Position Paper

Utilisation and Storage of CO_2

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1 Executive summary

Among all greenhouse gases in the atmosphere, CO_2 plays a special role due to the magnitude of its anthropogenic emissions. This Position Paper is based on a Discussion Paper, compiled by DECHEMA, which analyses artificial CO_2 sources and presents and discusses various technical options for dealing with CO_2 emissions in detail. The present Position Paper summarises the main findings, establishes **criteria** for the evaluation of the various technological options, formulates **political requirements** and identifies **research and development needs**.

Any overall strategy for CO_2 management should be based on three main elements: **mitigation**, **storage** and **chemical utilisation**:

The **mitigation of CO_2 emissions** takes priority over *all* measures to store or utilise CO_2, the rationale being that all storage and utilisation options for CO_2 require additional energy input, which in turn produces additional CO_2. For this reason **energy saving**, also by reducing existing energy needs, has absolute priority. **The chemical industry** can make **vital contributions** towards energy saving by efficient use of materials and technologies, intelligent use of energy, and enhanced efficiency of production processes. These contributions are specified in the Position Paper "Energy Supply of the Future" compiled by German chemical organisations.

Chemistry and chemical engineering provide the key enabling technologies for highly economic, energy-efficient **capture and purification** of CO_2 (e.g. from power plants or industrial processes by flue gas scrubbing, CO_2 absorption, chemical looping, etc.) and also for subsequent storage or utilisation. By these means, chemistry facilitates reliable, economic CO_2 capture and storage on an industrial scale.

The storage of CO_2 using carbon dioxide capture and storage (CCS) strategies is extremely expensive. Since all measures for the storage or utilisation of CO_2 require additional energy, thus generally producing additional CO_2, it is meaningful to draw up criteria for the assessment of CO_2 storage options (storage capacities, state of technology, safety and public acceptance, follow-up costs). In principle, CO_2 storage must remove *more* CO_2 from the atmosphere than is *released* by the *additional* energy required for its capture and storage.

For the chemical industry CO_2 storage merely represents an interim solution. Wherever possible, CO_2 should not be stored as "waste", but used as a chemical building block for the production of high-quality products, e.g. polymers. **Chemical utilisation** creates value.

CO_2 is a major product from the combustion of fossil fuels. For this reason adequate availability of non-fossil energy sources (renewable sources or nuclear energy) is a prerequisite for chemical utilisation of CO_2 on an industrial scale. It is, therefore, essential to **step up** the **development of new technologies** for energy production (particularly photovoltaics and photocatalysis), energy transport and energy storage.

Admittedly, the **chemical industry** can only make a minor direct contribution towards reducing the overall amount of CO_2 emissions: according to current estimates, it could convert at most **around 1% of global CO_2 emissions** into **chemical products** and **around 10%** into **fuel**. Chemical utilisation, however, coupled with the concomitant value added can **contribute to the cost effectiveness** of an overall strategy for CO_2 management.

Criteria are formulated (energy and CO_2 balance of the total process, value creation, product properties) for an assessment of the chemical utilisation of CO_2. The potential of CO_2 utilisation is discussed in DECHEMA's "Discussion Paper: Verwertung und Speicherung von CO_2" (currently only available in German)[1].

In the following a summary of the conclusions is presented in the form of **8 statements**. Furthermore, **areas requiring further research** are specified.

[1] All additional documentation is available on the DECHEMA website or on request.: http://www.dechema.de/Forschung_und_Forschungsf%C3%B6rderung-p-123211/Studien_und_Positionspapiere.html

2 Introduction

The scientifically based forecast of climate change induced by anthropogenic emissions of CO_2 and other greenhouse gases, fuelled by the publication of the Fourth Assessment Report of the Intergovernmental Panel on Climate Change (IPCC) in 2007, has given rise to an intensive public debate. In this context sweeping measures for the mitigation of CO_2 emissions and for more efficient use of energy as well as for the exploitation of novel energy sources and the partial transformation of our energy system from fossil fuels to renewable sources have top priority. Here, chemistry can play a key role. Its contributions to a sustainable energy supply are discussed in detail in a paper compiled by the "Chemical Energy Research" coordination group of several German chemical associations[2].

