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ABSALT: Accelerating Basic Solid Adsorbent Looping Technology



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The authors bear the entire responsibility for the content of this report and for the conclusions drawn therefrom.



Zusammenfassung

Das ABSALT-Projekt beabsichtigt, die Integration der Silica-Polyethylenimin-basierten CO₂-Abscheidungstechnologie in ein Zementwerk umfassend zu verstehen. Die Ziele des Projekts sind die Optimierung der Silica-PEI-Zusammensetzung, die Entwicklung von Regenerationsstrategien für Silica-PEI und die Untersuchung der Skalierung der Produktion von Silica-PEI. CEMEX ist direkt an den technoökonomischen und LCA-Studien beteiligt.

Bisher zeigen technisch-ökonomische Ergebnisse, dass, obwohl eine Vorbehandlung der Abgase in Betracht gezogen werden sollte, um die Temperatur-, NO_x- und SO_x-Anforderungen zu erfüllen, die Technologie mit dem MEA-System konkurrieren kann, da CO₂ an den Partikeln adsorbiert statt absorbiert wird (wie im MEA-System), was zu einem geringeren Energiebedarf für die Regeneration führt. In Bezug auf LCA wurde die Zusammenstellung der Input- und Output-Inventardaten abgeschlossen und vorläufige Ergebnisse werden Anfang 2023 erwartet.

Die nächsten Schritte werden die techno-ökonomischen Simulationen weiter optimieren und die LCA-Bewertung vervollständigen.

Résumé

Le projet ABSALT vise à comprendre en profondeur l'intégration de la technologie de capture du CO₂ à base de silice-polyéthylèneimine dans une cimenterie. Les objectifs du projet sont d'optimiser la composition silice-PEI, de concevoir des stratégies de régénération de la silice-PEI et d'étudier la mise à l'échelle de la production de silice-PEI. CEMEX est directement impliqué dans les études technico-économiques et l'évaluation du cycle de vie.

Jusqu'à présent, les résultats technico-économiques montrent que, même si un prétraitement des gaz d'échappement doit être envisagé pour répondre aux exigences de température, de NO_x et de SO_x, la technologie peut concurrencer le système MEA, puisque le CO₂ est adsorbé sur les particules au lieu d'être absorbé (comme c'est le cas dans le système MEA), entraînant une baisse de la demande d'énergie pour la régénération. En ce qui concerne l'évaluation du cycle de vie, la compilation des données d'inventaire des entrées et des sorties est terminée et les résultats préliminaires sont attendus début 2023.

Les prochaines étapes permettront d'optimiser davantage les simulations technico-économiques et d'achever l'évaluation de l'évaluation du cycle de vie.



Summary

The ABSALT project intends to deeply understand the integration of the Silica- Polyethylenimine based CO₂ capture technology into a cement plant. The project's objectives are to optimise the silica-PEI composition, to devise regeneration strategies for silica-PEI and to study the scaling up production of silica-PEI. CEMEX is directly involved in the techno-economic and LCA studies.

So far, techno-economic results show that, although a pre-treatment of the exhaust gases should be considered to meet temperature, NO_x and SO_x requirements, the technology can compete with MEA system, since CO₂ is adsorbed on the particles instead of absorbed (as is in MEA system), leading to lower energy demand for regeneration. Regarding LCA, the compilation of input and output inventory data has been completed and preliminary results are expected in early 2023.

Next steps will further optimise the techno-economic simulations and complete LCA assessment.



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CCGT: Combined Cycle Gas Turbines

Cf.: Concentration Factor

LCA: Life Cycle Analysis

LCI: Life Cycle Inventory

MEA: Monoethanolamine

MW: Molecular Weight

PCC: Post-combustion CO₂ capture

PEI: Polyethylenimine

SALT: Solids Adsorption Looping Technology

SPEI: Silica- Polyethylenimine

TEA: Techno-economic analysis

Base Case Plant – Simulation Plant (all values taken from simulation)

Reference Cement Plant – Cemex Plant (all values taken from data provided by Cemex)



1 Introduction

1.1 Background information and current situation

Of the CO₂ capture technologies currently being developed, amine scrubbing is the most mature having been adapted from natural gas separation. However, it has drawbacks, including high energy demand for regenerating the solvent and reactor corrosion, which are not completely solved by using mixed amines rather than monoethanolamine (MEA). These factors result in relatively high capture costs and this has catalysed the development of alternative or second-generation technologies (IEAGHG, 2018; Gardarsdottir et al., 2019). Although showing considerable promise, solid adsorbents are still at a relatively earlier stage of development and have not been investigated extensively at pilot-scale and demonstration scale.

Silica-PEI has received considerable attention as the leading candidate amongst strong basic adsorbents for both PCC and air capture, with a vast literature covering the impact of silica and PEI properties and composition and additives to improve kinetics and stability, which is summarised under “state of the art” in Section 3. The driving force behind the vast research effort on silica-PEI is the potential to reduce regeneration energies compared to advanced MEA and other amine systems. Regeneration energies have been calculated to be 2.5 GJ/tCO₂ for both coal and natural gas power plant using conservative operating parameters (Zhang et al. 2016, 2017), including a dynamic adsorption capacity of 5% compared to 3.3 GJ/tCO₂ for advanced MEA systems (IEA, 2011; Abu-Zahra et al., 2007; Li et al. 2016). This reduces to 2.2 GJ/tonne CO₂ if the dynamic working capacity can be increased to 7% and this translates into efficiency improvements of over 2%, as was demonstrated in the pilot-scale testing to date by UNOTT (Kim et al., 2019 and 2021).

The key challenges to the successful implementation of silica-PEI in SALT, at demonstration level and then commercially are addressed fully by the project objectives and the targets set. Firstly, maximising the working dynamic CO₂ adsorption capacity at high capture efficiencies and, secondly, keeping the adsorbent replacement costs below ca. 10 € per tonne of CO₂ captured, comparable to those for MEA in amine scrubbing, require the scientific and technical challenges of improving the stability of silica-PEI to be met. This translates to increasing adsorbent lifetimes to approaching 12 months, assuming conservative performance parameters. Thirdly, can costs be reduced further by addressing the scientific challenge of recovering the silica from spent adsorbent and converting the spent PEI to chemical feedstocks? The economic challenge of obtaining reliable estimates of material replacement costs that will arise from meeting the scientific and technical challenges. This will be met by conducting comprehensive TEA and LCA of SALT (WP6 and 7).

1.2 Purpose of the project

Although considerable attention has been given to silica-PEI sorbents for the post-combustion CO₂ capture process, no work has been conducted on its potential application on a commercial scale in the cement industry, even though it could be a solution to decarbonize the cement process. This project provides a detailed insight into the energy penalty reduction, the environmental performance improvement and costs savings by integrating the Silica-PEI based CO₂ capture technology into the cement plant. The work is of interest for cement manufacturers, who can get an idea of the real cost and performances of retrofitting CCS solutions to the cement plant, but also to policy makers, who can find benchmarking of CO₂ emissions and cost of carbon capture and storage in cement plants and understand the opportunity to eventually support the technical solution.



