

A Solatier & NetMix Chemergy system proposal

To realize a less CO2 emitting Cement Industry,
 Initiating a CO2 neutral Chemical industry and
 ultimately reach Type 3 (CO2 emission by users) neutral fuel companies
 under the assumption of rising CO2 waste cost level of 10 Eurocent/kg (100 E/t)

Creating a competitive advantage in the cement industry once CO2 taxes reach 100 Euro per ton using hydrated CO2/CH4 storage technologies.

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using the 2020 information from the C5lab and Net4CO2 Portuguese Colabs and the 2012 TNO chemergy concept

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1. Introduction

The cement industry is a very competitive industry with little room for profits. It operates in an international market at a 2019 average price level of 60 dollar/euro per 1-ton cement. With a CO2 taxation/trading scheme at any level, the price of 1-ton cement will “explode”:

60 Euro/1000kg Cement	Y kg CO2/1000 kg Cement					
X Euro/1000kg CO2	1000	800	600	400	200	0
30	90	84	78	72	66	60
100	160	140	120	100	80	60
300	360	300	240	180	120	60

Spreadsheet cell formula: $60 + (X (=CO2\text{-cost}) * Y (=CO2\text{-emission})) / 1000$

With increasing CO2 taxation, formulated positively, any extra CO2 reduction will lead to a relative competitive advantage. Once green politics rise CO2 taxation rapidly, doing nothing will soon lead to significant market loss and bankruptcy. Be proactive in CO2 reduction. Political decision can be implemented faster than research results can be achieved & implemented at any significant level coping with the needs (green) politicians on behalf of society soon might formulate.

What implies for the cement industry, with relatively the highest CO2 emission, will in a similar way also be the case in the chemical industry and the fossil fuel industries. With the difference that the cement industry has the “benefit” of a high CO2 point concentration, the chemical industry is already facing less high CO2 sources and the fuel industry ultimately will need to get their CO2 source from the air. In the subsequent text the focus is on the cement industry.

One remark: the whole vision will fly once it is not allowed to dump CO2 in the air and is charged as waste at 100 Euro/ton or 10 eurocent/kg levels.

2. Create a competitive advantage with CO2 taxation, if possible

Initial reaction regarding CO2 taxation is that it will hurt companies. However, if it is inevitable, then a proactive approach can lead to a competitive position for early companies as shown in the introduction. But it does require a level playing field.

If green policies lead to higher Euro/ton CO2 taxation, then a European border tax on CO2 will be needed to maintain a level playing field at global level. If such a tax is created, it is logically that the exported cement should get a CO2 refund. In trade deals an average added CO2 cost will be used to charge imported cement. Expect that CO2 tax to be based on high CO2 waste costs. However, the exported cement from a significant CO2 reduced cement producer will lead to a high CO2 refunding and an improve relative competitive position.

For a CO2 import tax at 600 kg CO2 tax/1000 kg cement at 100 E CO2 tax/1000 kg CO2 and an advanced cement producer at 400 CO2 waste/1000 kg produced cement, the benefit will be that cement produced for 60 E cement and 40 E CO2 gets refund of 60 Euro CO2 tax, enabling the producer to sell internationally for 60 E with a 20 Euro profit. In other words, an aggressive CO2 taxation at EU level with a proper border tax could even benefit European cement producers. But only if they become proactive and turn research results into real industrial use. What research is possible already today?

