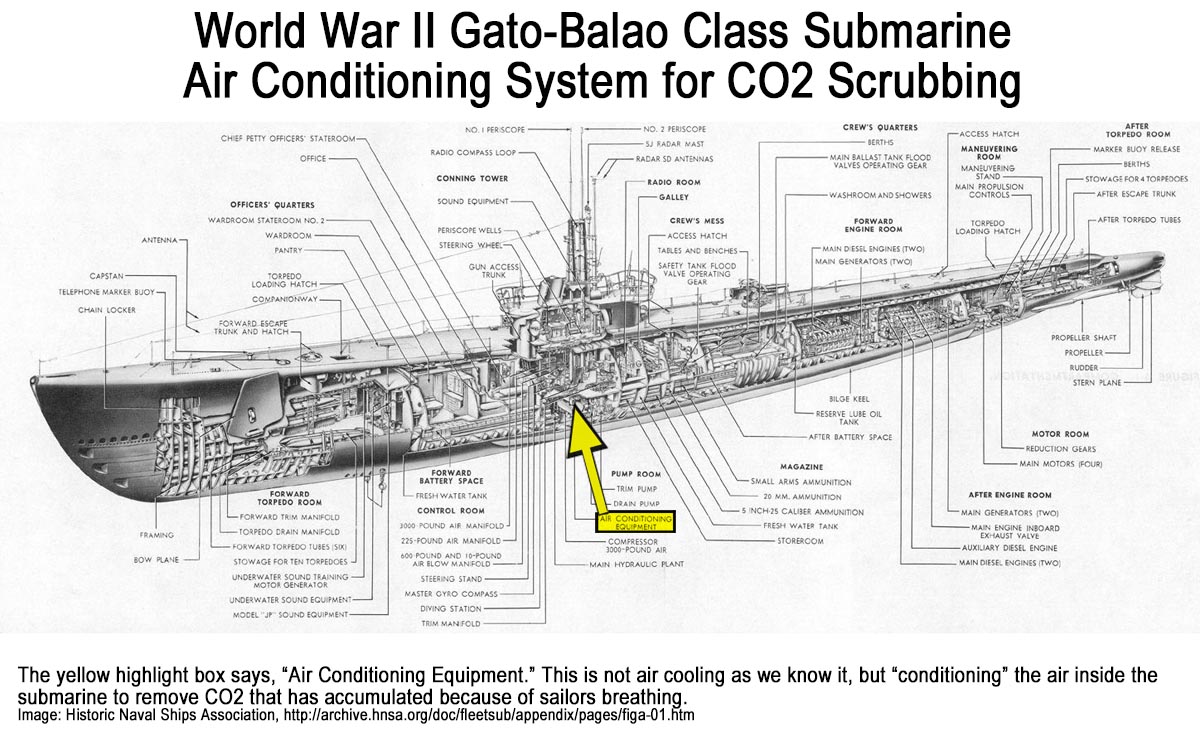
***History of Carbon Dioxide Removal***

How Century-Old Processes Related to Beer, Vitamines (Note the Spelling), Submarines, Baking Soda, and Bats  
Can Save Us From Climate Change

*It was illegal to brew beer in the warm months in Bavaria in the 19th century,   
until the refrigeration process that made liquefaction of air possible. (Wikicommons)*

**Air Liquification and the Beer Connection…**

Nobel Prize nominee Carl von Linde was the first to remove carbon dioxide from air in a meaningful way. His technology was developed from his refrigeration discovery that itself was first used in the 1870s to help the brewing industry overcome limitations on summer season brewing and beer storage that was plagued by bacterial contamination. Literally, brewing beer in the warm season was banned in Bavaria because of this problem. By 1890 Linde had sold 747 of his “ice machines.” In 1892 Guinness contracted with Linde to build a CO2 liquefaction plant to sell excess CO2 from fermentation as a feedstock in the newly industrialized world. This set in motion the ultra-cold refrigeration technology that Linde later used in cryoseparation to distill the components of air into usable products that included, oxygen, nitrogen, carbon dioxide and argon. The cryoseparation technology first supercools air to a liquid, then evaporates the liquid in a tall column where the temperature rises upwards in the column, condensing individual components of air (oxygen, nitrogen, carbon dioxide and argon…) at different temperatures, much like water vapor condenses in clouds.