The key drivers to the successful implementation of silica-PEI in SALT (solids adsorption looping technology) are:

- 1) Maximizing the working dynamic CO₂ adsorption capacity at high capture efficiencies.
- 2) Keeping the adsorbent replacement costs below ca. 10€ per ton of CO₂ captured, which will be comparable to those for MEA in amine scrubbing.

Our goal is to demonstrate that basic silica-PEI in solids adsorption looping technology (SALT) can achieve low capture costs. This will involve optimising the silica-PEI composition to minimise the adsorbent replacement cost and regeneration energy, with the extensive pilot-scale testing programme and the techno-economic and life cycle analyses providing the platform for accelerating SALT with silica-PEI to full demonstrations.

1.3 Objectives

The overall aim of the proposed two-year research project is to accelerate the development of SALT by optimising silica-PEI composition, to achieve low costs comparable to other capture technologies. This will be accomplished by maximising the dynamic CO₂ adsorption capacity in continuous operation, which will reduce the regeneration energy to approach 2.0 GJ/ton CO₂.

$$\text{dynamic sorption capacity (wt,\%)} = 100 \times \frac{\text{captured CO}_2 \text{ mass flow rate at the sorption reactor (kg/h)}}{\text{solid circulation rate (kg/h)}}$$

The specific objectives are:

(i) To optimise the performance of silica-PEI in terms of the working dynamic CO₂ adsorption capacity and the physical and chemical stability with respect to flue gases representing PCC from industrial processes, such as cement and lime production. This will first involve modifying PEI for optimal stability whilst maintaining high adsorption capacities and investigating a few silicas at a laboratory-scale in work packages (WPs) 1-3. The optimum silica-PEI formulations will then be evaluated using the SALT pilot-scale facility available at UNOTT.

(ii) To devise regeneration strategies for silica-PEI so that the silica can be recycled and, when PEI degrades, it can be pyrolyzed to yield platform chemicals. This new approach will involve a detailed mechanistic study of PEI degradation, optimising the production of amines and other N-containing organics that potentially have high market value (WP5).

(iii) To scale up production of silica-PEI to ca. 100 tons for future demonstrations operating at 10 MWe equivalent, comprehensive techno-economic analysis (TEA) [9] and life cycle analysis (LCA) of SALT are conducted, including the material replacement costs (WP6 and 7, with CEMEX involvement). The information will be used to obtain an initial high-level design of a demonstration facility for a cement/lime plant as a platform to accelerate SALT with silica-PEI to TRLs of 7/8.

Achieving the above objectives will enable SALT to be bench marked in relation to amine scrubbing and oxyfuel combustion, both for natural gas CCGT power plants and cement//lime production and provide the platform for taking silica-PEI SALT to full demonstrations.

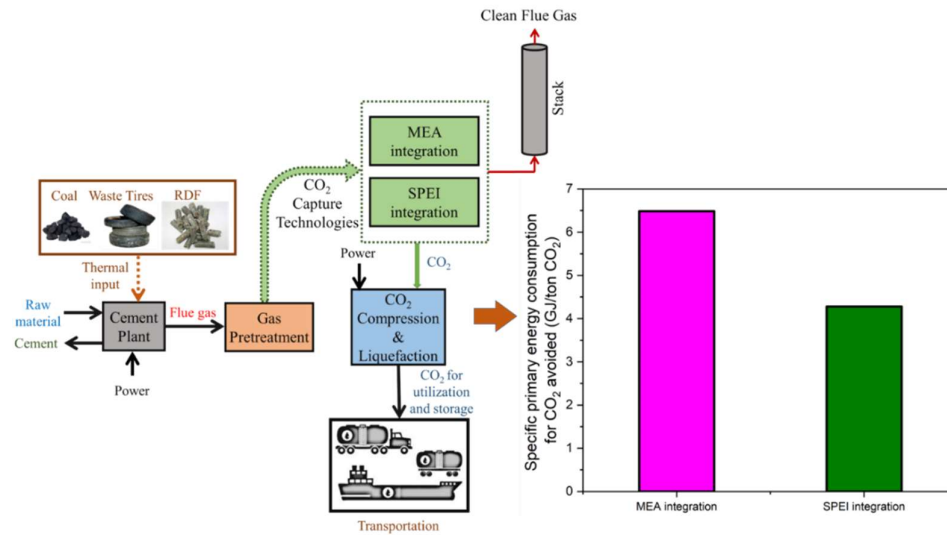


Figure 1. Comparison between the MEA and SPEI integration in Cement Plant [9]

2 Description of facility

Pilot-scale testing will be conducted using 5, 20 and 100 kg quantities of silica-PEI in the facilities at UNOTT (University of Nottingham) and KIER (Korea Institute of Energy Research). All the samples will be produced at UNOTT, 5 and 20 kg batches will be tested onsite, and 100 kg batch will be sent and tested at KIER. The sorbent based on PEI is essentially composed of a silica support material that has been impregnated with PEI and utilized in a circulation fluidized bed or bubbling fluidized bed reactor for CO₂ capture. The design and arrangement of the fluidised beds is similar in the different units. Figure shows the schematic diagram of the units comprising a bubbling fluidized-bed type sorption reactor, a bubbling fluidized-bed type desorption reactor, and a cyclone for separating gas and solids. For adsorption, a circulating fluidized bed can also be used, and this has the advantage of greater throughput with more rapid solid circulation. For solids handling, a transport system was placed to circulate adsorbents from the sorption reactor to the desorption one. The solid circulation rate is controlled by manipulating rotary valves. The rigs have gas recirculation systems for the CO₂-rich gas discharged from the desorbers. The unit at UNOTT, operating with 5 kg (bubbling bed adsorber) and 20 kg (circulating bed adsorber), and the 100 kg at KIER [1] with a bubbling bed adsorber are shown in 2(b) and (c), respectively. The rigs can run on both actual and simulated flue gas.