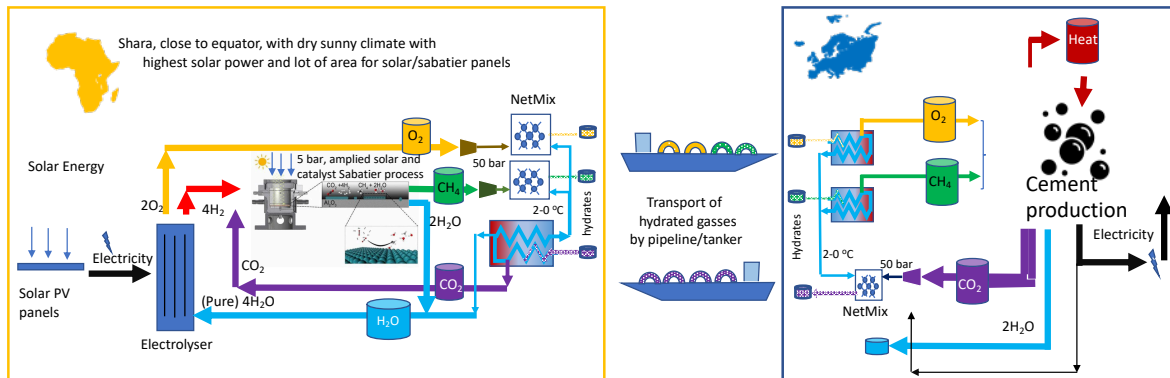
3. The basic idea

Disclaimer: the following numbers are assumptions based on (too) little information and must be validated (improved and completed) by an expert with cement production knowledge. It might even be that a different path is more suited. Below is a first suggestion, any improvement on the idea and numbers are (very) welcome.

For cement production one needs the cement ingredients (sand, etc.) and a 1000+ (1450) Celsius heated oven using e.g. CH₄/fossil fuel as burner fuel. We assume that half of the CO₂ production in the cement industry is related to the use of fossil fuel and the other half of the CO₂ is the result of the clinker process in the oven. We assume that during a daily production a significant portion of that CO₂ can be captured.

From this CO₂ and electrolyzing water into H₂ we could create (a part of) the daily CH₄ burner fuel needs. This way we reuse some of the CO₂ from the clinker production to replace the fossil CH₄ by CH₄ from the burner fuel/clinker CO₂ and effectively lower the total CO₂ waste. And lower CO₂ waste in the future implies less future CO₂ taxation. But what are the costs and benefits? And what could be a roadmap towards the end goal of industrial scale implementation?

SOLATIER for large scale CO2 neutral energy transport and storage for cement production
 a high-tech system using a combining of SOLar power driven SabATIER, gas-2-hydrates mixing and isolated slurry transport to reduce the CO2 load by the cement industries.



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Still to be done: mass/energy balance with all materials (H₂, CH₄, CO₂, H₂O, O₂) for simple small scale business case and at national volume

4. Calculation basics and assumptions for a 4-step roadmap

The creation of CH₄ from CO₂ costs (a lot of) energy. And that energy must be from a sustainable source. It must be solar/wind generated electricity at the moment they are at a peak and green electricity (spot) prices are low. However, in that case one needs to store CO₂ for more than several hours. Below we will use a daily cycle of continuously CO₂ capture, daily storage and peak CH₄ production from CO₂ during the periods of very low electricity prices. (The alternative with a dedicated Sahara solar park follows latter, but for the first roadmap phase, national low peak prices during surplus hours and enough electricity network capacity between source and user are assumed.)

Assume a daily (24h) production at a factory:	5.000.000 kg cement/day
Assume 20% CO₂ capture from clinker process ¹ :	1.000.000 kg (1000-ton) CO ₂ /day
Assume CO ₂ capturing costs:	30 Euro/ton CO ₂ (here 30K E/day)
1 m ³ of hydrated CO ₂ contains:	710 kg H ₂ O and 290 kg CO ₂
Storing 1.000.000 kg CO ₂ at 1 atm/0 °C requires:	~ 500.000 m ³
Storing 1.000.000 kg CO ₂ as liquid requires:	~ 1000 m ³ (at 1 atm and -37 °C)
Storing 1.000.000 kg CO ₂ hydrate requires:	3448 m ³ (88 seacontainers and 2448 m ³ H ₂ O, at 1 atm, 0-3 °C)

Storing the daily CO₂ as air is not doable, so it is dumped in the atmosphere. But that will become too costly. Cooled liquid CO₂ requires cooling energy. Storing it as hydrate with cold water and mixing with NetMix² at 60 bar CO₂ and then storing it in 3448 m³ isolated tank could cost 10K Euro. Later on, we reuse the once cooled water, so it is reused/recycled

¹ Today 1000 kg cement results in total in 674 kg CO₂, we assume here that 50% is from the clinker production, the rest is from heating the kiln by a flame using CH₄ as burner gas (say 25%) and transport etc (25%). From the say of 337 kg CO₂ (50% of the CO₂ from clinker and 168 kg CO₂ from CH₄ we here capture for the calculation in the example case an arbitrary 20% (100 kg from the 505 (337+168) kg coming out of the kiln), although other levels up to 100% (or say 505 kg) are possible too.

