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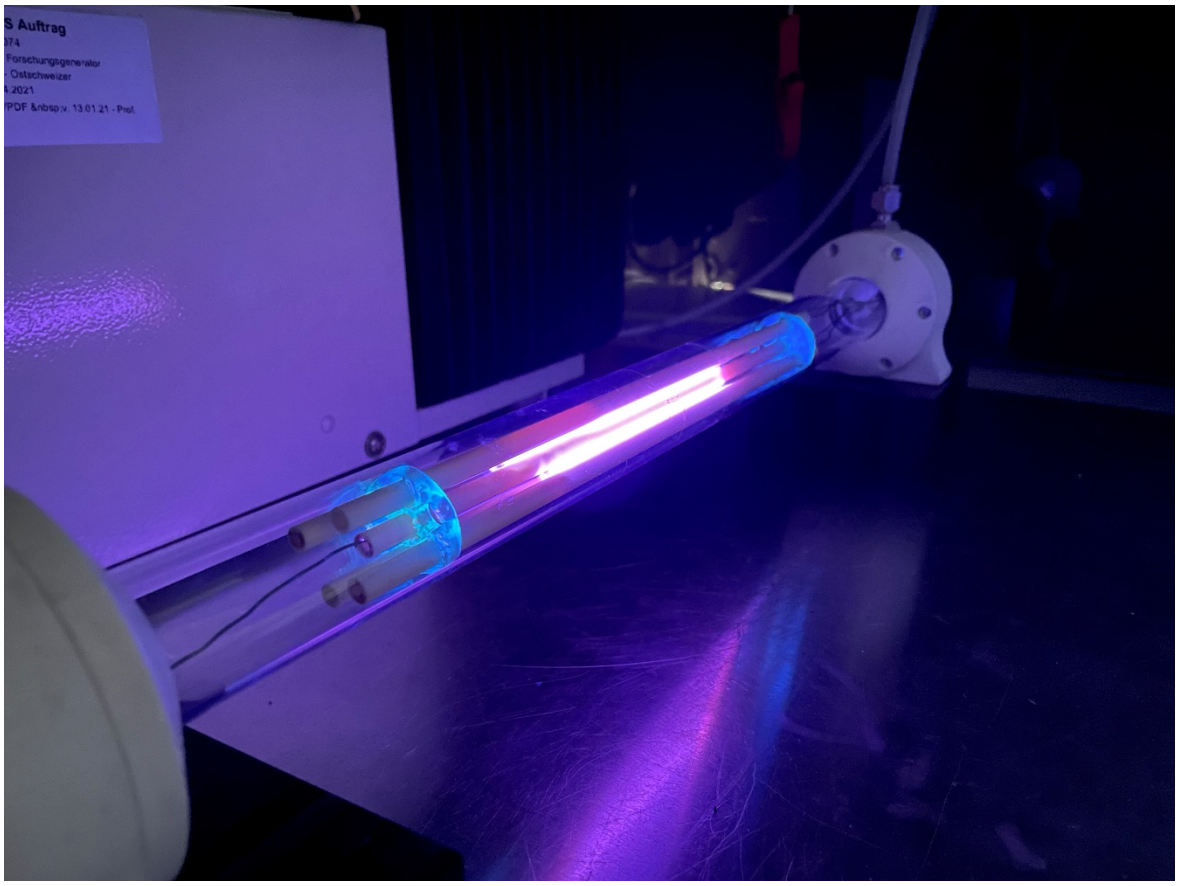
Final report dated 30 August 2022

COPlasma - Plasma assisted CO_2-Upcycling

Final Report



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Zusammenfassung

In dieser Machbarkeitsstudie wurde eine neue Technologie zur Erzeugung erneuerbarer Brennstoffe für ein Zementwerk entwickelt. Sie basiert auf einem plasmagestützten Upcycling von CO_2 und kann direkt auf einen CO_2-reichen Abgasstrom eines Zementwerks angewendet werden, um ein CO-reiches Brennstoffgemisch zu erzeugen. Die Reoxidation versorgt die Anlage mit der notwendigen thermischen Energie für den Kalzinierungsprozess und somit kann ein geschlossener Brennstoffkreislauf aus dem Abgas erzeugt werden. Im Rahmen des Projekts wurde ein völlig neuer Plasmaaufbau auf der Grundlage einer dielektrischen Barriereentladung (DBD) aufgebaut und betrieben. Die Entwicklungen umfassen die Konstruktion neuer Hardware wie mehrere Plasmareaktoren (Rohr- und Plattenreaktor) und eine LabVIEW-basierte Betriebssoftware. Darüber hinaus wurde eine erfolgreiche Industriekooperation mit Materiallieferanten und Plasmaanlagenherstellern aufgebaut, um die industrielle Implementierung zu gewährleisten. Das Ergebnis ist eine optimierte, voll funktionsfähige, hocheffiziente Plasmaeinheit, die auf einem skalierbaren Industriedesign für die spätere Industrialisierung basiert.

Im experimentellen Teil werden die höchsten CO_2-Umwandlungen (~20%) bei hoher Leistung oder geringen Durchflüssen erreicht und können durch Verdünnung des CO_2 (~25%) weiter gesteigert werden, was typischen Industrieabgaskonzentrationen entspricht. Die energieeffizienteste CO_2 Umwandlung erreicht man bei einer CO_2 Umwandlung von 10% mit einem Energieeintrag von nur 17 W. Dies wird durch die modernisierte und verbesserte industrielle Konfiguration erreicht. Zusätzlich wurde die Bildung unerwünschter Nebenprodukte per Massenspektrometer untersucht, wobei nur NOx in so vernachlässigbar geringen Mengen festgestellt werden konnte, dass diese keine umweltrechtliche Relevanz aufweisen. Der Einfluss von dielektrischen Materialien und Metallkatalysatoren auf die CO_2-Umwandlung wurde ebenfalls untersucht. Der Wechsel von einer Quarzbarriere zu einer Al_2O_3-Barriere führte beispielsweise zu einer Steigerung der CO_2-Umwandlung um mehr als 500%. Die größten Herausforderungen sind das Materialdesign und die anschließende Einführung der katalytischen Pulver in die Reaktionszone. Im Allgemeinen verbessert aber die Anwesenheit von Dielektrika und katalytisch-aktiven Metallen in der Plasmazone schon die CO_2-Umwandlung

Die Anwendbarkeit des Konzepts auf die Parameter eines Zementwerks wird positiv bewertet. Bei einem angenommenen Prozesswirkungsgrad von 62% (elektrische Leistung zu Reaktionsenthalpie) und einem derzeitigen Strompreis von 7 Rp/kWh (01/2022) beträgt der Beitrag der Stromkosten zum Preis der nutzbaren thermischen Energie ca. 114 CHF pro MWh Brennstoff. Aus unseren Ergebnissen lässt sich abschätzen, dass die am Anlagenstandort zurückgewonnene Elektrizität ausreicht, um 1.4% der benötigten Brennstoffmenge mit Hilfe des Plasmas bereitzustellen. Dies würde einer CO_2-Einsparung von 554 kg/h entsprechen. Eine vollständige Elektrifizierung der evaluierten Anlage zu 100% ist technisch machbar und könnte CO_2-Einsparungen von 40 t/h oder 350000 t/a erbringen.

Sintesi

In questo studio di fattibilità è stata sviluppata una nuova tecnologia di produzione di combustibile rinnovabile per un cementificio. Si basa sull' «upcycling» di CO_2 mediante plasma e può essere impiegata direttamente per produrre una miscela di combustibile ricca di CO da un flusso di gas di scarico ricco di CO_2 proveniente dal cementificio. La riossidazione fornisce all'impianto l'energia termica necessaria per il processo di calcinazione permettendo così di ottenere un ciclo chiuso di combustibili dai gas di scarico. Nell'ambito del progetto, è stata costruita e messa in funzione una configurazione di plasma completamente nuova, basata su una scarica a barriera dielettrica (DBD). Gli sviluppi includono la costruzione di nuovo hardware, come diversi reattori al plasma (a tubo e a piastra) e un software operativo basato su LabVIEW. Inoltre, è stata avviata una fruttuosa collaborazione con i fornitori di materiali e i produttori di impianti al plasma per garantire l'implementazione industriale. Il risultato è

un'unità al plasma ottimizzata, completamente funzionale e altamente efficiente, basata su un design scalabile per una successiva applicazione a livello industriale.

Nella parte sperimentale, le conversioni più elevate di CO_2 (~20%) si ottengono ad alta potenza o a bassi flussi e possono essere ulteriormente aumentate diluendo la CO_2 (~25%), che corrisponde alle concentrazioni tipiche dei gas di scarico industriali. La conversione di CO_2 più efficiente dal punto di vista energetico si ottiene con una conversione del 10% di CO_2 con un consumo energetico di soli 17W. Questo risultato è stato raggiunto attraverso una moderna e ottimizzata configurazione industriale. Inoltre, la formazione di prodotti secondari indesiderati è stata analizzata tramite spettrometro di massa, che ha permesso di rilevare solo NOx in quantità trascurabili, tali da non avere alcuna rilevanza per la legislazione ambientale vigente. È stata inoltre analizzata l'influenza dei materiali dielettrici e dei catalizzatori metallici sulla conversione della CO_2. Ad esempio, il passaggio da una barriera di quarzo a una barriera di Al_2O_3 ha portato a un aumento della conversione di CO_2 di oltre il 500%. Le sfide principali sono la progettazione del materiale e la successiva introduzione delle polveri catalitiche nella zona di reazione. In generale, tuttavia, la presenza di dielettrici e metalli cataliticamente attivi nella zona del plasma migliora già la conversione della CO_2.

L'applicabilità del concetto ai parametri operativi di un cementificio è valutata favorevolmente. Ipotizzando un'efficienza di processo del 62% (energia elettrica/entalpia di reazione) e un prezzo attuale dell'elettricità di 7 Rp/kWh (01/2022), il contributo dei costi dell'elettricità al prezzo dell'energia termica utilizzabile è di circa 114 CHF per MWh di combustibile. Dai nostri risultati, possiamo stimare che l'elettricità recuperata nel sito del cementificio con l'uso del plasma è sufficiente a fornire 1.4% della quantità di combustibile richiesta dall'impianto. Ciò corrisponde a un risparmio di CO_2 di 554 kg/h. Una completa elettrificazione del cementificio in esame è tecnicamente fattibile e permetterebbe un risparmio di CO_2 di 40 t/h o 350000 t/a.

Summary

In this feasibility study a new technology was successfully evaluated to generate renewable fuel for a cement plant. It is based on a plasma-assisted upcycling of CO_2 and can directly be applied to a CO2-rich exhaust gas stream of a cement plant to generate a CO-rich fuel mixture. Reoxidation of this fuel will supply the plant with the necessary heat energy for driving the calcination processes and can thereby generate a closed fuel cycle. Within the project a completely new plasma setup based on a dielectric barrier discharge (DBD) principle was established and operated. Developments include the design of new hardware such as several plasma reactors (tube, plate, etc.) and a LabVIEW based operating software (PlaTec) in addition. A successful industry cooperation was established with material and plasma plant suppliers. This resulted in an optimized, fully functional, high-efficiency plasma device that is based on an industrial design for the later scale up.