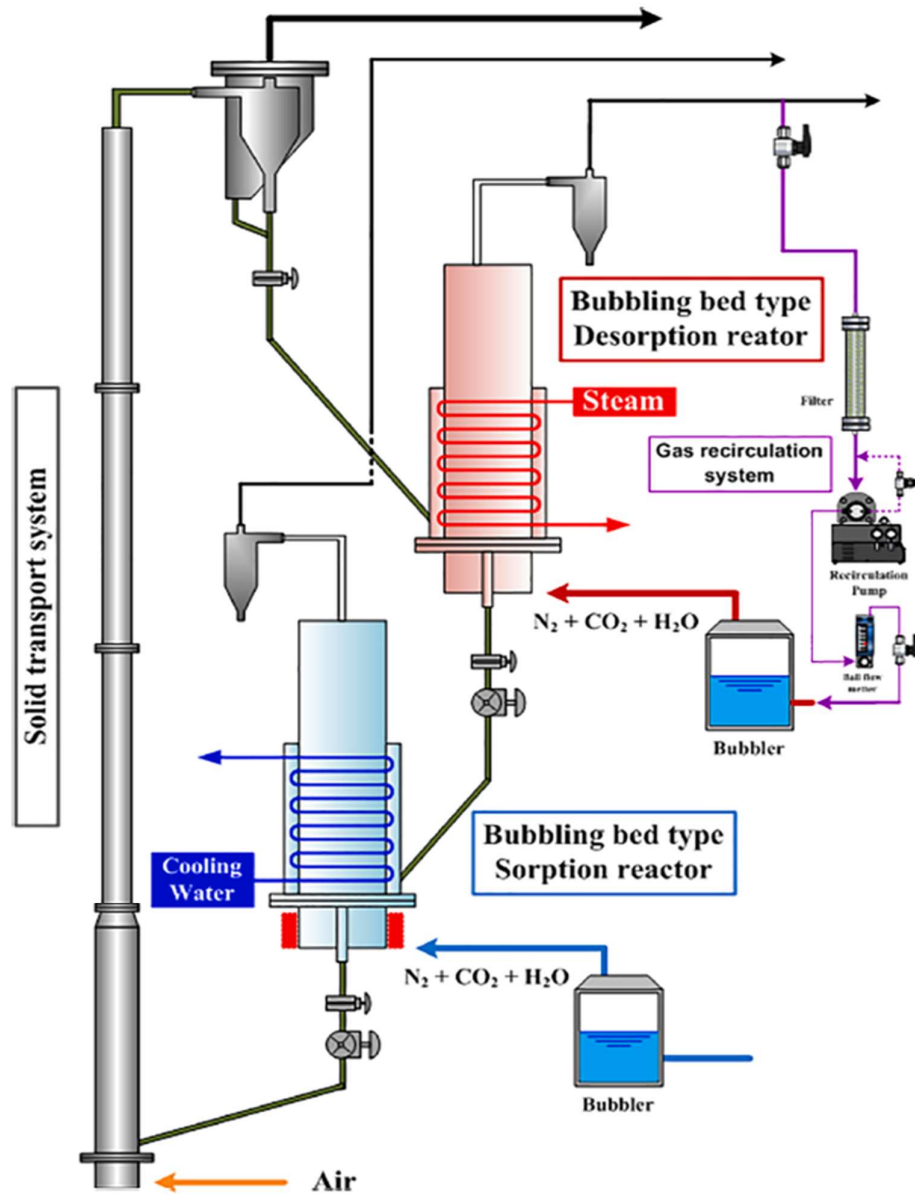


Figure 2 - (a) Schematic of SALT pilot facility [1]



Figure 2 - (b) Pilot unit at UNOTT for 5 and 20 kg of adsorbents and (c) unit at KIER for 100 kg adsorbent [9].

Process modelling, techno-economic evaluation of full-scale process integration for the integrated cement plant with ABSALT CO₂ capture was conducted by CERTH, CEMEX and ULSTER by using **Aspen Plus™** and **ECLIPSE** simulation software.

Environmental Assessment via Life cycle Analysis (LCA) and Project Risk Assessment was performed by ULSTER, CEMEX and CERTH by using **SIMAPRO™** and **RISK 8™** software.

3 Procedures and methodology

The proposed methodologies to achieve the successful outcomes of ABSALT by meeting the project objectives combine expertise in different areas. These, which comprise the technical WPs 1-7, are shown below:

1. Silica preparation and properties (WP1).
2. PEI preparation and properties (WP2).
3. The expertise on mixing, additives and PEI composition will be combined to optimise the composition of silica-PEI at a laboratory-scale for the pilot-scale tests (WP3).
4. SALT Pilot-scale testing (WP4). The test programme using the optimised silica-PEI from WP1-3 will meet the objective of optimising the performance of silica-PEI in terms of the working dynamic CO₂ adsorption capacity and the physical and chemical stability under flue gas conditions.



5. Pyrolysis of silica-PEI where initial findings described for WP5 have established the feasibility of this route to recover and recycle silica and potentially derive valuable (platform) chemicals from the PEI degradation products.

6. Techno-economic analysis (TEA) of CO₂ capture process was performed in order to benchmark ABSALT against other capture technologies, with the focus being on cement manufacture and to complete a high-level design for a demonstration plant (WP6). Detailed boundary assumptions for TEA and LCA are going to be described in the deliverable report D6.1, some information is already publicly available in the accepted paper [9]. The KPIs will be: TEA-CO₂ emission rate, specific primary energy consumption for CO₂ avoid (SPECCA), breakeven selling price (BESP) of Clinker/Cement; CO₂ avoidance cost, etc. LCA Endpoint and Single Score Results- ecosystem, resources and human health. Midpoint single indicator global warming, fossil resource scarcity and mineral resource scarcity.

7. The environmental impact assessment associated with ABSALT process integrated with cement plants is performed through life cycle analysis (LCA) in WP7, to evaluate the environmental aspects, global warming potential and sustainability, using the commercial software SimaPro™ (in compliance with ISO 14040-14044 standards). The environmental benefits to be identified are linked to the capture of CO₂ emissions in a cement plant. To ensure consistency with LCA, the following approaches are adopted: 1. comprehensive process modelling 2. detailed mass and heat balance. 3. data validation using test results and real process information. 4. using dedicated LCA software (for this study, the SimaPro software is used. The ISO 14040 series is specific to LCA. ISO 14000 series is a set voluntary environmental management standards, guides, and technical reports, in which ISO14040 sits.) comparing with the data derived from published results and literatures.

4 Activities and results

4.1 Summary of activities in WP1 and WP5 performed to date

WP1: Silica selection and properties (PQ Corp.)

- In total, 7 silicas were selected, including one silica of biogenic origin with lower greenhouse gas footprint.
- Extensive testing of those silicas is progressing in WP3, including testing with normal PEI. Maximum loadings have been identified.
- A third-party will perform explosivity testing on the silica-PEI.
- PQ Silicas has the capability to prepare mix silica and PEI at a scale of up to 100 kg, although only 5-10 kg is currently needed for pilot-scale testing. The silica and alkoxyated PEI to be used for the first large-scale batch will now be selected.

WP2: PEI preparation and properties (BASF)

- Initially, BASF has supplied 14 samples of alkoxyated PEI for testing at UNOTT. After, BASF has supplied 17 samples (2 patents have been filled by Prof. Snape (UNNOT) and BASF) more of alkoxyated PEI for further testing at UNOTT. The samples are mainly based on the PEI with a molecular weight of ca. 800. The results are described under WP3.
- BASF has provided 3 kg of an alkoxyated PEI for the first large batch (5 kg) preparation.
- Alkoxyated PEI synthesis without organic solvents and with no or 50% water has been demonstrated and viscosity appears not to be an issue. When methanol is used as a solvent, it competes in the alkoxylation and reacts with propylene and butylene oxides; Bu and residual levels of the alkylnoxide (2000 ppm) are evident.



