



Methanation of cementbased CO₂ emissions without prior CO₂ separation

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Vorwort der Begleitgruppe

Zement ist als Werkstoff für die Herstellung von Gebäuden und Infrastrukturbauten in jeder modernen Gesellschaft ein zentraler und unverzichtbarer Baustoff. Weltweit wird für die nächsten Jahre und Jahrzehnte ein markanter Anstieg der hergestellten Zementmengen erwartet.

Bei der Herstellung von Zement wird prozessbedingt eine grosse Menge von CO2 freigesetzt. Seit man sich der CO2- Problematik bewusst ist, hat die Schweizer Zementindustrie grosse Anstrengungen unternommen, um den spezifischen Ausstoss von CO2 bei der Herstellung von Zement zu reduzieren. Zement ist heute ein weitaus oekologischerer Baustoff als noch vor 30 Jahren.

Damit weitere Fortschritte auf dem Weg zur CO2- neutralen Herstellung von Zement erzielt werden können, braucht es Massnahmen, um das prozessbedingte CO2 binden, und einer weiteren Anwendung zuführen zu können.

Die vorliegende Arbeit untersucht die Möglichkeit, CO2 direkt aus den Emissionsgasen heraus zu methanisieren und dadurch einen Stoff herzustellen, der für weitere industrielle Prozesse genutzt werden kann. Neben der technischen Machbarkeit wird auch die Wirtschaftlichkeit einer solchen Massnahme untersucht. Die vorliegenden Resultate helfen mit, auf dem Weg zur CO2- neutralen Zementherstellung einen weiteren Schritt voran zu kommen.

Jan Patrik Niklaus, Vigier Ciment SA

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Dr. Martin Tschan, Leiter Umwelt, Technik, Wissenschaft, cemsuisse





Final report

CemCOO

Methanation of cement-based CO₂ emissions without prior CO₂ separation

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Contents

1	Summary	3
2	Project goals and status	4
2.1	Goals	4
2.2	Status	4
3	Results	5
3.1	Effect of oxygen on the CO2 conversion and safety of catalytic methanation	5
3.2	Effect of carbon monoxide on the activity of a sorption enhanced methanation catalyst	7
3.3	Sorption enhanced methanation with cement plant gas compositions	8
3.4	SO2 poisoning of a sorption enhanced methanation catalyst	9
3.5	Methanation of cement plant gases	11
4	An economical evaluation on large scale methane production from cement industry origination CO2	ng 13
4 4.1	An economical evaluation on large scale methane production from cement industry origination CO ₂	ng 13 13
4 4.1 4.2	An economical evaluation on large scale methane production from cement industry origination CO ₂ Introduction General technical considerations for the applied model	ng 13 13 15
4 4.1 4.2 4.3	An economical evaluation on large scale methane production from cement industry origination CO ₂ Introduction General technical considerations for the applied model Costs estimation for the power-to-gas model	ng 13 13 15 18
4 4.1 4.2 4.3 4.4	An economical evaluation on large scale methane production from cement industry origination CO2 Introduction General technical considerations for the applied model Costs estimation for the power-to-gas model Overall costs	ng 13 13 15 18 21
4 4.1 4.2 4.3 4.4 4.5	An economical evaluation on large scale methane production from cement industry origination CO2 Introduction	ng 13 13 15 18 21 22
4 4.1 4.2 4.3 4.4 4.5 5	An economical evaluation on large scale methane production from cement industry origination CO2	ng 13 13 15 18 21 22 24
4 4.1 4.2 4.3 4.4 4.5 5 6	An economical evaluation on large scale methane production from cement industry origination CO2 Introduction	ng 13 13 15 18 21 22 24 25





1. Summary

The CemCOO project is a feasibility study aiming at the demonstration of a catalytic CO_2 methanation without prior CO_2 separation for the valorisation and utilisation of CO_2 in waste gas from cement plants to reduce primary fossil fuels consumption and CO_2 emissions in the manufacturing process. A novel catalytic principle – the so-called sorption enhanced methanation process – was used for this purpose.

The catalyst was first tested with laboratory gas mixtures mimicking challenging cement plant gas compositions, the latter being provided by industrial partners. Crucial aspects of typical cement gas compositions and their effect on the catalytic performance were addressed, namely the effect of in nitrogen-diluted CO_2 , residual oxygen and carbon monoxide in such gas mixtures and the influence of poisoning SO_2 , which can deactivate the catalyst even in trace amounts. None of these issues was identified as a stopping criteria from the feasibility point of view. O_2 and SO_2 thresholds were defined, above which the technology is critically affected from the performance and economic points of view. As long as these thresholds are taken into account, proper engineering of the sorption enhanced methanation technology can help facing them without critical performance losses.

The process was then brought to demonstrator scale in the laboratory, which could be applied as prototype in real environment. Operation parameters adapted to the composition of cement plant gases could be found. The demonstrator performance shows that 100% of the CO_2 in cement exhaust gases can be converted directly and into CH_4 with regenerative H_2 . And this, despite the presence ballast gases such as N_2 and O_2 . This is shown for the first time and is a uniqueness for catalytic methanation systems. Finally, a gas specimen was taken on-site at an industrial partner and transported to the lab to be tested in the demonstrator. The results show that the catalyst performance can still be maintained with "real life" gas mixtures.

Finally, an economic evaluation was performed in order to assess in numbers the relevance of CO_2 methanation of cement plant gases in Switzerland.





2. Project goals and status

2.1 Goals

The main goal of the CemCOO project is to perform a feasibility study for the valorisation and utilisation of CO₂ in waste gas from cement plants without prior CO₂ separation. A first work package is dedicated to the collection of data from the three industrial partners involved in the project: Holcim, Jura Cement and Vigier Ciment. The confidential data provided by the individual companies concerns the composition and temperature of cement gases at different stages of the cement production process. This first step was necessary in order to define meaningful experimental parameters for the experiments, i.e. to be able to simulate the cement plant gases with laboratory gas mixtures and bring these mixtures into contact with the catalysts. A second work package focuses on the laboratory testing of the catalysts, first by confronting them with laboratory gas mixtures and second by collecting "real life" gas specimens at the companies mentioned above. Milestones involved direct methanation without CO_2 separation, notably with the use of a N_2 ballast, evaluation of the methane yield as a function of the amount of H_2 added to the gas stream, influence of residual O_2 and SO_2 contaminant in the cement gases, definition of optimal process parameters and evaluation of the operating feasibility of the methanation process. Finally, a third work package concerns the economic aspects of the proposed technological solution for the conversion of waste cement plant gases.

2.2 Status

The CemCOO project is now completed. All of the planned tasks were accomplished according to the schedule. WP1 was completed in the early stages of the project, including deliverable D1.1. The WP2 is complete, including the collection of specimen from an industrial partner and laboratory testing for methanation. Meaningful economic statements, notably connected to the applicability of the proposed methanation technology, are discussed in Section 4.



Fig. 1: Schedule and deliverable plan of the 12 month project period.