In the experimental part, the highest CO_2 conversions (~20%) are achieved at high power or low flows and can be further increased by diluting the CO_2 (~25%) as it is typical for industrial exhaust gas. The most energy-efficient CO_2 conversion is achieved at a CO_2 conversion of 10% with an energy input of only 17 W. In addition, the formation of undesirable by-products was investigated, whereby only NOx could be detected in such negligible quantities that they have no relevance to environmental legislation. Influences of dielectric materials and metal catalysts on CO_2 conversion was also investigated. The change from a quartz to an Al_2O_3 barrier resulted in an increase in conversion of >500%. Major challenges are the material design and the subsequent introduction of catalytic powders into the plasma zone but in general, the use of dielectrics and catalytic active metal nanoparticles in the plasma zone improves the CO_2 conversion.

The applicability of the concept is positively evaluated within the parameters of a cement plant. With an assumed process efficiency of 62% (power-to-reaction enthalpy) and an electricity price of 7 Rp per kWh, the contribution of electricity costs to the price of thermal energy is 114 CHF per MWh of fuel. From our results it can be estimated that recovered electricity at the plant site is sufficient to provide

1.4% of the required fuel quantity by means of the plasma. This would correspond to a CO_2 saving of 554 kg/h. Complete electrification is technically feasible and could deliver CO_2 savings of 40 t/h or 35000 t/a.

Main findings

- The COPlasma feasibility study demonstrated that with the developed cold atmospheric plasma technique a CO-based alternative fuel can be generated with an outstanding energy efficiency (power-to-reaction enthalpy) of 62%.
- The estimated expenditures for the required electricity amount to CO fuel costs of 114 CHF per MWh of fuel, assuming an electricity price of 7 Rp/kWh (as of project end 01/2022).
- With the same price assumptions, CO_2 reduction costs are about 200 CHF/tCO_2 in terms of electricity based OPEX costs.
- Our initial results show that the use of functional materials (dielectrics and catalysts) has a positive influence on CO_2 conversion. Thus, it is believed that the potential of the technology is far from being exhausted and further increases in efficiency and cost reduction can be expected from future developments.

Contents

Abbreviations

DBD	Dielectric Barrier Discharge
NTP	Non-Thermal Plasma
MS	Mass spectrometry
LST	Lanthanum Strontium Titanate
PZT	Lead Zirkonium Titanate (PbZr0.52Ti0.48O3)
PFN	Lead Iron Niobate (PbFe0.5NbO.5O3)
CCT	Calcium Copper Titanate (Ca0.25Cu0.75TiO3)
MgTiO3	Magnesium Titanate
CaTiO3	Calcium Titanate
BaTiO3	Barium Titanate
SrTiO3	Strontium Titanate
SrTiO3Ag	Silver doped Strontium Titanate
SrTiO3Cu	Copper doped Strontium Titanate

1 Introduction

1.1 Background information and current situation

Clinker production for the formulation of cement requires a tremendous amount of energy. According to the annual cemsuisse report (2019), the total energy consumption per ton clinker was 3.5 gigajoule in 2018. The essential step is the thermal transformation of $CaCO_3$ to CaO that requires high temperatures up to 1500°C. Predominantly, the six Swiss cement plants draw this energy by burning fossil fuels (oil, coal) or waste products (tires, plastics etc.) that also origin from fossil fuels. Therefore, the total emission of CO_2 results to 60% from unavoidable contributions from the chemical transformation of $CaCO_3$ (geogenic) as well as it results to 40% from the power generation via fossil fuels. Due to the development of new technologies on base of renewable energies during the past century, alternative solutions are nowadays available for fossil fuels. Such renewable energy carriers would have a significant impact by reducing the total fossil CO_2 emission by 40%. Furthermore, the emission of geogenic CO_2 into the atmosphere could also be reduced by a valorization into products such as fuels or liquids (Power-to-X). However, since the CO_2 concentration in the exhaust gas is only about 25%, mainly “useless” nitrogen (~69%) exists in the exhaust stream, and therefore huge separation plants are needed, what is very costly and economically unreliable up to date. The presence of nitrogen is referred to the usage of oxygen from air as oxidant during the clinker calcination process during heat generation. Additionally, 80% of environmental air is nitrogen, which is again counterproductive due to its additional heat consumption. Therefore, the upcycling of geogenic CO_2 in the exhaust to a “smart fuel”, potentially without any nitrogen, could change the energy and CO_2 balance and contribute to a reduction in emission.

1.2 Purpose of the project

A reasonable way to avoid additional emission of CO_2 is either to electrify the processes and supply the power by renewable and emission-free technologies such as solar, water or wind power, or to use hydrogen as fuel. The retrofitting of an existing cement plant into so-called oxyflame processes, which is operated on pure oxygen and renewable hydrogen from renewable electricity, is a big challenge and economically unattractive due to the necessary financial investments. Such an oxyflame-based retrofitting is economically and technically out of the scope and the integration even uncertain for new built cement plants.

Therefore, a radical new idea and an innovative "alternative fuel" is suggested: From several possibilities as alternative fuel, e.g. hydrogen, renewable methane or liquid fuels, CO seems to be the most suitable fuel candidate for the authors, according to equation 1:

$$CO + ½\ O_2 \rightleftharpoons CO_2 \qquad \Delta H_r = -283.0\ kJ/mol \qquad (Eq.1)$$

1) The caloric value of 12.6 MJ/m^3 (from -283.0 kJ/mol) is in the range of the currently used fossil fuel based gas mixture (6 MJ/m^3).
2) According to Eq. 1, CO can be generated by the dissociation of CO_2, available at the plant.
3) Combustion of the CO/O2 mixture does not require additional oxidants, since the exact stoichiometry is already given from the CO_2 dissociation. Addition of further oxygen and nitrogen via air (21%:79%) is minimised and additional energy savings are possible.
4) New exhaust composition from power generation would contain mainly CO_2, no further counterproductive N2.

This fuel is either generated with internally recuperated electricity (see section 2.4) or externally produced renewable electricity from water, sun and wind, which would represent a full electrification of a cement plant if the CO generated from the plant's exhaust were the only fuel used.

It is a "smart strategy" to reuse the emitted but unavoidable geogenic CO_2 from the raw materials and convert it into a CO/O2 mixture to subsequently apply this CO as "alternative fuel" by using the exothermic oxidation enthalpy of the reaction to replace a fraction of fossil fuels. The new approach is here: the dissociation of CO_2 will be realized by a so-called non-thermal and therefore cold plasma-assisted catalytic process at room temperature and atmospheric pressure.

1.3 Objectives

Dielectric Barrier Discharge (DBD) based non-thermal plasma is a suitable and promising technology, but still a relatively unknown technology in the community for environmental & energy applications as well as exhaust gas treatment. The only two well-known industrial applications are plasma-based ozonisation for disinfection and surface cleaning for electronic circuits (Kogelschatz et al. 1999, Hess et al. 2008). Nevertheless, the technology has the potential to replace conventional "hot catalysis" because a plasma can introduce the necessary vibrational energy into molecules via an electric high voltage power plasma and subsequent emitted electrons instead of activating molecules by heat. However, with the current but not well developed DBD plasma technique, offering 10% energy efficiency and 30% conversion, 238 MW electric energy (10 eV/molecule CO_2) has to be invested to reach the requested 70 MW thermal energy input which is too high for complete replacement of fossil fuels (Snoeckx et al. 2017). But, some very specialized plasma techniques operated at high vacuum and low flows, already reached conversions and efficiencies of 90% (Snoeckx et al. 2017), which demonstrates the huge potential of plasma technique.

Typically, physicists and electric engineers apply high voltage plasma technologies, but they are not very familiar with catalysis or chemical reactions and how to influence them. Current references in literature emphasize therefore rather physical plasma characteristics while catalytic materials or chemical aspects are mainly neglected. Here, UMTEC provides the necessary expertise from material science, chemical catalysis and analysis to bring it to a higher level and success, i.e. the **reuse and upcycling of CO_2 as precursor molecule for the application of CO as alternative fuel, to replace fossil ones**. Additionally, an associated high voltage and plasma laboratory is available at OST to deal with plasma technology.

In general, there is rather little DBD plasma literature available, but the given references show the huge potential, if materials science expertise is involved and finally implemented. From this, the authors will identify in this scientific pre-study the relations and interactions of

- plasma conditions (voltage, current and frequency) with
- processing parameters (gas flow and composition, its residence time and reactor geometry in terms of gap width) in combination with
- tailor-made materials/catalysts and microstructure of DBD materials (dielectric properties, antenna-like microstructures for DBD material

and how these influence

- CO_2-to-CO conversion efficiency and energy consumption
- recombination rate of dissociated molecules
- unwanted by-products such as O_3 or NOx

from realistic gas compositions of a cement plant.

Finally, it is the overall aim to estimate the potential for an upscaling and process implementation in a real cement plant on basis of the existing 1.6 MW recuperated electricity. Further on, to spread non-thermal plasma technology into the community and realize its application in environmental protection and energy technology or potentially replace them in the future by the gained knowledge.

2 Work packages, objectives and results

2.1 WP1: Non-thermal atmospheric plasma reactor with a modular, scaleable and upgradeable design

Objective

The objective of this work package is to build up and operate an industrial scalable Dielectric Barrier Discharge (DBD) based plasma reactor for CO_2 conversion at atmospheric pressure.

Results

Prior to the design of the reactors a suitable test infrastructure was set up (Figure 1). It is composed of four different modules 1) gas source and regulation 2) reactor 3) plasma generation & monitoring 4) gas analysis. Because of the need to ensure safety with regard to the high voltage (U>400 V) used, all parts that were under high voltage were housed in a custom-made safety cage. It has additional protection and safety mechanisms that only allow the plasma system to operate when the housing is closed. The housing and reactor exhaust are connected to the ventilation system to prevent the emission of potentially toxic gases (CO, O_3). All the experiments listed were carried out in dynamic operation, i.e. under flow conditions. For the gas supply, CO_2 (technical), N_2 (5.0), argon (5.0) and compressed air were fed on demand into the system by use of mass flow controllers (Bronkhorst; MFC). The flow range used is between 0.05 – 1 l/min. A research plasma generator from AFS (Horgau, Germany) with a maximum power of 500 W was used to operate the reactors. Its components are of industrial design and thus directly transferable to industrial plants; it generates a plasma according to the resonance principle. In the circuit diagram, the reactor is regarded as a capacitor which, together with an inductor, forms an oscillating circuit. This is fed by further resonant circuits. The advantages of this technology compared to conventional high-voltage transformers are the higher efficiency, the variability of the plasma ignition frequency and the high peak power that can be achieved. The research generator itself is externally controllable and can be operated in a continuous as well as in a pulsed mode. The option of external control allowed it to be integrated into our own custom-programmed, LabVIEW-based process software (PlaTec). The mass flow controller and the measurement analysis (mass spectrometer) were integrated into this software, what allowed a complete process automation. The contacting of the reactors was done via high-voltage cables. To prevent the formation of plasma on the outer electrode, it was insulated with capton adhesive tape. A calibrated mass spectrometer (Pfeiffer Omnistar) and a newly acquired gas chromatograph (Shimadzu GC-2030) were used to determine the composition of the treated gases.