- Performance with respect to CO₂ uptake and oxidative stability tests on these samples is underway at UNOTT (WP3).
- Currently the final selection is between 3 candidates.
- 20-40 kg max may be produced on lab scale in multiple runs which is enough for the pilot scale testing.

WP3: Silica-PEI screening (small-scale tests, UNOTT)

- To accelerate degradation, the oxidation temperature has been increased from 70 to 80°C (10 days). This has been used to (i) provide a detailed comparison of the FG and G100 PEI samples and (ii) test the latest batch of 17 alkoxyated PEIs (FG PEI) from BASF. The 17 samples investigated were impregnated onto the reference silica to give a PEI loading of 45% w/w.
- Alkoxyated PEIs degrade much more slowly than normal PEI, but the rate of degradation is dependent on several factors, including PEI MW, the degree of alkoxylation and whether antioxidants are used.
- Tests were conducted at 25, 30, 40, 50, 60, 70 and 75 °C to identify the optimal temperatures for the FG PEI and 17 alkoxyated samples.
- The results confirmed that G100 PEI is more stable than the FG sample for all the PEI loadings tested, although G100 has a lower equilibrium uptake than FG (12 cf. 14% w/w in 15% CO₂).
- For the alkoxyated FG PEIs, the rate of degradation is considerably slower and decreases with increasing alkoxylation. Further, alkoxylation shifts the maximum CO₂ uptake to lower temperatures which also reduces the desorption temperature needed to release the CO₂.
- Only a few further alkoxyated PEIs remain to be tested to finalise the decisions for scale-up.

WP4: Pilot-scale testing (UNOTT)

- Commissioning of the pilot-plant for the large-scale tests has commenced.
- Part of the commissioning of the pilot-plant has been delayed due to the company who constructed the rig having personnel shortages. The first commissioning tests with normal silica-PEI will investigate stability at 60-70°C high humidity conditions, typical of industrial flue gases.

WP5: Regeneration strategies for PEI (UNIBO, CERTH).

- UNIBO has developed analytical procedures for analysing water-soluble products and condensates. As previously reported, sonification in methanol is being investigated for the extraction of oxidised PEI from silica to facilitate characterisation.
- UNIBO is analysing the dark and light liquid products provided by CERTH from their pyrolysis experiments. Progress on the quantification of the dominant pyrazines was summarised.
- A researcher has been recruited for the pyrolysis plant experiments at UNIBO.
- The pyrolysis experiments at CERTH are on-going with normal and oxidised PEI being compared and slower heating rates being used.
- Catalyst testing at CERTH is also underway using zirconia, titania and magnesium oxide, basic catalysts giving lighter, less viscous products.
- Liaison with BASF will start on pyrolysis products, to ascertain which have potentially the greatest commercial value.
- Py-GC-MS has shown that high temperatures and the presence of silica favours the formation of pyrazines. Besides pyrazines, other aromatic amines were formed, among these are alkylated pyrroles and imidazoles. Aliphatic acyclic oligomers and piperazines are evident for low molecular weight PEI.



- UNIBO has characterised 8 of the dark and light liquid products provided by CERTH from their pyrolysis experiments and pyrazines dominate in all the samples.
- Overall, there is quite a high similarity between the fixed-bed pyrolysis products provided by CERTH and the flash heating Py-GC-MS experiments at UNIBO.
- Sonification in methanol is being investigated as an alternative to pyrolysis for the removal of oxidised PEI from silica. A significant fraction of the more highly oxidised PEI is not extracted. For the PEI extracted, the viscosity increases with oxidation. Further, FTIR and ¹³C NMR analysis has indicated the preponderance of oxygen functional groups in the oxidised PEI.
- At CERTH, the characterisation of the silica-PEIs supplied has been completed, including textural properties. For the silicas, differences between samples were as expected.
- Fast and slow pyrolysis of silica-PEI has been confirmed in the fixed-bed reactor operating at 600°C with 5 g of sample. Generally, the differences in product distribution were relatively minor with slow heating favouring monomeric products, including pyrazines.
- Comparison of fresh and oxidised PEI has indicated the fresh sample gives more of the lighter liquid phase product.
- Catalyst screening at CERTH has been carried out in the fixed-bed reactor using zirconia, titania and magnesium oxide. The catalysts generally reduce liquid and increase gas yields. However, the proportions of monomeric products, including, pyrazines increase. Further, absolute yield of pyrazines appears to increase.
- Liaison with BASF will start on the values of the pyrolysis products, particularly pyrazines, as to their potential commercial value.

4.2 Summary of activities in WP6 and WP7 performed to date

Within the ABSALT project, CEMEX is engaged in WP6 (Techno-economics/high level plant design) and WP7 (Environmental and project risk assessments), involved in the tasks related to process definition, system integration and operational risk assessment.

1. CEMEX has provided Raw meal chemical composition and raw mix proportions as well process information like fuels composition, fuel consumptions, heat demand, clinker production and raw meal consumption, flue gases, emissions, etc. related to a 3200 ton per day clinker plant.
2. The process definition for the full-scale cement integration has been completed. The size of the pilot plant corresponds to 5 to 10 MW of electricity. Industrial application would require 10 to 12 units, as in the case of the base line pilot plant. The energy integration will be a challenge of the project: recovering the waste heat from the process using heat exchangers;. Transferring the heat recovered to the stripper using fluidised bubbling beds. Regarding technical analysis we develop process models and generate detailed mass and energy balance. To optimise the process an exergy analysis will be carried out.
3. The deliverable report of operating conditions has been submitted.
4. Detailed process modelling and simulation was carried out and the results were generated.
5. A technical analysis has been carried out (including the calculation of specific CO₂ emissions, SPECC, CO₂ avoidance cost, etc.) and is already in the process of review for released to the public [9].



WP6: Comparative techno-economic analysis of the integration of MEA-based scrubbing and Silica PEI adsorbent-based CO₂ capture processes into cement plants

- The base case cement plant simulation has been completed with the results being close to an actual plant (data from CEMEX) with differences no more than 7%.
- Modelling of the integration of the cement plant with both SALT and amine scrubbing has also been completed and this has been supported by a steady-state mathematical model (steady state) for the adsorber and desorber in SALT.
- The benefits of SALT in terms of lower operating costs compared to advanced amine systems have been demonstrated with the cost of CO₂ removal estimated at 42€ per tonne for a cement plant is lower than that of amine scrubbing. However, a sensitivity analysis is on-going with key parameters relating to performance being evaluated such as the rate of replacement of adsorbent where rates of ca. 0.01% per hour are realistic based on stability results obtained.[9]

WP7 Environmental Assessment via Life Cycle Analysis (LCA) and Project Risk Assessment

- Initial LCA has showed how clinker production and heat recovery for the base case cement plant can affect CO₂ emissions and the potential health advantages that silica-PEI and alkoxylated PEI have over amine scrubbing. Data for the calculations was taken from base case cement plant and reference cement plant.