3. Results

3.1 Effect of oxygen on the CO₂ conversion and safety of catalytic methanation

At the start of the project, the presence of oxygen in cement plant gases was considered a priority object of study. In general, working with hydrogen (H₂) oxygen (O₂) mixtures in high temperature environments is avoided for safety reasons. In the case of the present project, the oxygen concentration is much smaller than the hydrogen concentration, which makes such experiments possible. Additionally, the main concern and critical point from an industrial application and economic point of view is the precise quantitative influence of the oxygen concentration on the CO_2 conversion, a topic that usually is not addressed, since typical methanation gases are practically O_2 free.



Fig. 2: In-situ mass spectrometry measurement of the outlet gas composition of a sorption enhanced methanation catalyst bed (quartz tube reactor, 6 mm diameter) exposed at 300° C (a) and 400° C (b) to different simulated cement plant gas compositions, to which H₂ is added with a 5 mol.% overstoichiometry with respect to the Sabatier reaction.

The two experiments in Fig. 2 illustrate the complexity of the sorption enhanced methanation process. Although the experiment from Fig. 2a is performed at the temperature optimum for sorption enhanced methanation (i.e. 300°C, the best compromise between the water sorption capacity of the water adsorbing support and the catalytic activity of the active nanoparticles [1]), the methane signal is relatively weak because sorption enhanced methanation requires gas hourly space velocities (GHSVs) that are two orders of magnitude lower than the experiments from Fig. 2. Nevertheless, such experiments are highly valuable because they allow fast gathering of information on the catalytic activity while using minimal amounts of material (< 1g in powder form) and reactants. Additionally, any safety-related aspects of such potentially harmful experiments are easier to manage with small-scale setups. In a later stage of the experimental plan, when enough data is gathered to define safe operation parameters, large demonstrator-sized sorption enhanced experiments can be performed (see further sections below).

Abrupt changes in the outlet gas composition (e.g. Fig. 2a, 3 mol.% O_2 and 6 mol.% O_2) are regularly observed when performing catalytic runs of the Sabatier reaction with variable amounts of oxygen. The interpretation is obvious here: the production of water from H₂ and O₂ (Reaction (1)) releases much more heat than the Sabatier reaction itself (reaction (2)):





$4\mathrm{H}_2 + 2\mathrm{O}_2 \Rightarrow 4\mathrm{H}_2\mathrm{O}$	$\Delta H^0 = -1144 \text{ kJ/mol}$	(1)
$4\mathrm{H}_2 + \mathrm{CO}_2 \Rightarrow \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O}$	$\Delta H^0 = -165 \text{ kJ/mol}$	(2)

Consequently, even small concentrations of oxygen can perturb the process thermal balance. This is what can be seen through these abrupt changes, which correspond to either system overheating due to Reaction (1) causing an increase of the catalyst activity or system restabilising at the set temperature causing a decrease in catalytic activity.

In order to increase the methane signal and better identify trends as a function of the oxygen concentration, similar experiments were performed at 400°C (Fig. 2b). The trend is indeed very clear here: the more oxygen is in the cement plant gas, the less methane is produced by the Sabatier reaction. Here again, the interpretation is straightforward: Reaction (1) takes place at the expense of Reaction (2), and since H_2 is only provided with a slight overstoichiometry with respect to Reaction (2), there is not enough H_2 for the latter reaction above a certain threshold in O_2 concentration (which is defined here as the O_2 concentration above which consequent decrease of the methane yield is observed). In the case of Fig. 2b, the O_2 concentration threshold is 3 mol.% in the cement plant gas.



Fig. 3: In-situ mass spectrometry measurement of the outlet gas composition of a sorption enhanced methanation catalyst bed (quartz tube reactor, 6 mm diameter) exposed at 400°C to different simulated cement plant gas compositions, to which H_2 is added with no H_2 overstoichiometry (a) and full stoichiometry with respect to both Reactions (1) and (2) (b).

It becomes clear that the tolerance of sorption enhanced methanation to oxygen from cement plant gases depends on the amount of H_2 added to the gas stream prior to CO_2 conversion. For instance, providing stoichiometry only for Reaction (2) results in a lower O_2 concentration threshold of 2 mol.% (Fig. 3a), and providing stoichiometry for both Reactions (1) and (2) increases the threshold up to 6 mol.% (Fig. 3b). Even when providing enough hydrogen for both reactions, the methane yield becomes critically affected above 6 mol.% O_2 . Explanations for this could be the accumulation of water in the catalyst bed or a perturbation of the process thermal balance.

From a purely quantitative point of view (Fig. 4), the methane yield starts around 80% with no O_2 in the gas stream (again, this does not correspond to the performance of the real sorption enhanced methanation process and needed GHSV, it only serves as a reference point), and decreases by about 50% at relatively high oxygen concentrations.







Fig. 4: Evolution of the methane yield as a function of the oxygen concentration in a simulated cement plant gas. Processed data from Figs. 1b, 2a and 2b. the reaction temperature is 400°C

3.2 Effect of carbon monoxide on the activity of a sorption enhanced methanation catalyst

Carbon monoxide is another recurring compound in cement plant gases. It is well-known that CO is an intermediate of Reaction (2), halfway between CO_2 and CH_4 in terms of oxidation number [2]:

$$4H_2 + CO_2 \Rightarrow 3H_2 + H_2O + CO \Rightarrow 2H_2O + CH_4$$
(3)

From Reaction (3), it is clear that any CO molecule present in the gas stream will be preferentially converted over CO_2 . However, this is confirmed by an experiment under the load of diluting gases, here for analytic reasons with an Ar load of 43 mol.% (Fig. 5).



Fig. 5: Evolution of the outlet gas composition of a sorption enhanced methanation catalyst bed (quartz tube reactor, 4 mm diameter) exposed to an inlet gas stream of composition 10 mol.% CO_2 , 30 mol.% CO, 17 mol.% H_2 and 43 mol.% Ar at two different temperatures, measured by in-situ Raman spectroscopy.

Indeed, although the CO concentration is three times higher than the CO_2 concentration in this experiment, the outlet composition shows the opposite proportion, especially at 400°C where the catalyst is more active and almost all the hydrogen is consumed.





3.3 Sorption enhanced methanation with cement plant gas compositions

By using a water adsorbing support together with metallic nanoparticles that are active for the Sabatier reaction, the support removes the product water molecules away from the reaction centers, thereby acting according to Le Châtelier's principle. Such a catalyst is able to enhance the kinetics and yield of the Sabatier reaction [1,4]. However, the dynamics of water evolution through the catalyst bed is a rate-limiting process, namely, the catalyst is in pelletized form and the pellet size is an important parameter [3] and influences the diffusion path length. This means that the process only works under relatively low GHSVs compared to classical catalysts (on the order of 100 h^{-1}). One should also keep in mind that the operation temperature is a compromise between the water sorption capacity of the water adsorbing support (which decreases with increasing temperature) and the catalytic activity of the active nanoparticles (which shows the opposite behaviour).

The first reactor that was used for the sorption enhanced methanation experiments has a circular section of 2.4 cm in diameter and a length of 33 cm. This design is not optimal for the process performance but it provides relevant data with minimal material load (~100 g per specimen). Fig. 6 shows two methanation runs performed with and without carrier gas, the carrier gas being N₂, as in real-life cement plant gases. In Fig. 6a, the GHSV is 50h⁻¹, and one can clearly distinguish the sorption enhanced mode as the methane concentration forms a plateau in which the methane yield approaches 100%. Here, the sorption enhanced mode is defined as the time between introduction of CO₂ in the inlet gas stream (left vertical red line in both graphs) and apparition of CO₂ in the outlet gas stream (right vertical red line in both graphs).



