
(Wei et al. Corrosion Review 2015 33(3-4): 151-174)

Impurity gas content of CO_2 captured by technologies (Oosterkamp and Ramse n, POLYTEC, 2008)

Component	Oxyfuel combustion capture	pre-combustion capture	post-combustion capture
CO_2	>90 v%	>95.6 v%	>99 v%
C2+	--	<0.01 v%	<100 ppmv
N_2	<7 v%	<0.6 v%	<0.17 v%
CH_4	--	<350 ppmv	<100 ppmv
CO	Trace	<0.4 v%	<10 ppmv
H_2S	Trace	<3.4 v%	Trace
NO_x	<0.25 v%	--	<50 ppmv
SO_x	<2.5 v%	--	<10 ppmv
O_2	<3 v%	Trace	<0.01 v%
H_2	Trace	<3 v%	Trace
Ar	<5 v%	0.05 v%	Trace

Supercritical conditions for several substances

Solvent	Critical T (K)	Critical P (MPa)	Critical density (g/cm^{-3})
CO_2	304.3	7.4	0.486
NH_3	405.5	11.2	3.0~ 8.0
H_2O	667	22.1	0.322
SO_2	157.5	7.9	0.525
HCF_3	299.3	4.8	0.525
CH_3CN	547.7	4.8	0.237

2. Research Background

Cost of CO_2 Capture Technologies

Comparison of Advantages Disadvantages and Cost of Different CO_2 Capture Technologies

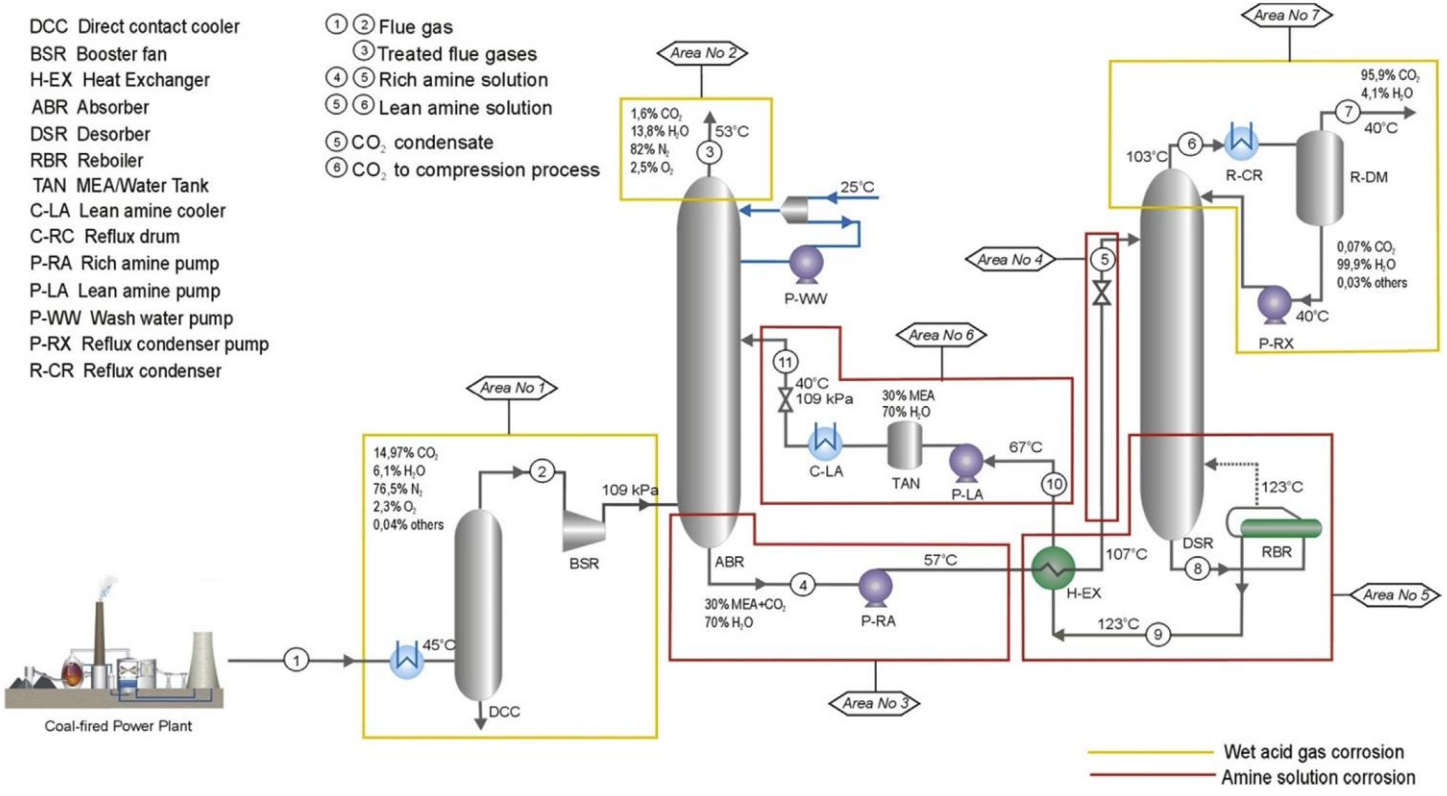
(Xiang et.al. Petroleum Geology and Recovery Efficiency, 2022, 29(4): 1-17. In Chinese)

Capture Technology	Advantages	Disadvantages	Application Areas	Capture Cost
Chemical Absorption	Mature technology, simple process modifications	High energy consumption, severe corrosion, loss of absorbent, high operational cost	CO_2 compression, such as in flue gas from power plants	**Amine absorption: 150-400 RMB/ton**
Physical Absorption	High absorption capacity, low energy consumption, non-corrosive equipment	CO_2 removal efficiency not high	CO_2 compression, such as in coal chemical industry, ammonia production	**Low-temperature methanol wash: 100 RMB/ton**
Adsorption Separation	Simple process, low energy consumption, high product purity	Frequent adsorbent regeneration, automation challenges, requires large adsorbent quantities	Suitable for industrial gases with CO_2 concentrations of 20-80%, such as in ammonia synthesis gas	**200-400 RMB/ton**
Membrane Separation	Low energy consumption, small equipment size, easy operation and maintenance	Membrane material prone to contamination, difficult to clean, high requirements for temperature and corrosion resistance	Mainly used in natural gas treatment	**500 RMB/ton (Guangdong Huayin Fenghai)**
Low-temperature Distillation	Produces high purity, liquid CO_2	Equipment is bulky, high energy consumption, separation efficiency varies	Suitable for high-concentration CO_2 recovery, such as in oil fields	**284 RMB/ton**
Pre-combustion Capture	High pollutant removal efficiency, low oxygen content	High operational cost, long construction period, low system reliability	IGCC (Integrated Gasification Combined Cycle)	**239 RMB/ton**
Oxy-fuel Combustion Capture	Low flue gas loss, high boiler efficiency, can retrofit existing boiler units	Energy loss due to oxygen and CO_2 compression, affects power plant efficiency	Currently in pilot testing	**780-900 RMB/ton**
Chemical Looping Combustion	High fuel conversion efficiency, low by-product generation of nitrogen compounds	Technology still in research, lacks experience in large-scale operation	Currently in chemical looping combustion reactor testing phase	**/**
Hydrate Separation	Simple equipment, easy operation, low capital investment	Technology still in research, lacks experience in large-scale operation	Applied in low-concentration CO_2 separation, potential for natural gas dehydration	**/**

2. Research Background

Amine Capture System

- Organic amine capture technology is **the most mature CO_2 capture technology**;
- Widely used in the field of natural gas purification. Also used in post-combustion capture of coal-fired power plants;
- Organic amines will suffer thermal, chemical & **oxidative degradation. They will volatilize into the CO_2 stream.**



Organic amine CO_2 capture system

(Krzemien, et al. Journal of Loss Prevention in the Process Industries 43 (2016) 189-197)

2. Research Background

Energy Consumption of CO_2 Capture

Costs of composite organic amines for capturing flue gas from a coal-fired boiler with a CO_2 concentration of 10% (Shasha Wang, Cost analysis of existing CO_2 capture technologies, 2023, (02): 62-64. In Chinese)

No.	Name	Unit	Utility Unit Price (RMB)	Consumption Amount (per ton of CO_2 product)			Operating Cost (RMB per ton of product)
				Pre-treatment	Absorption/ Desorption	Compression and Liquefaction	
1	Electricity	kW·h	0.5	50	36	130	108
2	Circulating Cooling Water	m^3	0.3	30	120	20	51
3	3-bar Steam	t	130	0	1.3	0	169
	Total						328

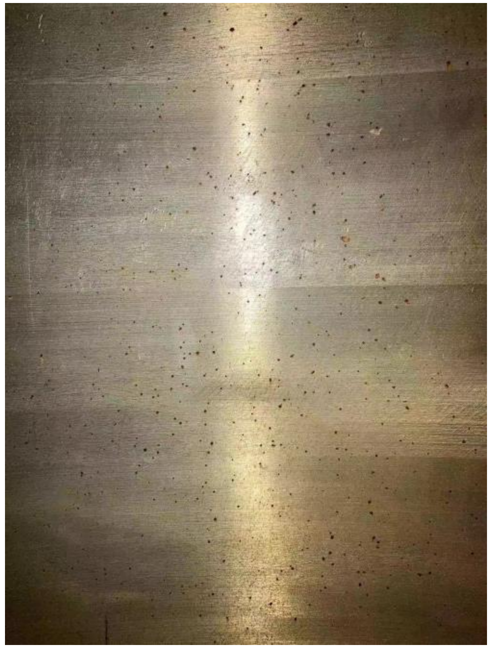
- Among the carbon sources of CO_2 emissions, they can be categorized into high concentration carbon sources (above 80%); medium concentration carbon sources (20% and 80%); and **low concentration carbon sources (below 20%).**
- High- and medium-concentration carbon sources, such as ammonia decarbonization gas and coal hydrogen tail gas, account for only a small portion; the vast majority are low-concentration carbon sources, **mainly flue gas.**

2. Research Background Corrosion of Capture System

- The CO_2 capture process causes severe corrosion from **acid gases** and **chloride ions**. Protection measures includes the use of **corrosion-resistant alloys, inhibitors and coatings**.
- NACE statistics show that 98% of **amine stress corrosion cracking** (ASCCs) are related to **improper post-weld heat treatment.**

Corrosion monitoring at the Technology Center Mongstad (TCM) .Results of corrosion of various materials during CO_2 absorption in aqueous MEA
(Flø, et al , International Journal of Greenhouse Gas Control 84 (2019) 91–110.)

materials	level	Type of test
Stainless steel (with weld)	316 L SS	Uniform and pitting corrosion
Stainless steels	316 L SS	stress corrosion cracking
Duplex steel	22Cr Duplex Stainless Steel	stress corrosion cracking
Super duplex steel	25Cr Duplex Stainless Steel	Uniform and pitting corrosion
Carbon steel	235 CS	Uniform corrosion
HNBR	—	degradation
EPDM-AL	—	degradation
EPDM-XH	—	degradation



Pitting corrosion of 30408 stainless steel in a domestic organic amine capture system

Corrosion cracking of impeller of poor amine solution transfer pump in CO_2 capture system

2. Research Background Transportation System

- Based on the failure causes of 29 reported accidents that occurred in U.S CO_2 pipeline from 1986 to 2008, it can be seen that corrosion is the main causative factor for CO_2 pipeline accidents **(45%).**