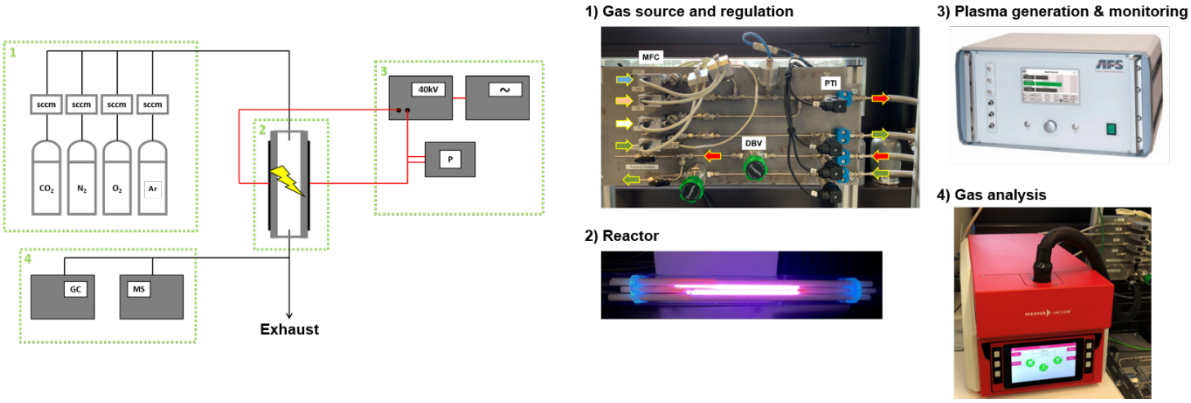

Figure 1: Illustration of plasma setup including micrographs of critical system parts.

With this equipment several DBD reactor geometry and concepts were evaluated. A custom-made tubular reactor (1) as well as a plate reactor (2) and a commercial exhaust gas treatment array (3). Following the technology of industrially established ozone generators (Kogelschatz et al. 1999), a tubular design was chosen for the CO_2 plasma reactor (Figure 2). The core of the reactor is made up of a cylindrical metal electrode (stainless steel) which is separated from the outer metal electrode (copper) by the discharge gap and a dielectric (Al_2O_3/Quartz). To prevent discharges at the outer electrode against air, it is insulated by capton adhesive tape. The size of the discharge gap (typically ≤3 mm) and the length of the discharge zone (10-20 cm) can be changed by varying the diameter of the inner electrode or the winding of the outer electrode. To fix the components and to ensure the necessary gas tightness, special gas distribution terminals were constructed. In order to allow highest design and operation flexibility, the reactor terminals were made from thermoplastic materials via a 3D printing technology at OST.

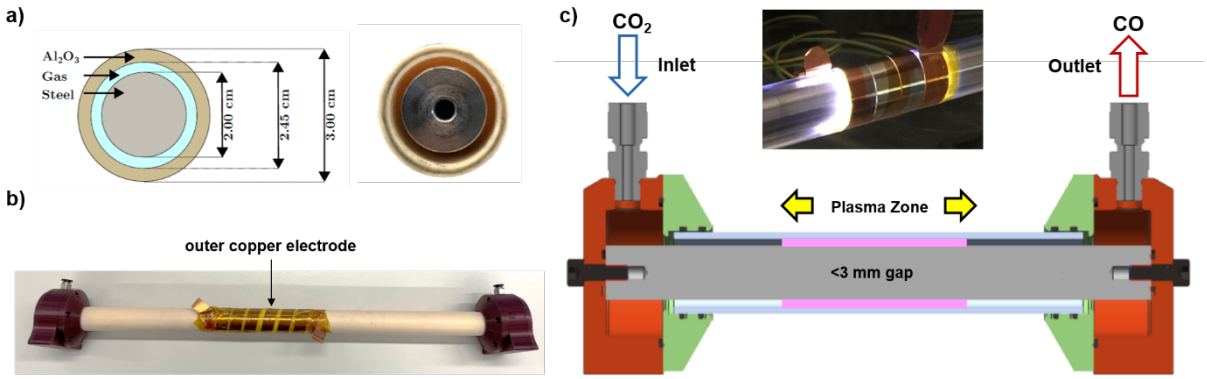

Figure 2: a) short-side crossection schematics and micrograph of the designed tubular DBD-Plasma reactor b) Micrograph the reactor with visible outer electrode c) long-side schematic crossectional view; the inset shows the system in operation with quartz as a barrier.

For a full electrical characterization of the system, current and voltage is recorded during operation at a resonance frequency of 37 kHz and a CO_2 flow of 500 ml/min (Figure 3). The course of the voltage (Figure 3a) is sinusoidal with a magnitude maximum ~6.6 kV. The course of the current (Figure 3b) is slightly shifted to the voltage and reaches a magnitude maximum of ~367 mA. The successful ignition of the plasma can be recognized by the noisy areas of the current curve (highlighted violet in the graph). Additional impedance measurements (not shown here) have shown that the capacity of the reactor is ~20 pF.

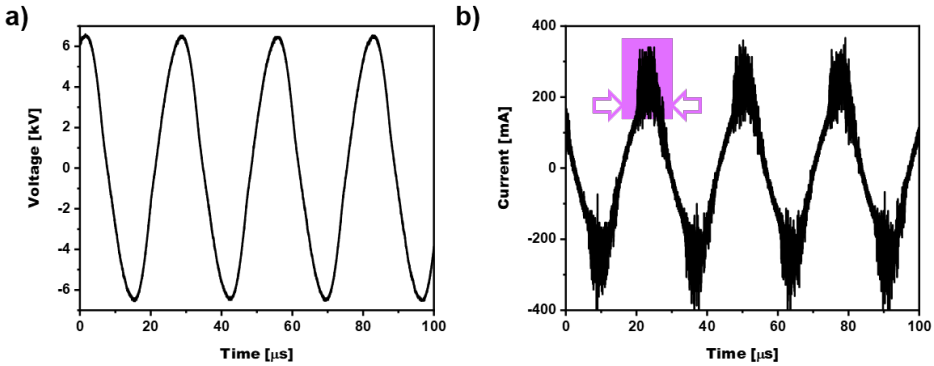

Figure 3: a) recorded sinusoidal voltage signal during operation of the tubular reactor b) corresponding current curve.

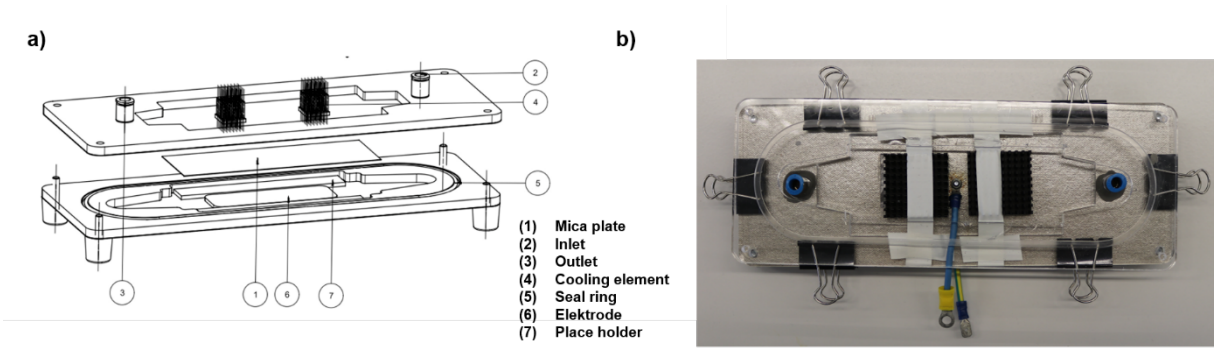

Figure 4: a) exploded view of the designed plate-reactor b) micrograph of the plate reactor.

A plate reactor is another tested design that has been developed (Figure 4) and was also built for scalability as well as high and easy sample throughput. In addition, the idea was to integrate a removable dielectric barrier. For the material tests, this could then be tested with different catalytic coatings, while a catalyst is complex to be integrated in a tubular design. Therefore, a sealed and stackable flat housing which is held together by clamps was manufactured. In order to avoid damage due to high temperatures, the hard plastic housing was laser-cut at the thermally stressed points and replaced by phlogopite plates, with a temperature stability up to 900°C. In addition, cooling fins were attached as heat sink to the back of the electrodes. The electrodes themselves are both located inside the reactor and are separated from each other by a removable dielectric barrier. This also consists of a phlogopite plate with a thickness of ~0.3 mm. The height of the discharge gap can be varied by using different thicknesses for the placeholders.

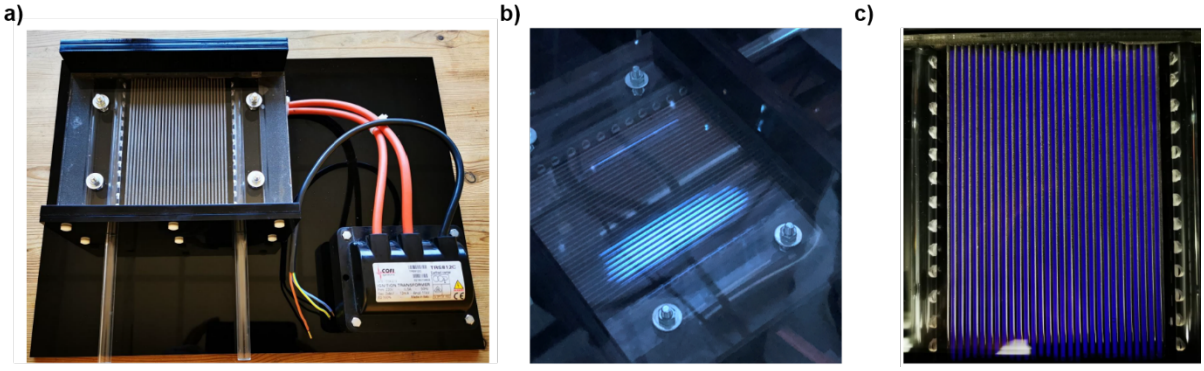

Figure 5: a) plasma module made by Oxytec b) in operation with CO_2 flow c) in operation with air flow.

