

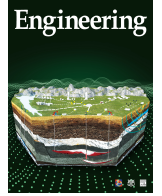


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## 二氧化碳捕集、利用与封存技术

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### ARTICLE INFO

#### Article history:

Received 12 July 2021

Revised 9 November 2021

Accepted 27 December 2021

Available online 16 February 2022

#### 关键词

二氧化碳捕集、利用与封存

二氧化碳捕集

二氧化碳利用

二氧化碳封存

化学吸收

电化学转化

封存机制

### 摘要

人类活动造成的二氧化碳(CO<sub>2</sub>)排放是引起全球变暖和气候变化的主要原因之一。绝大部分二氧化碳的排放来源于化石燃料燃烧,以及钢铁和水泥生产等工业过程。二氧化碳的排放会导致气候变化,而二氧化碳捕集、利用与封存(CCUS)是一种可持续性技术,在减排方面具有前景。从这个角度而言,二氧化碳捕集着重于化学吸收技术,主要原因在于其商业化潜力。本文对各种化学溶剂吸收二氧化碳的能力和速率进行了总结。二氧化碳的利用重点在于电化学转化途径,即将二氧化碳转化为具有潜在价值的化学品,这一途径已经备受瞩目。通过不同二氧化碳减排产品的法拉第转换效率,可对效率的改善情况进行说明。为了成功应用二氧化碳封存技术,需要更好地了解流体力学、地质力学以及反应运移,本文将详细讨论这几点。

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## 1. 引言

在工业化和城市化进程中,将温室气体排入大气已经导致全球变暖、造成气候变化。二氧化碳(CO<sub>2</sub>)是温室气体的主要来源,2018年,全球CO<sub>2</sub>排放量达到33.1 Gt,大约占温室气体排放量的67%。因此,大气中CO<sub>2</sub>的浓度显著增加(大约为百万分之412) [1–2]。二氧化碳捕集、利用与封存(CCUS)是潜在的颠覆性技术,有助于应对气候变化挑战。CCUS用于捕集发电厂、工业厂房等排放源以及大气中的CO<sub>2</sub>。捕集的CO<sub>2</sub>可用作原料,或者注入地表深处,被永久地安全封存。

CCUS(使用生物质时,也称为生物质能碳捕集、利用与封存)是一种能大规模实现净零排放的技术,可用于

现有的燃煤和燃气发电厂,有助于在发电时降低碳排放量。除了为供电行业做出贡献之外,对于在生产过程中会产生CO<sub>2</sub>的钢铁、水泥、玻璃、陶瓷、化学品制造等工业,要实现深脱碳,CCUS可能是唯一具有可扩展性和成本效益的选择。政府间气候变化专门委员会(IPCC)和国际能源署(IEA)开展的分析表明,CCUS是实现2050年“净零”(Net Zero)目标的关键;如《巴黎协定》[3–4]所述,CCUS有助于减少1/6的全球CO<sub>2</sub>排放量,能将全球气温升幅控制在1.5 °C以内。如果不能成功应用CCUS,应对气候挑战则会耗费更多财力。例如,在不应用CCUS的情况下,中国实现长期气候变化缓解目标需要多花费25%的费用[5]。

第2章着重讨论碳捕集的化学吸收,并对此展开了详

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细讨论。第3章的主题是电催化还原 $\text{CO}_2$ ，因为该方法在 $\text{CO}_2$ 利用方面颇具潜力。最后，第4章着重论述基本的 $\text{CO}_2$ 圈闭机制，该机制对于 $\text{CO}_2$ 封存具有重要意义。