Thermodynamic property

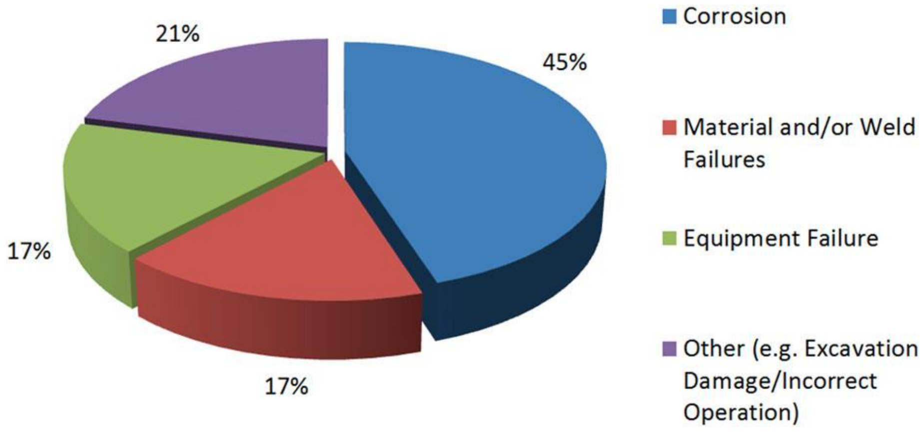
Transportation characteristics

Impurities in the carbon dioxide stream from CCUS

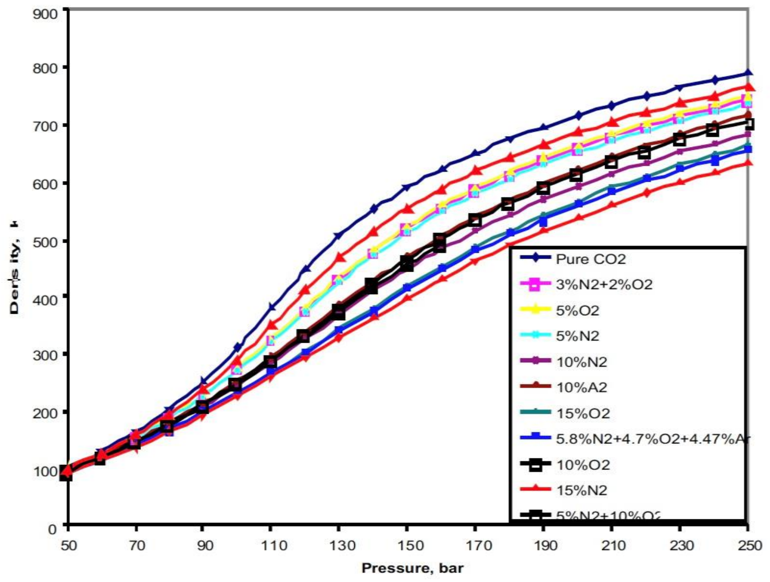
Economy and safety

Impurities:

N_2, Ar, O_2, H_2O, NO_x, SO_x, H_2S



Failure modes of CO_2 piping systems in the United States (Johnson, et al. 'Mapping of potential HSE issues related to large-scale capture, transport and storage of CO_2 (Det Norsk Veritas, Horvik. Norway)', 2008.)



Effect of impurities on the density of CO_2 mixtures
(Wang, et al. Energy Procedia 4 (2011) 3071-3078)

Impurities can affect the physical properties of CO_2 mixtures, which may have a significant effect on the **corrosion and hydrate formation.**

2. Research Background Transportation System

- Supercritical CO_2 may be converted to liquid CO_2 during pipeline transportation, collectively referred to as **dense-phase CO_2**. Corrosion of dense-phase CO_2 during transportation is affected by a variety of factors.

Medium

Water content

Impurity gases

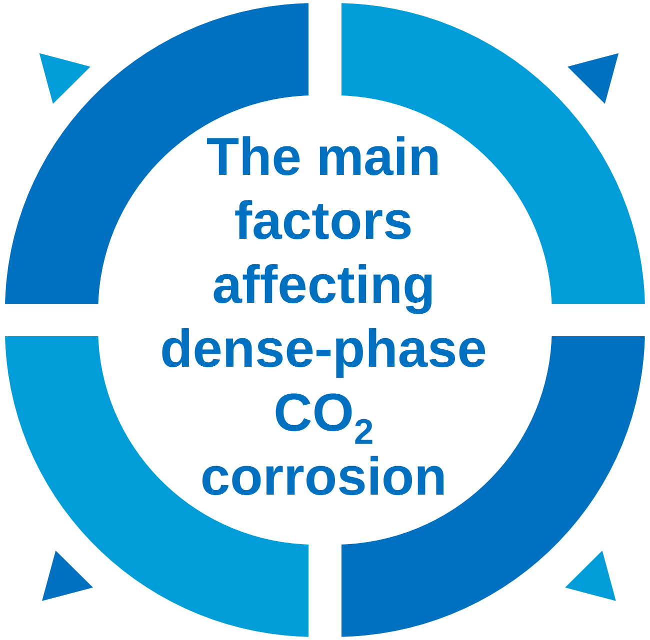
pH

Environment

Temperature

Pressure

Flow rate



Material

Chemical composition

Heat treatment

Microstructures

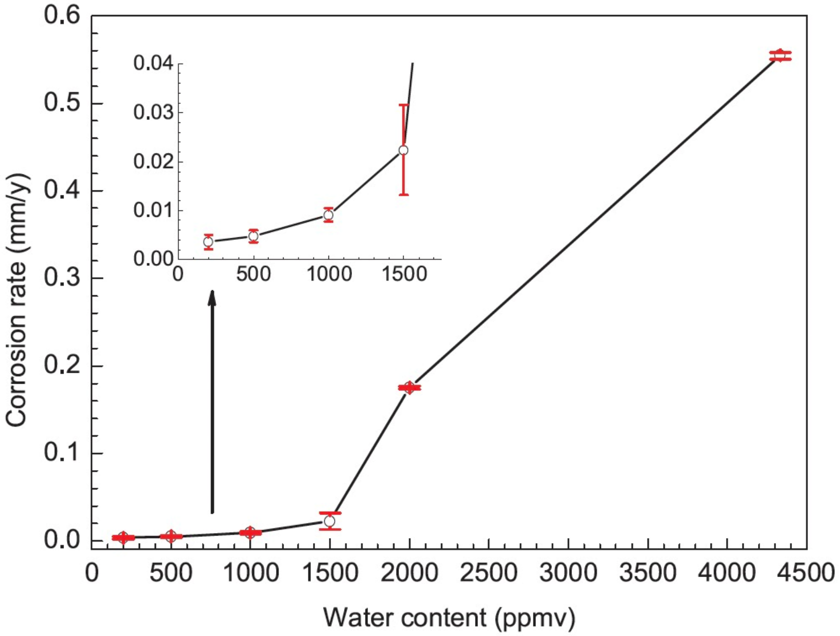
Surface roughness

Others

Service time

Coating

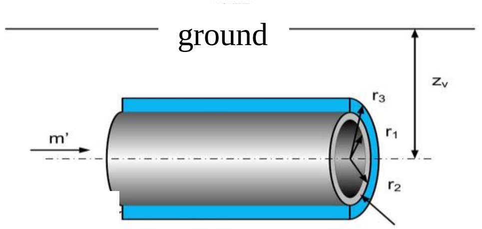
Inhibitor



Critical Relative Humidity in SC-CO_2 system

(Sun C, et al. Corrosion Science 137 (2018) 151–162)

2. Research Background



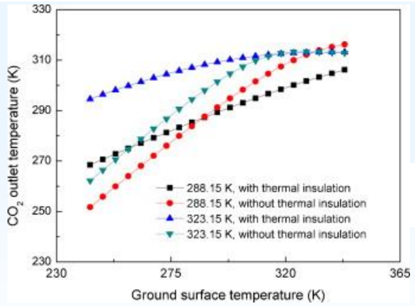
Schematic diagram of CO_2 pipeline heat transfer model

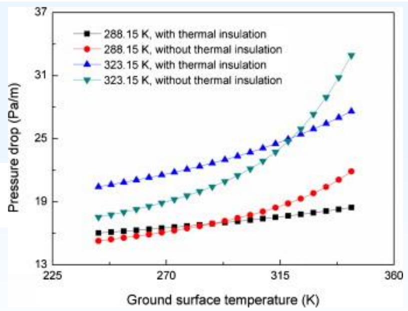
Mathematical model

$$U_c = \frac{1}{\frac{1}{h_c} + \frac{r_1}{k_p}\ln\left(\frac{r_2}{r_1}\right) + \frac{r_1}{k_{in}}\ln\left(\frac{r_3}{r_2}\right) + \frac{r_1}{k_{soil}}\ln\left(\frac{2z_v}{r_3}\right)}$$

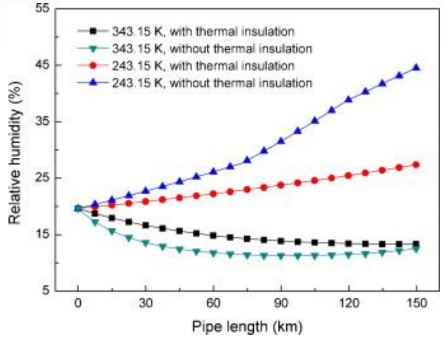
Mathematical expression of total heat transfer coefficient

Pressure drop calculation

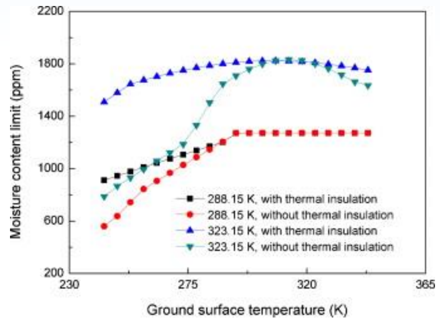




Relative humidity along the pipeline



Moisture content limit



- A thermodynamic model of the upper limit of the moisture content of pipeline CO_2 under extreme conditions was developed, and the prediction results were **in good agreement with the results of European DYNAMIS project.**

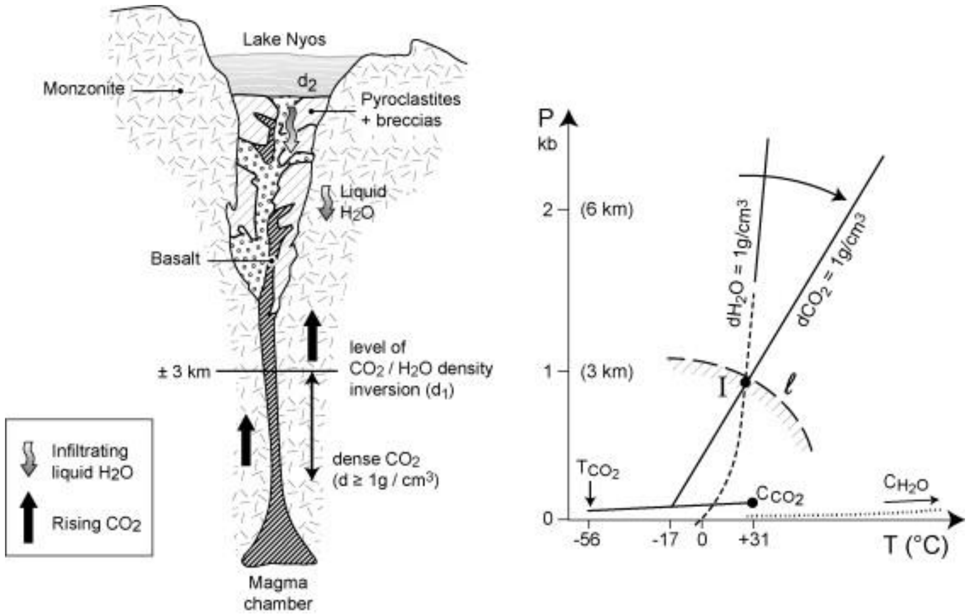
Corrosion Protection Measures in CO_2 Transportation Pipelines

- Moisture content has a huge impact on the corrosion process, and **dehydration** can effectively reduce the corrosion rate.
- **Use of stainless steel** for piping reduces the corrosion rate of the pipeline.