The search for an industrial partner as manufacturer of plasma electrodes revealed Oxytec AG (Zürich) which produces modules as shown in Figure 5a. Actually, such modules are used for the purification of room air from pollutants, bacteria, and viruses, and so there is no experience regarding CO_2 dissociation. The module itself operates autonomous via its own power supply (~100 W, 4 kV). The module is not based on the principle of the resonance circuit, as described above. It must be mentioned that the first approach to generate a homogeneous CO_2 plasma failed (Figure 5b) and it is assumed that the power of the electronics is not sufficient. Coupling the module to the more powerful RF plasma generator available at UMTEC, led to a spark breakdown of the electrodes or more precisely the electrode dielectric material and destructed the device. This clearly shows: the common commercial systems are not able to be operated with an enriched CO_2 flow to synthesise a fuel from CO_2, as proposed in this project. From this result, the commercial setup technology (Figure 5c) was therefore further developed with the manufacturer for the dissociation of CO_2. For this purpose, the electrodes were converted into a ceramic design, having a higher dielectric number and are thus more resistant to higher power input. Finally, a coupling with the RF plasma generator was possible. Initial tests in air showed a homogeneous plasma formation behaviour at higher powers levels of P > 80 W and gave rise to a promising system design (Figure 6a). The newly designed electrode array was therefore enclosed gas-tight in a glass tube for further testing (Figure 6b). The reactor terminals were again produced using 3D printing technology.

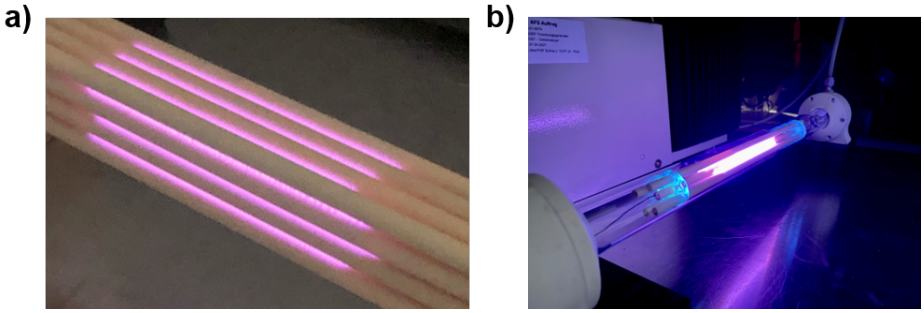

Figure 6: a) operation of an optimized electrode array in a ceramic design in air b) integration and operation of the module in a tubular housing.

2.2 WP2: CO_2 conversion efficiencies in non-thermal plasma

Objective

The dissociation of CO_2 into CO and O_2 in a DBD reactor is rarely reported in literature. Nevertheless, it was shown by some authors that the reaction is established in a non-thermal plasma setup, from which the CO_2 conversion (X_{CO2}) can be calculated as follows:

$$X_{CO2} = \frac{\Phi_{CO2,in} - \Phi_{CO2,out}}{\Phi_{CO2,in}} = \frac{\Phi_{CO,out} - \Phi_{CO,in}}{\Phi_{CO2,in}} = X_{CO}$$

Where $\Phi_{CO2,in}$, $\Phi_{CO2,out}$, $\Phi_{CO,int}$, $\Phi_{CO,out}$ are the inlet and outlet molar flows of CO_2 and CO, respectively Since $X_{CO2} = X_{CO}$ according to Eq. 1, the selectivity of the reaction towards CO is 100%. By knowing this equation and that the influence of diluting gases such as Argon or N2 has been investigated (Paulussen et al. 2010, Snoeckx et al. 2016), CO_2 conversions of about 10 - 20% were reported for DBD plasma (Snoeckx et al. 2017, Niu et al. 2019). However, for the implementation of the technology into an industrial plant the overall efficiency of the process must be further increased. Consequently, this WP aims for the optimization of the setup parameters for maximum CO_2 conversion rate by minimum energy input, but processing parameters also need to be adjusted to the gas composition of a cement plant exhaust gas.

Results

In addition to the tubular reactor described above (Figure 2), a smaller reactor with lower gas residence time was constructed. Initial experimental data on power, flow and frequency dependencies were carried out in this reactor whereas catalytic tests of materials were carried out in the larger reactor. Figure 7a shows a typical data set of a plasma-assisted CO_2 dissociation in the reactor.

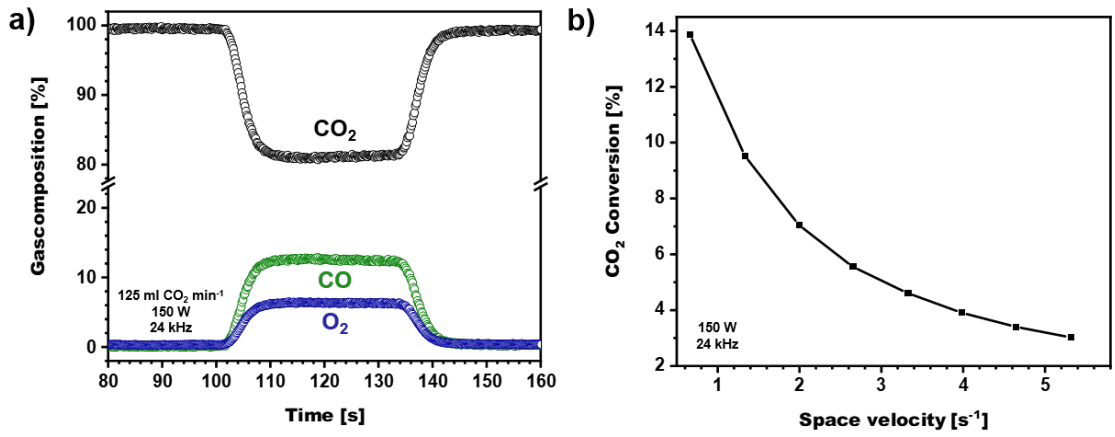

Figure 7: a) Gas concentrations monitored via MS during a typical plasma treatment of a 100% CO_2 flow (125 ml/min) in a tubular reactor. b) CO_2 conversion in dependence of the gas space velocity.

In the experiments of Figure 7, pure CO_2 was passed through the reactor at a flow rate of 125 ml/min. The plasma was ignited for a time period of 30 s with a power of 150 W at 24 kHz. As soon as the generator is switched on, the proportion of CO_2 in the total flow drops to 80.5%. At the same time, the two new products O_2 and CO are formed according to Eq. 1. After saturation their concentration is 13%

CO and 6.5% O2. With this the CO_2 conversion can be determined as 13.9%. The slope impressively shows the short reaction times to switching on and off.

The residence time of the molecules in a reaction zone is an important parameter in catalysis. It was therefore investigated how the flow rates of CO_2 affect its conversion in the plasma. For the experiment, the flow rate was varied between 125 ml/min up to 1 l/min, but expressed in space velocities for the independence of the results from the reactor geometry. The small reactor has a gap width of 2 mm, the plasma is ignited over a length of 50 mm and the distance from the inner to the outer electrode is 4.5 mm. Consequently, the plasma-filled volume is 3.14×10^3 mm^3. As an example: the reactor volume is exchanged 2.65 times per second at a flow rate of 500 ml min^{-1}. As can be seen (Figure 7b), the CO_2 conversion increases with decreasing space velocity. In the investigated flow range the highest CO_2 conversion is 13.9% at a space velocity of 0.66 1/s. With increasing GHSV (gas hourly space velocities), this results in a minimum value of 2.95% at 5.3 1/s. Since the slope is not linear, but rather exponential, it is assumed that with decreasing space velocities and higher residence times, the probability increases that a CO_2 molecule is split in the plasma. Consequently, the conversion is highest at low flows.

To evaluate the influence of the power, the flow rate was fixed at 500 ml/min and the input power was varied. As expected, the CO_2 conversion increases with increasing power (Figure 8a). Here, a maximum value of 6.2% is achieved at 200 W. The curve again shows a non-linear relation. At higher power levels, the curve flattens out and seems to saturate, while at lower power inputs, the conversion seems to decrease faster. The latter is due to the fact that a homogeneous plasma is not established at too low power levels. This reduces the probability of the molecules being ionised and the conversion is avoided. In contrast to this, a state of equilibrium seems to be reached at higher power inputs. This means that the reverse reaction, i.e. the recombination of CO and O to CO_2 becomes more pronounced, probably due to the increasing reactor temperature. Unfortunately, the reaction temperature could never be determined precisely, because of the high voltage applied in the system, and the fact that conventional metallic thermocouples cannot be integrated in the reactor, since it would disturb the plasma formation. In experiments with an infrared camera, for which a so-called material emission factor is needed, but not available for our material, it was at least possible to determine the temperature at the outlet, i.e. directly after the plasma zone. At this zone, the equilibrium reactor surface temperature was about 77°C for standard operation conditions used in the approach.

In addition to the gas flow rate and electric power as process variables, the plasma discharge frequency was varied. The resonance frequency present in the system is inversely proportional to the product of inductance and capacitance of a reactor system. The applied generator system is able to vary the frequency spectrum by changing the internal inductances in the oscillating circuits. The system is therefore able to adapt to the “frequency characteristics” of the used reactor system, what has a direct impact of the efficiency.

Interestingly, at lower power levels higher CO_2 conversions are reached at low frequencies compared to the higher frequencies (Figure 8b, 16.4 vs 84.6 kHz). This trend is reversed for high power levels above 120 W. Here, higher CO_2 conversion yields are reached at high frequencies. From the power-dependent experiments it is known that at low power the plasma seems to be non-homogeneous, i.e. not the complete possible volume is in a plasma state and as a consequence the conversions are drastically reduced. The frequency describes the number of discharges per time, if the power input into the DBD reactor is kept constant, like in the present case, lower frequencies will have a higher peak power per time than high frequencies as the number of discharges per time is reduced. Thus, lower frequencies are advantageous at lower power levels because of an increased plasma homogeneity. However, if a certain critical power is exceeded, here 120 W, this changes and the number of discharges is more important for an increased performance.

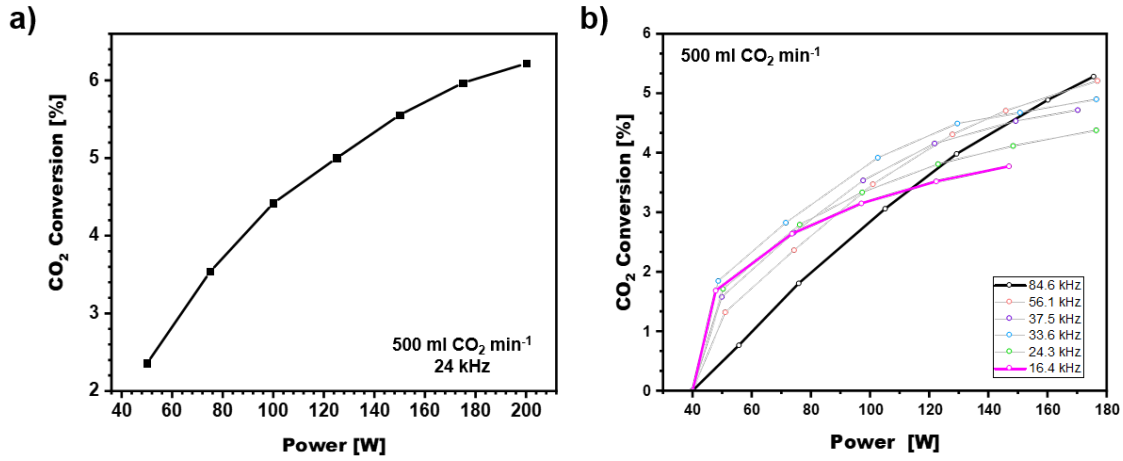

Figure 8: a) CO_2 conversions obtained in power-dependent measurements. The flow rate was fixed at 500 ml/min. b) CO_2 conversions for frequency-dependent measurement sequences.