Fig. 6: Evolution of the outlet gas composition of a sorption enhanced methanation catalyst bed (glass tube reactor, 24 mm diameter, pelletized specimens) exposed to an inlet gas stream of composition corresponding to the Sabatier stoichiometry at 300° C with (b) and without (a) carrier gas (77 mol. % N₂), measured by in-situ Raman spectroscopy.

In both Figs. 5a and 5b, the flow of reactants (H_2 and CO_2) is exactly the same, only the GHSV changes as a result of adding the (inert) N_2 carrier gas. As the GHSV roughly increases by 80%, the sorption enhanced mode shrinks by about 50%, and the characteristic plateau from Fig. 6a. This fully makes sense, since this parameter is directly linked to the sorption enhanced methanation kinetics, as mentioned above. Engineering can solve this issue, e.g. by adjusting the reactor design to the cement gas composition and flow. Similar experiments performed with small amounts of oxygen did not show significant differences, pointing out the possibility of a process tolerant to small quantities of oxygen.







Fig. 7: Evolution of the outlet gas composition (a) and spot temperature measurements (b) of a sorption enhanced methanation catalyst bed (plate aluminum reactor, 1.5 L inner volume, pelletized specimens) exposed to an inlet gas stream of composition 30 mol.% CO_2 and 70 mol.% Ar (with additional stoichiometric H_2) at 300°C.

After this preliminary study, the system was scaled up by using a plate reactor of 1.5 L inner volume containing 1.1 kg of pelletized catalyst exposed to a total reactant flow of 1.3 L/min. This demonstrator setup is optimised for the sorption enhanced process: here, the sorption enhanced phase lasts for more than one hour, with a simulated cement plant gas of 30 mol.% CO_2 and 70 mol.% Ar (Fig. 7a). This result is very encouraging with respect to potential applications because it shows that the performance of the sorption enhanced methanation process can be fully maintained despite the presence of an important concentration of inert gas, as it is the case in cement plants. The temperature data in Fig. 7b shows the characteristic propagation of a heat front through the reactor as the catalyst adsorbs water from the Sabatier reaction (see [1] for more details). As conclusion from these experiments it can be confirmed that the proposed sorption catalyst is able to convert the typical 30 mol.% of CO_2 in cement exhaust gas fully to CH_4 without prior CO_2 separation. This cannot be established by conventional catalyst.

3.4 SO₂ poisoning of a sorption enhanced methanation catalyst

Using the same experimental tools as for the study of the influence of O_2 on the activity of the sorption enhanced methanation catalysts, experiments were conducted in order to evaluate the catalyst resistance to poisoning. More specifically, efforts were directed towards SO_2 , a molecule that is typically found in cement plant gases. SO_2 is a well-known poison for





methanation catalysts [5], more generally Ni-based catalyst as the sorption enhanced methanation catalyst considered here. Moreover, it has to be mentioned, that there is no sulfur resistant Ni catalyst on the market, showing that this is a general and the most challenging task, which cannot be solved within such a short project time and focus as here. This is why the authors focus on showing the influence of SO₂ on this novel catalytic system.

Fig. 8 shows a typical poisoning experiment, where the catalyst is first exposed to a H_2/CO_2 mixture without SO₂, then poisoned with – in a catalytic sense – very high concentration of about 100 ppm SO₂ for 1 hour 30 min with an attempt of regeneration at the operation temperature in an oxidising environment.



Fig. 8: In-situ mass spectrometry measurement of the outlet gas composition of a sorption enhanced methanation catalyst bed (quartz tube reactor, 6 mm diameter) exposed at 300° C to an inlet gas stream of composition corresponding to the Sabatier stoichiometry, followed by 100 ppm of SO₂ and then oxidised at the same temperature.



Fig. 9: Relative intensity, as measured by mass spectrometry, of the recovered catalyst specimens with respect to the activity after poisoning as a function of the recovery temperature and poisoning pressure.

Obviously, it is not possible to regenerate this catalyst at the operation temperature of 300° C due to kinetic reasons. Different poisoning at lower levels (5 and 10 ppm SO₂) and regeneration (up to 575°C) parameters were considered, with more success, as can be seen in Fig. 9. An Final report – Project CEMCOO 10





intensity ratio of 1 means that catalyst regeneration was unsuccessful, as this is the case for the catalysts regenerated up to 500°C. But the catalysts regenerated at 575°C were more than recovered, since they show a higher activity than before poisoning. This is not really surprising since after oxidation, the system is slowly cooled down in a reducing atmosphere and since 575°C is above the catalyst initial reduction temperature (400°C). Nevertheless, this result is very encouraging in view of potential applications. One can also see the effect of the poisoning pressure on the extent of recovery. The "zone of interest" shown in Fig. 9 is the temperature region where full catalyst recovery is expected.

3.5 Methanation of cement plant gases

The final part of this project consists in the on-site collection of gases from cement plants of the industrial partners, followed by methanation experiments in the laboratory. A custom portable pumping station was designed for this purpose from Prematic (Switzerland). Special attention was paid to properties of the cement gases that are potentially harmful to such a system, e.g. moisture and temperature.



Fig. 10: Evolution of the outlet gas composition (a) and spot temperature measurements (b) of a sorption enhanced methanation catalyst bed (plate aluminum reactor, 1.5 L inner volume, pelletized specimens) exposed to cement gas (collected at Holcim Untervaz on 12.06.2019 at 3 pm; plus additional stoichiometric H_2 for reactions (1) and (2)) at 300°C. The constant N_2 signal was removed in order to only focus on reactive species.





The question of the spot for gas specimen collection was discussed with the industrial partners (including Prematic). The most problematic parameter for the integrity of the pumping station turned out to be the gas temperature, leading to the choice of the coldest spot available, i.e. about 90°C to 100°C at the chimney. On-site specimen gas collection was successfully carried out, as well as their transfer and experimentation in the laboratory.

Fig. 10 shows a sorption enhanced methanation experiment similar to the one described in Fig. 7 and related discussion. The important difference is of course the CO₂ source, this time exhaust cement gas from Holcim. This specimen contains about 71.8 mol.% N₂, 21 mol.% CO₂ and 7.2 mol.% O₂ (the other species are orders of magnitude below 1 mol.%). With the same total gas flow of 1.3 L/min as used in Fig. 7, one obtains a much longer sorption enhanced phase of about 200 min. Two reasons are behind this difference, and must be separately discussed.

First, the CO₂ concentrations are not identical to the prior lab experiments. The experiment from Fig. 7 in the laboratory was conducted with a "simulated" CO₂ concentration of 30 mol.% to cover all operation conditions at different plant locations and to check the catalyst performance. Since the duration of the sorption enhanced mode is directly connected to the concentration of CO₂ (the amount of water formed in the catalyst bed is directly proportional to the latter [1]), a longer sorption enhanced phase is expected as the CO₂ concentration decreases. One would roughly expect a 50% increase of the sorption enhanced methanation time observed in Fig. 6 if the CO₂ concentration was decreased by one third from 30% to 20%, i.e. at least reaching 100 min.