2. Research Background Storage System

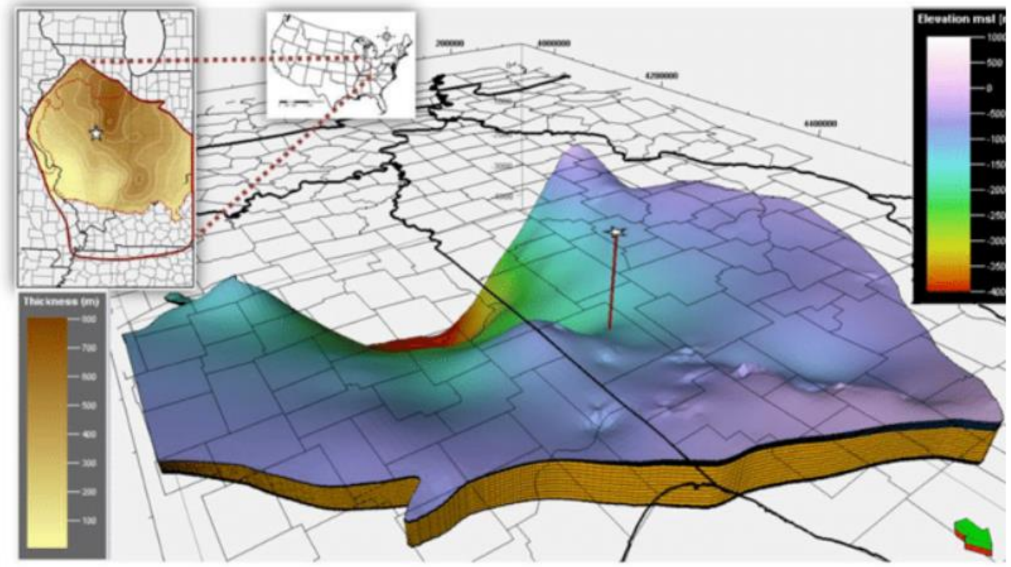
- In 1986, massive natural CO_2 erupted from the bottom of Lake Nyos in Cameroon, which spread to the surrounding low-lying areas in a short period of time, resulting in a serious accident in which around **1,700 people died.**

ADM's first major underground carbon sequestration facility in Illinois in the United States has experienced two leaks from a **corroded monitoring well** in March and July 2024. To date approximately **8,000 tons of liquid CO_2** and other fluids have flowed into uncontrolled areas. It is the **world's first CO_2 leakage** of CCS or CCUS projects!



Lake Nyos Volcanic System

(Jacques, et al. Was the lethal eruption of Lake Nyos related to a double CO_2/H_2O density inversion. 342(2010) 19−26)

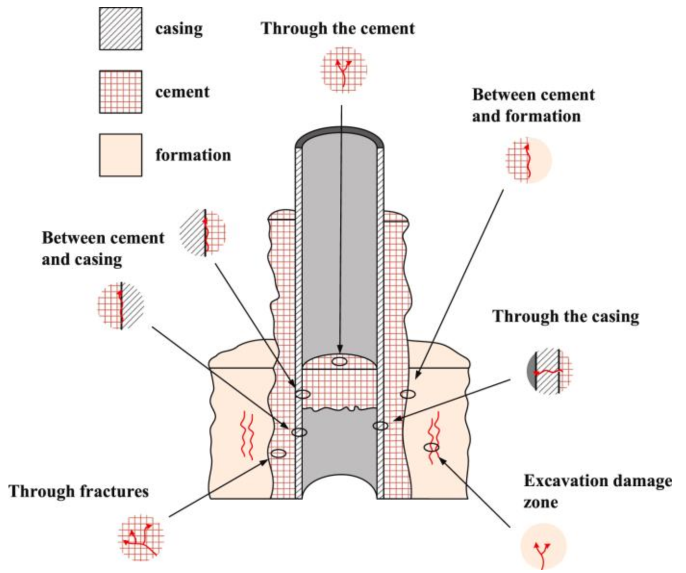


Illinois basin

2. Research Background   Storage System

CO_2-EOR well corrosion

Scaling on the inner wall of production wells



Potential leakage pathways in wellbore system

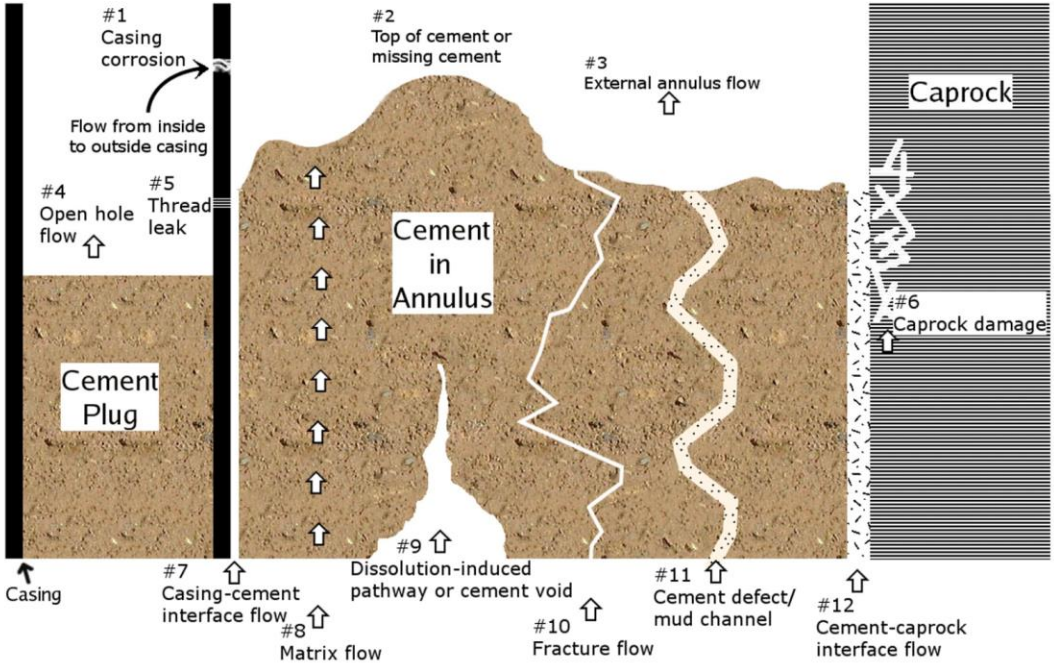
(Reinicke, et al. In: Sino-German Conference on Underground Storage of CO_2 and Energy, Beijing, China (2010) 6-13)

- The CO_2-EOR process and storage system may contain corrosive gases such as O_2, SO_x, NO_x, H_2S, which can cause **more serious damage** to the pipe column such as perforation and fracture.
- The main types of corrosion: **pitting, stress corrosion, microbial corrosion, galvanic corrosion and crevice corrosion, etc.**
- Producing wells under high mineralization conditions have serious **scaling problems** inducing under-deposit corrosion.

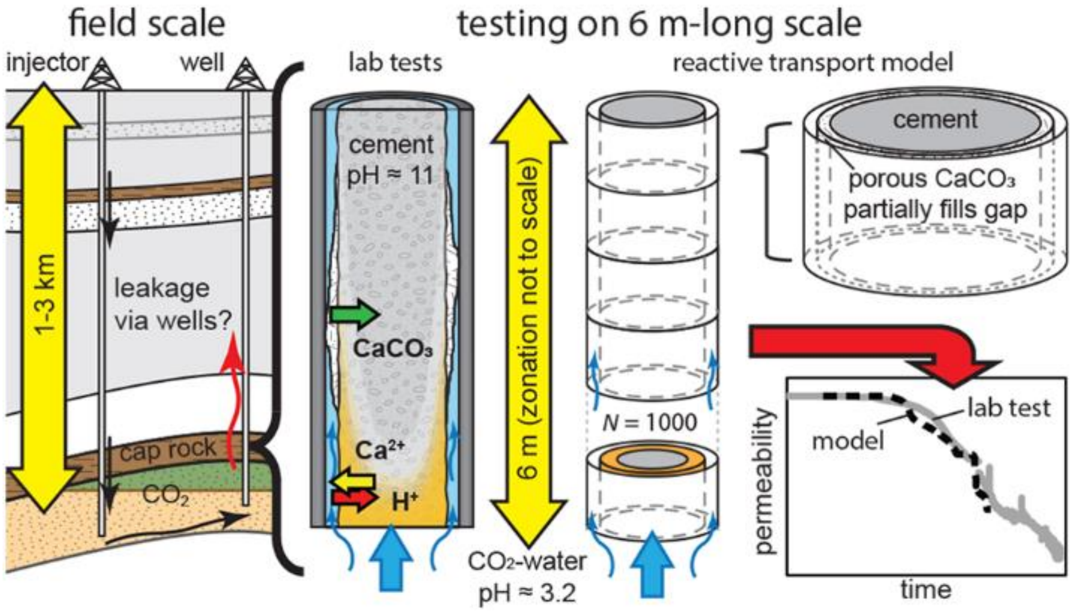
2. Research Background

Storage System

- Long-term, safe CO_2 sequestration is the goal of CCUS, so maintaining well integrity throughout the **entire life of the project (1000 year?)** is a key issue in ensuring the safety of CCUS.
- Failure of wellbore area integrity due to corrosion and degradation of materials under long-cycle containment and **CO_2 leakage from the wellbore area are issues of concern.**



Schematic diagram of CO_2 leakage path in the well region
(Carroll, et al. Int. J. Greenh. Gas Con. 49 (2016) 149–160)



Casing-cement interface defects undergo self-closing/opening behavior in the presence of CO_2-H_2O
(Timotheus, et al. Environ. Sci. Technol. 52(2018) 3786−3795)