 *The WWII Gato-Balao Class submarines were the first US subs to use the potash process to remove CO2   
from submarine air to keep our sailors safe from CO2 poisoning.*

**Lime-Potash Process for Removing Carbon Dioxide From Air…**

The recyclable lime-potash process has been used in various forms to remove CO2 from air since the late 18th Century. It involves two parts – capture with potash and release using lime in the baking soda production process. These two processes have been ubiquitous in industry since the mid- and late-1800s. Sodium bicarbonate (baking soda) has been used for thousands of years ago as a natural mineral deposited from hot springs among other places. French chemist, Nicolas Leblanc discovered the process to make baking soda (known as soda ash too) in 1791. In the late 18th century, soda ash was first used as a leavening agent in baking by John Dwight and Austin Church, in New York. It’s many other uses include: as an animal feed additive, as a bonding agent in dying, as a purifier and catalyst in the plastic industry, in the manufacture of rubber, as a softener in the food industry, as odors control in wastewater treatment, and it is widespread in pollution treatment of flue gases using the same chemistry as waster odor control, to remove sulfur pollution from the flue gas. It is widespread in the pharmaceutical industry and of course, as a leavening agent in bread and pastries since the 18th century. Potassium carbonate (potash) was first identified in 1742 by Antonio Campanella. It is made by the absorbent reaction with carbon dioxide. This defines the atmospheric carbon capture reaction used in the lime-potash process.

  
*Niacin (vitamin B3) rich foods, Harvard School of Public Health*

**Vitamines (Note the Spelling) and Amines…**

In 1930, Robert Bottoms was awarded a patent for removing CO2 from air with amines. The discovery of amines was first published in 1911 by Kazimierz Funk. Funk was inspired by Christiaan Eijkman work that showed eating brown rice reduced vulnerability to beri-beri, compared to those who at normal milled rice. (Beri-beri is a vitamin B deficiency that causes nerve and heart inflammation.) He was able to isolate the substance and because it contained an amine group he called it "vitamine". It was later to be known as vitamin B3 (niacin), though he thought that it would be thiamine (vitamin B1) and described it as "anti-beri-beri-factor". Amines have gone on to become one of the most important chemical groups in all of industry with processes that include: dyes, nylon, medicines, cooling systems, surfactants, cosmetics, agrochemicals, corrosion inhibitor, machining fluids, powder coatings, polyurethane, and epoxy coatings. Amines are a $32 billion industry in 2023.

**Baking S**  
*Bat guano was responsible for the Haber-Bosch amine process. (Wikicommons)*

**The Haber-Bosch Process (Amines) and Bat Guano in WW II…**

The Haber-Bosch process was an extremely important piece of chemistry developed just before WWI that allowed nitrogen production for use in explosives and fertilizers, with a key part of the process being the CO2 removal. It was a German invention because the Allies controlled all the bat guano deposits in caves that were the nitrogen source for fertilizers and explosives manufacturing. CO2 is a byproduct of the process produced as waste that must be removed, which is fundamental to the CO2 air capture process. The Haber-Bosch process is responsible for almost all fertilizers on Earth, one of the largest industries yet.