² NetMix from Prof. Jose Carlos Lopes (jose.carlos.lopes@net4co2.pt) is able to mix a hardly mixable bipolar gas with water using large scale, highly parallel turbulent liquid flows by pressurizing the gas and mixing it with icy water to produce the hydrate.

and only once cooled down from, say 20 C to 1 C. But every day, one need to warm the water a little just enough to release CO₂ for reuse as a base chemical to assembly CH₄.

Assume that every day there is a period of very low electricity pricing (wind/solar peak or need for a base load in middle of night). One could produce at such time-of-the-day green H₂ by electrolyzing (very clean) water (H₂O) into H₂ and O₂. (By the way this O₂ could be used to create higher flam temperature of burners using air + extra O₂). This H₂ might be used as momentary gas for the burners, but for later use it is difficult to store (e.g. 600 bar). Therefore, we want to use the green H₂ for CH₄ production, use the CH₄ as burner gas and store the temporary surplus of CH₄ for later use once the electricity pricing increases.

H₂ is difficult to storage but bring it directly after electrolyzing to 60 bar and reused 300 C from the flu gasses of the cement oven and put H₂ and CO₂ at 60 bars in the **Sabatier**³ process to get CH₄ (or syngas). Let's call this own CH₄, green CH₄. Then use this own green CH₄ instead of the purchased CH₄. The net effect will be that there is no CO₂ (tax) costs for the green CH₄. Today all this is not economically sensible, but with higher CO₂ taxation it become more sensible, all depending on the Sabatier or, as later described, Solatier⁴ process costs.

There is operational cost for CO₂ capture (say 30 E/ton), there is cost for CO₂ storage (say 10 E/ton) and there are cost for H₂ production. We will assume here that the electricity costs of Solar PV surpluses are (near) zero). And there are costs for the Sabatier process. The solar PV park, electrolyzer and Sabatier costs are mainly CAPEX and no/minimal OPEX. The question is the how much are these costs in relation to the CO₂ cost levels to make the business case realistic and might even provide the earlier assumed (temporary) competitive position? But this end picture cannot be determined yet. Therefore, a roadmap is proposed.

The following steps provide a conceptual roadmap toward the end solution. We start with the two scenarios: a CO₂ capturing and NetMix only N-scenario and a full Solatier S-scenario. (N stands for North Sea or Norwegian and S for Sahara or Saudi Arabia)

N-scenario:

Mine CH₄ in a cold climate (North Sea or Nordic ice sea) where the CH₄ is hydrated (at low energy cost for cooling the water to 0-2 C) for transport to a Portuguese cement plant (close to a sea harbor). Capture at the cement kiln the CO₂ during the clinker process where the CH₄ is used as fuel and hydrate the CO₂ (using the previous cold water from the CH₄ transport) for return transport. Motivation here is that e.g. the Dutch and/or Norwegian would be willing to participate in the production for climate neutral CH₄-usage as they are able to pump back CO₂ in depleted fields at sea locations.

³ Sabatier: traditional process 300 C, 60 bar CO₂ and H₂ to produce syngas/H₂ using catalyst reaction. Newer, solar/photonic and electrical accelerated Sabatier version (Solatier) require low pressure/temp (e.g. 5 bar, lower temp.).

⁴ Solatier, or SOLar PV enabled/enforced/accelerated Sabatier process is based on the work by Pascal Buskens (TNO) and the Univ of Hasselt (2017) Sunlight-Fueled, Low-Temperature Ru-Catalyzed Conversion of CO₂ and H₂ to CH₄ with a high proton-to-methane efficiency, Francesc Satre et al, ACS Omega, Vol 4, 2019, April, 23

The challenge in CO₂ storage in depleted oil/gas fields is probably the use of the hydrate slurry to be pressurized. But pressurizing a slurry is probably easier with a liquid than a gas. Of course, one would lose the cold water of the hydrated CO₂ by pumping it under ground, but in the Nordic situation there is enough cold available for the hydration of the CH₄.