Report Outline

01
Research Group

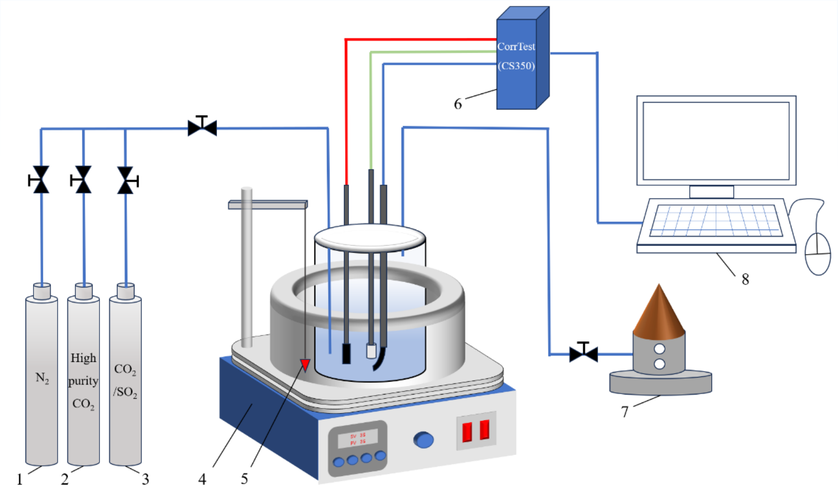
02
Research Background

03
Results and Discussion

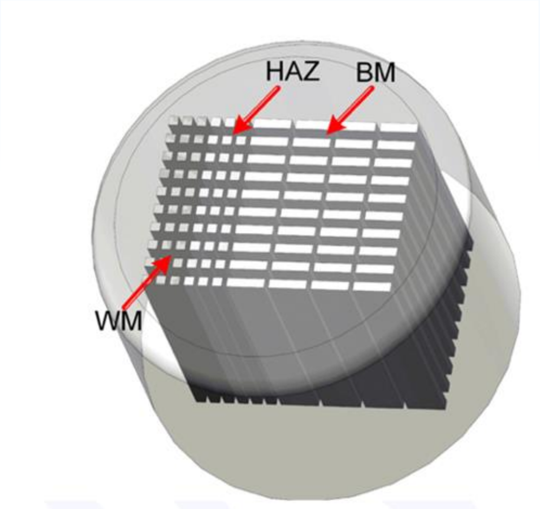
04
Conclusions and Prospects

3. Results and Discussion Experimental Setup

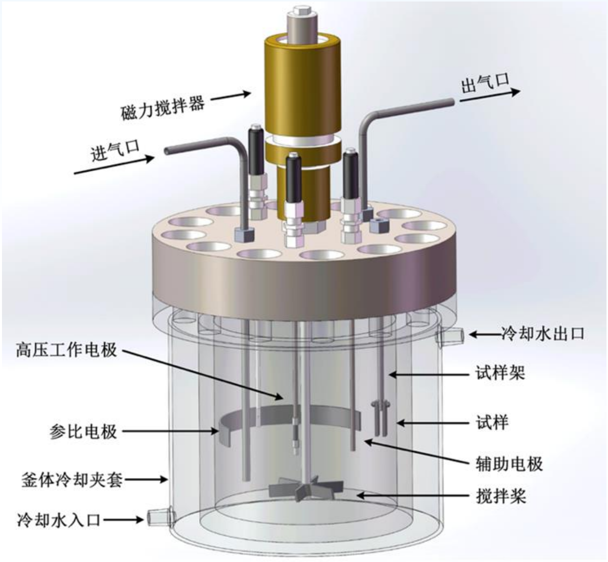
- The atmospheric pressure test is carried out in a glass cell; the high pressure test is carried out in an autoclave.
- The corrosion rate, morphology, and product film of the samples were analyzed **using weight-loss method, SEM, XPS, XRD, and 3D morphology**. High-pressure tests were conducted for high-pressure electrochemical measurements.



Experimental setup diagram:
(1. N_2; 2. high purity CO_2; 3. CO_2/SO_2; 4. reaction device; 5. thermocouple; 6. electrochemical workstation; 7. tail gas device; 8. computer)

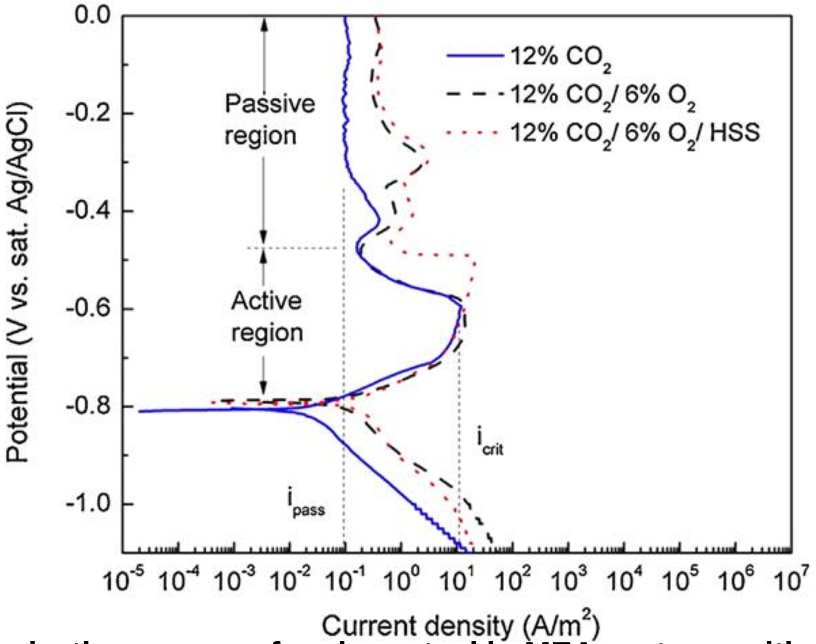


Welded joint electrode

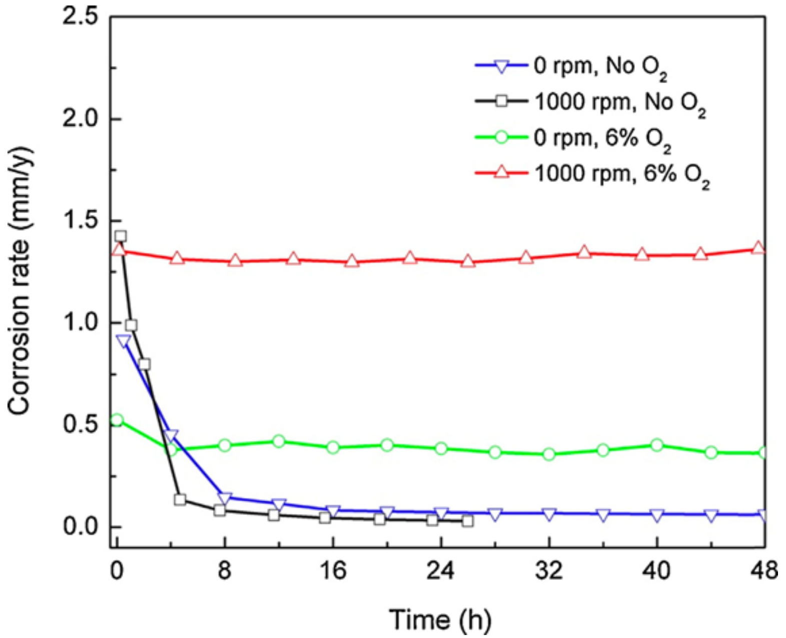


High-temperature and high-pressure autoclave

➢ Organic amine degradation and corrosion mechanism



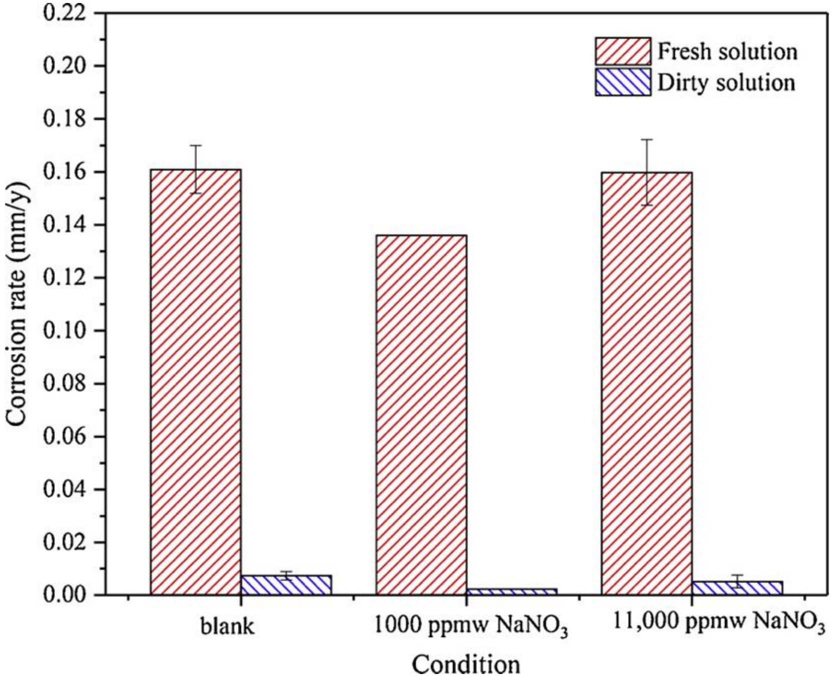
Polarization curves of carbon steel in MEA systems with O_2 and HSS (after 7-day exposure, 50 °C).



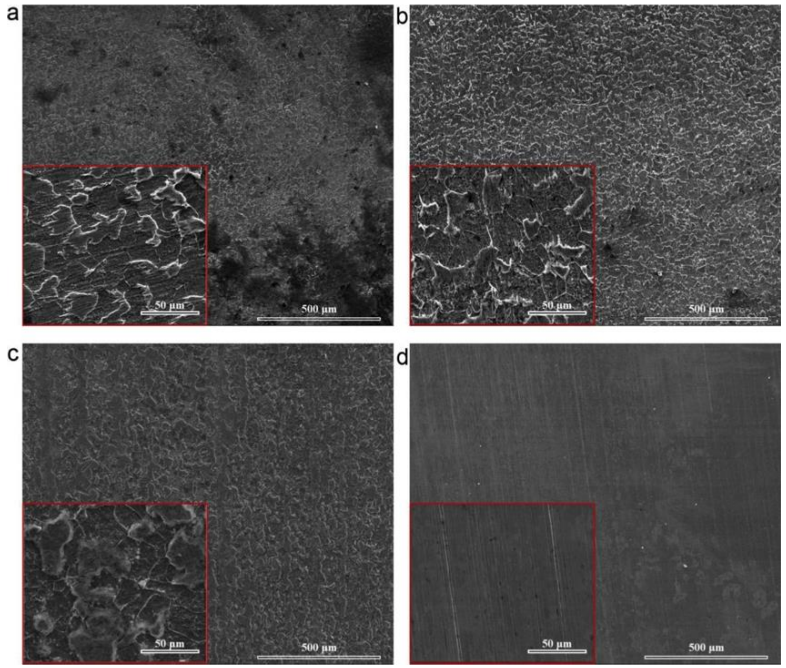
Effect of flow on the corrosion rate of carbon steel with time under different conditions.

- The addition of O_2 and heat stabilized salt (HSS) to the monoethanolamine (MEA) -containing solution revealed that the anodic reaction process had the activation and passivation regions, while the **cathode reaction was enhanced.**
- When oxygen and flow were both present, the corrosion rate did not decrease over time, **the flow increased the mass transfer process and accelerated corrosion.**

➢ Organic amine degradation and corrosion mechanism



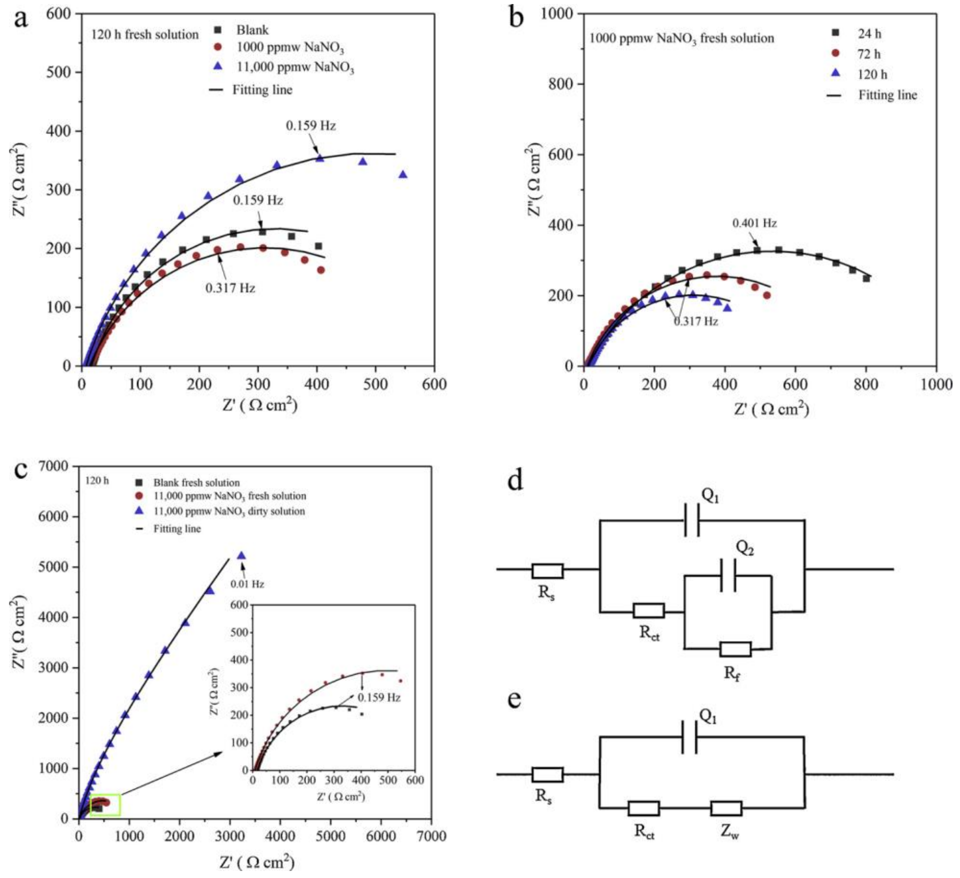
Corrosion rate of A106 steel in MEA solution before and after degradation (50°C, atmospheric environment)



Low corrosion rate of A106 steel after 120 h of MEA degradation(a) fresh solution, 24 h, (b) fresh solution, 72 h, (c) fresh solution, 120 h, (d) dirty solution, 120 h (exposed from 120 to 240 h)

- The corrosion rate of specimens in dirty solution was found to be **significantly lower than that in the fresh solution** by weight-loss method.
- Obvious corrosion happened on the surface of the specimen in the fresh solution, while grinding marks were observed on the smooth surface of the specimen in the dirty solution.