## 2. 碳捕集

在发电、工业生产以及能源转换过程中均会排放 $\text{CO}_2$ 。碳捕集技术分为三个途径：燃烧后捕集、氧燃料燃烧捕集以及燃烧前捕集。捕集技术中采用了多种物理和化学工艺，包括溶剂型吸收、吸附/吸收用固体吸附剂、薄膜、低温以及用于分离 $\text{CO}_2$ 的化学循环[6–8]。目前，化学吸收是商业上使用最广的技术（如加拿大每年100万吨 $\text{CO}_2$ （t $\text{CO}_2$ ）边界大坝 $\text{CO}_2$ 捕集厂项目[9]和美国每年140万t $\text{CO}_2$ 佩特拉诺瓦（Petra Nova）碳捕集与封存（CCS）项目[10]）。全球碳捕集项目的现行成本是60~110 USD·t $^{-1}$ ，预计到2030年会降至30~50 USD·t $^{-1}$ 。这有助于在商业规模上加强技术推广[11]。

鉴于燃烧后化学吸收对现有设施的改动最小，所以未来上市的潜力最大。化学吸收涉及使用化学溶剂吸收 $\text{CO}_2$ 的各种物理和化学捕集工艺。目前，捕集技术的采用主要受溶剂再生能耗高、毒性大、易挥发、成本高等因素的限制。当前，边界大坝和佩特拉诺瓦项目捕集 $\text{CO}_2$ 消耗的能源是0.25~0.3 MW·h·t $\text{CO}_2^{-1}$ ，导致能效损失。据估计， $\text{CO}_2$ 捕集率为90%时，发电厂（如煤粉超临界发电厂）的净发电效率将从41%~45%降至30%~35%，预计商业应用中的能耗会减少30%~40% [12]。

为了提高捕集效率和经济竞争力，开发性能高且能有效改良工艺配置的新型溶剂才是具有吸引力的研究领域。理想的 $\text{CO}_2$ 溶剂是化学吸收过程的核心，应具有吸收率高、吸收能力大、再生能量需求低等特点。还需要具备安全、稳定、环境友好、设备腐蚀性低和经济合理性等特点。图1和表1 [7,13–38]总结了不同类型的 $\text{CO}_2$ 捕集溶剂。单胺、胺混合物、相溶剂、贫水溶剂等胺系吸收剂用于实现更好的效率[39]。相溶剂的理念是将一种单相的吸收体系注入吸收器，然后转化成不相混的富 $\text{CO}_2$ 和贫 $\text{CO}_2$ 相[40]。贫水溶剂是有机稀释剂和胺的混合物。这些溶剂能增强传质特性，提升吸收能力，还能减少热量的产生。为了有效改良工艺配置，吸收过程中可采用中间冷却、富溶剂回收、贫溶剂分离等潜在的改进方法，而解吸过程可采用中间加热、富溶剂分离、闪蒸剥离等方法。这些方法是降低生产费用的关键基础。

除点源碳捕集之外，直接空气碳捕集（DAC）是直接

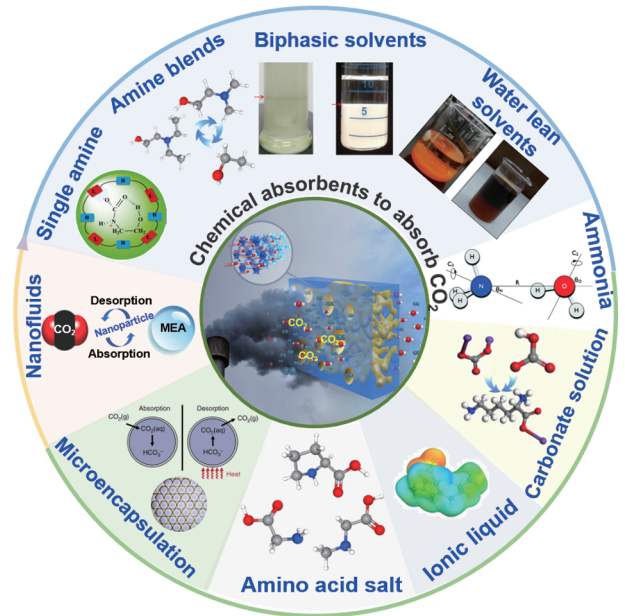


图1.  $\text{CO}_2$ 吸收用化学溶剂以及相关吸收能力和吸收速率（表1）。

术尚不完善，从中捕集 $\text{CO}_2$ 的成本也比从高浓度 $\text{CO}_2$ 排放源中捕集高。目前，根据选择的技术，试点规模内的直接空气碳捕集成本为94~232 USD·t $\text{CO}_2^{-1}$ 。预计到2040年的总成本大约会降至60 USD·t $\text{CO}_2^{-1}$ ，这将会加快该技术在商业上的可行性[41]。