Initially a small-scale setup using (12-ft) sea container size and multiples of 10.000 kg CO₂ (see calculation in S-scenario) could be used during an experiment, but ultimately it can be scaled up to weekly/monthly transport of small freight ship (1000-ton feeder type container ships). Capturing CO₂ at 20-30 E/ton, twice transport at 2x10 E/ton, twice hydration at 2x10 E/ton would result in a say 80 E/ton and be economic viable once (inside Europe) CO₂ prices of 100 E/ton are reached.

S-scenario:

This is the full scenario in a sunny (warmer) environment and to be evolved along a 4-step roadmap.

- (1) capturing a part of the CO₂ and use water electrolyzing and Sabatier to supplement the actual momentary CH₄ usage for the burners (mixture of fossil and green CH₄).
- (2) a parallel step with (1) is local storage (later usable at the full-scale version) of the continue CO₂ capturing in the form of hydrated CO₂.
- (3) in the third step a huge amount of needed green electricity is locally (next to a cement factory) available as surplus (solar field, windmill farms with can't put too much power on the network during peak hours due to network capacity constraints).
- (4) and (one the first three step are proven) scale up at a large solar/wind park where the electrolyzing and Sabatier process are done far away from the cement production and where transport (of CH₄ and CO₂) become necessary and is done by exchanging hydrated CH₄ and CO₂. That is done in the last roadmap steps.

In the following paragraphs these steps are explained in more details. But let's start with some more detailed assumptions and numbers.

If 1000 kg cement costs 673 kg CO₂ and (see footnote 1) we could assume that 168 kg CO₂ could be due to the burning of CH₄, then at a daily production of 5.000.000 kg cement/24 h, one needs (at 168 kg CO₂ equals 61 kg CH₄⁵) 305.000 kg CH₄/24 h = 12.727 kg CH₄/h or (at 0,657 kg/m³ at 1 atm, 20 C) 19.000 m³ CH₄/h (5 m³ CH₄/sec).

Assume we want to go all the way to 300.000kg CH₄ per day, then we need 825.000 kg CO₂ (but that will be in abundance with 5.000.000 kg cement/day) and 75.000 kg H₂/day or 3125 kg H₂/h or approx. 35.000 m³ H₂/h. Such an installation requires an electrolyzer in the order of 2x100 MW electrolyzer (see figure below).


⁵ 1 mol CO₂ is 12 + 2 x 16 = 44 versus 1 mol CH₄ is 12+4 = 16, therefore all things (atmospheric pressure, temperature) equal 168 kg CO₂ is equal to 61 kg CH₄

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<https://mcpny.com/en/our-products-and-solutions/electrolyzers/augmented-mclyzer/>

Our 100 MW platform:

- 25 modules of 4 MW
- Based on the same architecture as the 20 MW clusters
- A total footprint below 4,500 m²
- 20,000 Nm³/h of hydrogen, more than 42 tons per day
- 30 bar: high pressure production
- Fast dynamic response time
- High energy efficiency
- 10,000 Nm³/h of by-product O₂, 342 tons per day



A 2x100 MW solar park⁶ requires 50 m x 500 m (300 hectare) at appr 200 M Euro Capex, resulting in 20.000 E/day (divided by 10.000 days lifetime) costs for the solar park, plus ?? cost for the 2x100 MW electrolyzer plant. (Notice the additional oxygen that is produced by the electrolyzer one could use for the burner process.)

(The following it not full correct (yet) as a 200MWp solar park only provides the peak power during a few hours a day. So, for the calculation below we run the hypothetical electrolyzer installation only for a few hours a day. The rest, capturing installation, Sabatier (and some H₂ day buffering) could be running on a continuous 24 h daily basis.)

