

Methane removal and atmospheric restoration

Zeolites and other technologies should be evaluated and pursued for reducing methane concentrations in the atmosphere from 1,860 ppb to preindustrial levels of ~750 ppb. Such a goal of atmospheric restoration provides a positive framework for change at a time when climate action is desperately needed.

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Greenhouse gas concentrations and global temperatures continue to rise. Industrial emissions of carbon dioxide (CO₂) reached a record 37 billion tonnes (Gt) in 2018 after several years of little or no apparent growth¹. Global methane concentrations passed 1,860 ppb for the first time in 2018, two-and-a-half-times greater than preindustrial levels. Average global temperatures reached record highs in 2015 and 2016, and the Paris Agreement's goal of keeping temperature increases well below 2 °C — even 1.5 °C — grows more difficult each year².

Because of such challenges, scientists and policymakers are evaluating options beyond reducing greenhouse gas emissions, including direct CO₂ removal from the atmosphere^{3,4}. Such 'negative-emission technologies' (NETs) include biomass energy or direct-air capture of CO₂, coupled with carbon capture and storage. Recent studies have examined the feasibility of removing as much as 10 Gt of CO₂ a year^{3,4}, a quarter

of total anthropogenic emissions¹. NETs play an important role in most integrated-assessment-model scenarios that stabilize average global temperatures at 2 °C above preindustrial levels and almost every scenario at 1.5 °C (ref. ³). Negative emissions for other greenhouse gases, particularly methane, could provide a complementary approach to CO₂ removal alone (Fig. 1).

After CO₂, methane (CH₄) is the most dominant anthropogenic greenhouse gas. It is 84 times more potent than CO₂ over the first 20 years after release and ~28 times more potent after a century. A recent estimate of the cumulative radiative forcings for CO₂, CH₄, and nitrous oxide (N₂O) are 1.95, 0.62, and 0.18 W m⁻², respectively, for 1755 through year end of 2015 (ref. ⁵). Dominated by agricultural and fossil fuel sources, anthropogenic CH₄ emissions are currently ~60% of the global total of ~560 Tg yr⁻¹, with an imbalance to the atmosphere of ~10 Tg yr⁻¹ (ref. ⁶). Methane and other hydrocarbons also

react with nitrogen oxides and can lead to tropospheric ozone pollution.

In contrast to negative emissions scenarios for CO₂ that typically assume hundreds of billions of tonnes removed over decades and do not restore the atmosphere to preindustrial levels⁷, methane concentrations could be restored to ~750 ppb by removing ~3.2 of the 5.3 Gt of CH₄ currently in the atmosphere. Rather than capturing and storing the methane, the 3.2 Gt of CH₄ could be oxidized to CO₂, a thermodynamically favourable reaction (CH₄ + 2O₂ → CO₂ + 2H₂O; ΔH_r = -803 kJ mol⁻¹). The large activation barrier associated with splitting methane's C-H bond (435 kJ mol⁻¹) could in principle be overcome by metal or other catalysts. In total, the reaction would yield 8.2 additional Gt of atmospheric CO₂, equivalent to a few months of current industrial CO₂ emissions¹, but it would eliminate approximately one sixth of total radiative forcing. As a result,