## 3. 碳利用

关于 $\text{CO}_2$ 利用，建议通过有利地重复使用捕集的 $\text{CO}_2$ 来提升CCUS技术的经济竞争力。一般而言， $\text{CO}_2$ 利用包括将 $\text{CO}_2$ 直接用作干冰、灭火器、制冷剂，以及用于食品行业；其他方法包括通过不同的化学工艺（如通过化学方法转换成燃料和化学品、矿化）和生物工艺（如海藻培养）将 $\text{CO}_2$ 转换成高价值产品。使用 $\text{CO}_2$ 合成燃料的规模为每年1.0~4.2 Gt  $\text{CO}_2$  [42]。表2 [43–44]总结了典型化学品的市场情况以及 $\text{CO}_2$ 衍生技术的成熟度。电化学还原 $\text{CO}_2$ 是将 $\text{CO}_2$ 与可再生能源的燃料过程相结合的有效方法。

近年来，受再生电的影响，电催化还原 $\text{CO}_2$ 合成燃料和化学品引起了广泛的关注（图2 [45–65]）。经证实，通过精心设计和筛选电催化剂可将 $\text{CO}_2$ 转换成双电子还原产物（即一氧化碳和甲酸盐），法拉第效率（FE）高于95% [66]。此外，采用铜基电催化剂[67]才可获得分离性适中的深度还原产物（电子转移数大于2），但是该体系的稳定性仍需进一步改进。近来，采用气体扩散电极结构实现了在高电流密度（> 100 mA·cm $^{-2}$ ）下进行电催化还原

表1 CO<sub>2</sub>吸收用化学溶剂的吸收能力和吸收速率

Absorbents	Experimental apparatus	Absorptive capacity (mol CO <sub>2</sub> )·(kg solvent) <sup>-1</sup>	Reaction conditions	Absorption rate ((mol CO <sub>2</sub> )·(mol solute) <sup>-1</sup> ·min) <sup>-1</sup>	References
Single amine	Rapid screening apparatus	0.37~2.01	<ul style="list-style-type: none"> <li>• <math>T = 40\sim 80\text{ }^{\circ}\text{C}</math></li> <li>• <math>P_{\text{CO}_2} = 1.0\sim 9.5\text{ kPa}</math></li> </ul>	0.006~0.037	[13–15]
Amine blends	Bubbling reactor	1.35~1.77	<ul style="list-style-type: none"> <li>• <math>T = 40\text{ }^{\circ}\text{C}</math></li> <li>• <math>P_{\text{CO}_2} = 12\text{ kPa}</math></li> <li>• 15%~25% MEA</li> <li>• + 5%~15% MDEA (AMP, DETA, AEEA)</li> </ul>	0.015~0.017	[16–17]
Biphasic solvents	Bubbling reactor	1.25~2.15	<ul style="list-style-type: none"> <li>• <math>T = 40\text{ }^{\circ}\text{C}</math></li> <li>• <math>Q_{\text{CO}_2} = 2\text{ L}\cdot\text{min}^{-1}</math></li> </ul>	0.005~0.026	[18–20]
Water lean solvents	Wetted-wall column	0.66~1.05	<ul style="list-style-type: none"> <li>• <math>T = 25\sim 40\text{ }^{\circ}\text{C}</math></li> <li>• <math>P_{\text{CO}_2} = (15.0 \pm 0.5)\text{ kPa}</math></li> </ul>	0.007~0.011	[21–23]
Ammonia solution	Stirred tank apparatus	0.30~0.85	<ul style="list-style-type: none"> <li>• <math>T = 20\sim 60\text{ }^{\circ}\text{C}</math></li> <li>• <math>P_{\text{CO}_2} = 0.8\sim 30\text{ kPa}</math></li> </ul>	0.004~0.011	[24–27]
Carbonate solution	Bubbling reactor	0.27~0.30	<ul style="list-style-type: none"> <li>• <math>T = 25\text{ }^{\circ}\text{C}</math></li> <li>• <math>P_{\text{CO}_2} = 15\text{ kPa}</math></li> </ul>	0.001~0.014	[28–29]
Ionic liquid	Bubbling reactor	0.30~1.15	<ul style="list-style-type: none"> <li>• <math>T = 22\sim 40\text{ }^{\circ}\text{C}</math></li> <li>• <math>P = 1\text{ bar}</math></li> <li>• <math>m_{\text{ILs}} = 1.0\text{ g}</math></li> <li>• <math>Q_{\text{CO}_2} = 60\text{ mL}\cdot\text{min}^{-1}</math></li> </ul>	0.012~0.037	[30–31]
Amino acid salt	Bubbling reactor	0.20~0.32	<ul style="list-style-type: none"> <li>• <math>T = 40\text{ }^{\circ}\text{C}</math></li> <li>• Linear, sterically hindered amino acids: 1 mol·L<sup>-1</sup></li> </ul>	0.024~0.043	[32–34]
Microencapsulation	Pressure drop apparatus	0.55~1.78	<ul style="list-style-type: none"> <li>• <math>T = 25\sim 60\text{ }^{\circ}\text{C}</math></li> <li>• NDIL0309, NDIL0230</li> </ul>	—	[35–37]
Nanofluids	Bubbling reactor	0.58~0.95	<ul style="list-style-type: none"> <li>• <math>T = 40\text{ }^{\circ}\text{C}</math></li> <li>• 0.05 wt%~0.1wt% TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub></li> </ul>	0.004~0.013	[7,38]