The IPCC Report presents various emissions scenarios projecting the trend of atmospheric CO_2 concentration. These scenarios, however, demonstrate that CO_2 mitigation strategies alone will not suffice to stop climate change. This is the context of the ongoing debate concerning measures for CO_2 storage[3] which is now a priority on the political agenda.

The scientific and technical background of the present Position Paper is the topic of a DECHEMA discussion paper of the same title. The paper elaborates the different strategies for utilisation and storage of CO_2 emissions from power plants and industrial processes or directly from the atmosphere.

3 Political and economic context

The development and implementation of novel technologies is not only constrained by scientific and technical progress, but also by a number of political, social and economic factors. The various processes for the utilisation and storage of CO_2 are in different stages of development. Some are already in industrial use. Practically all the options presented here involve significant investments, both of capital and energy.

The key to the successful implementation of a new technology is its acceptance by the general public. The public not only needs to be convinced of the advantages of the new technology, but also has to accept the attendant impact on its daily life. This may entail considerably higher prices for energy, adverse effects of transportation routes (CO_2 pipelines through densely populated areas) and storage facilities as well as the risks perceived in conjunction with the technology concerned.

Furthermore the implementation of a new technology takes place within a specific economic context. Hence, the economic risks associated with investment costs of immature technologies, the trend of raw material prices, etc. need to be considered. Economic feasibility is the test of the competitveness of a new technology compared with a conventional one. For instance, novel power plants lose practically all the efficiency improvements gained over the last few decades due to the energy penalty of

[2] Energieversorgung der Zukunft – der Beitrag der Chemie, March 2007; Koordinierungskreis Chemische Energieforschung der Chemieorganisationen DECHEMA, GDCh, DBG, DGMK, VDI-GVC und VCI.
[3] W. Arlt, Verfahrenstechnische Möglichkeiten zur Verringerung des Anstiegs von Kohlendioxid in der Luft, CIT 2003, 74, 340-348.

CO_2 capture and storage: they require significantly higher primary energy input for the same amount of power output. Given rising prices for primary energy sources, this represents a considerable financial burden which, in turn, will significantly increase energy costs for the end-user. The situation improves if the captured CO_2 is used in conjunction with another process, e.g. enhanced oil recovery (EOR). The disposal of CO_2, directly or chemically modified and without any further value creation or utilisation options, constitutes a substantial cost factor. In a straight comparison with an efficient, conventional power plant, a CCS power plant is not competitive. Moreover legal issues and public acceptance of CCS technology still have to be clarified (see above). Long-term risk studies and insurance concepts regarding the impermeability of storage facilities and potential leaks are currently under discussion.

It is doubtful whether the critical mass required to implement complex, expensive technologies can be achieved globally, and particularly whether emerging countries with soaring energy demands and rapid economic growth are prepared to pay the extra price. If, however, only certain regions create the framework for CCS technology by taking measures to combat climate change, the resulting rise in energy prices will jeopardise the competitiveness of their own domestic, energy-intensive industry. Furthermore the predictable increase in consumption of primary energy will limit the availability of fossil fuels, rendering them even more expensive. The chemical industry in particular, however, depends on energy at internationally competitive prices for its innovation potential to flourish.

The economic viability and the impact~~s~~ of the technologies described above are strongly dependent on development in related sectors. Hence, none of the above-mentioned technologies enable the utilisation of CO_2 from the combustion of fuels in the transportation sector since it is produced by a multitude of small mobile sources. Should, however, the transportation sector make the transition to a hydrogen system, the hydrogen could be produced centrally, for instance from renewable sources or from nuclear power. Similar speculations can be made with respect to a transport system based on electricity.

4 Conclusions

Our industrial society will not be able to dispense with fossil energy sources in the foreseeable future. Their use, mainly in power generation but also as fuel, will engender a further increase in atmospheric CO_2 concentration. The related and predictable rise in temperature calls for measures to limit and mitigate CO_2 emissions.

The DECHEMA Discussion paper “Verwertung und Speicherung von CO_2” discusses storage options for CO_2 on the one hand, and utilisation strategies for CO_2 as a source of carbon and a reactant on the other. The utilisation strategies are geared towards creating new products and generating value added. They make an important contribution to CO_2 management, particularly in the light of the current excess of relatively pure CO_2 produced by the chemical industry itself. Compared with competing processes that do not use CO_2, their CO_2 balance is potentially more favourable. As a rule, however, detailed material, energy and CO_2 balances are not yet available for the technical applications and products discussed; this holds both for the chemical and biochemical processes under consideration and for the industrial use of microalgae.