The exhaust gas of a cement plant contains only about 25% CO_2, the remaining 75% is N2 (69%) and O_2 (6%). If a plasma technology is used to synthesise a fuel, it must be able to convert different lower CO_2 concentrations in the exhaust gas. Experiments here are therefore focussed on “diluted” CO_2 flows to test its suitability and influence. Due to overlaps of measurement signals in mass spectroscopy analysis for CO_2 and N2/O2 signals, the diluting gas N2 was replaced by argon. It was assumed that this does not significantly change the results with respect to the CO_2 conversion. 27% and 20% of CO_2 was selected as CO_2 concentrations in argon (Figure 9a), from which 21% and 25%, respectively, were converted. For comparison reasons, the conversion at 100% CO_2 is also included and is about 7%. This indicates a dilution effect and can be explained by the fact that the number of excitable CO_2 molecules decreases with decreasing CO_2 concentration in the gas. However, since the excitation power is not reduced, this means more energy for fewer molecules, if the diluting gas is not taking up energy from the plasma. The probability for an excitation and conversion of CO_2 thus increases. In addition, recombination becomes less likely due to the dilution effect, since the different species formed are spatially further apart from each other. Another observed effect is that the CO emissions decrease with increasing dilution from initial 7% for pure CO_2 to 5%. This means that the increase in conversion does not fully compensate for the overall lower fraction of CO_2 in the overall gas flow.

Argon cannot completely replace a N_2 in a N_2/O_2 gas mixture as a model substance, since Argon cannot dissociate and react with the activated species present in the plasma. Nevertheless, there are studies showing that N_2 and O_2 can form nitrogen oxides and ozone in plasma (Snoeckx et al. 2016). Hence it was examined qualitatively whether this is similar to be expected for the present system. As a representative of the nitrogen oxides, the ion current of NO was recorded in the mass spectrometer for different initial compositions (CO_2 /N_2/O_2). The data show that varying ratios between N2 and CO_2 do not lead to significant changes in the NO ion current (c.f. Figure 9b). However, when O_2 is added to the mixture, the NO signal increases and hence oxygen must be present to form NO, and in a CO_2-N_2 mixture it can only originate from CO_2 dissociation, since it is the only oxygen source. The present conditions seem not to favour the formation of NO compared to the direct presence of O_2 through admixture. Overall, it can be said that the measured ion current in the range 10^{-11} indicates a negligible amount of NO. O_3 could not be detected under any condition with the available measurement technique.

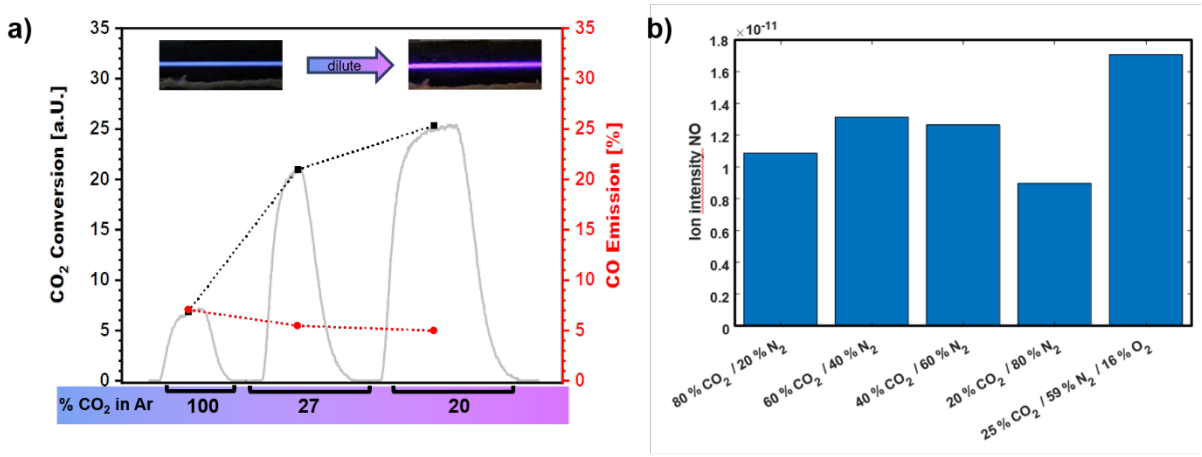

Figure 9: a) CO_2 conversion and CO emission at different CO_2 concentrations in argon b) ion intensity for NO at different gas compositions monitored by MS.

As already mentioned, higher temperatures in the reaction system seem to favour the unwanted recombination of dissociated species due to the higher thermal movement. However, attempts to influence this with a water-cooled electrode did not result in any significant improvement in the conversion. It is assumed that the heat exchange of the gas in the plasma volume with the cooled electrode is insufficient. Another possibility to lower the temperature in the system is to superposition the plasma frequency with a pulsed plasma operating, an available option of the research generator. Pulse and pause times can be set in the range 0.05 s to 60 s. In a tube reactor no improvement was observed.

But surprisingly, for the last electrode configuration, the electrode array shown in Figure 6, more than 10% CO_2 conversion is achieved by applying only 17 W of electric power (Figure 10). The authors observed such conversion rates for a tube reactor design only for a 10-fold higher power. The crucial point is that in the pulsed electrode array the peak power is actually still 185 W, but due to the shorter pulse duration of 0.1 s in combination with a subsequent pause of 1 s, the effective power is only 9% of this.

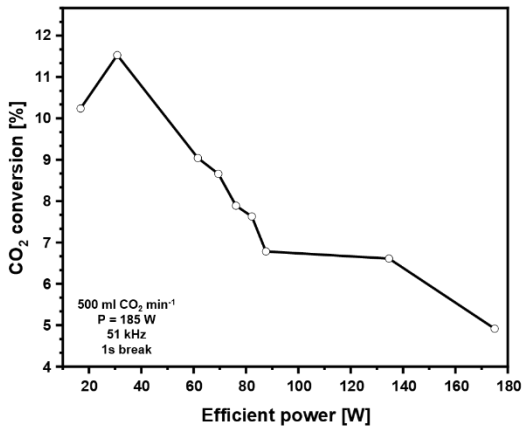

Figure 10: CO_2 conversion in pulsed operation of the optimised plasma electrodes.

2.3 WP3: Introduction of packing and/or catalyst in non-thermal plasma

Objective

The DBD reactor can be described as a capacitor in which a plasma is generated by the artificial breakthrough of the electrical current through the dielectric barrier. In electrical circuits this would normally destruct the capacitor. Here, it is the ignition of a plasma which forces the splitting of CO_2. Comparable to the classical capacitors the type of dielectric barrier seems to influence the performance of the system (Ozkan et al. 2017). Literature reports that CO_2 conversion can be increased by introduction of DBD materials such as titanates up to 35% (Xu et al. 2017). Consequently, in this work package a more systematic investigation on the impact of "tailor-made DBD" materials on the efficiency (low power and high conversion) is carried out.

Results

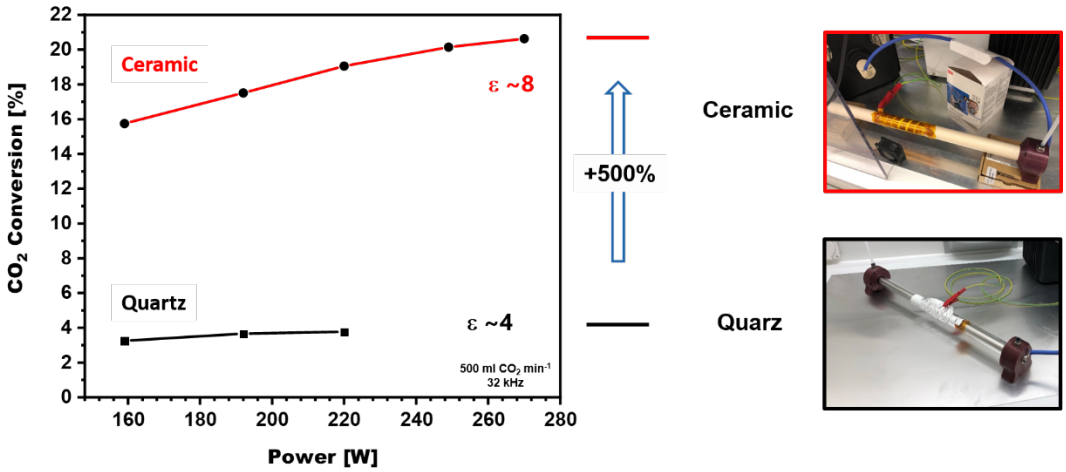

Figure 11: Power-dependent CO_2 conversion for the tubular DBD reactor with two different barrier types.

Dielectric materials are usually classified according to their dielectric constant - also called permittivity. Adding a dielectric to a capacitor increases its capacitance. Due to dielectric polarisation, there is a direct proportionality between dielectric constant and capacitance. Within the framework of the project, it was initially clarified whether the type of dielectric barrier itself has an effect on the DBD reactor, i.e. the CO_2 conversion. For the tubular reactor both, a quartz glass material and an Al_2O_3 ceramic were provided as dielectric barrier. According to the manufacturer's literature, the dielectric value is 3 and 8 for the quartz glass and the ceramic, respectively. In power-dependent measurements, a clear difference can be monitored (Figure 11). Compared to the ceramic barrier, the system with a quartz glass barrier shows a significant lower CO_2 conversion. At about 220 W, the conversion maximum of 3.7% is reached with the quartz glass, while the ceramic barrier provided a 19% conversion at the same power. Up to 20.6% at 270 W were observed with a further increase in power. In brief: While all other processing conditions remain identical, our new plasma reactor array design with a ceramic barrier achieves a 500% higher conversion than a commercial quartz glass barrier, as it is used for standard VOC treatment in exhaust gas applications.

Placing dielectrics directly in the plasma zone is associated with some industrialisation obstacles, e.g. the small gap width of 2-3 mm and the availability of very good dielectrics as powder or pellets to be

filled in. Therefore, preliminary tests were carried out to determine whether the plate reactor is suitable for testing different dielectrics. A phloghopite plate coated with a dielectric dispersion was inserted as barrier and tested. Due to a larger thermal expansion, the plate bended and subsequently a large measurement error resulted. Measurements were not reproducible, and a rapid screening was not possible. Based on that, a process was developed to pelletise dielectrics powders and to test them in the tube reactor. Apart from BaTiO3 (commercially available as powder), the dielectrics are custom-made and produced as well as characterised from UMTEC. A variation of the self-developed citrate route (Borgschulte et al. 2021) was used for this. Lead zirconium titanate (PZT), lead iron niobate (PFN) and calcium copper titanate (CCT) are common compounds with very high dielectric constant. Alkaline earth titanates are also known for their dielectric properties and form a series in which only one element is varied. $SrTiO_3$ has been additionally coated with surface metals, through an intrinsic reduction of the materials. According to a process developed from some of the report authors, metals ions can be released as nanoparticles and act as metallic catalysts (Burnat et al. 2016). After their synthesis, all materials are available as powder and therefore had to be pelletised for integration into the reactor. Gypsum was used as binder and carrier for dielectric powders for the pelletisation. Before curing, 2wt% powder of the dielectric material was added to the gypsum-based host and homogenised. After curing, the received gypsum-material-sheets were crushed and sieved for a fraction between 1-2 mm. The received pellets possess a suitable size to fit into the reactor and simultaneously cause only a negligible pressure drop (Figure 12a).