Besides this effect, in the meantime the heat distribution into the reactor was optimised, i.e. the temperature in the first zone of the reactor was adapted with respect to the average 300°C inside the reactor. This prevents overheating of the reactor inlet in the first stages of sorption enhanced methanation and later on allows this zone cooling down faster and thereby increasing the zeolite water sorption capacity, as can be seen in Fig. 10b. Indeed, the temperature of 300°C at the end of the sorption enhanced phase, but on Fig. 10b, most of the reactor comes back to 300°C (channels 3-5) while the inlet (channels 1-2) falls under 300°C. This optimisation shows how versatile the technology is as it can be adapted to different concentrations of reactive gas flows.

No effect of poisoning from SO_2 could be seen on the catalyst performance despite being exposed more than 3 hours to the gas stream. The SO_2 concentration at the time when the gas specimen was collected was 9 ppm. The poisoning experiments (see previous section) showed that such a concentration should already affect the catalyst performance on this time scale. Surprisingly, this is not the case here. An important difference between these measurements is that the poisoning experiments were not conducted in sorption enhanced conditions. The sorption enhanced conditions imply a different chemical configuration of the catalyst surface, i.e. lower water partial pressure/coverage due to Le Châtelier's principle [1]. This could hinder SO_2 adsorption and/or sulphide formation. This is another encouraging sign of the catalyst performances, however, unravelling this mechanism is out of the scope of the present project. Moreover, it must be specified here that long-term poisoning studies are necessary in order to fully assess the catalyst resistance to poisoning.

Furthermore, no clear effect of oxygen on the sorption enhanced methanation process could be identified. An oxygen level of 7.2 mol% should, according to section 3.1, lead to significant decrease of the methane yield. Here again, it seems that sorption enhanced methanation is not affected in the same way. Not only the surface configuration of the catalyst is different, but also the process thermal balance strongly differs from classic catalysed methanation.





4. An economical evaluation on large scale methane production from cement industry originating CO₂

Considering the fact that the production of cement in Switzerland accounts around 2.5 million tonnes for CO_2 emissions of which corresponds to roughly 7 % of the country's total CO_2 emissions, the following economic approach examines how this amount could be put to meaningful use in order to create a new value-added chain through CO_2 methanation, and thus use the produced CH_4 as fuel and reduce the consumption and import of fossil fuels of the cement industry in Switzerland. With power-to-gas technology, this CO_2 , along with regenerative hydrogen from photovoltaics, can be converted into methane, which can then be fed into the existing natural-gas grid. This economic evaluation gives a cost prediction for conversion of all the CO_2 from the Swiss cement industry into methane by using the technologies available today in order to replacing fossil methane imports.

4.1 Introduction

4.1.1 Origins of CO2 sources in Switzerland

Fig. 11 gives an overview on the distribution of the various CO_2 emitters in Switzerland without grey emissions [6].



Fig. 11: Distribution and percentage shares of the CO₂ emitters in Switzerland in 2015 [6].

Whereas the emission of CO_2 is highly decentralised and irregular in the sectors of transport, households, services and agriculture, emissions in the sectors of industry and waste management occur in large quantities both centrally and continuously. Particularly in industrial processes where CO_2 emissions cannot currently be reduced through either substitution or renunciation, it would make sense to feed the emissions into power-to-gas and produce a re-usable waste product. It is focused here on the use of the value-free but progressively more expensive CO_2 for producing a renewable energy vector, i.e. methane (CH₄) by applying the well-known Sabatier reaction for a power-to-gas application [7] and substitute natural gas imports (c.f. chapter about technical considerations).

4.1.2 The cement industry and CO_2 emissions

In 2015, the industry sector emitted 7.5 million tonnes of carbon dioxide. After waste incineration the cement industry, with an output of 2.5 million tonnes CO_2 is the second largest





emitter in the industrial sector [8]. The waste gas with 20 - 35% CO₂ in variable N₂ to O₂ ratios, emitted by the cement industry is made up, firstly, of the CO₂ from the combustion process (38.5 %) and, secondly, from the CaCO₃ dissociation of the feedstock (61.5 %) [9]. However, using these 2.5 million tonnes of mainly unavoidable CO₂ would offer a possibility to replace large amounts of natural gas and reduce fossil imports with corresponding emissions.

In Switzerland there are six large-scale installations for the production of cement. Given its centralised structure and the continuous occurrence of CO_2 emissions, it is this industrial sector that is particularly appropriate for the downstream addition of power-to-gas plants for converting CO_2 to methane in large quantities. Secondly, the process intrinsic high calcination temperatures necessary for the CaCO₃ processing are an ideal source of heat for some novel methanation reactor concepts, such as the sorption enhanced methanation, which are not self-sustaining at about 300°C.

As remark: cement industry is conscious of the fact that it emits large amounts of CO_2 and has been following various strategies for many years to counter these emissions. Measures implemented up until 2010 resulted in a reduction from 3.85 to 2.9 million tonnes CO_2 a total cut of 25 % in emissions [8,10]. Since only limited possibilities for further process optimisations are still available and since no alternative building material is going to exist for the near future, it is going to be necessary to consider additional approaches to reducing the high levels of CO_2 emissions or to putting these to other uses. The here proposed reuse of the emitted CO_2 in terms of its conversion to CH_4 is one possible scenario to do so.

4.1.3 Power-to-gas and its role in CO₂ reduction

Power-to-gas technology offers the possibility of using technical or electro-chemical conversion processes by use of electricity from renewable sources to produce hydrogen (H₂), thereby turning the electric energy into a chemical energy carrier, such as H₂ or subsequently to methane (CH₄) that can be long-term stored for any period of time until it is needed again for use [11]. The production of pure hydrogen faces challenges in the domains of storage, transport and shortage of consumers. Given the characteristics of the equipment currently installed by the end consumers, it is neither possible nor legally permissible to add large amounts of hydrogen to the natural-gas supply (max. 2 vol % H₂), because a higher percentage of hydrogen in natural gas changes the gas feed, flame conditions and combustion properties, which strongly influences the operation of the end consumer devices.

In the case of the here presented power-to-gas model, the hydrogen produced is put to further use and reacted with carbon dioxide (CO₂) to form methane, which is simpler to handle and transport. This process, which is also known as CO₂ methanation, is already in use today in small to medium-sized installations [12]. Fig. 3 illustrates the process for the model subject to an economic investigation in this study. The only technologies included here, were technologies that are already technically mature today. This examination is focusing exclusively on power from PV, since further PV installations are feasible in Switzerland, while e.g. hydro and wind power has very limited potential to be further increased or installed. Furthermore, there are several alternative technologies which may taken into account. But for the sake of a definite energy value chain, it is not further spread to other technologies. One example of this is large-scale electrolysis, which uses an alkaline electrolysis (AEL), a technology which provides since decades sufficient lifetimes and large hydrogen production rates (90000 h with up to 750 m³/h) [13]. It might be based on polymer electrolyte membrane (PEM) technology in future at such large scales. However, it is believed that at an industrial scale, as it is evaluated here, PEM electrolysis is nowadays still not the most reliable path for such an industrial scale as it is focussed here [14]. Table 1 provides a brief comparison of AEL and PEM electrolysis with the main advantages and disadvantages.