➢ Organic amine degradation and corrosion mechanism

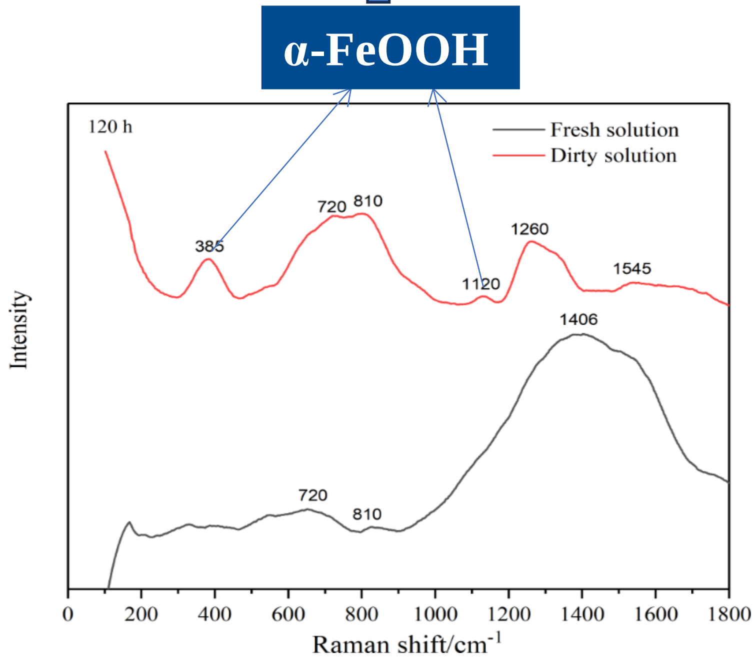


Nyquist plots of A106 steel in CO_2-O_2-MEA solution at 50 °C:
(a) with different concentrations of $NaNO_3$ in fresh solution after 120 h; (b) in fresh solution with 1000 ppmw $NaNO_3$ and different time durations; (c) in fresh and dirty solutions after 120 h with 11,000 ppmw $NaNO_3$; (d) equivalent circuit of fresh solution; (e) equivalent circuit of dirty solution.

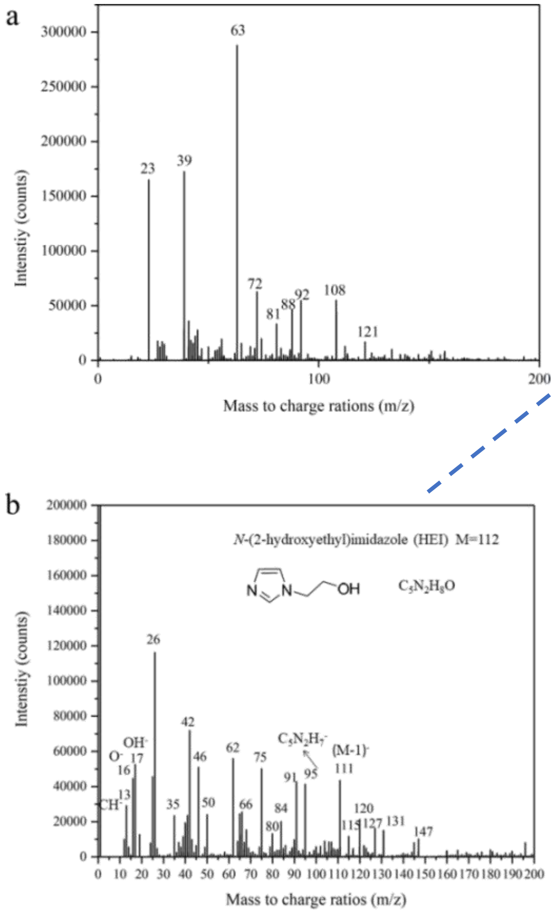
- The EIS results are in agreement with the weight loss method, and it was found that the diameter of the capacitive arc of the specimen in the dirty solution was significantly larger than that of the fresh solution, **the resistance was greater and the corrosion rate was lower.**
- The corrosion rate of A106 steel in 11000 ppmw $NaNO_3$-CO_2-O_2-MEA solution was lower than that of the blank group and 1000 ppmw $NaNO_3$ group.

➢ Organic amine degradation and corrosion mechanism

The 1120 and 385 cm^{-1} peaks in the dirty solution are α-FeOOH (ferric oxyhydroxide). 810 cm^{-1} peak may be related to the adsorption of organic molecules produced during the degradation of corrosion product films or MEA.



Raman spectra of A106 steel in 1000 ppmw $NaNO_3$-CO_2-MEA fresh and dirty solutions at 50 °C and 120 h

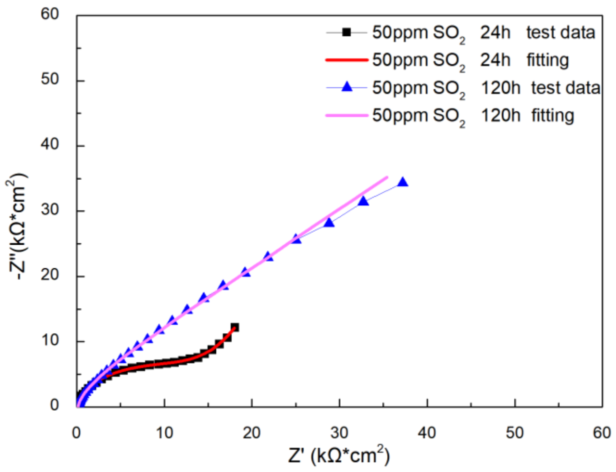


ToF-SIMS spectra of A106 steel in dirty MEA solution: (a) cations and (b) anions

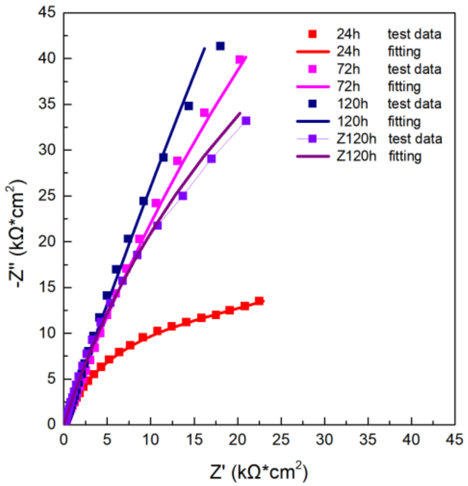
- Time-of-flight secondary mass spectrometry (ToF-SIMS) shows that **N-(2-hydroxyethyl) imidazole (HEI)** is present on the surface of A106 steel in dirty solutions.
- The lone electron pairs of nitrogen atoms can have adsorption interactions with metal surfaces . As one of the imidazoles, HEI may adsorb on the steel surface and inhibit its corrosion.

(COLOMBAN P, et al. New trends and developments in automotive system engineering: In Tech. 2011: 565-584.)
(STUPNISEK-LISAC E, et al. Corrosion, 1995, 51(10): 767-772.)

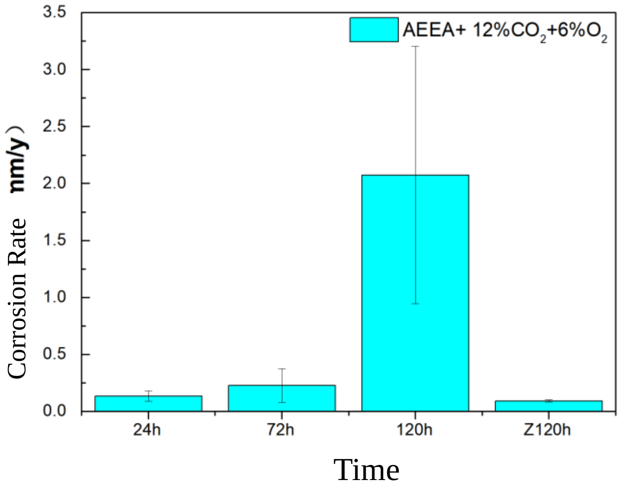
➢ Organic amine degradation and corrosion mechanism



Nyquist plots of 30408 stainless steel in a 30 wt% AEEA solution passed through 50 ppm SO_2 at different times in fresh solution

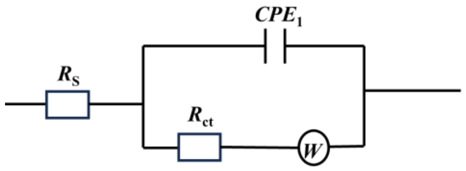


Nyquist plots of 30408 stainless steel in a 30 wt% AEEA solution with 12% CO_2 + 6% O_2 + 50 ppm SO_2 passed through it for different times in fresh solution.