In this context, the following conclusions can be drawn:

1.) On principle, the mitigation of additional CO_2 emissions by exhausting all measures to conserve energy, enhancing the energy efficiency of production and power plants, and increasing the use of renewable energy sources has priority and takes precedence over all other options for storing and utilising CO_2 that has already been produced. The position paper “Energy Supply in the Future – the Contribution of Chemistry” compiled by the Chemical Energy Coordination Group of the German chemical organisations describes in detail the role of chemistry and chemical engineering in this area.

2.) CO_2 mitigation measures alone will not, however, suffice to significantly reduce the increase in atmospheric CO_2. The next priority after mitigation of CO_2 emissions should be a consolidated strategy for value-adding processes in preference to dumping, which creates no value at all.

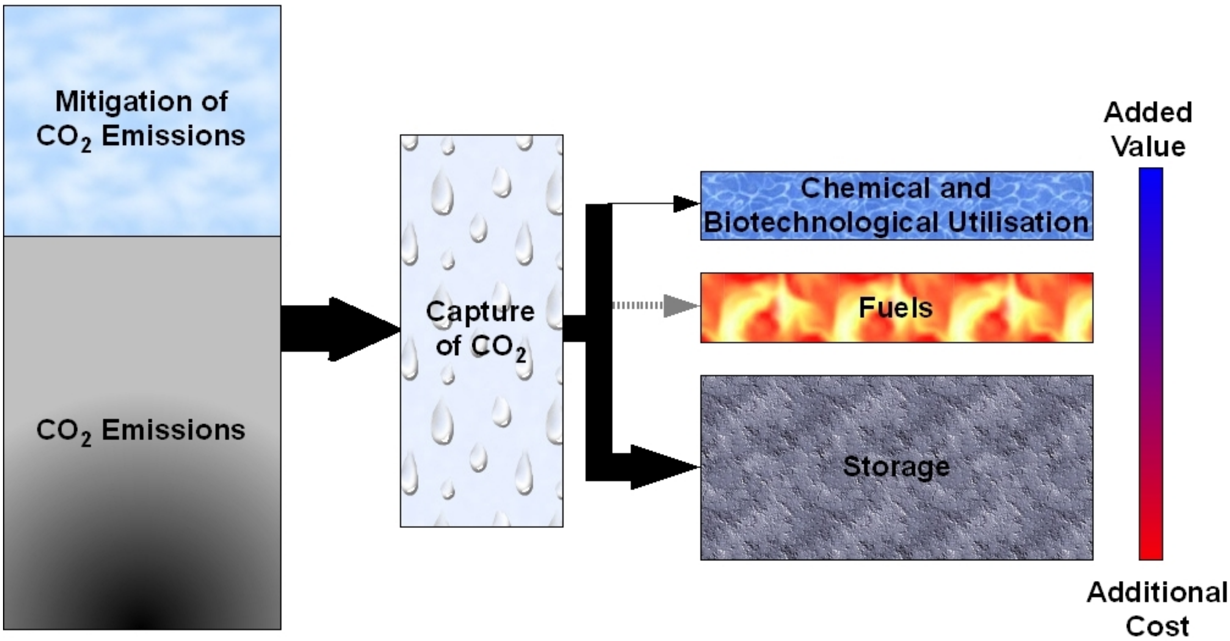


Figure 1: Options for CO_2 management: mitigation should have priority over all other options. The arrows represent CO_2 material flows: after capture and purification CO_2 can be utilised or stored. Processes that create value take precedence over those that do not. Utilisation as fuel is only meaningful provided that hydrogen is available from renewable sources or nuclear power.

3.) Any storage option for CO_2 involves an additional – in some cases, a substantial – energy input. When reviewing the various storage options, the starting point is society's readiness to bear the additional energy costs in return for the mitigation of atmospheric CO_2 emissions. Every CO_2 storage strategy must be measured against the following criteria:

- Potential volume of CO_2 to be stored
- Amount of energy required (and the amount of additionally produced CO_2)
- Storage time (time horizon for CO_2 removal from the atmosphere)
- Costs, including follow-up costs
- State of the technology
- Public acceptance of the process
- The time frame for the process to achieve industrial maturity and the anticipated research and development required (chemical engineering aspects, capture, purification and storage).