Table 1: Comparison of AEL and PEM [12, 13, 15].

	AEL electrolyser	PEM electrolyser
Electrolyte	- liquid	- solid
	- electrolyte solution 20-40 % KOH	- highly porous polymer electrolyte (Nafion)
Materials	- steel (frame)	- Titanium (bipolar plates)
	- Nickel (catalyst)	- noble metals (platinum, ruthenium,
	- Asbestos, Titanium, Zirconium (separator)	iridium)
Advantages	- technology already proven on a large scale	- good part-load and overload capability
	- low production and investment costs	- fast response and reaction times
	- high long-term stability	- high current densities
		- compact design
Disadvantages	- optimization needs for dynamic operation	- membrane sensitivity and lifetime
	- alkaline purity and gas cleaning	- only smaller installations tested to date
	- corrosive liquid electrolyte	- high investment costs
		- noble metals indispensable
Investment Costs	500 – 1500 €/kW (as of 2014)	2000 – 6000 €/kW (as of 2014)

4.2 General technical considerations for the applied model

A possible and reliable way for the production of methane with commercially available technologies from CO₂ emissions of the cement industry is investigated here (Fig. 12) [16].



Fig.12: Illustration of the power-to-gas process for cement based CO₂ emissions [17].

In the scenario considered here, the electricity needed for operation of the alkaline electrolyser is generated by conventional photovoltaic (PV) modules, attached to potentially appropriate





roof surfaces (about 140 km² in Switzerland) or on suitable facades (50 km²) [18, 19]. The technology used for electrochemical water splitting is the above-mentioned alkaline electrolysis with the following reactions and characteristics [12]:

Cathode reaction:	$4\mathrm{H}_2\mathrm{O} + 4\mathrm{e}^- \rightarrow 2\mathrm{H}_2 + 4\mathrm{OH}^-$		(4)
Anode reaction:	$40 \text{H}^- \rightarrow 0_2 + 2 \text{H}_2 0 + 4 \text{e}^-$		(5)
Total:	$2\mathrm{H}_2\mathrm{O}(\mathrm{l}) \rightarrow 2\mathrm{H}_2(\mathrm{g}) + \mathrm{O}_2(\mathrm{g})$	with $\Delta H_R = +571.7 \text{ kJ}$	(6)

Once the hydrogen has been produced, it can be converted into methane by reacting it with CO_2 in a catalytic fixed-bed reactor at atmospheric pressure according to the Sabatier reaction in Reaction (2). Atmospheric pressure is assumed here from the authors, since recent developments in catalysis showed methane yields up to 100 % already at atmospheric pressure for the so-called sorption enhanced methanation [4]. By this, the compression energy is also significantly lower since only methane must be compressed to natural gas grid pressure instead of CO_2 and H_2 , which needs 5 times more compression energy and a H_2 suitable technology. The reaction of CO_2 and H_2 to form methane via the Sabatier reaction runs at temperatures of between 200 and 700°C and pressures from atmosphere up to 80 bar depending on the type of reactor and catalyst [20, 21].

Although the correlated project with CemSuisse is focussing on a CO₂ methantion without prior CO₂ separation, we considered the supply of CO₂ from a separation process from the cement exhaust waste gases. In this case, we have a worst-case scenario in terms of separation costs. Additionally, since each cement plant provides different O₂ levels, and the project was evaluating the drawback of O₂ on the CO₂ conversion, it was calculate and implement varying O₂ levels. Therefore, while CO₂ concentration in the exhaust is between 20 and 35 % [17], typical separation costs arise of about 35 CHF/t CO₂ [22]. Methane, produced from this purified CO₂, has a composition corresponding to natural methane and can be directly used or even stored in the gas grid and retrieved as needed. This is also valid for the sorption enhanced methanation without prior CO₂ separation, since the O₂ is preferably converted with H₂ to H₂O. It is worth to note, that Switzerland's gas grid is fundamentally designed to rather distribute natural gas than to store it in large quantities. In normal circumstances, a maximum of 2.7 million m³ can be accommodated in various storage devices.

It is further recommended that the hydrogen production and methanation plant itself be installed in the immediate vicinity of the CO_2 emitters in order to minimise the problems and costs associated with the transport of hydrogen and CO_2 . Although, the particle emission and dust from such a cement plant may reduce the efficiency of the installed PV. The entire design of the plant later on and the calculation of the costs associated with it are based on the fact that photovoltaic generation of electricity in Switzerland is only available for approximately 1200 hours per year [23, 24]. That means that the plant must be operated in standby mode for the rest of the 7560 hours. It is to mention here, that a plant in existence today has not been designed for on/off operation. Operating at full load for only 1200 hours a year, which is assumed for the purpose of this study, might have negative effects on the degree of efficiency, gas quality, gas production and service life of the plant.

4.2.1 Energy losses and efficiencies

Each energy conversion step represents a technical process that is subject to a loss of efficiency. Table 2 shows the bandwidth between the best and worst case for the entire facility, both with and without the photovoltaics. The technologies available today result, in





dependency of the applied process chain, in an overall efficiency of between 41 and 65 % as worst case and best case scenario [25, 26].

Table 2: Typical efficiency values and chain efficiency of the overall power-to-gas processes by provision of solar electricity according to [25, 26].

Infrastructure	System efficiency in %
Power grid	95 - 100
Alkaline Electrolysis	64 - 80
Catalytic Methanation	80 - 85
Compression	85 - 95
Overall Process Chain	41 - 65

It might be possible to achieve further optimisation of overall efficiency by using energy and mass flows between the individual process steps, for instance by using the waste heat from methanation for electrolysis via solid oxide electrolysis and the provision of water vapour at 800 °C. However, such technologies are not mature nowadays. The interested reader may get further details from current research projects such as the Swiss "High Efficiency Power-to-Gas Plant" and EU project "Pentagon" [27, 28], integrating high temperature solid oxide electrolyser cells (SOEC) into a demonstration plant.

4.2.2 Mass flow consideration

To calculate the annual masses of the reactants of CO₂ (M_{CO2} = 44.01 g/mol), H₂ (M_{H2} = 2.02 g/mol) as well as of the products CH_4 (M_{CH4} = 16.05 g/mol) and H_2O (MH_{H2O} = 18.02 g/mol) [29], one can simply scale up the stoichiometric reaction from Reactions (2, 4-6) to the addressed 2.5 million tonnes of CO₂ from cement industry. The resulting mass flows in terms of per reaction and per cement plant and year are shown in Table 3. The methanation of these annual 2.5 million tonnes CO₂ from the year 2015 requires 0.46 million tonnes of H₂ (5.08 billion m³/a), which have to be produced through electrolysis. The reaction products are 0.9 million tonnes (1.26 billion m^3/a) of CH₄ and 2.04 million tonnes of H₂O. This amount of methane produced would correspond to roughly 33 % of the annual consumption of natural gas in Switzerland, which is as high as 119420 TJ (3.821 billion m³/a) [30, 31]. In comparison to that, in 2015 Germany produced 3.8 million m³/a of CH₄ by chemical methanation [12].