Stainless steel corrosion rate in organic amine AEEA degradation product solution less than fresh solution

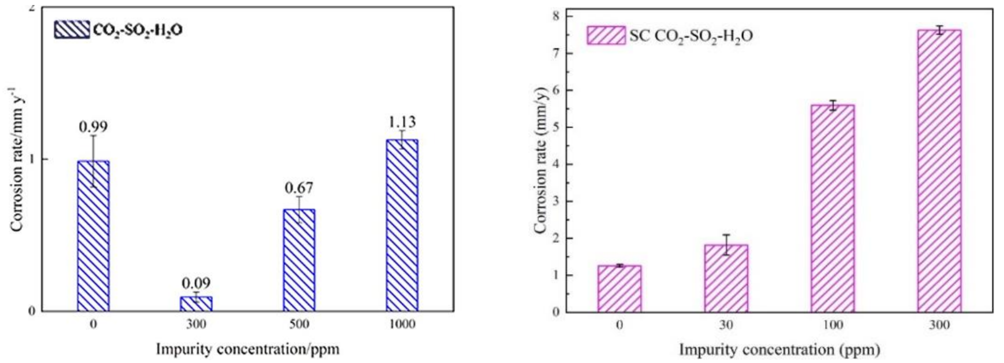
Equivalent circuit of EIS spectrum in 12% CO_2+6% O_2+50 ppm SO_2 environment and fitting parameter table

Time	R_s (Ω*cm²)	R_{ct} (Ω*cm²)	Y (Ω⁻¹*sⁿ)	n	equivalent circuit
24 h	184.98	30824	1.2016E-4	0.80755	
72 h	87.375	351170	1.7709E-4	0.77199	
120 h	63.295	1728300	1.9268E-4	0.77734	
Z120 h	26.318	170980	2.0848E-4	0.79976	

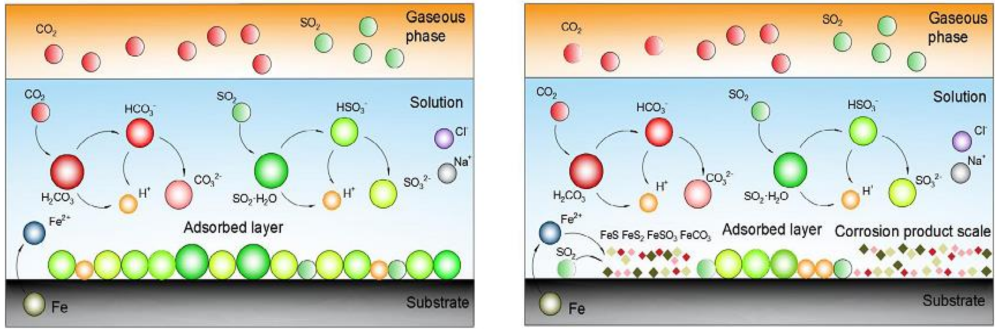
Degradation products of the organic amine AEEA (hydroxyethyl ethylenediamine) **also have an inhibitory effect on corrosion.**

3. Results and Discussion   Spontaneous Inhibition Phenomena

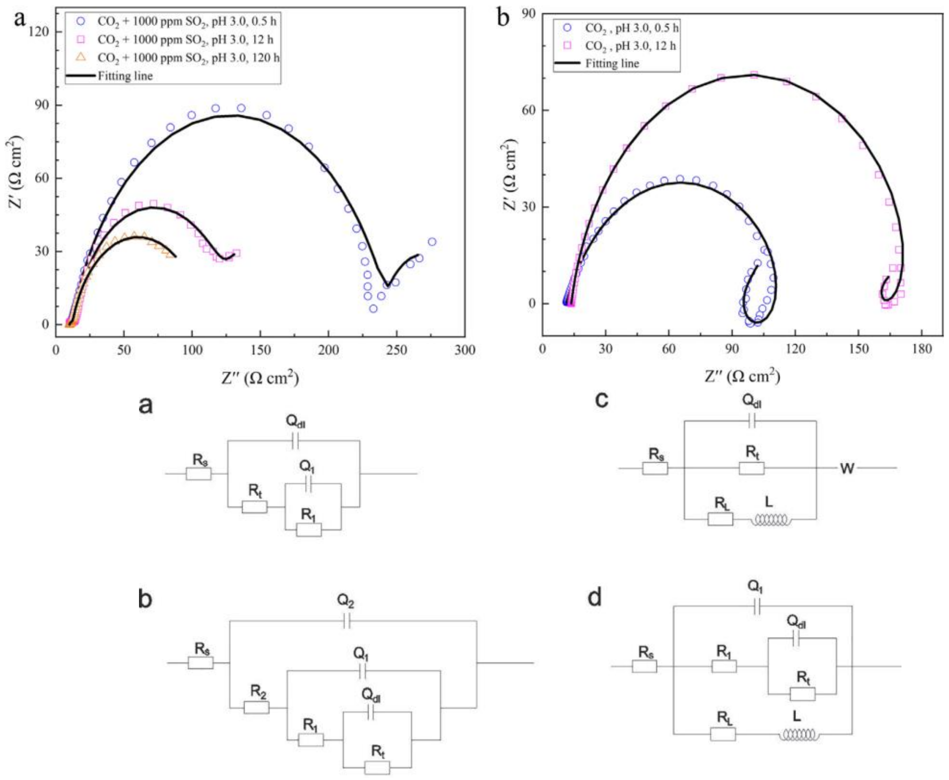
➢ CO_2-SO_2 coupling system corrosion mechanism



Differences in corrosion rates in atmospheric/supercritical CO_2 systems containing different concentrations of SO_2



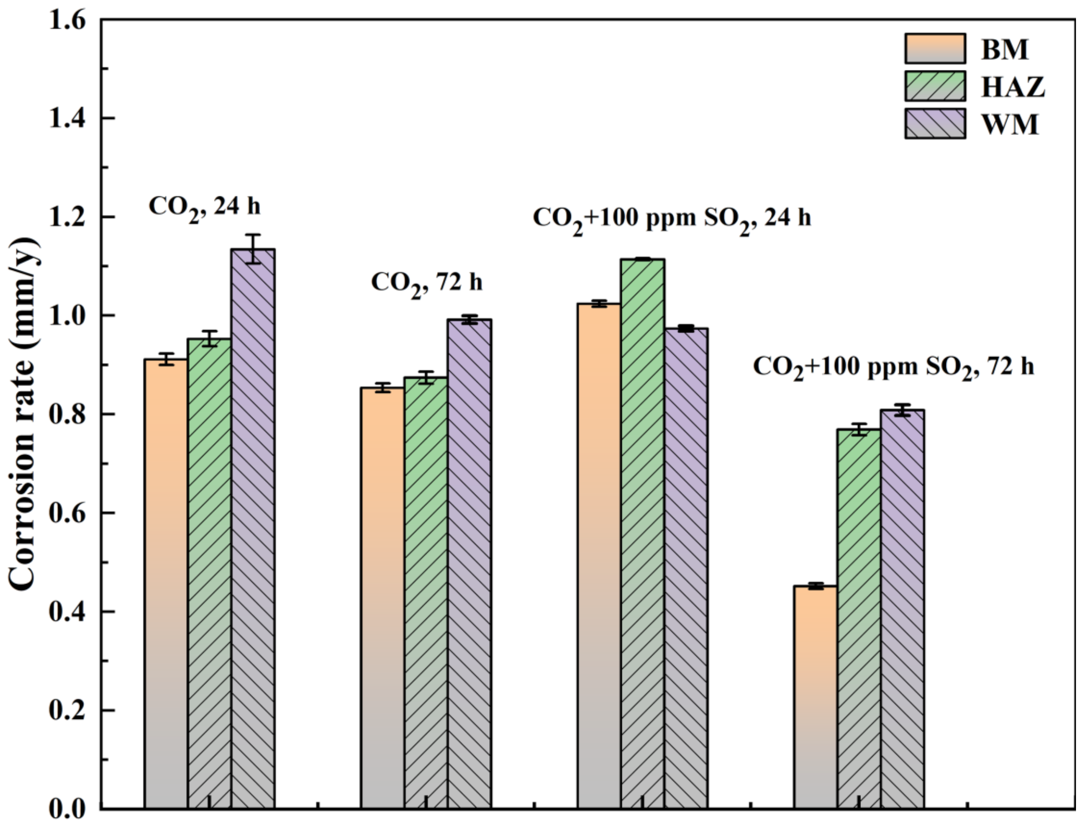
Schematic diagram of corrosion mechanism of X80 steel in CO_2/SO_2 system



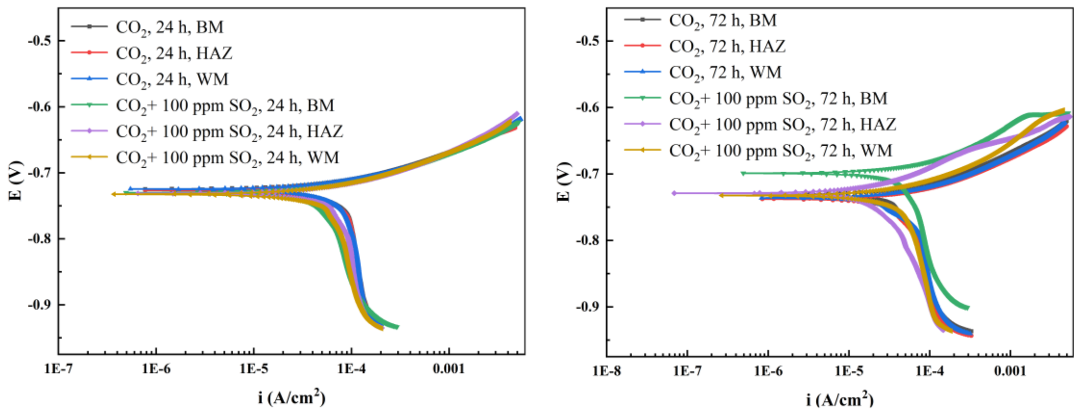
Impedance spectra and fitting circuits for X80 steel at the initial stage of corrosion in the CO_2/SO_2 system

● There is a significant difference in the effect of SO_2 impurities on corrosion in atmospheric CO_2 and supercritical CO_2 environments. **SO_2 inhibits corrosion during the initial stages** of corrosion in atmospheric CO_2 system.

➢ CO_2-SO_2 coupling system corrosion mechanism (welded joint steel)



Tafel slope extrapolation corrosion rate calculation results (35 ℃, atmospheric pressure environment)



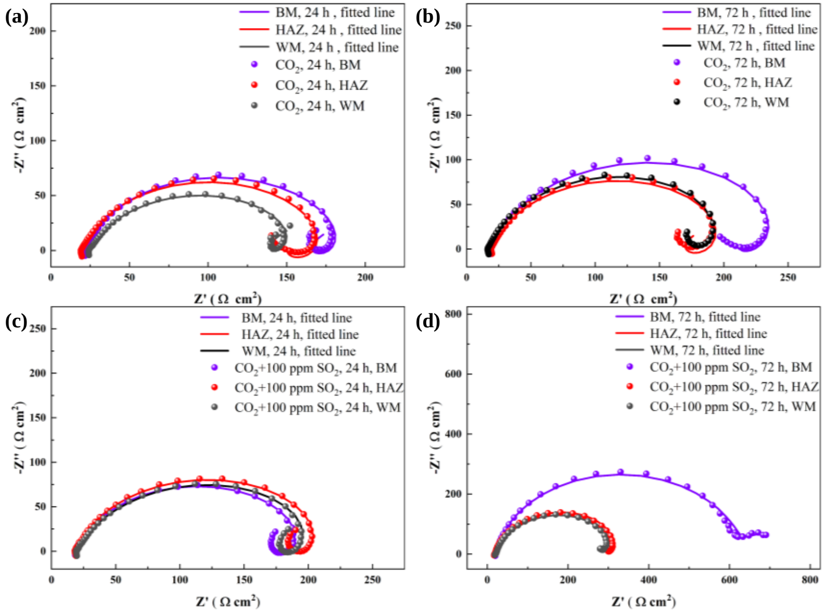
Polarization curve (35°C, atmospheric environment)

- It was found that in an aqueous solution saturated with CO_2, WM had the highest corrosion rate and BM had the lowest corrosion rate; after the addition of SO_2, **a significant decrease in the corrosion rate of BM was observed at 72 h.**

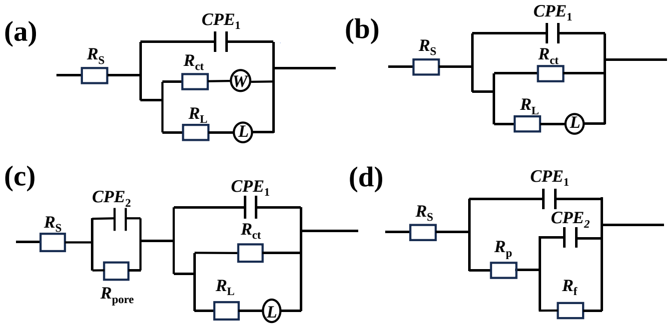
3. Results and Discussion

Spontaneous Inhibition Phenomena

➢ CO_2-SO_2 coupling system corrosion mechanism (welded joint steel)



Nyquist curve for X65 welded joints in CO_2/SO_2 saturated aqueous solution: (a) CO_2 24 h; (b) CO_2 72 h; (c) CO_2+100 ppm SO_2 24 h; (d) CO_2+100 ppm SO_2 72 h at 35°C, atmospheric pressure.