$T$ : temperature;  $P$ : pressure;  $Q$ : flow rate; MDEA: *N*-methyldiethanolamine; AMP: 2-amino-2-methyl-1-propanol; DETA: diethylenetriamine; AEEA: *N*-(2-hydroxyethyl) ethylenediamine; ILs: ionic liquids; NDIL0309 and NDIL0230: types of micro-encapsulated CO<sub>2</sub> sorbents.

表2 典型化学品的市场情况以及CO<sub>2</sub>衍生技术的开发水平[43–44]

Products	Market size (Mt·a <sup>-1</sup> )	Market price (USD·t <sup>-1</sup> )	Level of development
Urea	~180	300~450	Commercialization
Methanol	~65	380~500	Commercialization
Polyurethane	~18	1800~2250	Commercialization
Polycarbonates	~5	2900~4000	Commercialization
Calcium carbonate	~115	50~380	Pilot and demonstration
Ethanol	~80	450~580	Pilot and demonstration
Sodium carbonate	~62	50~390	Pilot and demonstration
Formic acid	~3	690~1000	Pilot and demonstration
Magnesium carbonate	~21	450~850	Lab research
Acetic acid	~16	450~750	Lab research
Acrylic acid	~6	1700~3000	Lab research

CO<sub>2</sub>操作, 这标志着在CO<sub>2</sub>电解槽方面取得显著进步[68]。而且, 碳-杂原子(如氮)键的形成与电催化还原CO<sub>2</sub>结合是在温和条件下制备增值化学品的有效途径[67]。随着

理论化学和数据科学的快速发展, 理论和数据辅助催化剂设计能明显加快高性能CO<sub>2</sub>还原电催化剂的探索进程[59]。此外, 在使用产品后, CO<sub>2</sub>通常会排向大气中。因