  
*Solvay Baking Soda Plant, Erie Canal, New York, 1917 (Wikicommons)*

**Baking Soda…**

The Solvay process in the 1860s first created baking soda in industry of natural, and is the most widely used process for baking soda production today, responsible for over 2 million tons per year. The CO2 capture process is simply described by the way baking soda works in cooking. Chemical leavening requires an acidic catalyst in the batter, such as yogurt or buttermilk. On contact with the sodium bicarbonate (baking soda), this causes the release of carbon dioxide in a simple acid-base reaction. Baking soda also releases its CO2 when heated above 50 C (122 F). The remaining sodium and carbonates can be reacted with CO2 to recreate the baking soda (sodium bicarbonate) in a loop. Twenty-five percent of all baking soda used worldwide is as an animal feed additive. It is widespread in the dyeing industry to make color bond permanently. It is used as a purifier and catalyst in the plastic industry. It is prominently included in the manufacture of rubber. Baking soda is used as a softener in the food industry. It not only controls odors in our refrigerators, it is widespread in the wastewater treatment industry to control odors too. It is widespread in pollution treatment of flue gases using the same chemistry as waster odor control to remove sulfur pollution from the flue gas. It has a disinfection property that makes it a common chemical in the pharmaceutical industry. And of course, to relieve indigestion. Oh, and as a leavening agent in bread and pastries since the 18th century using naturally occurring sodium bicarbonate or soda ash (same as baking soda).

***Discussion of Ongoing Industrialization of Carbon Dioxide Removal***

Right now there are over 200, 1 million ton per year atmospheric CO2 removal units committed under the IRA's IRS45Q enhancement, a significant majority of which are for direct sequestration, not enhanced oil recovery. There are three main processes in play, all 100 years or more old. [Keith 2018](https://pdf.sciencedirectassets.com/316494/1-s2.0-S2542435117X00135/1-s2.0-S2542435118302253/mainext.pdf?X-Amz-Security-Token=IQoJb3JpZ2luX2VjEHkaCXVzLWVhc3QtMSJGMEQCIDhzPMV0r64F2Z0BGh7W%2FKQbLFSKjkc7Va2rfiLZa8W6AiBHqM%2Fyx1%2F5KpG2k%2FdQfNfthpOCcHlwePfK2h8a74c%2F%2BCq8BQjC%2F%2F%2F%2F%2F%2F%2F%2F%2F%2F8BEAUaDDA1OTAwMzU0Njg2NSIMk3fyct5zBX3PTe6yKpAFoLcGp3b6vv%2BfsPSQo%2Fz4SXAYnkB230ddIXJyO2Ikmwaom1YY3489D4ebmLfJPQ0Jbao7GLQwwUlEX4vObOf%2Fi5QAi1rrXPxrfP%2BybSFu8ex8D4sQwdxXNtE4H5fiGNQWTorFIPnS6KvIaQ%2FxbvrKCeLaK%2FqGx8lAwdLwr%2Fbqu0BTtmtL0%2BjlUwjOi4Zz%2FPbLzTMaStB5WRXXiYX9tJQwqHqx1sDLxbaTihFrkMOcSOL82SaTm3XYiT8Epsq0pI8TwPLegOr0xRyJ4Lrh25uEeuqJP8AeF4OpDAbDMowr4ugR0fqvCQf2V%2F1iI0kR6pjiggzOa1VExqyEqzVPDwL8ytqq1Y2%2BIIEuvH%2F3Zd8nOY8yiDWMmO2nfJJ4YUBAdCiYiaBdNJjb5dtPOtM9l6sW3Bwuw80oSUS4TLwKKklusUF1l14ZOJui7uUjDIABwZOe4eXqsorwi6LZiIT9Bd6XdMYMwmsjEoEAWEWobLVMrewylY28lHcXoseqBcwNI0sk2WlEgSSpIy8SyBVOzr3R988BZrNgqDS49xt7MRk4CFyPktYdGxJfw62gU2e5wSuo9rbg80mlW9n5hA4Rg8Vou888CR2wdI6iVW6VWHAD11bcJbXezIwKBpz34Nav8OcGbdZaneaatHEkw6EWSSUqP5CZIScrvN1dVIpYuIg%2FXUqAynGAC%2B51nFaccJakJxdympvy6esjMH97Auf11vVdSg1UdvvoD0IRSLvAu169Xvl%2BgCE%2FS3CnfmMvAae4BO%2F6Tytj15ZwsWGKMaIhXavT4a3Usx5%2FWSvH%2Bod%2BIyuu2JHT3%2BjymdSTXJrZ5AJLLFw5v%2BU%2BjmZ%2F8vgE%2BdYfjTM1w9bIKrSXy71FYCtVCmOupMow88vjqgY6sgE%2B6ibjK8FJtLraQJBqjOOmbIfTBQ82MkCcoroIvUzNebOA1gIFs9or349ht5snRqyqOzChtQgoow8zQqKg2yiawwIgBCurhhkHY%2BLVOPQw%2Fn6T7JXkYIz%2FzmldKju%2F%2B8MmkMYgZZ3NX0JB1XoOvZoTwoTNvNDFlVMOGIMQl0NnT8oteIdnyEDuCPXuIUBLqPaxv3tR1NOAvN6YLCkkWaoyYLH4UwNcLqsqoUjUdv80brLF&X-Amz-Algorithm=AWS4-HMAC-SHA256&X-Amz-Date=20231118T164059Z&X-Amz-SignedHeaders=host&X-Amz-Expires=300&X-Amz-Credential=ASIAQ3PHCVTYTLEIAB5G%2F20231118%2Fus-east-1%2Fs3%2Faws4_request&X-Amz-Signature=4be4e6c84d10baf968d448606164249751b1cdbfb588a2bcce58188470341c8f&hash=01930a432c453c8d48a6d920d5b4f14df80bb9d7c06d6f584ab2d50cf3ff6cd4&host=68042c943591013ac2b2430a89b270f6af2c76d8dfd086a07176afe7c76c2c61&pii=S2542435118302253&tid=spdf-7f8c2ab6-0de0-49c6-bac2-57f1d424481d&sid=1b8a26858551a24daf2ae849eec9b7e59648gxrqa&type=client&tsoh=d3d3LnNjaW) describes a hypothetical 1 million ton per year recyclable lime-potash process with components widespread in industry with known scaling factors. This process is in the lead with a 45Q cash pay of $180 a ton - significantly in excess of process costs. Keith 2018 defines the classic "cheapest" cost at $100 a ton in popular press, where Keith's findings are based on Carbon Engineering's 1 Kton per year demonstration in Squamish BC that uses a best case $94 ton cost in the findings, including upstream emissions. This is for the studied scenario of at best $0.03 kWh natural gas energy with energy being 87% of process costs. With current $0.01 kWh renewable energy costs for new utility scale installations and about 60 percent of energy from renewables (some process energy must be flame energy to catalyze oxidation as in many hard of decarbonize processes), costs are below +/- $50 ton. There is no cap on pay, so it is very likely profits will be pushed back into design enhancement and further production to help realize a greater market share.