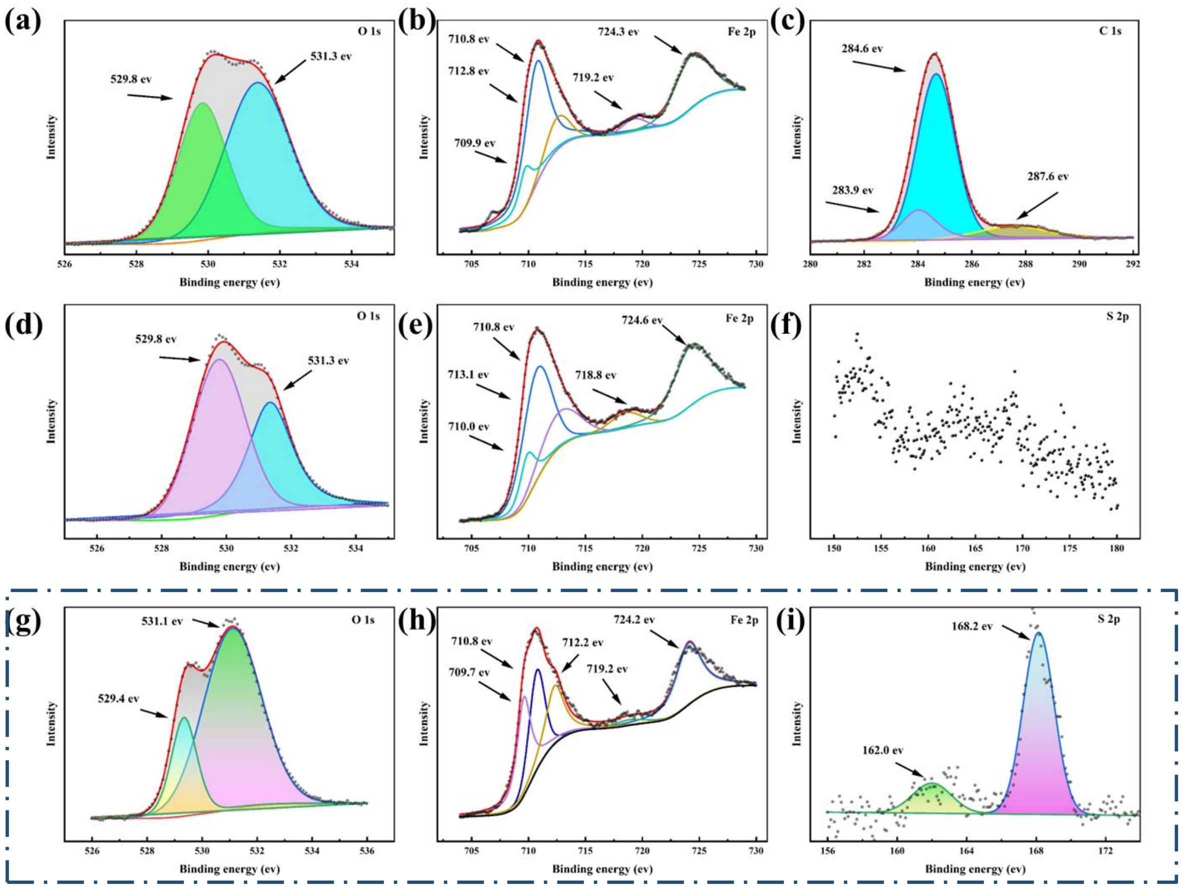


fitting circuit

- In CO_2 solution, the impedance spectrum showed capacitive characteristics related to the charge transfer process, while the low-frequency range exhibited **inductive characteristics associated with the adsorption of the $Fe(OH)^+$ [1]**.
- In CO_2 aqueous system containing SO_2 for 72 h, it was observed that in BM, HAZ, and WM showed different corrosion conditions, with the BM specimen showing the **largest diameter of the capacitive resistance arc.**

([1] Moradighadi, et al. Electrochim. Acta 400 (2021) 139460)

➢ CO_2-SO_2 coupling system corrosion mechanism (welded joint steel)



XPS of X65 welded joints in CO_2/SO_2 saturated aqueous solution for 72 h: WM (CO_2): (a, b, c); WM (CO_2 +100 ppm SO_2): (d, e, f); BM (CO_2 +100 ppm SO_2): (g, h, i) (35°C, atmospheric pressure)

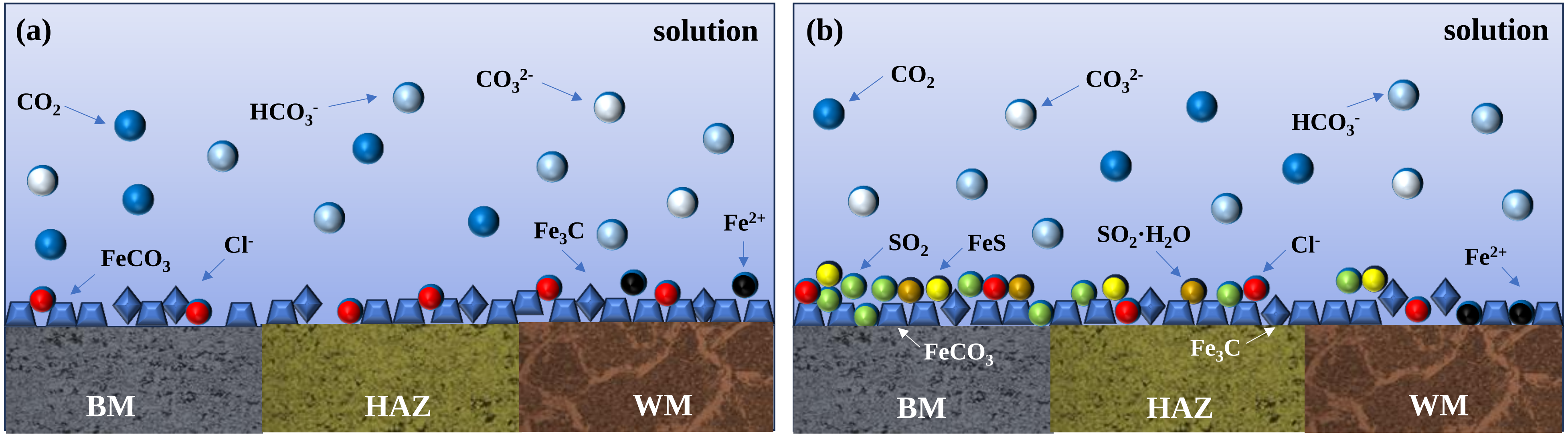
- WM analysis through XPS revealed that no sulfur-containing compounds were formed, regardless of the presence or absence of SO_2. The main reaction products detected were $FeCO_3$ and Fe_3C (cementite).
- In the presence of SO_2, SO_3^{2-} and **FeS** were detected. Therefore, we infer that the hydrolysis products of SO_2 are adsorbed on the substrate surface during the reaction, **forming FeS and inhibiting the corrosion of the BM.**

Transformation ⇩

$$SO_2 \rightarrow SO_3^- \rightarrow S_2O_4^- \rightarrow S_4O_6^- \rightarrow S_2O_3^- \rightarrow S \rightarrow S_5^- \rightarrow S_4^- \rightarrow S_3^- \rightarrow S_2^- \rightarrow S^-$$

(Hemmingsen, et al. Corrosion 48 (1992) 475–481)

➢ CO_2-SO_2 coupling system corrosion mechanism (welded joint steel)



Corrosion mechanism of X65 welded joints in CO_2/SO_2 saturated aqueous phase solution: (a): CO_2 ; (b): CO_2+SO_2

- In CO_2 solution, the metal substrate always maintains a high corrosion rate owing to Cl^- and Fe_3C will destroy the integrity of the $FeCO_3$ product film**, and the WM corrosion rate is always the highest.**
- In the presence of SO_2, the hydrolysis products of SO_2 will be preferentially and selectively **adsorbed on the surface of BM and form the FeS product film (why?)**, which prevents the further corrosion.

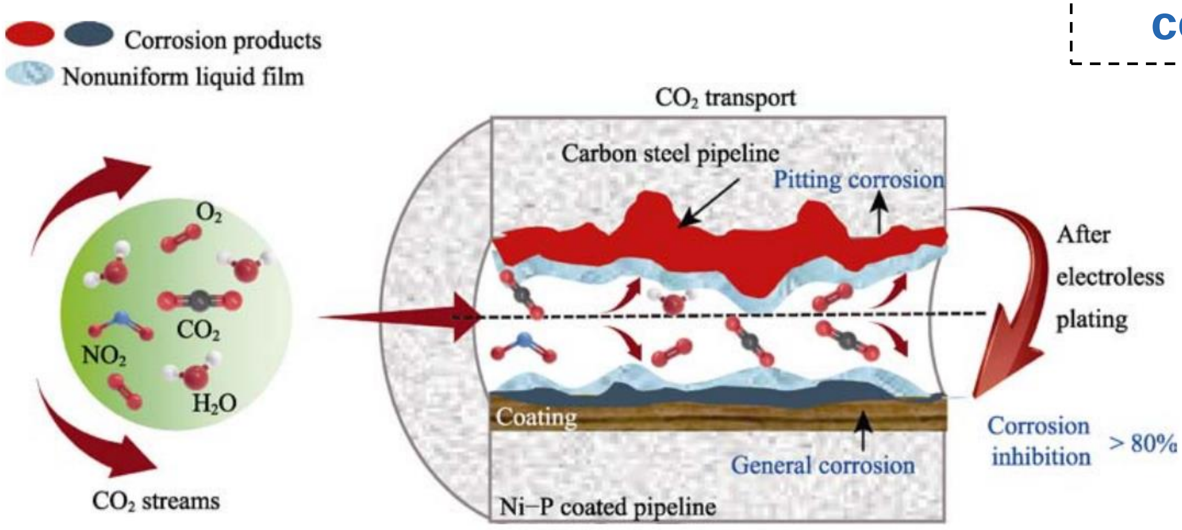
3. Results and Discussion

Intentional Corrosion Inhibition

➢ Coating protection technology

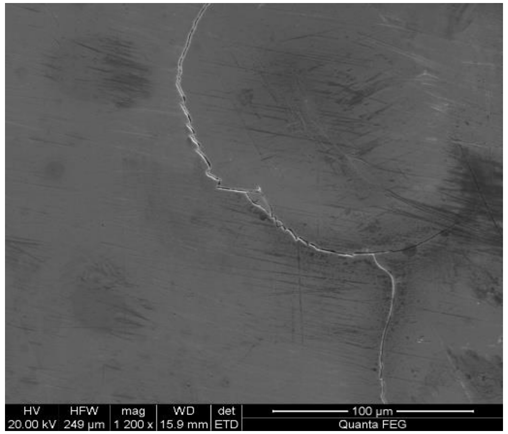
Coating → Organic polymer-based coatings; Metal Alloy Coatings

- **Metal Alloy Coatings:** Alloy coatings can enhance protective performance in CO_2 environments. **Ni–P (Phosphorus) coatings** achieve a corrosion inhibition rate of **over 80% in supercritical CO_2 environments containing H_2O–O_2–NO_2 impurities**.