Table 3: Overview of mass flows in methanation reaction on a molar and industry level.

	Input			Output	
	CO ₂	H ₂		H₂O	CH₄
stoichiometry	1	4	-	2	1
molar weight (g/mol)	44.01	2.02		18.02	16.05
industry level (million tonnes)	2.5	0.46		2.04	0.9

For the needed 0.46 million tonnes of H₂, the electrolyser consumes 4.1 million tonnes of fresh and deionized water and produces another 3.6 million tonnes of oxygen (O₂) according to Reaction (6) and Table 4. Further use and economic aspects of the oxygen as well as a possible water circulation from the methanation to the electrolyser to compensate the water consumption were not considered in this study. If a suitable consumer for the oxygen would be available, e.g. oxyfuel combustion process or ozon-based purification of waste water in sewage-treatment facilities, it might have a further positive impact on the economic perspective. Especially if the necessary combustion heat for the cement plant is provided by Final report – Project CEMCOO 17





an oxyfuel process and air is avoided as oxygen source, massive energy could be saved from the avoidance of heating up air-based N_2 . Additionally, the oxygen level in the exhaust gas can be lowered which is again reducing the H_2 needs.

	Input		Output	
	H₂O		H ₂	O 2
stoichiometry	2	-	2	1
molar weight (g/mol)	36.04		2.02	32
industry level (million tonnes)	4.1	_	0.46	3.6

Table 4: Overview of mass flows in electrolysis on a molar level and industry level for 2.5 million tonnes of CO₂.

4.2.3 Energetic consideration for H_2 production by alkaline electrolysis and its conversion to CH_4

The reaction in the electrolyser requires a great deal of energy to split water into H₂ and O₂. The specific energy consumption of an alkaline electrolyser is given as 4.2 kWh/m³ and 4.7 kWh/m³ of H₂ including the power electronics, respectively [32]. For the production of a total mass of 0.46 million tonnes of H₂, corresponding to 5.1 billion m³ (ρ_{H2} = 0.0899 kg/m³), the necessary annual energy input is 23900 GWh. Expressed in terms of the lower heating value (LHV) or net calorific value (NCV) of H₂ (H_i = 3.00 kWh/m³), the output amounts to 15255 GWh, with an average electrolyser efficiency of about 64 %.

The subsequent conversion of this H_2 with CO_2 is assumed to take place at ambient pressure and 300°C, since these conditions are technically feasible to reach 100 % CO_2 conversion with state-of-the-art for common nickel catalysts [4]. The authors furthermore assumed for this case study that compression of one unit of CH_4 is more efficient and more economic than compressing 5 units of reactant gasses under stoichiometric conditions, i.e. 4 units H_2 and one unit of CO_2 and therefore, compression on gas grid conditions takes place after methanation. Despite that, an additional electrical energy of 0.4 kWh per m³ synthetic natural gas [12] is calculated to heat the CO_2 and H_2 mixture (1:4) up to 300°C for the catalytic reaction. In best case, this energy can be saved, if exhaust heat from the cement kiln can be recuperated and used for this heating purpose.

4.3 Costs estimation for the power-to-gas model

As a general remark prior to the detailed cost analyses, is has to be mentioned that the cost calculation is based on the net present value method [33]. The interest rate was set at 3.5 % and the investment period has been fixed at 30 years.

4.3.1 Photovoltaics

According to the considerations made in 2.3 the annual energy needed for producing hydrogen via PV amounts to 24403 GWh/a, from which 23900 GWh are for electrolysis to receive H₂ and 503 GWh for the conversion to CH₄. Losses of about 5 % occur in the inverter system, therefore, the system must be designed for 25095 GWh/a. The following calculations that are summarized in Table 5, assume a PV module efficiency of 16 %, but a loss of about 20 % of the output in the course of a service life of 30 years has to be considered [34]. For this reason, the plant was oversized by a further 10 % to balance these losses off, and finally the whole system needs to be dimensioned for 27604 GWh/a. With an operation of 1200 full load hours





per year a necessary system performance of 23 GW results. While the peak output per unit area of present-day modules is about 0.23 kW/m² [34] an overall surface area of 100 km² is required for the installation of these modules. One should know, that the roof area that can sensibly used for photovoltaics in Switzerland is indicated as 100 to 150 km² [18].

To calculate the investment costs, the first step is to estimate 1000 CHF/kW of installed capacity [35, 36]. Considering the quantity of the installations involved and the resulting effective economies of scale, a 10 % reduction is a commonly applicable reduction for the investment costs [32]. The investment costs or capital expenditures (CapEx) for all the photovoltaic installations therefore amount to 20703 million CHF.

The operating costs or operating expenditures (OpEx) consist of the cost depreciation and interest (697 million CHF/a), replacing the inverters twice during the total running time (428 million CHF/a), the roof rent (286 million CHF/a), as well as other costs such as administration, insurance, repair, cleaning and control (571 million CHF/a) [37]. Together, OpEx costs are 1982 million CHF/a and for an annual production of 25095 GWh/a mean operating costs are assumed to 0.09 CHF per kWh (c.f. Table 5).

Table 5: Breakdown of the costs for the photovoltaic plant for a total installed plant power of 23 GW.

CapEx (Capital expenditures)	
investment costs	23003 million CHF
10 % saving through quantity of installation	- 2300 million CHF
investment costs	20703 million CHF
investment costs/power	900 CHF/kW

OpEx (Operational expenses)	
depreciation and interest	697 million CHF/a
replace inverter (1.5 Rp/kWh)	428 million CHF/a
roof rental (1 Rp/kWh)	286 million CHF/a
administration, insurance, repair (2 Rp/kWh)	571 million CHF/a
total	1982 million CHF/a
costs/energy consumption	0.09 CHF/kWh

4.3.2 Alkaline electrolysis (AEL)

The economic appraisal for the AEL design is based on data of the German Aerospace Center (DLR) in its study into planning a demonstration plant for the production of hydrogen [32]. The DLR study is evaluating plants designed for two different sizes, 5 MW and 100 MW, respectively. The cost estimation presented in this study is based on the data for a 100 MW plant, with an amortisation time of 30 years. With a hydrogen production rate of 20000 m³/h, which is typical for plant of this size and with the plant operating time of 1200 h/a, the annual H₂ production rate is 24 million m³. For production of the annual amount of 5.1 billion m³ of hydrogen calculated above, 212 installations like this are needed to reach a power of 21188 MW. The DLR report indicates the investment costs for a 100 MW plant as being 52.1 million EUR or 56.5 million CHF (exchange rate used for the calculation: 1 EUR = 1.084 CHF from





May 2017). The total investment sum for all 212 plants is 14968 million CHF. Under consideration of a 10 % cost reduction attributable to economies of scale, the necessary investments for the alkaline electrolysers are 13471 million CHF. With an overall system output of 21188 MW, the result is 636 CHF/kW. In Addition to the costs for depreciation and interests (454 million CHF/a) another 7 % of the investment costs are estimated for the OpEx costs. The major part of these costs is the exchange of components in the electrolyser at an interval of 8 years. In addition, there are costs for cleaning, evaluation and administration, summing up to 943 million CHF/a. The mean operating costs are assumed to 1397 million CHF/a or 0.11 CHF per kWh (listed in Table 6).