Public acceptance of CO_2 storage will play a pivotal role: underground CO_2 storage facilities close to populated areas could encounter massive public resistance.

Moreover, in contrast to CO_2 utilisation approaches, most CCS strategies do not create added value. Exceptions include processes for enhanced oil/gas recovery, enhanced coal-bed methane production and the potential extraction of methane from methane hydrate in deep-sea sediment by CO_2 exchange.

4.) Chemistry can make considerable contributions to cost-effective technical implementation of CCS technologies (e.g. flue gas scrubbing, CO_2 absorption and chemical looping).

5.) The conversion of CO_2 into a storable product must fulfil the criterion of removing more CO_2 from the atmosphere than is released by the additional energy required for conversion and storage.

6.) Chemical utilisation of CO_2 as a building block for chemical synthesis has to stand the test of the following criteria:

- Energy and CO_2 balances of the process
- Value-added generated
- Process alternatives
- Product properties

Options by which, in comparison with the state-of-the-art, more CO_2 is released than they convert do not achieve the goal of a reduction of CO_2. If this is borne in mind, CO_2 can be used as a building block for chemical synthesis and is viable from both an economic and a technical point of view. The existing technical process used should serve as the reference. Given these framework conditions, the following aspects are important:

- The production of high-value products can create added value; this can make a process economically self-supporting (in contrast to all pure storage strategies).
- CO_2 can serve as a source of carbon, thus reducing input from other carbon sources.
- The chemical utilisation of CO_2 could form part of an overall strategy to reduce CO_2 emissions.

7.) The sources of CO_2 in the required purity and amount for chemical utilisation can be provided from sources other than flue gases from power plants. Nevertheless, the chemical utilisation of CO_2 will not make any significant contribution towards reducing CO_2 emissions in the foreseeable future.

8.) The future of chemical utilisation of CO_2 on an industrial scale depends on the availability of non-fossil energy sources.

5 *Identification of research needs*

The **mitigation of CO_2 emissions** should be the target of all CO_2 management strategies. The same holds for the respective research and development initiatives. However, mitigation strategies are explicitly not the subject of this paper. The research needs identified in this chapter are complementary to activities in the area of CO_2 emission mitigation, they do not compete with them.

The processes for utilisation and storage of CO_2 under discussion are in different stages of their technical development. In some cases there is still a **considerable need for more research and development**. Germany is leading-edge in the advancement of existing processes and research into novel options due to its strength in the necessary core disciplines: process engineering, catalysis and synthetic chemistry, among others.

5.1 CO_2 capture

Economically sustainable capture and purification are a prerequisite for further utilisation or storage of CO_2 from flue gases. Purification needs to take into account the required quality standards of the subsequent process. Separation and purification are energy-intensive steps, thus the **optimisation of existing systems** and the **development of new processes** aimed at **reducing energy needs** are of utmost importance.

From an economic standpoint, the feasibility of absorption capture processes is determined on the one hand by the lifetime of the absorption substances used (especially under conditions of a flue gas atmosphere in post-combustion set-ups), and on the other hand by the energy required for their thermal regeneration. Further research and development should target suitable **absorption media and mixtures** thereof with **significantly enhanced lifetime**, **faster loading and unloading capabilities** and **reduced heat requirements for regeneration** to compete against existing systems.

Current concepts for processes in the field of chemical looping combustion are promising. This requires the **development** of suitable, **highly selective oxygen carriers with good long-term stability** and satisfactory resistance to abrasion under high turnover conditions. On the chemical engineering side, development should focus on cycling the **solid looping substance** between the reactor and the regenerator with separation on the gas side and on reducing abrasion of the oxygen carriers to a minimum. These concepts then have to be scaled up to **pilot plant level** to demonstrate the proof-of-concept on a technically relevant scale.

Research on oxyfuel processes should address replacing cryogenic air separation by **oxygen transport membrane technology**; this is a prerequisite for its economic feasibility.

In addition to the capture methods discussed, emphasis should be placed on **further developing methods of pre-cleaning flue gas** in order to optimise the separation step, while obtaining CO_2 as efficiently as possible and in the required purity for the subsequent steps (transport, and utilisation or storage).