此，直接空气碳捕集在进一步降低空气中CO<sub>2</sub>的浓度方面发挥着至关重要的作用。

CO<sub>2</sub>利用在CO<sub>2</sub>减排方面有很大的潜力。虽然已经提出通过CO<sub>2</sub>的利用降低CCUS成本，但是许多利用技术本身在经济上尚不具有可行性。CO<sub>2</sub>的绝大多数化学转化（矿化期间的酸碱中和反应除外）需要投入外部能源，另外还需要额外的成本推动转化过程。从这个意义上说，尽管考虑到预期的性能改进，将CO<sub>2</sub>转化成某些产物（如甲烷）在价格上无法与现有的石油化学途径竞争[69]。因此，CO<sub>2</sub>转换成聚碳酸酯和丙烯酸酯塑料等高价化学用品[70]可能是可行的利用途径。CO<sub>2</sub>利用期间还应考虑的另一因素是物流成本。应避免CO<sub>2</sub>排放源、利用设施和终端用户之间的长途运输，从而降低CCUS的总成本。

## 4. 碳封存

碳封存是将CO<sub>2</sub>注入地下（如石油/天然气储层、不可开采煤层以及咸水层）并进行永久封存的过程。政府间气候变化专门委员会和国际能源署表示，任何应对气候变化的可行净零排放途径均涉及全球范围内的碳封存[3,71]。近年来，提高石油/天然气储层的石油采收率技术（EOR）和提高不可开采煤层的气采收率技术（ECBM）已经成为颇具吸引力的CO<sub>2</sub>地质利用技术。注入CO<sub>2</sub>，提取额外的石油和天然气，同时封存CO<sub>2</sub>。CO<sub>2</sub>驱油技术的原理是通过非混相驱或混相驱将CO<sub>2</sub>注入储层孔隙，进而增强孔隙尺度的替驱效率。通过该技术能额外采收30%~60%的石油，抵消一些成本，目前该技术已被广泛应用[72]。CO<sub>2</sub>驱采煤层气的机制是基于较甲烷（CH<sub>4</sub>）而言CO<sub>2</sub>在煤微

孔表面的选择性吸附情况。目前，由于CO<sub>2</sub>驱采煤层气技术在将CO<sub>2</sub>注入低透水性的不可开采煤层方面还存在技术困难，且钻井还需花费额外的成本，所以该技术还未上市。虽然深层盐水层碳封存具有较大的潜力，但是现在还没有投入商用。地质系统中通常有4种CO<sub>2</sub>封存类型：由非渗透岩石组成的盖层形成地层圈闭、溶解捕集（CO<sub>2</sub>在盐水中溶解）、矿物捕集（CO<sub>2</sub>与容矿岩发生反应）、残留或毛细管捕集[周围的液体将CO<sub>2</sub>以液滴的形式圈闭在孔隙（或神经节）中][73-74]。

在过去几十年中，已经开发出孔隙尺度成像技术用于从孔隙尺度层面可视化量化多孔岩石中的多相流动[75]。深层盐水层和石油/天然气储层碳封存机制与润湿性相关，目前已经有充分解释（图3[76]）。CO<sub>2</sub>通过毛细管捕集可被封存在盐水层中：水润湿岩石表面，流过润湿层，然后让非润湿相CO<sub>2</sub>以不连续的团块留在大孔隙中心，此时，大量的CO<sub>2</sub>会被圈闭在地下。将CO<sub>2</sub>封存在油气储层时，如果地质时期多孔岩石中的碳氢化合物使得润湿性更倾向于油湿性，那么孔隙中存在水、油和CO<sub>2</sub>，CO<sub>2</sub>-水流的概念不可被简单地加以应用。据观察，润湿性取决于孔隙结构和流体特性：CO<sub>2</sub>可能是最不润湿相，占据着最大的孔隙，促进流动并实现毛细管圈闭。在其他情况下，水不润湿岩石表面，将CO<sub>2</sub>限制在低渗透层的孔隙中，阻碍毛细管圈闭。

从科学的角度而言，虽然CO<sub>2</sub>封存概念和机制已经得到证实，但是按照预想将CO<sub>2</sub>注入地下后的封存效率及其长期命运仍是令人关注的问题。CO<sub>2</sub>地质利用和封存相关的问题仍然存在：如何将CO<sub>2</sub>圈闭在孔隙中以及圈闭会如何造成沉积盆地、枯竭油田或疏水层等地质系统以及页