Table 6: Breakdown of the costs for AEL for total plant power of 21188 MW.

CapEx (Capital expenditures)	
investment costs for plant	14968 million CHF
10 % saving through quantity of installation	- 1497 million CHF
investment costs	13471 million CHF
investment costs/power	636 CHF/kW

OpEx (Operational expenses)	
depreciation and interest	454 million CHF/a
materials, repairs, personnel, etc. (7 % CapEx)	957 million CHF/a
total	1397 million CHF/a
costs/energy consumed	0.11 CHF/kWh

4.3.3 Methanation

The cost estimation of the methanation process is based on today's plants with a power consumption of up to 5 MW. These plants are generally composed of electrolysers and methanation collectors. Based on this configuration, the cost of the methanation part is estimated to be between 208 and 440 CHF per kW [12]. Given the expected scale effects due to the enormous project size, the most optimistic value of 208 CHF per kW is used for further calculations and the resulting investment is 4405 million CHF.

The costs for depreciation and interests are 148 million CHF/a. Due to a lack of experience, especially over long periods of time, there is currently little usable data available. However, various plant builders estimate a range of 1 - 3 % of investment costs. A safety margin of 5 % is additionally used and sum up to a total of 220 million CHF, required for the operation of the plants. These costs include the replacement of the catalysts, the cooling media and the handling of the necessary water. Another 88 million CHF/a are included the separation of CO_2 from the exhaust gases of the cement industry (32.6 \in /t CO₂; [21, 38]). In summary, operating costs for the methanation plant add up to a total of 457 million CHF/a or CHF 0.04/kWh (Table 7).





Table 7: The costs of methanation at an installed capacity of 419 MW.

CapEx (Capital expenditures)	
investment costs	4405 million CHF
investment costs/power	208 CHF/kW
OpEx (Operational expenses)	
depreciation and interest	148 million CHF/a
material, repairs, personnel, etc. (5 % CapEx)	220 million CHF/a
CO ₂ separation	88 million CHF/a
total	457 million CHF/a
costs/energy consumed	0.04 CHF/kWh

Is has to be mentioned explicitly that neither the waste heat of the methanation process at 300° C affects the cost estimation, since the methanation is expected to be heated from the exhaust heat of a cement kiln. Nor is the water produced catalytically during the methanation processes taken into account. In the best case, this relatively pure water can be recirculated to the electrolysis and used a water source. From an engineering point of view, a heat and mass flow exchange between two complex systems increases the system complexity even more. Therefore, the extent to which heat and water can be used as input into the electrolysis and how great the resulting benefit is, need to be clarified elsewhere. Decoupling the methanation processes from the electrolysis through the possible interim storage of the H₂ may be a possible solution for better use of the electricity and for coping with the problems of modulating operation, but this additional infrastructure could not be addressed by this activity.

4.4 Overall Costs

Everything considered, the investment volume required for the power-to-gas process in terms of an annual 2.5 million tonnes of CO_2 conversion to methane amounts to CHF 38579 million CHF. The annual operating costs are highest at 1982 million CHF for photovoltaics. Next come the operating costs for alkaline electrolysis at 1397 million CHF, while methanation accounts for a further 457 million CHF per annum, including 88 million CHF/a for CO_2 separation from the cement kiln exhaust gas. Additional annual operating costs for the whole plant have to be considered and amount to a total of 3836 million CHF per annum. Overall economic calculations for the individual processes are comprised in Table 8.





Table 8: Costs of the power-to-gas concept for the twofold use of CO2 from Swiss cement works, process chain: photovoltaics, alkaline electrolysis and methanation.

	photovoltaics	alkaline	methanation*	total
		electrolysis*		
CapEx in million CHF	20703	13471	4405	38579
CapEx/power in CHF/kW	900	636	208	
OpEx in million CHF/a	1982	1397	457	3836
OpEx in CHF/kWh	0.09	0.11	0.04	0.24

*: Electric power costs for alkaline electrolysis and methanation have been included in the investment calculation for the photovoltaics and separation costs of CO_2 have been included in the methanation.

For an annual processing of 2.5 million tonnes of CO_2 from cement industry, the resulting costs per tonne of CO₂ are about 1500 CHF. 1.26 billion m³ of renewable methane are produced during the processing of the carbon dioxide. This results in methane costs of 3 CHF/m³ and 0.30 CHF/kWh, respectively. No costs were related to any transport or storage of hydrogen as well as the feed-in costs of methane into the natural gas network were not included in this calculation, since the project addresses a direct use of methane as fuel for the cement plant. The energy price published for natural gas in 2016 was 0.084 CHF/kWh. Without including the conversion factor and taking the net calorific value of methane of 9.97 kWh/m³, the costs are calculated to be 0.84 CHF/m³. Consuming 1.26 billion m³ of methane from the natural-gas grid therefore costs 1.059 billion CHF a year. Synthetically produced methane from the power-togas process thus costs 3.6 times more than fossil methane.

These costs do vary with the economic assumptions, especially on such as electricity prices or PV operation hours per year for the H₂ production. However, overall costs of 0.30 CHF per kWh for synthetic methane from cement-based CO₂ under the specific Swiss conditions, still is in the range of 0.07 to 0.42 CHF per kWh reported elsewhere [39-44]. These values strongly depend on the plant scale and technology maturity.

4.5 Conclusion

Within the current energy turnaround activities in Switzerland a huge momentum for a reduction of CO₂ emissions and replacement of fossil fuels is given, if locally available CO₂rich sources like the 2.5 million tonnes of CO₂ per year from the Swiss cement kiln plants are converted into even transportable and storable methane under the use of renewable H_2 . This study examined the costs of applying the current state-of-the-art technologies for a large-scale CO₂ methanation process. Since the CO₂ emissions from Swiss cement industry are emitted by only six large plants.

Using the technology chain of PV, alkaline electrolysis and catalytic methanation for the investigated CO₂ valorization path, it is possible to produce 0.9 million tonnes or 1.26 billion m^3 of synthetic CH₄ per year by applying the CO₂ from the exhaust gases of all cement plants. Not less than 32.9 % of the annually required 3.82 billion m³ of natural gas imports could be compensated by the produced CH₄, thus reducing the CO₂ emission from natural gas by the same amount of 32.9 %.

The investment costs of the whole power-to-methane infrastructure amount to a total of 38579 million CHF. This comprises installation costs of 20703 million CHF for electricity generation by photovoltaics, 13471 million CHF for alkaline electrolysis and another 4405 million CHF are required for the installation of the methanation plants itself. Final report – Project CEMCOO 22





Besides these installation costs annual running expenses have to be considered. Separation and conversion of the annually emitted 2.5 million tonnes of CO_2 to 0.9 million tonnes CH_4 are estimated at 3836 million CHF per annum. Without prior CO_2 separation, we have identified that approximately 4-5 % of H₂ can be "economically wasted" before safety issues become obvious and due to the fact that residual O_2 is not removed. This has to be considered for upcoming activities. The highest individual costs are 1982 million CHF per year for the production of the electricity by photovoltaics (51.7 %), followed by 1397 million CHF/a for alkaline electrolysis (36.4 %) and 457 million CHF/a for the methanation (11.9 %).