With such an installation, next to the cement factory (in a sunny spot), one would save (1/4 of the total CO₂) 168 x 5000 kg CO₂/day, or 840.000 kg or 84.000 Euro/day if CO₂ price would be 100 E/ton(1000kg). Next to the 20.000 E /day for the solar PV and the ?? for the electrolyzer platform, one also needs to add the cost for CO₂ capturing (say in its high concentration, that that can be done for say 20 E/ton, so the 840 ton capturing of the CO₂ would costs per day 16.800 E/day and the ?? costs of a Sabatier installation where the H₂ and CO₂ are processed into CH₄. The ?? for the electrolyzer can be determined easily as electrolyzers are commercially available products. The ?? for the Sabatier is less clear. In any case, daily saving of 84K E CO₂ tax (at 100 E/1000 kg CO₂) costs at least 16,8K E capturing, 20K E electricity and ?? electrolyzing H₂ and ?? CH₄ forming from CO₂ and H₂. So the costs of electrolyzing the H₂ and the Sabatier production of CH₄ must be possible below 47K per day.

⁶https://www.academia.edu/31082576/An_Approximate_DESIGN_of_a_100MW_Solar_Power_Plant_for_Zimbabwe by Takura Kutsoma – we assume solar intensity in Zimbabwe similar to e.g. Portugal

5. First, begin minimal scenario proposal of only a few parts of the whole chain.

The first experiment will be dimensioned to produce some small amount of green CH₄ that can be used continuously in the oven. Just capturing the CO₂ and electrolyze water once electricity is at a very low prices level and directly use the CO₂ with the H₂ in the Sabatier process, so no H₂ storage is needed (only maybe some buffering in intermediate vessels).

For an first step, start with a 4 MW electrolyser (CAPEX/OPEX ?) and a small 4MW (of more) solar park (4 M E CAPEX?) (of high capacity (4kAV+ electrical power connection to the power grid network). With such an installation one might produce 800 m³ H₂/h, resulting in 72 kg H₂ and producing with a Sabatier process then 300 kg CH₄ and saving 825 kg CO₂ per hour. Say for a day with 6-hour peak solar electricity, that would imply that on such a day 5-ton CO₂ could be avoided with such an experimental, pilot installation. No CO₂ storage is needed if the capacity of the CO₂ capturing during the 6-hour peak is large enough.

6. A parallel step with CO₂ (capture) storage on daily basis

Once sufficient (green) electricity is available and electrolyzing H₂ (and O₂) and the Sabatier process are working properly one can scale up the production to a 4 MW capacity reaching the situation for a peak hour use. However, CO₂ capturing can be continuously, but that need to be stored be stored with local storage tanks ready to be "Sabatier"-ed once the H₂ is generated during peak electricity. Now we assume that during the solar day peak the above 5000 kg CO₂ is used and that we want to have at least always 5000 kg CO₂ at hand.

Storing 5.000 kg CO₂ at 1 atm/0 C requires: ~ 2.500 m³

Storing 5.000 kg CO₂ hydrate requires: 17 m³, that is ½ sea container (of 39m³)

To store 5000 kg CO₂ in 24 h, requires a 200 kg/h installation or one stack (size of one man) of NetMix (40 plates) modules. And one still needs to get (once) 15 m³ of ice water and of course the costs for the NetMix system (say at 10 E/ton, then 5000 kg is 50 E/day).

Intermezzo: Solatier in combination with a Solar PV park

The Sabatier process to do the opposite of burning a fossil fuel as CH₄ with O₂ into CO₂ and H₂O requires a lot of energy in the form of a high temperature and pressure to break open the stable O=C=O molecule and replace the oxygen binds with H-binds. Due to the high temperature/pressure such a process can only be done at a very large (economy of scale) site where enough heat is available.

Recently, see footnote 4, an alternative Sabatier process has been demonstrated where the same process is accelerated with photons such that the high temperature/pressure are not needed anymore. It does require amplified sunlight (high energy photons). A reason to call it Solatier (Solar enforced Sabatier). In the context of the discussion here, once one has a large

solar PV park, it logical to expand it with an electrolyzer to produce H₂, a CO₂ source as input to such a solar driving Solatier installation to produce the syngas/CH₄.