Below is a history of these three main removal process that is quite surprising, and easily contradicts the understated reticent findings of the scientific method. Why understated? It's the scientific process. First, findings are based on scenarios studied and Keith 2018 is an excellent example. Though Keith himself says $100 ton in popular literature, the best studied scenario of his work is $94 ton. This rounding --rounding upwards-- exhibits this classic reluctance to focus on the best case and demands that the full scientific range of scenarios studied be recited. In this case, Keith used two scenarios, $0.03 and 0.06 kWh energy, all natural gas. Though Keith's scenarios describe a hypothetically scaled 1 million ton per year process from the existing industry components with known scaling factors, he does not look forward to energy costs less than $0.03 kWh natural gas, which also carries a 10 percent carbon penalty from the natural gas consumed. Also not discussed are further costs reductions from process refinement. Further understatement in Keith 2018 comes because of high energy use, where new utility scale energy will most likely be generated on site with no transmission costs or profit to the energy provider. Another really interesting likelihood is that because almost all air capture will be done by the fossil fuel industrial complex, and their producer costs of natural gas are likely significantly below $0.01kWh, the additional 10 percent carbon penalty from natural gas can easily be overcome by scaling their units 10 percent larger.

Occidental Petroleum (Oxy) uses Carbon Engineering's (Keith) recyclable lime-potash process and they have committed to 100, 1 million ton per year units by 2035. This first flush of 200+ committed units under 45Q will very likely see rapid advancement of process efficiency bringing costs down significantly.