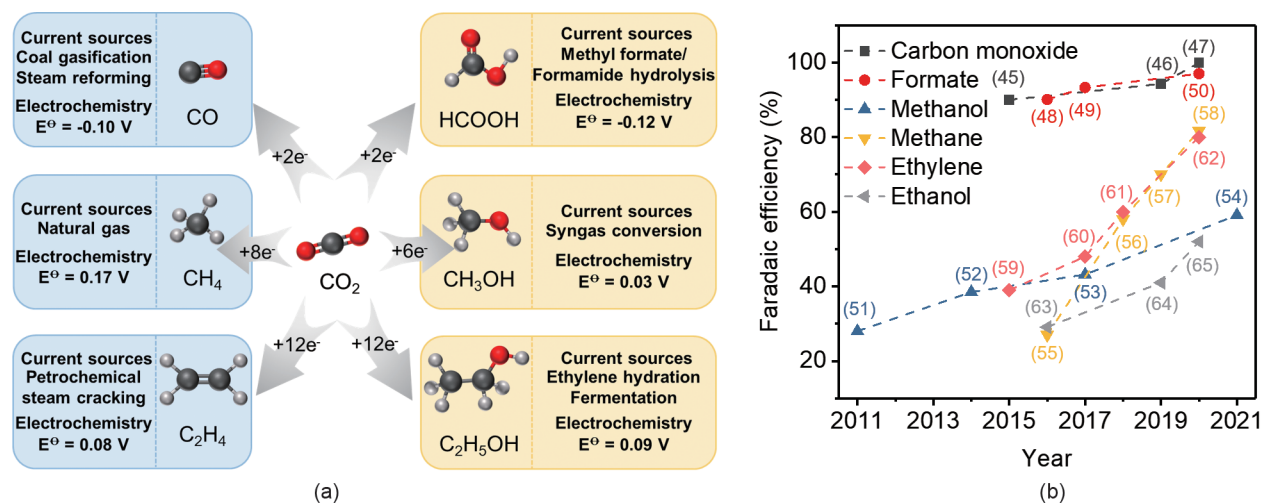


图2. 电催化CO<sub>2</sub>转换用于燃料和化学品生产。(a) CO<sub>2</sub>可能产生的典型产物的电流源以及相应电化学反应条件。(b) 电流密度大于10 mA·cm<sup>-2</sup>时实现的典型CO<sub>2</sub>还原产物的法拉第效率趋势，包括一氧化碳[45-47]、甲酸盐[48-50]、甲醇[51-54]、甲烷[55-58]、乙烯[59-62]和乙醇[63-65]。E<sup>0</sup>: 标准电极电势。