4.3 ABSALT integration into a cement plant

ULSTER, CEMEX and UNOTT provided the basis of design and the boundary conditions for WP6 and WP7. Figure 3 shows an integration of the ABSALT process into a cement plant.

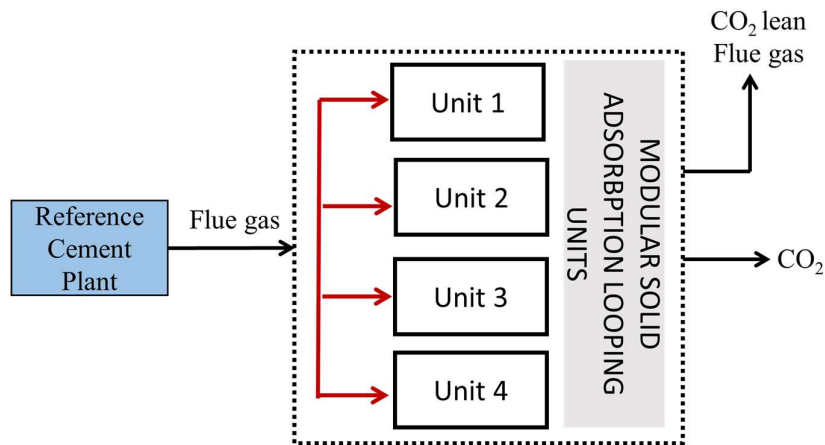
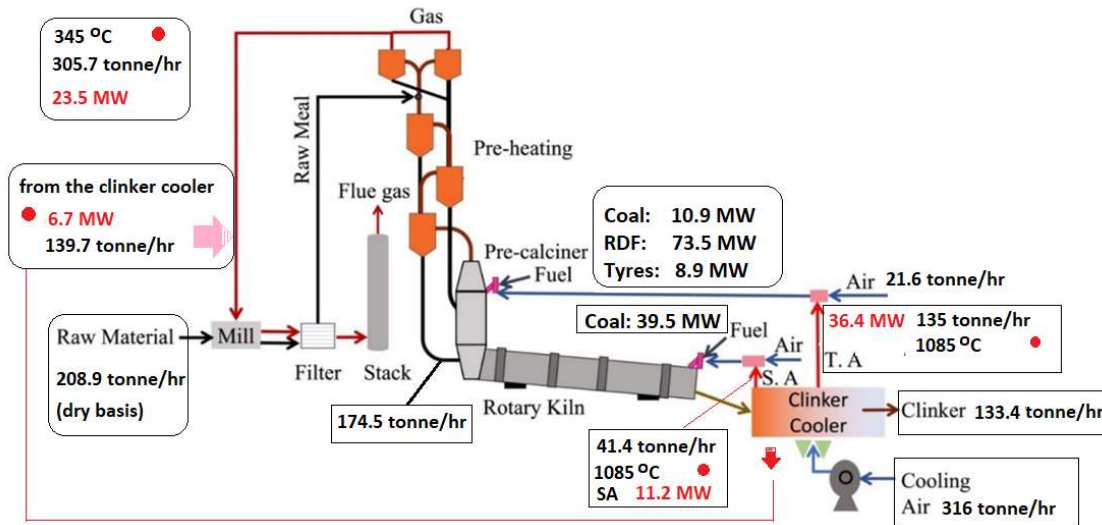


Figure 3 - Schematic diagram of SPEI-based carbon capture system [9]

4.3.1 Cement Production Process

Cement production involves the process of selecting mineral raw materials to produce a synthetic mineral mixture (clinker) that can be ground to powder together with other supplementary cementitious materials (SCM), having the specified chemical composition physical properties of cement, as shown in 4. As a new cement plant constructed in Europe would generally produce about 3000 to 4000 Ton clinker per day, the total capacity of the selected cement plant in this study is assumed to be 3200 tons per day (133.4 tons per hour) of clinker produced. A raw meal input of 208.9 tons per hour is considered. The plant operates for 8000 hours using coal, RDF and/or tires as fuel sources.



4.3.2 Silica-PEI based carbon capture system

The CO₂ rich silica-PEI sorbent is then heated with the lean silica-PEI sorbent stream from the desorber using heat exchanger. The CO₂ rich silica-PEI sorbent is then transferred to the desorber by the mean of an air conveying system. In the desorber, steam and CO₂ is added to improve regeneration of sorbent. The CO₂ released is recovered from the desorber and treated further for storage. The lean solid sorbent is recovered from the bottom of the desorber and recycled back into the adsorber after purging and cooling. Since the silica-PEI sorbent is stable, the purge rate is lower because of less sorbent deactivation, therefore sorbent makeup requirement is lower [6].

4.3.3 Silica-PEI-based carbon capture unit operating conditions

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silica-PEI sorbent. The CO₂ capture rate is maintained at 90 % in the adsorber, the CO₂ uptake in the adsorber is calculated at 2.05 mmol/g. Since the sorbent/CO₂ ratio significantly affects the carbon capture rate and the regeneration of sorbent, an optimised sorbent/CO₂ ratio of 10 (in weight %) is considered for this study.

From the adsorber, the CO₂-rich sorbent is conveyed to the bubbling bed desorber, where almost 100 % of the CO₂ is desorbed thermally from the sorbent in the desorber at the temperature of 110-120 °C. The heat for the desorption is provided by the regenerator. After desorption, the lean silica-PEI sorbent stream is then recycled back into the adsorption reactor after purging the recycle stream at 0.1% and cooling at the temperature of 50 °C. The adsorption temperature, carbon capture rate, sorbent/CO₂ ratio, desorption temperature, and CO₂ desorption rate values are based on the assumptions presented by Kim et al., [6] and Zhang et al., [7].