In 1981 I helped build an advanced cryoseparation unit on the Houston Ship Channel for Air Products, founded by Carl von Linde, Nobel Prize nominee in 1913 for his refrigeration process where Guinness contracted with Linde in 1892 to use the high pressures generated from compression with refrigeration, to liquefy brewing air waste and distill CO2 for sale as a chemical feedstock in industry.

**REFERENCES AND NOTES…**

**Cryoseparation of air…** Nobel Prize nominee Carl von Linde was the first to remove carbon dioxide from air. His technology was developed from his refrigeration discovery that itself was first used in the 1870s to help the brewing industry in Bavaria overcome limitations on summer season brewing and beer storage that was plagued by bacterial contamination that soured the beer, where from 1553 to 1850 summer brewing was literally banned between April 23 and September 29. After 1850, brewers learned to brew over produce in march and April and store their beer in caves where they had stockpiled winter ice. By 1890 Linde had sold 747 of his “ice machines” and summer brewing was flourishing. In 1892 Guinness contracted with Linde to build a CO2 liquefaction plant to sell excess CO2 from fermentation as an industrial chemical. This set in motion the ultra-cold refrigeration technology that Linde used in cryoseparation to distill the components of air into usable products that included not only carbon dioxide but, oxygen, nitrogen, and argon. The cryoseparation technology first supercools air to a liquid, then evaporates the liquid in a tall column where the temperature rises upwards in the column, condensing individual components at different temperatures, much like water vapor condenses in clouds to make rain.

**Potash/Potassium Carbonate…** A US patent granted in 1904, described a process for absorbing CO2 in a hot solution of potassium carbonate and then stripping the solution by pressure reduction without additional heating (Behrens, 1904).

**Potash/ Lye…** Giammarco was the first to patent an activated potash solution in 1955, and there are now a number of such processes - Kohl and Riesenfeld mentions some - they are still widely applied.

**WWII – Lime/Potash and Amines: Keeping our sailors safe from CO2 Poisoning… The history of CO2 removal in submarines begins in World War II…** "Air monitoring was by colorimetric tubes, soda lime was used to remove carbon dioxide and oxygen candles provide a source of oxygen replenishment." With the advent of long submerse times with nuclear submarines , amines were used to scrub CO2 from submarine air.

Mazurek, Key developments in submarine air monitoring and purification, SAMAP Proceedings, October 2015.  
<https://www.sonistics.com/wp-content/uploads/SAMAP-15-Proceedings.pdf>

Mention of soda ash and amines…  
<https://www.sonistics.com/wp-content/uploads/A-Brief-History-of-Submarine-Air-Quality.pdf>

**History of Baking Soda...** Sodium bicarbonate (baking soda) has been used for thousands of years ago as a natural mineral deposited from hot springs among other places. French chemist, Nicolas Leblanc discovered the process to make baking soda (known as soda ash too) in 1791. In the late 18th century, soda ash was first used as a leavening agent in baking by John Dwight and Austin Church, in New York.

Sodium Bicarbonate (Baking Soda) , Production, History and Uses, Iranian Labour News Agency, April 14, 2021.  
<https://www.ilna.ir/Section-economy-4/1062921-sodium-bicarbonate-production-history-and-uses#:~:text=In%20the%20late%2018th%20century,carbon%20dioxide%20and%20sodium%20carbonate>

**Uses of Baking Soda…** Twenty-five percent of all baking soda used worldwide is as an animal feed additive. It is widespread in the dyeing industry to make the color bond permanently. It is used as a purifier and catalyst in the plastic industry. It is prominently included in the manufacture of rubber. Baking soda is used as a softener in the food industry. It not only controls odors in our refrigerators, it is widespread in the wastewater treatment industry to control odors too. It is widespread in pollution treatment of flue gases using the same chemistry as waster odor control, to remove sulfur pollution from the flue gas. It has a disinfection property that makes it a common chemical in the pharmaceutical industry. And of course, to relieve indigestion. Oh, and as a leavening agent in bread and pastries since the 18th century.