Protection mechanism of Ni-P coatings in supercritical CO_2 environment

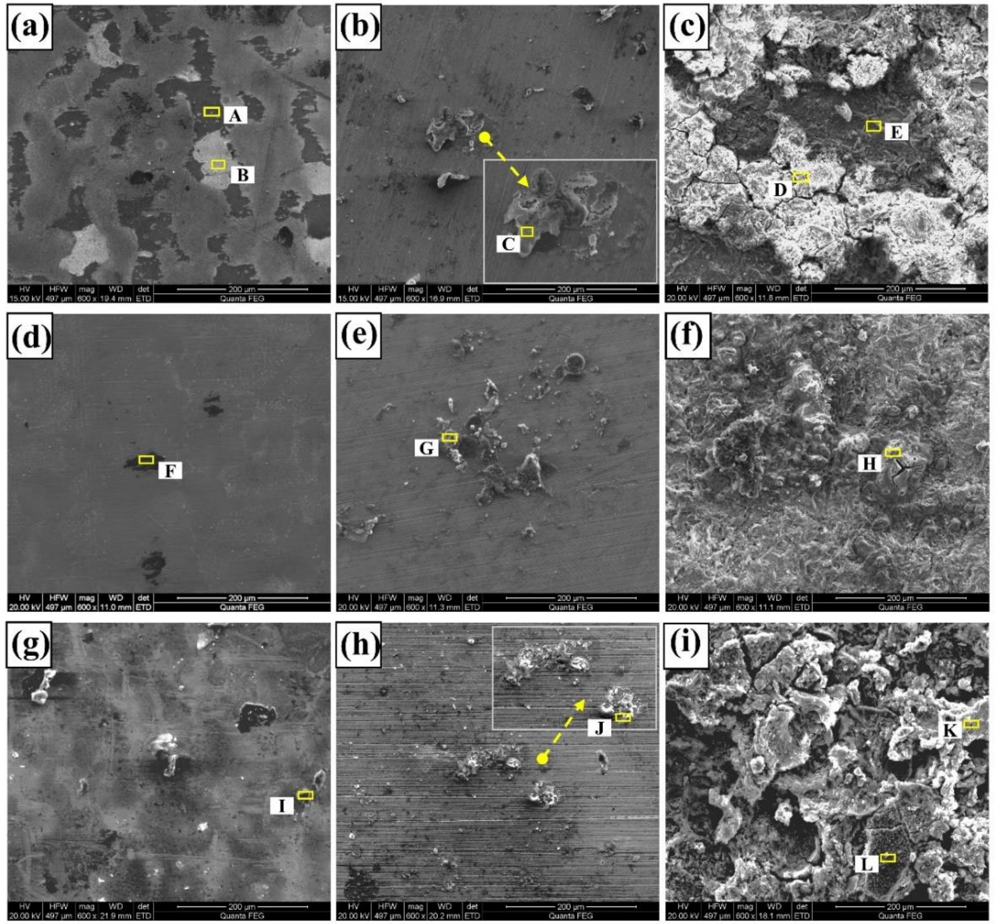
(SUN, et al. ACS Applied Materials & Interfaces, 2019, 11(17): 16243-16251)



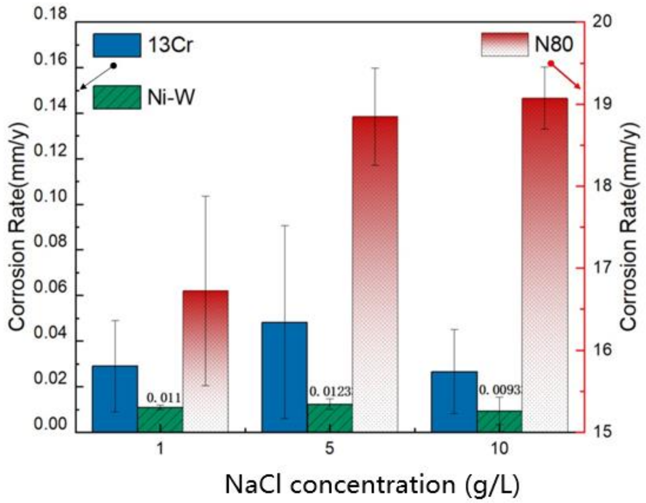
Ni-W (Tungsten) coating have exhibited **cracking** under CO_2-EOR downhole conditions, with significant amount of corrosive media entering the annulus.

3. Results and Discussion   Intentional Corrosion Inhibition

➢ Coating protection technology



SEM images of Ni-W coating, N80 and 13Cr steel after corrosion in rich aqueous phase for 72 h at 8 MPa, 35 °C and different Cl^- concentrations (a) Ni-W coating-1 g/L (b) 13Cr-1g/L (c) N80-1g/L (d) Ni-W coating-5 g/L (e) 13Cr-5 g/L (f) N80-5 g/L (g) Ni-W plating-10 g/L (h) 13Cr-10 g/L (i) N80-10 g/L



Corrosion rate plots of Ni-W coating, N80 and 13Cr steel after 72 h of corrosion in rich aqueous phase at 8 MPa, 35°C and different Cl^- concentrations

- The **Ni-W coating** consistently maintains **a low corrosion rate** at different sodium chloride concentrations.
- Ni-W coating surface almost had no obvious corrosion products. 13Cr steel surface had a small amount of products. Corrosion of N80 carbon steel was severe.

➢ Coating protection technology

- **Organic polymer-based coatings:** organic coatings offer numerous advantages, including a wide variety of types, ease of application, and high performance cost ratio.

- Traditional organic coatings exhibit **poor stability in SC-CO_2 and even show significant permeability under harsh conditions.**
- The failure of organic coatings in medium- to high-pressure CO_2 environments is mainly manifested through local **blistering**, overall blistering, and non-blistering failure phenomena.

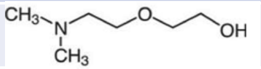
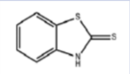
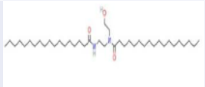
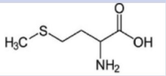
Blistering of the coating was observed under a high-pressure environment at 110 ˚C
(Sun, et al. Surface Technology 51 (2022) 43–52)

- Organic coatings are characterized by low cost; however, this kind of CO_2 corrosion protection coatings are still in the exploratory state (with several applications in the U.S). **Further research and development are needed to create organic coating systems capable of withstanding harsh CO_2 environments.**

3. Results and Discussion   Intentional Corrosion Inhibition

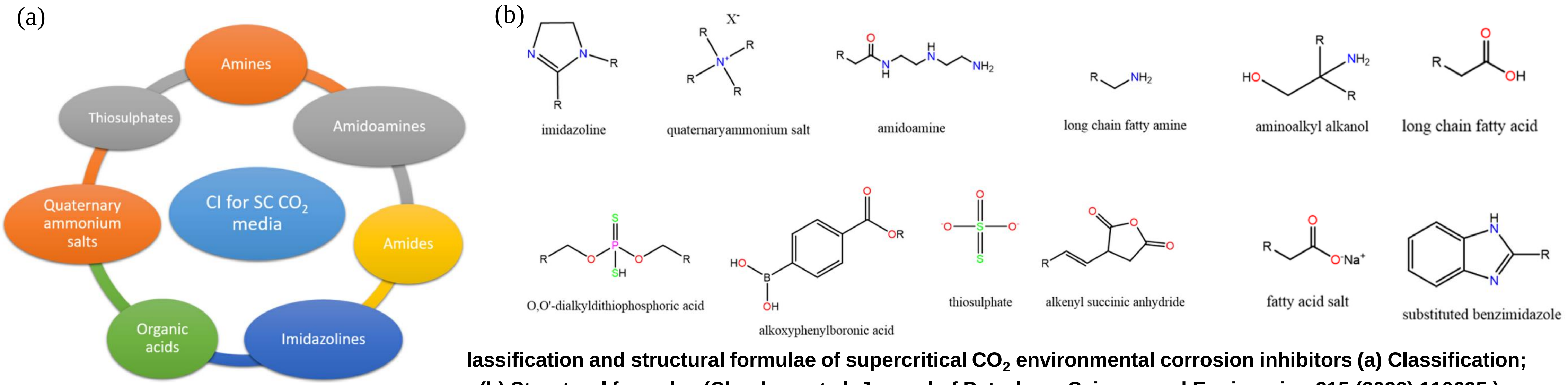
➢ Carbon Capture System Corrosion Inhibitors

Organic Amine Trap System Corrosion Inhibitors Summary (Zhao et al., *Separation and Purification Technology*, 2023)

Name	Inhibitor Type	Material	Condition	Organic Molecule Structure Diagram	Main Conclusion
Na_2SO_3	cathodic	Carbon Steel	MDEA Acid Solution	——	Removes oxygen
Sodium Sulfite	cathodic	Carbon Steel 1020	0.565 mol CO_2/mol MEA	——	Inhibition efficiency close to 80%
Long-chain Fatty Amine	cathodic	Carbon Steel 1020	0.565 mol CO_2/mol MEA	——	Inhibition efficiency close to 80%
$CuCO_3$	Anodic	Carbon Steel 1018	MEA Acid Solution	——	Inhibition efficiency ≥ 80%
VND	Anodic	Carbon Steel 1020	MEA Acid Solution	——	High inhibition efficiency and stability
Tannic Acid	Anodic	Carbon Steel 1020	0.565 mol CO_2/mol MEA	——	High inhibition performance (up to 92%)
Na_2S	Anodic	Carbon Steel A36	MEA Acid Solution	——	Inhibition rate: 96.7%
$Na_2S_2O_3$	Anodic	Carbon Steel A36	MEA Acid Solution		Inhibition rate: 91.3%
2-[2-(Dimethylamino)ethyl] Ethanol	Mixed	API X120 Steel	CO_2 and 3.5 wt% NaCl Solution		87.75% inhibition rate at 25°C
2-Mercaptobenzothiazole (MBT)	Mixed	Carbon Steel 316	MEA Acid Solution		It works at low temperature with 100 ppm
1-Vinyl-3-methylimidazolium tris(fluoromethanesulfonyl)methide	Mixed	Soft Steel	Ionic Solution	[Cnmim]TCM，n＝2、4、6和8	Inhibition efficiency increases with alkyl chain length
N-[2-(2-aminoethyl)aminoethyl]-9-octadecylamine	Mixed	Carbon Steel 1018	CO_2-saturated 5% NaCl Solution		Inhibition efficiency depends on temperature and concentration
Methyltetrahydrophthalic Acid (MTI)	Mixed	Carbon Steel 1018	MEA Acid Solution		MTI is a mixed inhibitor

➢ Supercritical CO_2 corrosion inhibitor

- Common supercritical phase corrosion inhibitors are: **imidazolines, quaternary ammonium salts, organic amines, organic acids, thiosulfates, volatile corrosion inhibitors**.



lassification and structural formulae of supercritical CO_2 environmental corrosion inhibitors (a) Classification; (b) Structural formulae (Chauhan, et al. Journal of Petroleum Science and Engineering 215 (2022) 110695)

- At present, the supercritical CO_2 conditions of corrosion inhibitor research is lacking, engineering experience is relatively scarce, and **the impact of impurities on the corrosion inhibitor is unknown. We have to develop a more efficient and green corrosion inhibitor.**

Report Outline

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Conclusions and Prospects

4. Conclusions and Prospects

Conclusions:

- In the capture system, the corrosion rate of carbon steel in degraded organic amine solution for a period of time was **significantly lower than that in the fresh solution**, which was related to the **adsorption of degradation products**.
- Low concentrations of SO_2 during transportation and storage systems initially reduce the corrosion rate **which is related to the generation of FeS**. In the weld joint region FeS is more inclined to be generated on the BM.
- **Imidazolines and quaternary ammonium salts** as the main corrosion inhibitor is current commonly used high-pressure CO_2 corrosion inhibitors, while the metal coating is also an important means of corrosion protection.

Prospects:

- In the capture process there will be a variety of impurities, the corrosion mechanism of these impurities on the pipeline system, injection tubing, production tubing and storage well is a future concern.
- In the future, developing an **environmentally friendly and highly efficient corrosion inhibitors and protective coating systems** will be crucial in addressing the corrosion issues of CCUS systems.

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Thank you!

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