Table 1 - Boundary conditions for the modelling of SPEI based carbon capture unit

Parameters	Value
Flue gas cooler temperature (°C)	50
Adsorption temperature (°C)	50
CO ₂ avoided from flue gas (%)	90
Sorbent to CO ₂ ratio	10
Desorption temperature (°C)	110-120
Waste stream-Purge rate	0.1%
CO ₂ recycle rate (%)	50
SPEI working capacity (mmol/g)	1.25
Sorption capacity (wt.%)	5.5

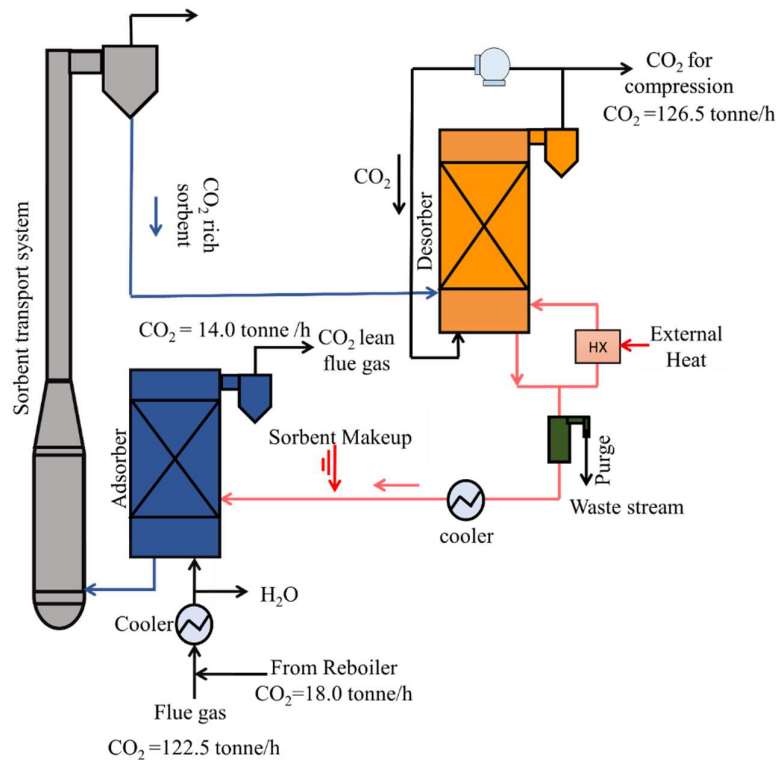


Figure 1 - Process flow diagram of SPEI-based carbon capture unit [9]

4.4 Results of ABSALT integration into a cement plant

The simulation model was developed based on the real time data provided by CEMEX using ECLIPSE process simulator, which is a personal computer-based package with built-in programs for mass and energy balance and capital cost estimation. There is a high degree of agreement found between the simulation results and real time data with percentage error at less than 10 %.

The results after simulation can be found in Table 2,

The concentration of flue gas leaving the base case cement plant contains; CO₂ at 16.5 vol. %, N₂ at 58.2 vol. %, O₂ at 6.8 vol. %, argon at 0.39 vol. % and H₂O at 18.1 vol. %. The emission rate of CO₂ from the base case cement plant is estimated at 123 tonne CO₂/hr which corresponds to 0.92 tonne CO₂/tonne clinker.

The simulation results showed that the 64 wt. % of the direct CO₂ emissions are from the calcination process through the decomposition of CaCO₃ into CO₂ and CaO. The remaining CO₂ is produced by burning fuels in the kiln burner. If 0.27 tonne CO₂/MWh of CO₂ emission factor for electricity generation



is considered, the indirect CO₂ emissions showed the equivalent CO₂ emissions at 0.95 tonne CO₂/tonne clinker.

The detailed technical results with energy performance indicators are given in Table 3.

Table 3 Technical results of reference cement plant – Cemex data

Main process data	Value
Raw meal input (tonne /hr, dry basis)	208.9
RDF input (tonne /hr, as received)	14.0
Tyres input (tonne /hr, as received)	1.4
Coal input (tonne /hr, as received)	7.0
Total thermal input (MWth)	133.4
Clinker production (tonne /hr)	133.4
Raw meal/clinker ratio (dry basis)	1.57
Power consumption (MWe)	16.3
Specific power consumed (MWh/tonne Clinker)	0.12
Specific direct heat required (GJ/tonne Clinker)	3.60
Specific indirect heat required (GJ/tonne Clinker)	0.71
Equivalent specific heat required (GJ/tonne Clinker)	4.31
CO ₂ emissions on-site (tonne CO ₂ /hr)	122.5
Specific direct CO ₂ emission (kg CO ₂ /tonne Clinker)	919
Indirect CO ₂ emission (kg CO ₂ /tonne Clinker)	34
CO ₂ emissions (kg CO ₂ /tonne Clinker)	952



Table 2 - Reference cement plant operating conditions - CEMEX data

Parameter	CEMEX
First stage cyclone temperature	370 °C
Second stage cyclone temperature	563 °C
Third stage cyclone temperature	737 °C
Fourth stage cyclone temperature	880 °C
Secondary air temperature	1000 °C
Tertiary air temperature	973 °C

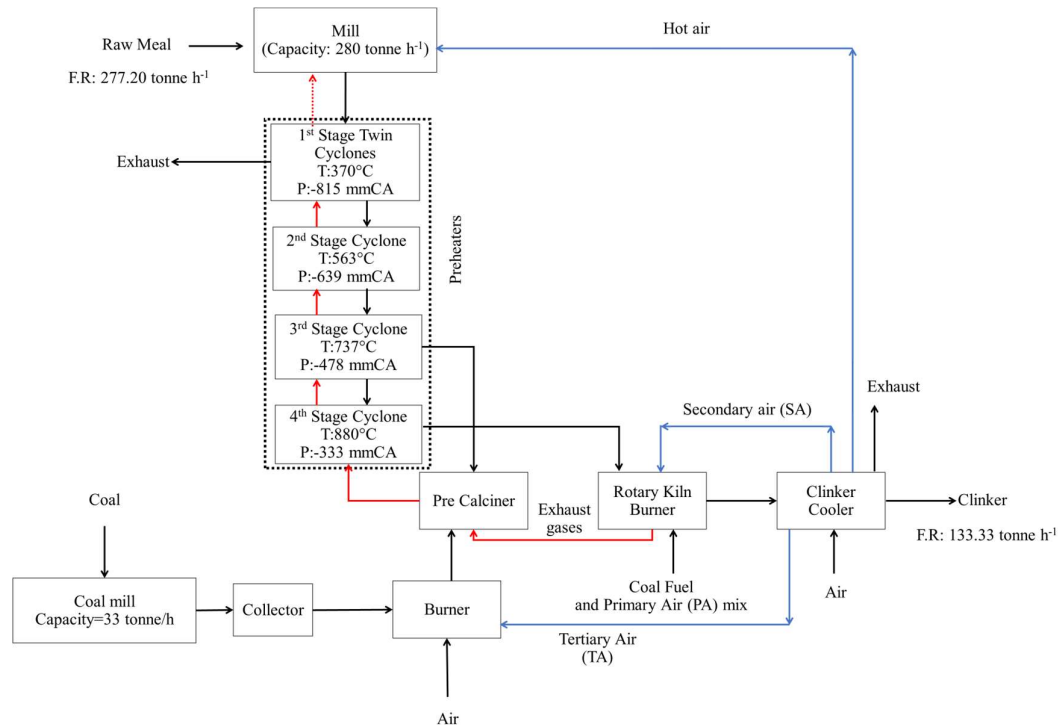


Figure 6 – Main operating parameters of the reference cement plant [9]

The concentration of flue gas leaving the base case cement plant contains; CO₂ at 16.5 vol. %, N₂ at 58.2 vol. %, O₂ at 6.8 vol. %, argon at 0.39 vol. % and H₂O at 18.1 vol. %. The emission rate of CO₂ from the base case cement plant is estimated at 123 tonne CO₂/hr which corresponds to 0.92 tonne CO₂/tonne clinker.