5.2 Utilisation of CO_2

Chemical utilisation of CO_2 is mainly limited by its low energy content. The **investigation and refinement of potential routes for CO_2 activation** is essential to the further development of its chemistry. This also entails evaluating the upstream and downstream processes, e.g. the intelligent production of reactants with high-energy content. Another focus of the work should be research on product properties. This involves investigating the **material properties** of target products from copolymers that can already be produced with CO_2 and of potential **novel, complex polymers** together with an evaluation of their **marketability**. Life-cycle assessments with CO_2 balances must be performed for all these products.

To boost the chemical use even of less pure CO_2, efforts are needed to develop efficient, robust catalysts that are less susceptible to catalyst poisoning.

New strategies for using CO_2 as a C1 building block represent long-term research goals, often referred to as ‘dream reactions’, such as **hydrogenation to produce long-chain alcohols**, **hydrocarboxylation of ketones and imines**, **isocyanate and carbamine conversion**, and **olefin copolymerisation**. To date, these products cannot be produced, or only with insignificant yields. Catalysis holds the key to these targets.

In the long run, the most attractive variant is **photocatalytic activation** of CO_2, since it inherently uses sunlight as a renewable source of energy. Basic research should concentrate on this field of photocatalysis together with **photocatalytic water splitting**.

Currently any evaluation of the options for the biotechnological utilisation of CO_2 via microalgae is thwarted by the lack of **reliable data**. The collection of these data is indispensable to an assessment of their potential.

Since data on existing microalgae are negligible, extensive **taxometric studies** and **targeted screening of naturally occurring algae strains** are essential.

At this point in time many challenging chemical engineering aspects concerning the utilisation of microalgae still remain to be solved. The **development of a robust downstream process chain** must be prioritized to facilitate their use on a technical scale. This also applies to **integration in modern biorefinery concepts** with utilisation of residual biomass in biogas plants. These different process chains need to be evaluated on the basis of a **comprehensive life-cycle assessment**.

5.3 Storage of CO_2

The storage of CO_2 in geological formations calls for an **inventory of geological criteria** and their **independent validation**. This is crucial in terms of public acceptance.

The future extraction of methane from methane hydrates by CO_2 exchange appears particularly promising since it creates value. Besides the **exploration of geological sites**, research should be intensified on **process options on laboratory and pilot scale**. Furthermore this should be complemented by refining processes to convert methane on-site into transportable liquid fuel by **gas-to-liquid technology (GTL)**.

Thanks to its harmless end-products, mineral carbonation has met with relatively wide public acceptance and should be pursued as an alternative storage option. In addition to **optimising the process parameters**, further technical development should rapidly switch to a demonstration of the **proof-of-concept** in a pilot plant to permit a **sound evaluation** of the process. This should include an energy balance incorporating the preceding energy-intensive process steps, particularly the milling of the oxide reactant. An energy balance is crucial to establishing the eligibility of mineral carbonation as a storage option. An alternative possibility would be to evaluate the **use of fly ash**; admittedly this would eliminate the milling step, but at the same time it would significantly reduce the quantity of CO_2 to be stored.

5.4 Life-cycle assessment

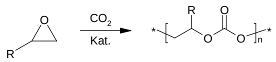
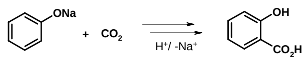
To make an informed choice between various technologies it is essential to have an objective, commensurable evaluation which takes into account all the preceding and succeeding steps. This requires on the one hand **valid data**, which for many of the options discussed do not exist, and on the other the **further development or adaptation of LCA methods**. Comparability of the assessments necessitates the **precise determination of the system boundaries** of all the technological options, reflecting **the variation of time horizons for CO_2 storage**.