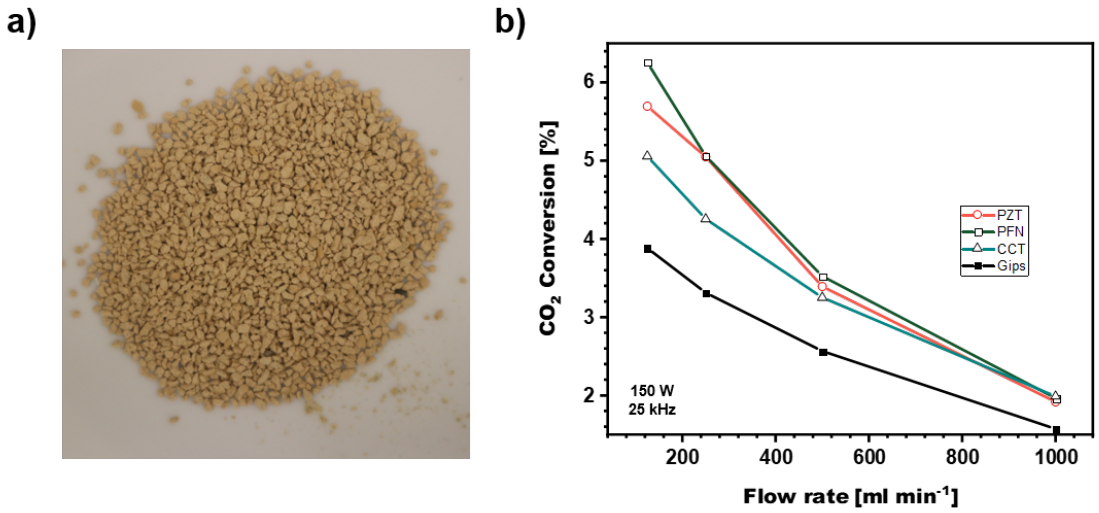

Figure 12:a) Tailor-made Gypsum-material pellets (size range 1-2 mm) used for the plasma reactor b) Flow-dependent CO_2 conversions for different dielectric admixtures (PZT, PFN and CCT) and pure gypsum.

As reference, pure gypsum was also pelletised and packed into the reactor. According to the literature, PZT has a dielectric constant of approx. 500, and PFN as well as CCT have dielectric constants >10,000. In the flow-dependent CO_2 conversion (Figure 12b), clear trends can be seen. On the one hand, all reactor fillings with admixed dielectric show higher conversions than pure gypsum. For example, the gypsum only achieves 3.9% conversion at 125 ml/min, whereas the PFN-containing material achieves 6.3%. On the other hand, the dielectric samples yield different conversions at low flow rates, but are similar at high flow rates. It is assumed that the residence time of the molecules in the plasma zone is too low at high flow rates and therefore a linear relationship in the conversion results. The reactor used has a space velocity of 0.42 1/s (500 ml/min) when empty. Due to the confined space and the particle distribution between 1-2 mm we assume the maximum possible packing density of 74% as an extreme case with this the value increases to 1.4 1/s in the packed state. However, this still does not consider any blocked channels or preferential flow directions, and an even higher space velocity can be assumed. This means that the gas exchange is about 4 times higher compared to the empty reactor. At high flow

rates, the system seems to be kinetically dominated, whereas at low flow rates the influence of the dielectrics increases.

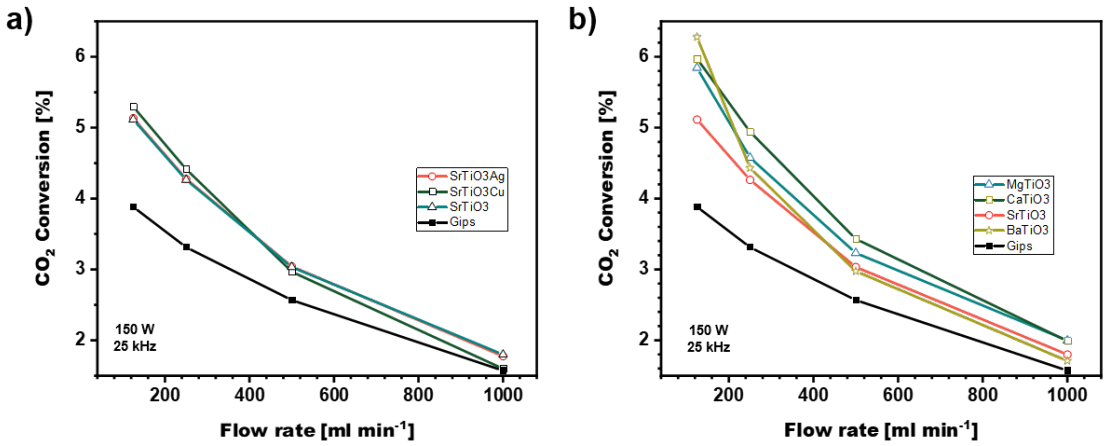

Figure 13: Flow-dependent CO_2 conversions for a) metal doped SrTiO3 and b) the alkaline earth titanates.

As mentioned, the influence of a catalyst present in the reaction zone was investigated. For this purpose, perovskite materials based on $SrTiO_3$ were used. The perovskite host structure can resist to a certain amount of substitution cations without structural changes, here Ti was partially replaced by either 5mol% Cu ($SrTiO_3Cu$) or 5mol% Ag ($SrTiO_3Ag$), which can be released by reduction as metal nanoparticles on the surface. First, the materials were investigated without H2-based reduction, i.e. they are considered as pure oxide dielectrics (Figure 13a). Here, all conversions are again higher than in comparison to pure gypsum. The values for $SrTiO_3$, $SrTiO_3Cu$ and $SrTiO_3Ag$ are very similar for all fluxes. This suggests that the simple introduction of a metal cation into the oxide host structure has no influence on the CO_2 conversion. As a final investigation of the pure dielectrics, a series of alkaline earth titanates from $MgTiO_3$ to $BaTiO_3$ was examined (Figure 13b). The highest conversion of approx. 6.3% is achieved by $BaTiO_3$ at a flow rate of 125 ml/min. It is interesting to note that the conversion decreases for $BaTiO_3$ stronger with an increasing flow rate than for the other alkaline earth titanates. According to the measured conversions as function of the element (i.e. Ba>Ca>Ca>Mg), there is no correlation to the element position in the periodic system of elements. This could also be related to the fact that the dielectric constant is not only dependent on the material composition but also on the frequency. Certain frequency ranges could thus be associated with significant dielectric losses in the material, which minimises the energy input into the plasma. Once again, pure gypsum had the worst conversion rate.

For the activation of the perovskites, i.e. the formation of metal nanoparticles on the surface, the system needed to be stimulated by reduction with hydrogen gas. $SrTiO_3Cu$ was therefore pelletised with the aid of binder and pore former (Hoelderich 1986). The quantity obtained was sufficient to fill the small tube reactor. An unreduced sample without $Me^{+/-0}$ species on the surface was compared to a sample which was reduced and therefore exhibits activated $Me^{+/-0}$ species on the surface. As it can be seen from the results in Figure 14, the activated sample gives higher CO_2 conversions than the non-activated sample for all flow rates. The absolute difference is about 0.5%, but this is still 25 – 30% higher than non-activated surfaces, proofing the catalytic activity. The conversion of ~3.2% (500 ml/min) seems to be relatively low, but compared to the empty reactor (Figure 7b) the space velocity at ideal packing density is about 10 1/s. As indicated in the scheme, it is assumed that the presence of metal nanoparticles influences the discharge behaviour, i.e. a higher plasma density is generated at the particle surfaces. However, it cannot be excluded that the copper itself has a catalytic effect on the CO_2 dissociation

reaction. Further studies are needed for a more detailed investigation, since this could not be clarified in the short term.

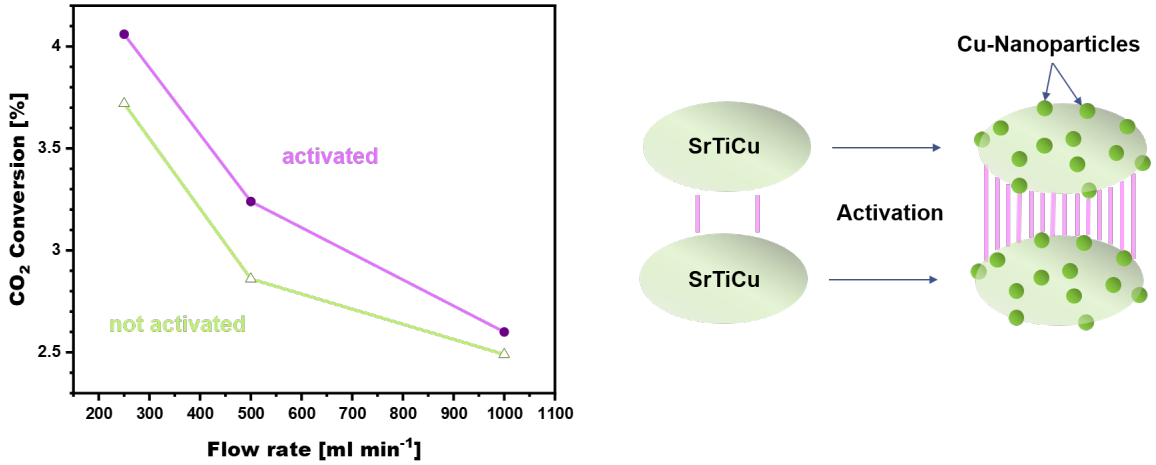

Figure 14: Flow-dependent CO_2 conversions of native (not activated) and hydrogen (activated) pretreated SrTiO3Cu.