The simulation results showed that the 64 wt. % of the direct CO₂ emissions are from the calcination process through the decomposition of CaCO₃ into CO₂ and CaO. The remaining CO₂ is produced by burning fuels in the kiln burner. If 0.27 tonne CO₂/MWh of CO₂ emission factor for electricity generation is considered, the indirect CO₂ emissions showed the equivalent CO₂ emissions at 0.95 tonne CO₂/tonne clinker.

The detailed technical results with energy performance indicators are given in Table 3.



Table 3 Technical results of reference cement plant – Cemex data

Main process data	Value
Raw meal input (tonne /hr, dry basis)	208.9
RDF input (tonne /hr, as received)	14.0
Tyres input (tonne /hr, as received)	1.4
Coal input (tonne /hr, as received)	7.0
Total thermal input (MWth)	133.4
Clinker production (tonne /hr)	133.4
Raw meal/clinker ratio (dry basis)	1.57
Power consumption (MWe)	16.3
Specific power consumed (MWh/tonne Clinker)	0.12
Specific direct heat required (GJ/tonne Clinker)	3.60
Specific indirect heat required (GJ/tonne Clinker)	0.71
Equivalent specific heat required (GJ/tonne Clinker)	4.31
CO ₂ emissions on-site (tonne CO ₂ /hr)	122.5
Specific direct CO ₂ emission (kg CO ₂ /tonne Clinker)	919
Indirect CO ₂ emission (kg CO ₂ /tonne Clinker)	34
CO ₂ emissions (kg CO ₂ /tonne Clinker)	952



4.5 Comparison of ABSALT and MEA systems

Figure 2 details a schematic diagram of a MEA based capture system, with the process flow diagram shown in Figure 3.

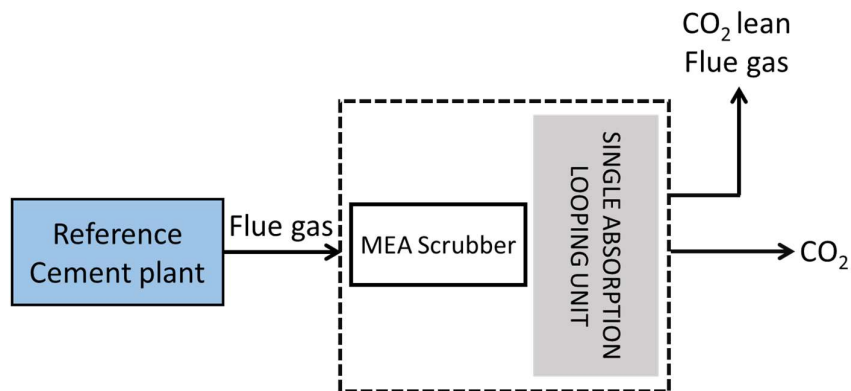


Figure 2 - Schematic diagram of MEA carbon capture system

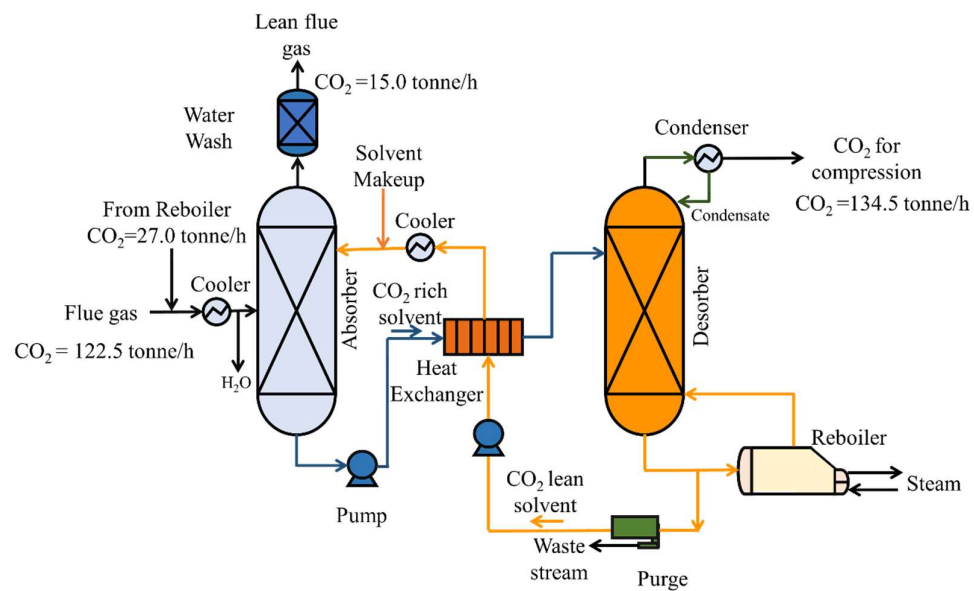


Figure 3 - Process flow diagram of MEA-based carbon capture unit

Comparison of technical results for reference cement plant versus ABSALT and MEA Scrubbing are presented in the table 4.



Table 4. Technical results comparison between 3 scenarios

Main process data	Value	Value	Value MEA
	Reference Plant	ABSALT	Scrubbing
Raw meal input (tonne /hr, dry basis)	208.9	208.9	208.9
RDF input (tonne /hr, as received)	14.0	-	-
Tyres input (tonne /hr, as received)	1.4	-	-
Coal input (tonne /hr, as received)	7.0	-	-
Total thermal input (MWth)	133.4	133.4	133.4
Clinker production (tonne /hr)	133.4	133.4	133.4
Cement production (tonne /hr)	146.6	146.6	146.6
Raw meal/clinker ratio (dry basis)	1.57	1.57	1.57
Power consumption (MWe)	16.3	29.8	31.0
Specific power consumed (MWh/tonne Clinker)	0.12	0.22	0.23
Specific direct heat required (GJ/tonne Clinker)	3.60	-	-
Specific indirect heat required (GJ/tonne Clinker)	0.71	-	-
Equivalent specific heat required (GJ/tonne Clinker)	4.31	-	-
CO ₂ emissions on-site (tonne CO ₂ /hr)	122.5	14.1	15.0
Specific direct CO ₂ emission (kg CO ₂ /tonne Clinker)	919	108	112
Indirect CO ₂ emission (kg CO ₂ /tonne Clinker)	34	61	64
CO ₂ emissions (kg CO ₂ /tonne Clinker)	952	169	176
Energy supply for SPEI/MEA regeneration (MWth)	-	101.4	162.8
Required regeneration energy (GJ/tonne CO ₂)	-	2.36	3.53
Equivalent specific energy required (GJ/tonne Clinker)	4.31	7.66	9.34
CO ₂ captured (tonne CO ₂ /hr)	-	126.5	134.5
CO ₂ capture rate (%)	-	90	90
Equivalent specific CO ₂ emissions (kg CO ₂ /tonne Clinker)	952	163.5	175.8
Equivalent CO ₂ emissions avoided (kg CO ₂ /tonne Clinker)	-	754,5	742.9
SPECCA (GJ/tonne CO ₂)	-	4.3	6.5