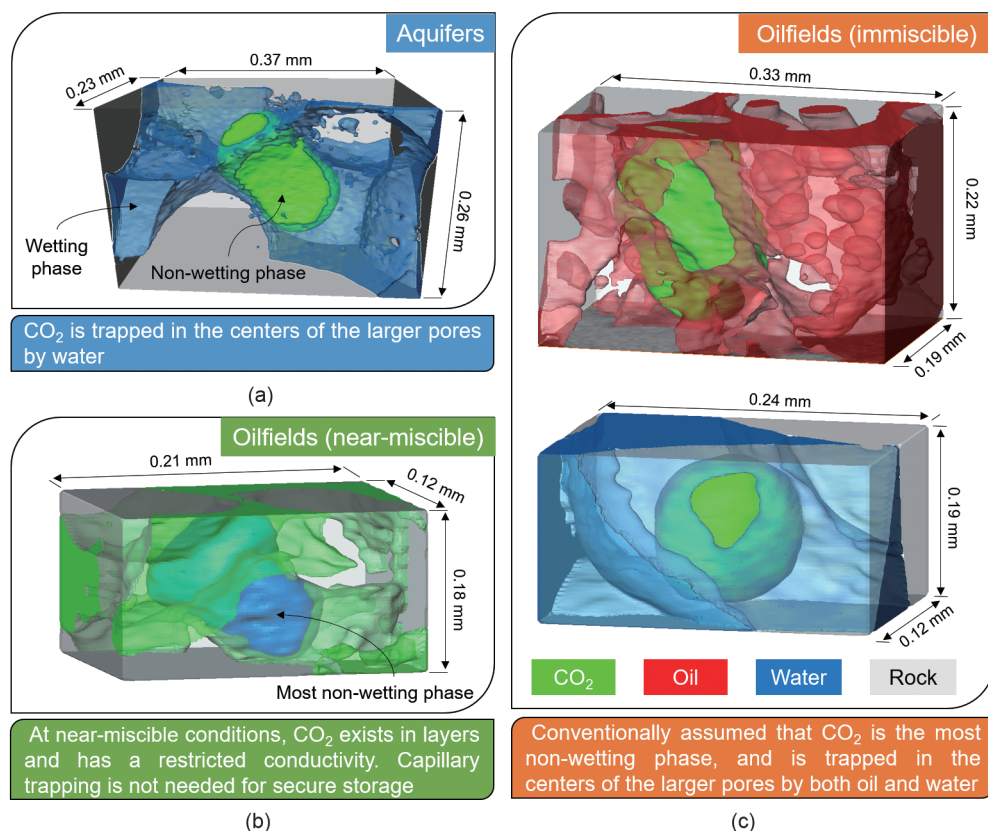


图3. CO<sub>2</sub>封存机制以及地质地层中已封存CO<sub>2</sub>的润湿状态。(a) 盐水层中的CO<sub>2</sub>是非润湿相，可以被圈闭在更大孔隙的中心。(b)、(c)在非混相条件下，油田中的CO<sub>2</sub>是最不润湿相，可以被（顶部的）石油或（底部的）水圈闭。在近混相条件下，水是最不润湿相，随之是CO<sub>2</sub>和石油。CO<sub>2</sub>存在于水相周围的层内，其流动性受到了限制[76]。

岩、煤层和破碎岩石等非常规环境的变化？物化非均匀性对封存有何影响？如何设计CO<sub>2</sub>注入使封存安全性最大化？CO<sub>2</sub>封存如何与提高石油采收率技术和提高气采收率技术相结合，以便被永久封存并且有效、经济实惠地生产燃料？若要获得问题的答案，需要良好地了解下述三个重要方面，这三个方面有助于设计提高封存效率的注入和封存策略。

(1) 应力状态和上覆压力等地质力学对孔隙结构和流动特性（如渗透性）变化的影响。

(2) 反应运移（例如，在储层条件下，孔隙中若存在CO<sub>2</sub>时岩石会溶解）及孔隙结构、流动路径和流动特性变化对其产生的影响。

(3) 孔隙中多个流体相的复杂流体力学。

## 5. 结论和观点

大气中CO<sub>2</sub>排放量增多成为主要的环境问题，引发全球变暖和气候变化。对CCUS的一些特定技术已经进行讨论。就CO<sub>2</sub>捕集而言，化学吸收是可用作商用的潜在解决方案。但是，要求技术成本降至30~50 USD·t<sup>-1</sup>，捕集

CO<sub>2</sub>的能耗大约低于0.21 MWh·tCO<sub>2</sub><sup>-1</sup>。为实现这一目标，需要采用高效且再生成本低的吸收剂，以便在成功应用该技术时降低捕集成本。就CO<sub>2</sub>利用而言，电化学转换具有将CO<sub>2</sub>转换为有价值的化学品的潜力。未来该技术的发展方向是开发高活性、高选择性和高稳定性的电催化剂，优化电解槽设计，在试点规模内推广示范，有利于评估该过程的整体能源效率和成本。在地下封存CO<sub>2</sub>这一途径极具潜力，其中CO<sub>2</sub>封存可与能源生产相结合（如提高石油采收率技术和提高气采收率技术），创造经济效益。虽然已经解释了CO<sub>2</sub>圈闭的基本原理，但是进一步研究流体力学、地质力学、反应运移以及这些过程如何与CO<sub>2</sub>封存结合并且如何对其产生影响，从而实现优化和安全封存要求仍具挑战性。采用无损成像层析技术等先进新颖的技术可以解决这一问题。

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