6 Appendix

6.1 Overview: options for CO_2 capture

Option	Absorption processes	Chemical looping	Membrane processes	Adsorption processes	Oxyfuel
Additional energy requirement	High (15-20% of a power plant output)	High (15-20% of a power plant output)	Not known	High (20% of a power plant output)	Currently very high due to cryogenic air separation
Cost	>20 €/t CO_2 (capture)	Not known	Not known	Not known	Not known
State of technological development	Already used in industry	First pilot trials	Laboratory scale	First pilot trials	Concepts and pilot trials
Time horizon	Medium-term	Long-term	Long-term	Long-term	Medium-term
Research requirements	Absorption media: - improved life time - rapid loading and unloading - reduction of heat requirements for regeneration	- Development of highly selective oxygen carriers with good long-term stability - Concepts for cycling solids with minimum loss of material - Transfer to pilot scale	- Development of robust membrane processes for CO_2 capture	Adsorption media: - improved life time - rapid loading and unloading	- Development of robust membrane processes for air separation (oxygen transport membrane)
	-Refinement of flue gas scrubbing techniques				

6.2 Overview: options for CO_2 utilisation

Option	Polymer synthesis	Fuel synthesis	Chemical synthesis	Microalgae	Artificial photosynthesis
Potential quantities	e.g. For polycarbonates 50 kt a^{-1}	max. 2.05 Gt CO_2 a^{-1}	max. 178 Mt CO_2 a^{-1} e.g. urea 94 Mt a^{-1}	Limited by area requirements, < 5% of a given power plant, with max. area of 25kt/km^2	Not known
Examples	e.g. Polycarbonates 	e.g. Methanol production via dry reforming $CH_4+CO_2 \rightarrow 2CO+ 2H_2$ $CO+2H_2 \rightarrow H_3COH$	e.g. Synthesis of urea: $2NH_3 + CO_2 \rightarrow CH_4N_2O$ e.g. salicylic acid 		Not known
Additional energy requirement	Process-oriented	High, only meaningful if renewable energy sources or nuclear power are used	Process-oriented	Solar power input and process energy	Solar power input and process energy
Overall CO_2 balance	Depending on the process compared to the reference process	Net emissions, if H_2 is not available from renewable sources or nuclear power	Depending on the process compared to the reference process	Net emissions	Not known
Cost	Reference: existing technical process	Reference: fossil fuel and bio-based fuels	Reference: existing technical process	0.40 – 2.50 € /t algae biomass [4]	Not known

[4] Biotechnology Advances 25 (2007)294–306

State of technological development	Technically implemented examples (see e.g.) and exploratory routes	Some process steps in industrial application, pilot plants under development (e.g. Mitsui Chemicals)	Technically implemented examples (e.g. salicylic acid, urea) + exploratory routes	Raceway ponds and algae photobioreactors state of technology, but low-tech and cost-intensive; considerable efficiency increases possible	Basic research
Value creation	Polymers	Fuels	Chemicals	Fine chemicals, fuels, biogas	Chemicals
Time horizon	In development	Partial implemention	Individual applications	Individual applications on pilot scale	Not known
Research needs	- Develop potential reaction routes - Intelligent synthesis of highly reactive molecules - Analysis of products' marketability	- Catalysis	- Establish potential of 'dream reactions' - Catalysis - Development of possible reaction routes	- Reliable data collection of process parameters - Taxometric screening of natural algae strains - Development of robust downstream processes - Integration into biorefinery concepts	- Photocatalytic activation of CO_2 - Photocatalytic water splitting
	Life-cycle assessment methods				

6.3 Overview: options for CO_2 storage

Option	Geological storage	Methane hydrates	Mineral carbonation
Potential quantities	High, 100% of captured CO_2 emissions of a power plant	Not known, estimated to be high	High, 100% of captured CO_2 emissions of a power plant
Additional energy requirement	Additional energy required for CO_2 transport and injection	Not known	Currently 30% of power plant output
Storage time	Depending on storage; approx. 1000 a	Dependent on oceanographic conditions, approx. 1000 a	Mineral storage, geological time scale
Cost	> 10 €/t CO_2 (storage)	Not known	> 55 €/t CO_2 (storage)
State of technological development	Pilot trials; industrial scale 2020 at the earliest	Research and development stage	Research stage
Value creation	None, few exceptions (EOR, EGR)	Methane	None
Public acceptance	Problems foreseen for underground storage in densely populated areas	Neutral if far away from the coasts	Neutral, harmless storage products
Time horizon	Medium-term	Long-term	Long-term
Research needs	- Collection and independent validation of geological criteria	- Geological exploration of storage sites - Development of extraction process - Development of efficient gas-to-liquid (GTL) technology	- Optimisation of process parameters - Evaluation of the process, including comprehensive energy balance - Proof-of-concept on pilot scale using fly ash