*SPECCA - Specific Primary Energy Consumption per CO₂ Avoided



Table 5. Economic factors and indices to calculate CO₂ capture and CO₂ avoidance cost

Economic factors	Baseline
Project life (years)	25
Plant operating hours/year	8000
Discount cash flow rate (%)	6
Owner Cost (%.EPC)	10
Contingencies (%.TCI)	10
Maintenance cost (%.TCI)	4
Insurance cost (%.TCI)	1.5
Raw meal (€/tonne)	4
RDF cost (€/tonne)	-75
Coal cost (€/tonne)	51.4
Waste tyres cost (€/tonne)	-153
MEA makeup (€/tonne)	1600
SPEI (€/tonne)	6500
Electricity price (€/MWh)	115
Natural gas price (€/MWh)	25
Fresh water price (€/tonne)	2

4.6 Life Cycle Analysis

Life cycle assessment (LCA) evaluates the environmental impact of product or process throughout the cycle of production. This analysis in ABSALT will be done using both midpoint (process-oriented) and endpoint (damage-oriented) approaches.

Initial LCA has showed how clinker production and heat recovery for the reference cement plant can affect CO₂ emissions and the potential health advantages that silica-PEI and alkoxylated PEI have over amine scrubbing.

Data for LCA is taken from reference cement plant and from simulations.

For this study, the SimaPro software is used. The ISO 14040 series is specific to LCA. ISO 14000 series is a set voluntary environmental standards, guides, and technical report, in which ISO 14040 sits.



5 Evaluation of results to date

5.1 ABSALT integration into a cement plant – Discussion

Comments from Cemex's perspective as a potential user:

Post combustion best installation location:

- Best location in the cement production process of clinker for the installation of the SPEI has been defined just before the exhaust gases achieve the main stack of the plant which is the official emissions control point by the authorities.
- The exhaust gases expelled by the plant varies from plant to plant in the range of 100 to 120°C.
- Waste heat is rarely found nowadays in the clinker production process. When available WH is used for drying purposes of raw materials and fuels (primary and alternative fuels).
- Exhaust gases at 300-400 °C from the preheater might be used however they contain high dust load (around 100 g/Nm³) which makes them almost impossible to be used directly. The dust load of this flow stream is removed and controlled by filtration in the main bag house collector installed after the raw meal grinding process where the heat of the preheater exhaust gases is used for drying of the raw materials.

Pre-treatment of exhaust gases:

- Consortium has been advised about the need of installation of a pre-treatment and/ or preconditioning of the exhaust gases of the main stack (feed into the SPEI system) regarding:
 - Temperature of the exhaust gases is 106°C and must be decreased to 40-50°C as required by the silica-PEI system.
 - SO₂ is in compliance with the environmental requirement however the emitted SO₂ release could impact on the operational life of the adsorbent.
 - NO_x is also in compliance with the environmental requirement however the emitted SO₂ release could impact on the operational life of the adsorbent.
 - Water content could also impact or influence the operation of the SPEI, therefore it has to be considered.
 - Heat sources for SALT process are waste heat from the flue gases and auxiliary boiler.



5.2 ABSALT and MEA comparison – Discussion

Under consideration of the results of simulations presented in Point 4.5 (table 4) comparing the total thermal input (natural gas) (GJ/ton CO₂) of 2.4 for the ABSALT capture process Vs the 3.5 of the MEA scrubbing, it is expected to have from now on this main impact of lower thermal demand reflected among all further calculations (i. e. LCA, TEA) before heat recovery. If the process of heat recovery from the cement plant is considered both economic and environmental performance of the ABSALT will be improved more than that of MEA.. That is why is fundamentally recommended to clarify this difference in thermal regeneration of the adsorbent during the stripping of the PEI.

A detailed technoeconomic analysis of two post-combustion carbon capture processes (i.e., the MEA-based carbon capture process and SPEI-based carbon capture process) has been undertaken and the following conclusions can be drawn:

- 1) Both the studied processes can potentially remove ≥ 90 % of the CO₂ from the flue gas. MEA-based carbon capture process shows the SPECCA at 6.5 GJ/tonne CO₂. While the SPECCA for the SPEI carbon capture process is lower compared to MEA based carbon capture process at 4.3 GJ/tonne CO₂.
- 2) The CO₂ capture cost of the MEA scrubbing process and SPEI-based processes is estimated at 61.4 and 49.8 €/tonne CO₂ , respectively. The CO₂ avoidance cost of the MEA scrubbing process and SPEI-based carbon capture process is estimated at 84.7 and 62.2 €/tonne CO₂, respectively.
- 3) The sensitivity analysis shows that the minimum carbon capture cost is observed at 55.4 and 45.7 €/tonne CO₂ for the MEA-based carbon capture process and SPEI-based carbon capture process when the natural gas price is 20 €/MWh.
- 4) If carbon tax is implemented, the BEBP of the cement plant increases significantly. At a carbon tax above 60 €/tonne CO₂, the cost of clinker produced with the cement plant integrated with the SPEI-based carbon capture process is lower than the cement plant. When the carbon tax is approximately 85 €/tonne CO₂, the BEBP of MEA-based carbon capture process is lower than the cement plant.
- 5) A maximum of 53.9 MWth of heat can be recovered from the cement plant. If a 100% of the available heat is recovered from the cement plant, the total CO₂ emissions reduces to up to 6.5 % for the MEA-based carbon capture process. While, for the emissions reduces to up to 6.9 % for the SPEI-based carbon capture process.
- 6) In the case of the 100 % heat recovery from the cement plant, the cost of CO₂ capture for the MEA-based and SPEI-based carbon capture processes reduces to 48.0 €/tonne CO₂ and 35.6 €/tonne CO₂ respectively. Furthermore, the CO₂ avoidance cost for the MEA-based and SPEI-based carbon capture processes reduces to 57.5 €/tonne CO₂ and 44.5 €/tonne CO₂ respectively. [9]



6 Next steps

- Pending information from pilot testing in Nottingham and relevant risk assessment from technical point of view.
- Ongoing arrangement of visit in KIER, where 100 kg alkoxyated SPEI will be tested.
- Ongoing preparation of risk assessment.

7 National and international cooperation

Three monthly progress reports have been accepted by the Research Council of Norway, the coordinating body for the ACT programme.

8 Communication

The paper, "A technical and environmental comparison of novel Silica PEI adsorbent-based and conventional MEA-based CO₂ capture technologies in the selected cement plant" has been accepted by the journal of carbon capture science & technologies for publication (7th December 2023) [9].

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