If it is considered, that only 61.5 % of the CO₂ emissions are of unavoidable geogenic origin, it becomes clear that the remaining 38.5 % CO₂ from fossil fuels can be completely replaced. In this case, all estimated values from PV plants size, over methanation installations to annual operation costs can be reduced by these 38.5%. However, the amount of hydrogen to be used is directly correlated to the installed PV power and related limitations. It is a social difficulty if all Swiss PV capacity is exclusively needed for hydrogen production to replace fossil imports. Here, other production ways, such as additional renewable power sources or at least foreign PV plants with higher operations hours, become necessary. Alternative production ways for renewable power is needed as long as energy consumption is that high in Switzerland. The economic appraisal shows that the costs estimation is about 1500 CHF per tonne of CO₂. Compared with that, a tonne of CO₂ is currently sold for only 26 CHF in international CO₂ trade (as per September 2019), but this value already increased by nearly 90% during the 12 months of this project.





5. Conclusions

As a conclusion to this report, the applicability of sorption enhanced methanation, as well as the perspectives of the current project, are highlighted here. From a purely technical point of view, starting with a simplified situation, it was demonstrated that a gas stream containing CO_2 only as a secondary compound, can nevertheless be directly used to convert all the CO_2 into methane. This is a novum in methanation technology.

But in practice, cement plant gases contain more compounds than simply ballast N₂. Namely, residual O₂ cannot be avoided in an operational cement plant. It was shown that the presence of oxygen leads to reaction with H₂ – favoured over methanation – to form water and release large amounts of energy that can perturb the process thermal balance. Additionally, every O_2 molecule present in the gas stream consumes two H_2 molecules. This significantly affects the economy of the technology, knowing that hydrogen is the most valuable chemical involved here. Depending on the H_2 concentration added to the gas stream, O_2 thresholds were defined, above which mainly the process safety and performance are critically affected, i.e. the maximum admissible O₂ concentration is 3 mol.% if H₂ is provided stoichiometrically to the Sabatier reaction, and goes up to 6 mol.% if H₂ is also provided for its reaction with O₂. The economic aspects are clear, since every O_2 reduces the economic benefit. Therefore, it must be an aim to reduce the residual O_2 level as much as technically feasible to maintain the cement quality. The presence of CO in any concentration is not a problem regarding sorption enhanced methanation, since CO is basically a secondary reactant towards methane whose conversion is even more straightforward than CO₂. Poisonous gases are also present in typical cement gases, the most problematic being SO₂. Experiments were conducted with SO₂ levels corresponding to the cement industry. It was shown that poisoned catalysts can be regenerated in oxidising environments at high temperature. Repeating the procedure regularly is a part of the solution to this problem, the other part being a thorough control of the SO_2 concentration an optional bypass of the methanation reactor during SO_2 peaks, where the poison concentration can be potentially lethal for the catalyst. Not included in this project are long-term studies, due to the rather short project time and influence on particulate matters from the production process.

On-site specimen collection from an industrial partner, followed by methanation experiments in the laboratory, was then carried out. The results show that CO_2 in cement gases can be converted to methane with a yield of 100% without prior CO_2 separation. Surprisingly, no significant effect of O_2 and SO_2 could be identified, suggesting that sorption enhanced methanation is more resistant to these species than classic catalysed methanation. Again, one should note here that these conclusions are only valid on a relatively small time scale of a few hours.

The economic evaluation showed that methanation of cement plant gases in Switzerland from Swiss resources remains expensive. Methanation itself is only about 10-12% of the overall costs. Neither price of the methanation reactors and catalysts, nor their performance - as shown in Section 3 - is the problem here. It comes down *in fine* to the hydrogen-related technologies, i.e. photovoltaics and electrolysis and the relatively low sun shine period of about 1200 h. Cooperation with other countries having access to more renewable energy sources seems a viable option. The market dynamics - price of CH₄, taxes on CO₂ - is a key parameter as well, as it continuously evolves in favour of power-to-gas.





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7. Financials

Remark:

From the financial data can be seen that overall costs are higher than the project budget. The amount over the guaranteed budget is covered by own contribution in terms of other party funding from ZHAW.

Function	Name	Hourly	Expenses / h			
			Project Year 1			
		CHF / h	Total	cemsuisse	3rd	ZHAW
ZHAW - IMPE						
Project Leader	Andre Heel	110	75	25	0	50
Scientist	Renaud Delmelle	74	850	600	0	250
Assistant	N.N.	63	0	0	0	0
			0	0	0	0
Total			925	625	0	300
Function	Name			Expense	s in CHF	
Function	Name			Expense Project	s in CHF Year 1	
Function	Name		Total	Expense Project cemsuisse	s in CHF Year 1 3rd	ZHAW
Function ZHAW - IMPE	Name		Total	Expense Project cemsuisse	s in CHF Year 1 3rd	ZHAW
Function ZHAW - IMPE Project Leader	Name Andre Heel		Total 8.250	Expense Project cemsuisse 2.750	s in CHF Year 1 3rd 0	ZHAW 5.500
Function ZHAW - IMPE Project Leader Scientist	Name Andre Heel Renaud Delmelle		Total 8.250 62.900	Expense Project cemsuisse 2.750 44.400	s in CHF Year 1 3rd 0 0	ZHAW 5.500 18.500
Function ZHAW - IMPE Project Leader Scientist Assistant	Name Andre Heel Renaud Delmelle N.N.		Total 8.250 62.900 0	Expense Project cemsuisse 2.750 44.400 0	es in CHF Year 1 3rd 0 0 0	ZHAW 5.500 18.500 0
Function ZHAW - IMPE Project Leader Scientist Assistant 0	Name Andre Heel Renaud Deimelle N.N. 0		Total 8.250 62.900 0 0	Expense Project cemsuisse 2.750 44.400 0 0	s in CHF Year 1 3rd 0 0 0 0	ZHAW 5.500 18.500 0 0

Personnel costs:

Individual costs by type:

Cemsuisse

ZHAW - IMPE

Cost type	Project Year 1	Total
Personnel costs	47.150	47.150
Subcontracts *	0	0
Investments	0	0
Consumables	3.750	3.750
Travel costs	400	400
Total	51.300	51.300





Financial overview and request:

Expenses

Zhaw - Impe	Project Year 1				ZHAW - Impe
	Cemsuisse	3rd	OC		Total
PhD student	0	0	0		0
Salaries other personnel	47.150	0	24.000		71.150
Investments	0	0	0		0
Materials, supplies, other costs	4.150	0	0		4.150
Total	51.300	0	24.000		75.300

Funding request and overall amount (in CHF)

Project CemCOO				
	Cemsuisse	3rd	00	Total
ZHAW - IMPE	51.300	0	24.000	75.300
-	0	0	0	0
Sum	51.300	0	24.000	75.300
Overall Request	48.000			