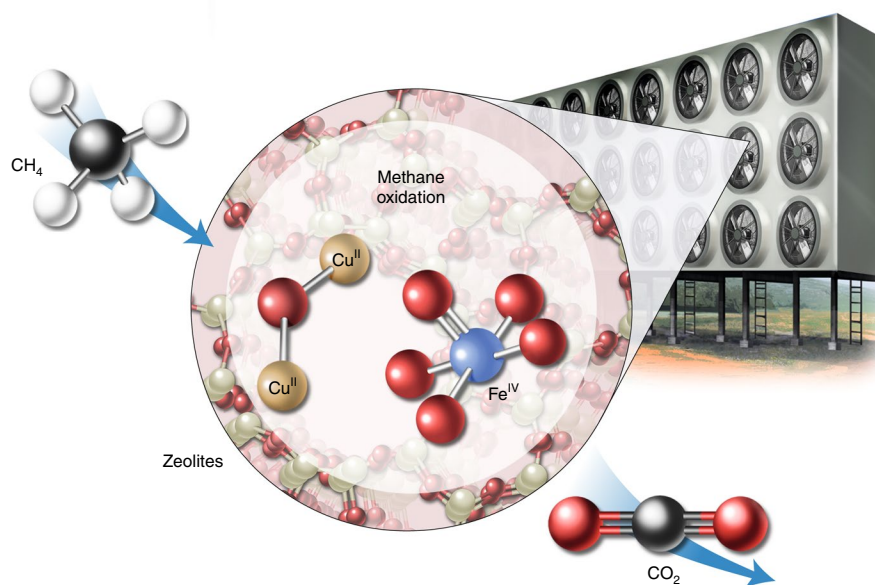


Fig. 1 | A hypothetical industrial array oxidizing CH₄ to CO₂. See text for additional details regarding the use of zeolites and other materials for CH₄ oxidation¹¹. Credit: Image by Stan Coffman

methane removal or conversion would strongly complement current CO₂ and CH₄ emissions-reduction activities⁸. The reduction in short-term warming, attributable to methane's high radiative forcing and relatively short lifetime, would also provide more time to adapt to warming from long-lived greenhouse gases such as CO₂ and N₂O.

Despite this thermodynamic favourability, capturing CH₄ from air is in other ways more challenging than capturing CO₂. CH₄ is found in the atmosphere at concentrations two-hundred-fold lower than CO₂. CO₂ has a strong quadrupole moment that can be exploited, and it is weakly acidic, allowing commercial capture using acid–base reactions and amine solvents. Its linear structure makes physical capture simpler than for the symmetrical, tetrahedral CH₄ molecule that lacks an obvious point of catalytic entry. The C–H bond in methane is also difficult to activate⁹. Traditional liquid solvents lack sufficient CH₄ affinity to be of commercial use, and traditional enrichment of even relatively concentrated methane flows requires a large number of cycles and, hence, energy.

One promising family of materials for trapping CH₄ is nanoporous zeolites^{10–12}. Zeolites have been identified for concentrating methane in industrial applications based on their favourable sorption capacities and CH₄/CO₂ and CH₄/N₂ selectivity. These materials raise the possibility of weakly binding methane molecules within their porous system using oxygen groups on the zeolite framework, utilizing methane–methane interactions in the cavities to oxidize the molecule (Fig. 1); we acknowledge that the same interactions could in principle also bind other species such as water that are more concentrated in the atmosphere.

The goal of most previous zeolite research with methane has been to oxidize it partially to methanol (CH₃OH), a chemical feedstock, rather than fully to CO₂. Low-temperature methane reactivity for conversion to methanol has already been observed in several Cu- and Fe-zeolites (for example, Cu-ZSM-5 and Fe-ZSM-5)^{11,13,14}. The characterization of active site formation and differences in geometric and electronic structure and reactivity for conversion to CO₂ could all build upon previous methanol research. Selective hydrocarbon oxidation in Fe-zeolites (α -O), for example, has been identified for an Fe^{IV}=O species with exceptional reactivity derived from the constrained geometry of the zeolite lattice¹¹. Such studies of Fe- and Cu-zeolites provide a foundation of insights needed to convert methane to CO₂. Unlike for methanol, which must be extracted from the zeolites,

CO₂ could be released to the atmosphere, eliminating the need for capture.

Potential complements to zeolites are porous polymer networks¹⁵ (PPNs), polymeric materials that contain small pores that can be used to capture, trap, and store compounds such as methane, and photocatalytic approaches for oxidizing methane¹⁶. One advantage of PPNS compared with zeolites is the ability to tune specific chemical interactions with methane by introducing functional groups on the polymer backbone, while taking advantage of favourable methane–methane interactions within micropores. Other families of materials, including carbon-based adsorbents, graphene-based materials, or metal–organic frameworks, appear to have poorer selectivity. Future research and deployment will determine the most desirable technologies and potential commercial viability.