2.4 WP4: Development and evaluation of processing concept: (proof of concept for scale-up)

Objective

The objective of this WP is to develop a realistic processing concept for a renewable power driven plasma reactor and its integration into the industrial setting of a cement production plant in Wildegg to save fossil CO_2 emissions. The current situation at the industrial partners site in Wildegg allows to recuperate about 1.6 MW of electricity from a recently installed ORC-based turbine (14 GWh/a, 800 m^3 ORC plant size). This electricity could be used as recovered power to operate a plasma system as described in the technological part. Since such a recuperation system is not common and only available at the partner's site, we will evaluate the feasibility for 2 different scenarios:

1) Scenario 1 (Wildegg): Availability of 1.6 MW (14 GWh/a) of electricity from ORC for a plasma technology
2) Scenario 2 (100% electrification): External renewable power input needed, to substitute all fossil energy carriers by a plasma generated CO fuel from purely geogenic CO_2

Results

The following paragraph presents – for a better understanding and clearity – the basis facts of the cement plant including energy needs and emission values:

- 70 MW fossil energy input is needed for calcination of $CaCO_3$
- 878`000 t of CO_2 are emitted per year
- 1.6 MW (equal to 14 GWh/a) of electricity is recuperated from waste heat (ORC plant)

- 200'000 m^3/h exhaust gas, from which 25% are CO_2 (fossil and geogenic) and 75% are N_2/O_2 (from air as oxidant)
- CO_2 originates to 60% from unavoidable $CaCO_3$ and 40% from avoidable fossil fuels

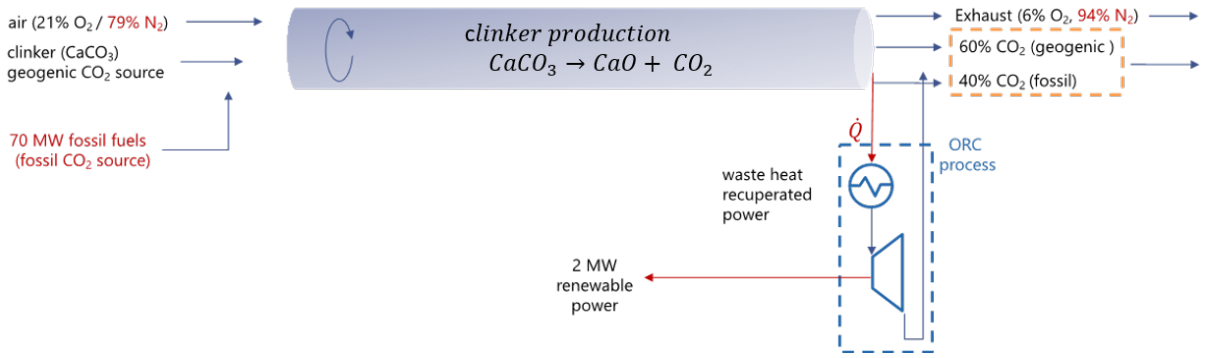

Figure 15: Current process scheme of the Wildegg cement plant.

In the current state (Figure 15) and during normal production rate the exhaust volume from the clinker production plant in Wildegg is about 200'000 m^3/h, from which 75% or 150'000 m^3/h mainly consist of N_2 from air as oxidant. The remaining 25% and 50'000 m^3/h, respectively, are CO_2. 60% thereof, i.e. 30'000 m^3/h are of geogenic origin ($CaCO_3$) and 20'000 m^3/h of CO_2 result from the fossil fuels used in the calcination process of the raw materials.

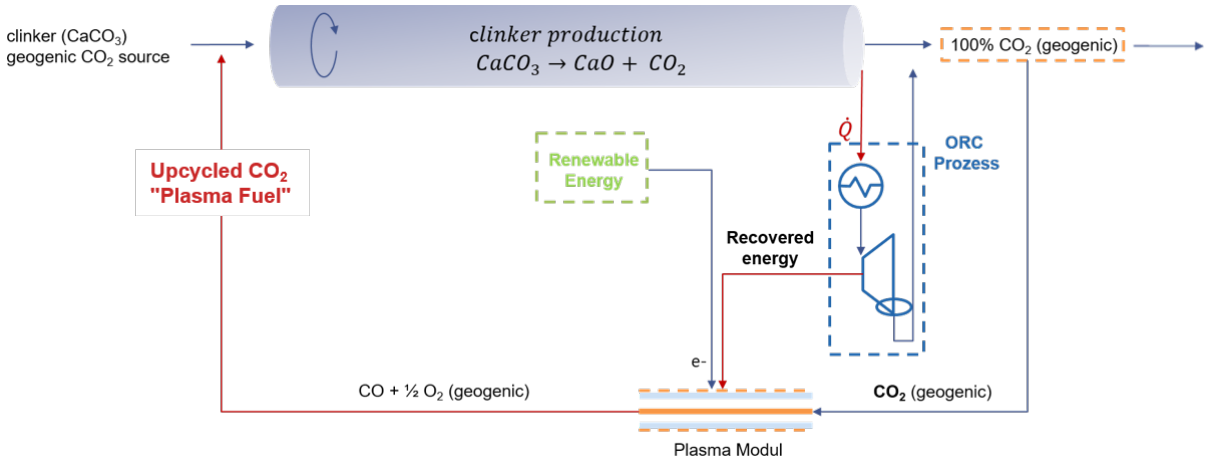

Figure 16: Electrified process scheme of the Wildegg cement plant.

According to the authors suggested "upcycling process" (Figure 16), a fraction of the exhaust gas stream is initially applied with the newly developed non-thermal plasma-assisted CO_2-to-CO reactor system. Within the non-thermal plasma, CO_2 is dissociated to CO and O_2 in stoichiometric amounts, and that at a temperature level near to room temperature. In case a cement plant is equipped with a heat-to-power recuperation system, similar to the 1.6 MW ORC plant of Jura cement in Wildegg, this "renewable power" can be applied to operate the proposed plasma system. This would result in a partial use of CO_2 emissions, its upcycling to a CO/O_2 mixture and its subsequent use as alternative, CO-based fuel in the clinker calcination production. It is worth to mention, that the needed oxidant, – usually O_2 from external air, but together with a large fraction of 79% N_2 – is already included here.

For the existing industrial plant and its production rate, our plasma approach has the potential to reduce CO_2 emissions of about **20'000 m^3/h or 40 t/h,** if all CO_2 emissions could be converted by a plasma technology. The required amount of CO to cover the requested thermal energy of 70 MW from fossil fuels is equivalent to 20'000 m^3 CO per hour (Eq. 1: 1 mol CO is formed from 1 mol CO2) and taking the reaction enthalpy of CO oxidation into account (c.f. reverse equation of eq. 1). This means in turn: for every single per cent of the fossil fuel, which is replaced by upcycled CO, the plant reduces its fossil CO_2 emission by 3500 t/year. On base of these facts, one can calculate the CO_2 savings, in case only a certain fraction of fossil fuels can be replaced by the here proposed plasma process (Figure 17). For instance, the available recuperated energy (1.6 MW) from the ORC process used for the conversion of the CO_2 emission in the exhaust gas would safe 2355 t/year if an energetic efficiency of 30% is assumed during the plasma process.

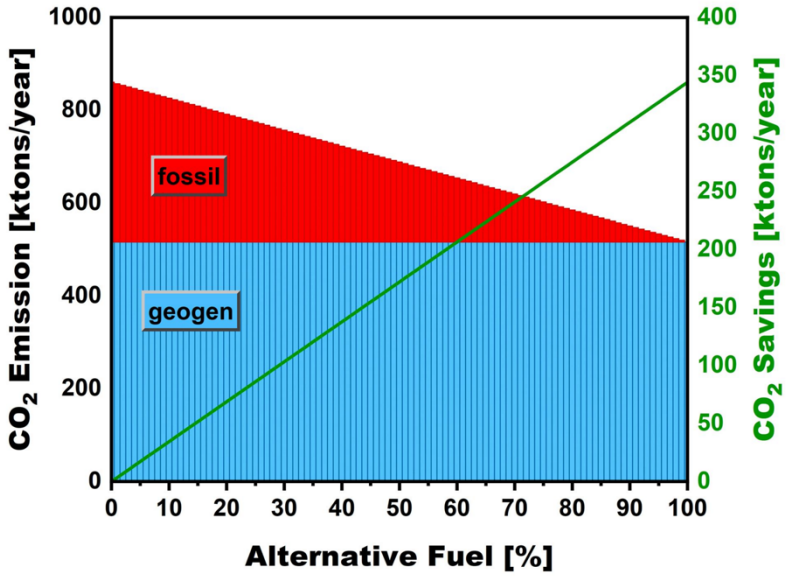

Figure 17: Illustration of the total CO_2 emission of the cement plant in dependence of the ratio of replaced fossil fuels from 1 to 100%. Data calculated from the authors on base of the Wildegg plant provided by the industrial partner.

For the discussion of the two scenarios -ORC operation and full electrification-, experimentally determined CO_2 to CO conversion and required electrical energy are extracted from Figure 10. They are in the range of 10% and 17 W. As the CO_2 input flow during the experiment is also known (500 ml/min) the produced amount of CO can be calculated from the conversion to 50 ml/min (10% of CO_2 input). Considering CO as ideal gas, with a molecular volume of V_m = 22.414 l/mol this equals 2.23 mmol/min or taking the molecular weight M(CO) = 28 g/mol into account 3.75 g CO/h. In other words, it requires 17 Wh to produce 3.75 g CO which is an energy demand of 4.5 kWh or 16.3 MJ extrapolated to 1 kg (267x17 Wh). A comparison with the calorific value of CO (10.103 MJ/kg) gives an assumed process efficiency of 62% (power-to-reaction enthalpy of fuel oxidation) meaning 10.103 MJ of heat energy can be generated by investing 16.3 MJ electric energy into the plasma-based fuel generation.

In **scenario 1**, the total CO output from the plasma process is ~353 kg/h if only the recuperated energy of the existing ORC plant (1.6 MW) is used. According to Eq. 1 the consumption of CO_2 is equimolar to the generation of CO thus, the CO_2 input equivalents to the plasma can be calculated by multiplication of the CO amount with a factor of 1.57 ($M(CO_2)/M(CO)$ = 1.57) this corresponds to a reduction of ~554 kg/h of CO_2 emissions. From the 353 kg/h CO a thermal energy by means of combustion energy of 1 MW/h is obtained, which corresponds to 1.4% of the total demand. For simplicity a cuboid

(2 cm x 2 cm x 15 cm, i.e. 0.06 l) is assumed for the reactor to extrapolate and estimate the required reaction volume for the scenario. With the current production rate of 3.75 g CO/h a reaction volume of ~5.6 m^3 is required which fits into a standard ship container (33 m^3), for instance.

Scenario 2 represents the full range electrification of the clinker production process, for which 70 MW/h of thermal energy is needed. According to the calorific value of the CO combustion, this requires 25 t CO per hour. The plant in its current existing condition and production throughput would require then 113 MW/h of electricity and ~40 t/h of CO_2 to provide the necessary amount of CO gas as alternative fuel. As the plasma fuel generation can be run as a circular process and the burned CO is recycled as CO_2, the plant would only have to run for ~7h under geogenic emission (58 t/h) to produce the total amount of CO_2 that is necessary for a permanent fuel provision. Since only electric energy and no further fossil fuel is needed after this point, the CO_2 saving from this point amounts to 40 t/h. Again, the plasma technology takes up only a small amount of space, according the present data the required reaction volume is estimated at 400 m^3. This equals 13 standard ship containers and is therefore way smaller than typical coal or waste deposits that are normally required for firing of the plants. However, it must be taken into account that due to the modular design, even more space savings of at least 50% can be expected.

Table 1: estimated process parameters for scenario 1 and 2.