Of importance in this context is that one does not have to storage H₂. Although not impossible the storage of H₂ is a fundamental problem and therefore rather costly technology. The whole idea in this proposal is to avoid the storage and transport of H₂, but to use the same trick as nature does already for billions of years do it with hydrocarbons (as CH₄).

7. Large storage covering weekly basis (low costs weekend electricity, multi day lack of low peaks)

Expand storage with hydrated CO₂ and CH₄ for a next research phase with a cement factory and solar/wind farm close by (e.g. 100 km) and truck transport in an experimental phase (in practice, offloading the peak loads that the solar/wind park can't put on the network and wants to use local storage by converting surplus electricity into H₂ and then into CH₄ which it cannot put in a gas network, so it puts it into hydrated CH₄).

Here we assume a 100+ MWp (Wp is Watt peak power) park that cannot put a surplus peak every day for 2 hours at 100 MW on the grid. Using this 2-hour 100 MW can be used to electrolyze H₂O into H₂. Let's assume it then produces 40.000 m³ H₂ or 3600 kg H₂ during those two hours. This can be converted ("Sabatier"-ed) into 14400 kg CH₄ and that should then be stored in hydrate CH₄ at (115 kg CH₄ goes into 1 m³ hydrate) 125 m³ (and needing 110 m³ icy H₂O), roughly the equivalent of 3 (20 ft, 39 m³) sea containers (two trucks). Of course, the power site needs then also 40.000 CO₂. At 290 kg CO₂ per 1 m³ hydrated CO₂ that means 138 m³, the equivalent of 4 sea containers (the same two truck driving daily between the two sites).

At the cement site the capturing and NetMix of CO₂ needs to be scaled up to from 5000 kg/day to 40.000 kg/day. The NetMix then goes to 1666 kg/h and 8 man-height NetMix racks.

8. Exchange/long distance transport of hydrated CO₂ and CH₄

At large scale local CH₄ production will run into limited availability of electricity/network capacities. In that case an exchange by hydrated CH₄/CO₂ tank (sea) transport become sensible. Capture CO₂ at the cement oven, hydrate it and transport it next to a dedicated (Sahara type, max solar energy) solar/wind field where, during over-capacity and network blockage, locally the hydrate CO₂ is used in the green CH₄ production and which green CH₄ is then hydrated (reusing the cold water from the hydrated CO₂) and then transported back with the same tanker.

On a daily basis we want to process 300.000 kg CH₄ and 825.000 kg CO₂ at both sides. This amount needs a hydrating amount of (2500/2850, say) 3000 m³ hydrated gas/day. That is equal to say 75 20-ft sea containers and on a monthly trip the sailing requires around 2000 20 ft or 1000 40-ft sea containers fitting on a medium sized (Feeder container) ship. Or a small sea bulk tanker equipped with isolated tank of 40.000 m³ would in case of hydrates be

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able to carry 10.000 m³ and might travel one a week up and down with the CO₂/CH₄ hydrates.

In other words, one can sketch a roadmap to an ultimate goal of reaching a 20% reduction of CO₂ in the production of cement at plant and even national level. (especially if a cement plant is close to a sea harbor).

9. Transport discussion

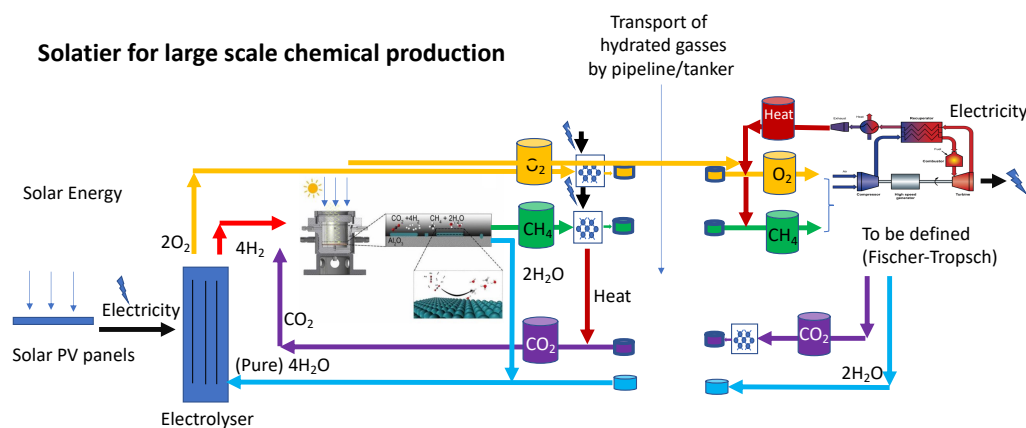
Today CO₂ and CH₄ cannot be transported by the same liquid gas tankers. But with hydrated slurries at 1 atm and around 1-2 C, that is no problem (and avoid the complex tank procedures and riskier transport as with liquid (CH₄) gas). Road/sea tanker transport will add extra costs (sea bulk tanker transport is around 8 Euro/ton).