The Many Uses of Sodium Bicarbonate (Baking Soda), Bell Chem. Accessed on October 10, 2022.

<https://www.bellchem.com/news/the-many-uses-of-sodium-bicarbonate>

**Discovery of the Modern Baking Soda Process in 1838…**

Several scientists had investigated ammonia–soda methods for preparing soda ash. Essentially, these methods involved saturating a concentrated brine solution with ammonia to form ammonium salts and then with carbon dioxide (made by burning lime). This produces ammonium bicarbonate, which reacts with the brine to form ammonium chloride and sodium carbonate. The sodium carbonate, in the presence of excess carbon dioxide, is converted to sodium bicarbonate, which precipitates out of solution and can easily be decomposed to soda ash (potash) by heating. The resulting carbon dioxide can be recycled, and the ammonium chloride treated to recover reusable ammonia.

Kiefer, Soda ash, Solvay Style, Today’s Chemist at Work, February 2002.  
<https://pubsapp.acs.org/subscribe/archive/tcaw/11/i02/html/02chemchron.html>?   
**The Science of Baking Soda…** The Solvay process in the 1860s first created baking soda in industry of natural, and is the most widely used process for baking soda production today, responsible for over 2 million tons per year. The CO2 capture process is simply described by the way baking soda works in cooking. Chemical leavening requires an acidic catalyst in the batter, such as yogurt or buttermilk. On contact with the sodium bicarbonate (baking soda), this causes the release of carbon dioxide in a simple acid-base reaction. Baking soda also releases its CO2 when heated above 50 C (122 F). The resulting sodium and carbonates can be reacted with CO2 to recreate the baking soda (sodium bicarbonate) in a loop.   
Graves, The Science of Baking Soda, American Chamical Society, 3, 2018>  
<https://axial.acs.org/cross-disciplinary-concepts/the-science-of-baking-soda>

**Potash in the Lime/Potash Process for CO2 Removal…** Potassium carbonate (potash) was first identified in 1742 by Antonio Campanella. It is made by the absorbent reaction with carbon dioxide. This defines the atmospheric carbon capture reaction used in the lime-potash process.

Potassium Carbonate (Potash), from A Dictionary of Science, Oxford University Press, 2003 by ChemEurope.com. Accessed on October 10, 2022.

<https://chemeurope.com/en/encyclopedia/Potassium_carbonate.html>

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**Amines…** In 1930, Robert Bottoms was awarded a patent for removing CO2 from air with amines**.** The discovery of amines was first published in 1911 by Kazimierz Funk. Funk was inspired by Christiaan Eijkman work that showed eating brown rice reduced vulnerability to beri-beri, compared to those who at normal milled rice. (Beri-beri is a vitamin B deficiency that causes nerve and heart inflammation.) He was able to isolate the substance and because it contained an amine group he called it "vitamine". It was later to be known as vitamin B3 (niacin), though he thought that it would be thiamine (vitamin B1) and described it as "anti-beri-beri-factor". Amines have gone on to become one of the most important chemical groups in all of industry with processes that include: dyes, nylon, medicines, cooling systems, surfactants, cosmetics, agrochemicals, corrosion inhibitor, machining fluids, powder coatings, polyurethane, and epoxy coatings. Amines are a $32 billion industry in 2023.

(Thanks to Richard Darton, Emeritus Professor, University of Oxford, for information on the importance of potash in the early development of CO2 processes in industry.)

**Haber-Bosch process…** This was an extremely important process developed just before WWI that allowed nitrogen production for use in explosives and fertilizers, with a key part of the process being the CO2 removal. It was a German invention because the Allies controlled all the bat guano deposits in caves that were the nitrogen source for fertilizers and explosives manufacturing. CO2 is a byproduct of the process produced as waste that must be removed, which is fundamental to the CO2 air capture process.

Betts, The Haber Process: How the Need For Bombs 100 Years Ago Has Saved Your Life, Early Navigation through Advanced Chemical Topics, July 29, 2022.

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