Conversion of CO_2 to CO*	10%	
Electrical Power	17 W	
Electricity Input to plasma process	4.5 kWh/kgCO	
Reactor volume	0.06 l	
Contribution of electricity cost to Price of CO fuel**	0.32 CHF/kg CO 114 CHF/MWh	
	Szenario 1	**Szenario 2**
Total CO output from plasma process	353 kg/h	25 t/h
CO_2 Equivalent input to plasma process	554 kg/h	40 t/h
Electricity Input to plasma process	1.6 MW/h	113 MW/h
Thermal Energy Output as CO fuel	1 MW/h	70 MW/h
Electricity Costs for CO fuel production	114 CHF/h	7980 CHF/h
Required reaction volume	5.6 m^3	400 m^3

*pure CO_2 stream ** assuming 0.07CHF/kWh

With the available data (Table 1) a discussion about all expenditures in advance (CapEx) as well as operational expenses (OpEx) for the new technology is possible. However, as the system size of this feasibility study is orders of magnitude smaller than it would be required for a cement plant this is only done on a qualitative level due to expected scaling effects. CapEx costs will be dominated by the

contribution of the ceramic based plasma electrodes as well as by the electrical hardware (RF-plasma generator) equipment. Compared to state of the art glass based plasma electrodes and to standard low frequency transformers (see 2.1 "commercially available plasma module") the developments might be more expensive. However, both of these parts are very robust technologies with expectable long lifetimes. Thus, higher CapEx might be compensated by lower OpEx contributions from the equipment e.g. for maintenance. Besides maintenance or personal hours for operation of the system we expect the OpEx to be dominated by the electricity costs. As the cement production facility in Wildegg has its own ORC plant, electrical current is available cheaper than the average price on the free market. In the costs calculations we use the expected price for electricity from the ORC plant, which is 0.07 CHF/kWh and extrapolate it also for the case of a fully electrified plant. Compared to the online available data from ElCom this is roughly 50% cheaper than the free market price (14.52 Rp./kWh). Based on the upper calculations and on the assumed price for electrical current ~1.6 MWh electrical energy have to be invested to generate 1 MWh thermal energy. Therefore, the contribution of electric costs to the price of CO fuel for the provision of 1 MWh of thermal energy is 114 CHF (1628 kWh x 0.07 CHF/kWh). In that perspective it is comparable with the production costs of hydrogen from electrolysers (Kober et al. 2019). Here, the dominant contribution to the price is also electricity. However, as the proposed technology does not require any other chemicals or additives for the production of fuels it is supposed to be more cost efficient than various other carbon capture and utilization processes as they require mostly hydrogen and additional energy for driving the processes e.g. Power-to-Gas (H2 for methane). The contribution of electric costs to the price per t CO_2 equivalent removed is 200 CHF. This value may be higher than some expected costs for carbon capture and storage systems (Schmelz et al. 2020) but it does not include the added value by the generated CO fuel.

For the further technical implementation several considerations have to be made in advance. It has to be evaluated at which intersections in the plant the recycling should take place. One challenge could be the well-known dust load in the exhaust gas. Clogging of the electrodes from settled particles could cause a pressure drop or a complete blocking due to the small electrode gaps present in the system. However, even SCR systems with similar “mesh sizes” are applied nowadays in the exhaust gas of cement plants without clogging problems. In this context, also contaminations with other by-products from cement production (NH3, H2S, etc.) should be examined for their interaction with other components. However, since the plants are equipped with several cleaning stages, finding the right quality of exhaust gas should not be a major issue. In addition, the ceramic design of the electrodes is relatively resistant against cleaning methods (mechanical/chemical) if necessary. The implementation must also take into account that the calorific value of the produced gas mixture is constant or at least given in order to ensure compatibility with the already existing infrastructure. One conceivable option here would be the use of modern sensors to determine and monitor the calorific value permanently. This would also be advantageous for energy balancing.

3 Conclusions

A new technology was successfully evaluated to generate renewable fuels for the cement industry. It is based on a plasma-assisted upcycling of CO_2 and can directly be applied to a CO2-rich exhaust gas stream of a cement plant or other CO2-rich emission streams, to generate a combustible CO/O2 fuel mixture. Reoxidation thereof will supply the plant with the necessary heat energy for driving the calcination processes and can thereby generate an alternative, but closed fuel cycle. Within the project a completely new plasma setup based on a dielectric barrier discharge (DBD) principle was evaluated, established and operated. The activities include the design of new hardware such as several plasma reactors (tube, plate, etc.) and a LabVIEW based controlling software (PlaTec). Industry cooperations were successfully established with material, electronics and plasma plant supplier for future large-scale implementation. As one result, an optimized and fully functional high-efficiency plasma device was established, which is based on an industrial design for the later industrialization and scale up.

In the experimental part of the project various general aspects such as process design as well as more complex features such as material design were considered for an operation as optimized system. For example, flow-, power-, frequency- and gas composition-dependent experiments were conducted and evaluated according to their influence on the CO_2 conversion. The results are given here for the most affecting processing variables as trends and are listed in Table 2. The highest CO_2 conversion of a pure CO_2 stream was of about 20% and was achieved at high power or low flows. However, this conversion can be further increased by diluting the CO_2 down to ~25%, which corresponds to realistic industrial gas compositions in the exhaust. The most energy efficient conversion is about 10% at 17 W energy input, which could be reached by custom-made modifications to an improved industrial plasma configuration. Additionally, various N_2/O_2/ CO_2 mixtures were examined qualitatively for the formation of undesirable by-products but only NO_x was found at negligible small amounts. These results confirm the suitability of the technology to be applied in cement plants and its typical gas compositions.

Table 2: Overview of the general trends in CO_2 Conversion for variation of different parameters.

Parameter	Trend	CO_2 Conversion
Flow	↓	↑
Power	↑	↑
Frequency	↑	↑ (for high powers)
Dilution	↑	↑

The complex investigations dealt with material design that was used in the plasma zone, i.e. the influence of dielectric materials and metal catalysts on CO_2 conversion. It turns out to be a crucial design aspect for the plasma technology as for example the change from a quartz barrier ($\varepsilon = 4$) to an Al_2O_3 barrier ($\varepsilon = 8$) resulted in a 500% higher CO_2 conversion. Material design was identified as a major challenge and especially the subsequent introduction of catalytic materials into the reaction zone, which could probably be solved with pelletisation of such materials to receive the proper mechanical and plasma related stability in the plasma reaction zone. In general, the use of dielectric materials in the plasma zone improves CO_2 conversion. However, it must be noted that the residence time of CO_2 in the plasma zone decreases substantially due to the reduced accessible volume. It was shown that the presence of a copper-containing strontium titanate nanopowder improves the conversion, but potential and influence may be underestimated due to the strong flow dependence, which could not be adapted to the reactor concept in the short project time.

Overall, the applicability of the plasma concept to the parameters of a cement plant is positively evaluated. With an assumed process efficiency of 62% (power-to-reaction enthalpy of fuel oxidation)

and an electricity price of 7 Rp, the contribution of electricity cost to the price of thermal energy is 114 CHF per MWh of CO fuel. From our results it can be estimated, that 2.28% (i.e. available recuperated 1.6 MW per needed 70 MW) of recovered electricity from the ORC plant is sufficient to provide 1.4% of the required fuel quantity by means of the plasma. This would correspond to a CO_2 saving of 554 kg/h. Complete electrification also seems feasible and could deliver CO_2 savings of 40 t/h for the chosen plant specification.

4 Outlook and next steps

With about 62% energy efficiency (power-to-reaction enthalpy of fuel oxidation) and electricity cost contribution to thermal energy which is about 114 CHF/MWh, the plasma-based CO_2 upgrade exceeds the initial expectations of 30% efficiency by far and is therefore already now an attractive method to produce alternative and regenerative fuels for the cement industry and others. For this reason, the next step should be a demonstrator plant with higher output levels. A realistic time frame for the realization is estimated to be within approximately three years to address the challenges for an industrial implementation.

Although the research plasma generator used operates according to industrial standards, it is not fully adapted to the DBD application for CO_2 dissociation. In order to increase the energetic efficiency and avoid losses, the current developments in electrical engineering (loss-free switching, MOSFET, etc.) should be taken into account and implemented. In this regard, the design of the reactors, especially how the gas is guided through the plasma zone was adapted to older technologies to a certain extent. In the next steps this should be carefully evaluated also by the aid of flow and plasma modelling and could be optimized by a new arrangement of the plasma electrodes in the CO_2 stream.

The investigations have shown the development potential of DBD technology with respect to the use of ceramic dielectrics. The bottleneck here is the integration of the new materials into the reaction zone which is very time consuming. For a further increase in efficiency, which is undoubtedly possible, it is therefore recommended to produce tubes of the specific materials in order to use them as full-fledged dielectric barriers. The hurdle here is not only to identify the best material composition but also the special development required for the production of the ceramic green compacts. However, technical ceramics are playing an increasingly important role in high-tech products, which is why finding a development partner could be successful.

Although the feasibility study showed that metal nanoparticles can have a positive influence on the conversion, there is still great potential for development in this respect. It must first be clarified whether the improvement results from a change in the dielectric constant or from a catalytic effect of the metal particles on the surface. If the latter is the case, systematic search should be made for a metal that specifically catalyses CO_2 dissociation in the plasma.

In the near future, thistechnology could become even more important, as synthesis gas (H_2/CO) is needed for the production of synthetic fuels and other strategically important platform chemicals. Excess CO_2 from the cement industry could also be used in this way. Finally, company authorities still have to clarify how the use of the technology affects the eligibility of reductions in CO_2 emissions in current and future GHG trading and subsidy schemes.

5 National and international cooperation

During the overall project it was of high importance to identify local industrial partners, but at the same time it was highly challenging, too, especially due to the Corona constraints. Secondly, this research

grouphad the intention and general strategy to bring plasma technology relatively fast to an industrial level and to proof its applicability. With respect to this the following cooperations have been established so far:

- The cooperation with the company Oxytec AG turns out to be very fruitful and will be continued even more intensively in the future. A strategy for a “common partnership” is in the planning to guarantee the later industrial implementation and market entry.
- Jura Cement put much effort in the project by providing data and sharing experiences regarding plant operation. Several meetings and discussion rounds have proven the interest of the cement producer in the technology and the overall feedback is positive. A future implementation of the technology in the plant in Wildegg is currently considered
- AFS (Germany) – as supplier for electronic hardware - is interested in a further development of the electronic components for an industrial scale.

6 Communication

- UMTEC Newsletter, Q1, 2021 (print version).
- https://www.ost.ch/de/die-ost/organisation/medien/forschungspreise-fuer-co2-plasma-reaktor-und-nano-pipettenspitzen
- https://www.futur.ch/Forderung-Start-ups-und-Innovation/Angebote/Technologietransferpreis
- https://goldkueste24.ch/articles/136860-zwei-ost-projekte-erhalten-forschungspreise
- https://march24.ch/articles/137011-zwei-ost-projekte-erhalten-forschungspreise

7 Publications

Bachelor Thesis 2021 (EEU) Samuel Hecht

Bachelor Thesis 2021 (EEU) Jana Niggli

Semester Project work 2021 (EEU Bachelor) Pascal Landolt

Semester Project work 2021 (Electrical Engineering Master) Urs Fischli

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9 Appendix

not applicable