10. Temporary conclusion for the cement industry

20% CO₂ reduction by the cement industry is possible. It will become economically realistic once CO₂ tax level evolve towards 100 Euro per ton CO₂. And it will require a roadmap toward that solution which will take a few years to evolve.

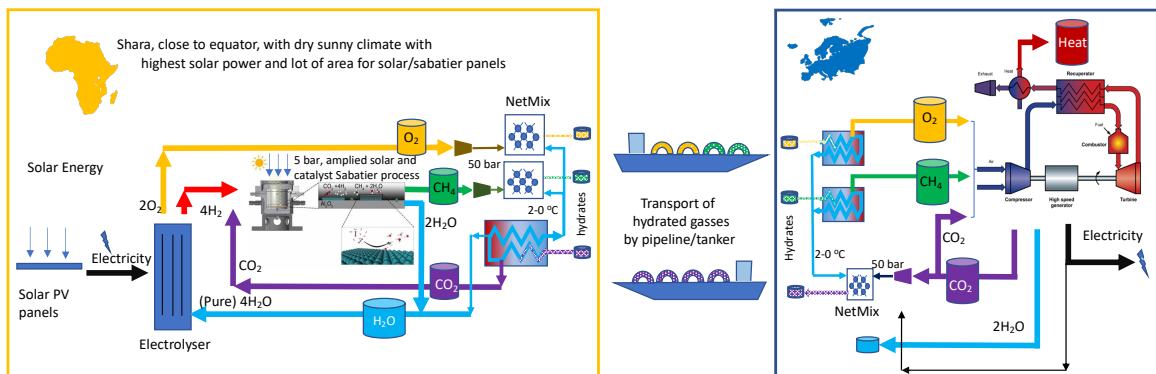
11. Beyond the cement industry (with its relative high CO₂ emission)

Other industries that need to be CO₂ neutral, but which will use hydrocarbons as base material or fuel are the chemical process industry and the fuel energy companies. There the challenge is to produce them out of CO₂, ultimately extracted from the air, and not fossil sources. For these industries any progress at the cement industry is of great interest. Therefore, the cement industry might search for cooperation with these process industry as in those industry some of the (chemical) technologies that are needed are more common than in the cement industry. In particular today's fossil fuel companies might be extremely interested and capital powered to join the described roadmap.



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SOLATIER for large scale CO2 neutral energy transport and storage for electricity production
 a high-tech system using a combining of SOLar power driven SabATIER, gas-2-hydrates mixing and isolated slurry transport between Europe and Sahara-Countries to lower Russian & fossile gas dependency.



Put a CO₂ import tax border around Europe at 0,3 €/kg (or 100-300 €/ton) with refund once CO₂ slurry is exported for Solatier, then any imported non-solar CH₄, i.e. Russian/European mined, gets a CO₂-added tax with higher prices such that the chemery (proces & energy) sector can be CO2 neutral and competitive despite the hydrating costs.

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Still to be done: mass/energy balance with all materials (H₂, CH₄, CO₂, H₂O, O₂) for simpel small scale business case and at national volume

Source (still to be completed)

See footnote for references

Chemery (https://www.ejsol.dse.nl/DSE/Presentations_files/Chemery%20v5.pdf)

Wikipedia

Google (e.g. on chemery)