The economics of scaled CH₄ conversion to CO₂ (or CH₃OH) still need to be resolved. A price on carbon emissions or a policy mandate would be required; current market prices of \$10 to \$30 per tonne CO₂ (for example, European Emissions Allowances; values in US dollars throughout) rise quickly to \$50 to \$500 or more per tonne this century in most integrated-assessment-model scenarios of 1.5 °C and 2 °C stabilization³. Such CO₂ prices would generate potential revenues of ~\$1,250 to \$12,500 per tonne CH₄ using a 100-year global warming potential of ~28 for CH₄ relative to CO₂ (and subtracting for the 2.75 tonnes of CO₂ emitted per tonne of CH₄ removed). A 100 m × 100 m array processing air at a wind speed of 20 km hr⁻¹ and converting 20% of the methane in air could in principle generate ~\$500,000 to \$5,000,000 of income a year operating at 90% capacity. Methane conversion would likely be more expensive per tonne than negative emissions for CO₂, and its potential cost and profitability remain uncertain, but it could yield greater climate and economic value because of methane's greater potency as a greenhouse gas.

Research is also needed for scaling methane removal industrially. Methane and CO₂ removal share the requirement to expose large volumes of air to catalysts (for CH₄) or aqueous reactants typically for CO₂. Electric fans would likely drive this forcing, ideally using no-carbon fuels. Catalysts in powdered, pelletized, or other forms could be exposed to air in tumbling bulk chambers or, instead, in parallel segmented chambers or packed reactors to optimize catalyst exposure while minimizing pressure drop through the system. The spent zeolite or other catalyst would then be heated in

O₂ to form and release CO₂ (or in H₂O to release CH₃OH). The specifics of scaling will strongly influence the efficiency and cost of methane removal.

Sustained efforts in methane removal, even after atmospheric restoration, could provide additional advantages for offsetting CH₄ emissions from agriculture and industry. A recent marginal cost-abatement curve for methane in the oil and gas sector¹⁷ estimated that almost half of methane emissions could be mitigated at no net cost; however, abatement costs rose steeply beyond that point. Sustained methane removal could offset the most expensive emissions effectively permanently, with research needed to determine the extent to which removal efficiency decreases and cost increases as methane concentrations decrease. Similarly in agriculture, some methane emissions from rice and meat production seem inevitable, even after substantial efforts to reduce them. Here, too, methane removal might counterbalance the most intractable emissions.

In principle, approaches used for methane could also apply to N₂O and other greenhouse gases¹⁸. Nitrous oxide is a potent, long-lived gas whose concentration of ~330 ppb today is more than 20% higher than preindustrial levels. It is also the dominant gas associated with current ozone depletion in the stratosphere. Global population growth and the need to produce more food and biofuels will make eliminating N₂O emissions difficult. The decomposition reaction N₂O → N₂ + ½O₂ is exothermic ($\Delta H_r = -163 \text{ kJ mol}^{-1}$), as it is for methane oxidation, but catalysis of the reaction is similarly difficult to facilitate¹⁹.

Both the Fe and Cu active sites in zeolites that activate H-atom extraction from CH₄ can be generated using N₂O, providing a possible scenario for the abatement of both greenhouse gases²⁰. Alternatively, the Cu active site but not the Fe site can also be generated with O₂, for reasons not yet fully understood. The zeolite lattice plays critical roles in the unique reactivity of active Fe and Cu sites in providing both a rigid framework that activates the metal site, lowering the barrier for reactivity, and a pore configuration that can limit radical escape and enhance selectivity.

Atmospheric restoration of all gases to preindustrial levels may seem unlikely today but, we believe, will eventually occur. Such a goal could provide a positive framework for social change at a time when climate action is sorely needed. It could complement numerous United Nations Sustainable Development Goals, including Climate Action and Affordable and Clean Energy, boosting innovation and technological

opportunity. One example for atmospheric restoration already underway is the Montreal Protocol and its amendments, which are reducing concentrations of man-made chlorofluorocarbons and other ozone-depleting compounds such as trichloroethane (CH₃CCl₃).

Overall, the conversion of CH₄ to CO₂ in the atmosphere is energetically favourable and could, in time, yield cost-effective climate benefits. Its economic feasibility will depend on effective mechanisms for trapping and catalytic oxidation. If and when suitable materials are identified, methane conversion could also be more attractive for climate benefit than CO₂ removal alone because of the much smaller scale (that is, ~3.2 billion tonnes CH₄ in total removal) and relative importance (about one sixth of total radiative forcing). It could also be applied to systems where CH₄ concentrations are higher than in background air but lower than concentrations needed for combustion (~50,000 ppm). We propose

a new initiative to assess the feasibility of large-scale methane conversion and, ultimately, atmospheric restoration. □

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