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Highlights and main findings from the 8 year SOLVit R&D programme – Bringing solvents and technology from laboratory to industry

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Abstract

SOLVit is an eight year (2008 – 2015) and 37 million Euro research programme focusing on developing energy efficient and environmental friendly post combustion carbon capture systems for large-scale industrial CO_2 emissions. The programme is coordinated by Aker Solutions. Work has been conducted within the fields of solvent development, process optimisation and operational understanding through pilot plant testing. Several new solvents have been developed in the project offering up to 35% improvement in energy consumption relative to MEA along with significantly improved degradation and environmental performances. SOLVit has improved the maturity of Aker Solutions' Advanced Carbon Capture^{TM} process significantly.

Peer-review under responsibility of the organizing committee of GHGT-13.

Keywords:Post-combustion capture; Research programme; Solvent development; Pilot plant testing

1. Introduction

SOLVit is a major R&D programme on improvement of solvent and process technology for CO_2 post combustion capture [1]. The project was initiated in 2008 and concluded in December 2015. The project is owned and coordinated by Aker Solutions and the research activities have been managed and performed by the group for CO_2 Capture Processes at SINTEF Materials and Chemistry jointly with Aker Solutions and NTNU,

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Department of Chemical Engineering. Also several partners from the industry and potential end-users of carbon capture technologies, EnBW, E.ON, Scottish Power and Statkraft, have participated actively in different parts of SOLVit.

The project has been co-funded by the strategic Norwegian research program CLIMIT, and the Norwegian Research Council. Budget is 332 million NOK (approx. 37 million EUR) of which 132 million NOK has been received in funding from CLIMIT.

The overall aim of the SOLVit programme has been to reduce the costs of CO_2 post combustion capture technology through development of more energy efficient solvent systems as well as adapted process design. In addition it has been the aim to develop more environmentally friendly solvents and technology that may reduce the environmental impact of solvent based CO_2 capture processes. Finally it has been the aim to demonstrate the performance improvements of the novel solvents in pilot scale.

This paper provides and overview of the key learnings and main results from the entire SOLVit programme from 2008 to 2015.

2. Programme overview

The SOLVit project has been carried out in three phases, where each phase builds on learnings from the previous phase. The focus of the programme has been adjusted along the way in order to accommodate new findings and change in focus caused by external drivers e.g. environmental issues, market conditions, etc. Below is highlighted the main focus areas of the different phases of SOLVit:

- **Phase 1 – Development of functional solvents (2008-2010)**
  - Develop solvent screening methodology
  - Develop full flow sheet simulation tool (CO2SIM) for SOLVit solvents
  - Addressing urgent requirement for solvent process by working on 1st generation solvent concepts
  - Establishing laboratory test facilities and full height pilot plant at SINTEF Tiller
- **Phase 2 – Testing of Development of (2011-2012)**
  - Characterization, pilot testing and model development of first generation solvents
  - Focus on development of green solvents and reducing environmental impact of solvent processes
  - Work on breakthrough concepts/3rd generation solvent systems
- **Phase 3 – Bringing solvents from laboratory to industry (2013-2015)**
  - Focus on qualification of 1st generation solvents through pilot testing on different real industrial exhaust gases (cement, coal, natural gas, refinery catalytic cracker) at four full height pilots
  - Demonstration of 1st generation solvents at 2-10% of full-scale (Technology Centre Mongstad)
  - Proof-of-principle for 3rd generation solvent concepts by testing in full height pilot plant (Tiller)
  - Technology and process developments to reduce cost of CO_2 capture
  - Concluding the programme

The work in SOLVit has been organised in four main subprojects:

- Fundamental Studies
- Modelling
- Technology Development
- Pilot Plant Testing and Demonstration

In addition, an educational programme at NTNU (sponsored separately by the Norwegian Research Council and

Aker Solutions AS) has been carried out in conjunction with SOLVit, contributing with more fundamental research on solvent based capture processes.

The Fundamental Studies subproject has focused on solvent development, degradation chemistry, environmental impact and development of chemical analysis for solvents and their degradation products. The activities have mainly been conducted by SINTEF and NTNU.

In the Modelling subproject SINTEF has developed a full flow sheet in-house process simulator “CO2SIM” for solvent based CO_2 capture processes. Solvent models have been developed for all the solvent systems tested in pilot plants. CO2SIM has throughout the project been used to validate data from the pilot plant campaigns.

The Technology Development subproject has focused on developing and qualifying new technical solutions, improved hardware and less expensive construction materials for use in solvent based capture processes. The activities have been closely linked to the Pilot Plant Testing and Demonstration subproject.

The Pilot Plant Testing and Demonstration subproject has been a very significant part of SOLVit. Focus here has been do demonstrate and validate the performance of first and third generation solvents as well the technology improvements developed in the SOLVit programme. More than half of the total budget has been used on construction, modification and operation of pilot plant facilities. Five different pilot plants have been used in the project: Research pilot plants at NTNU and Tiller. Aker Solutions’ Mobile Test Unit, EnBW’s pilot plant at Heilbronn coal-fired power station and the large amine plant at Technology Centre Mongstad (TCM).

The contents of the different subprojects and how they are interlinked are illustrated in Figure 1.

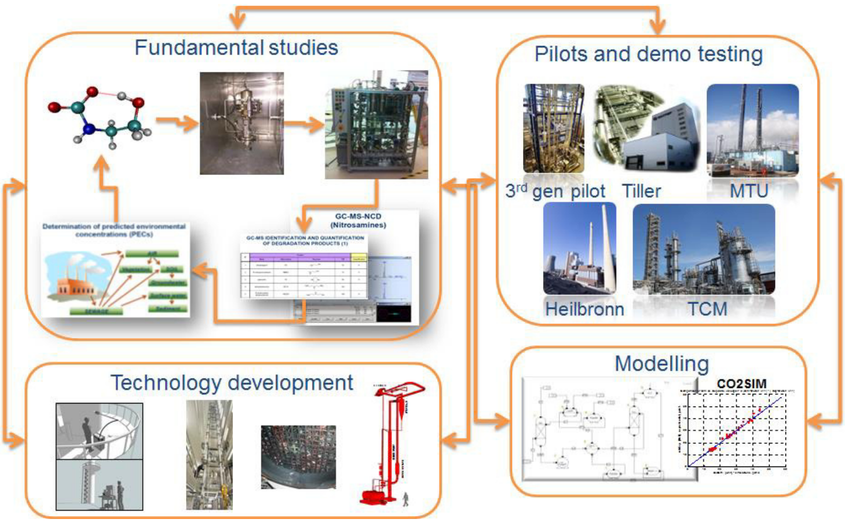


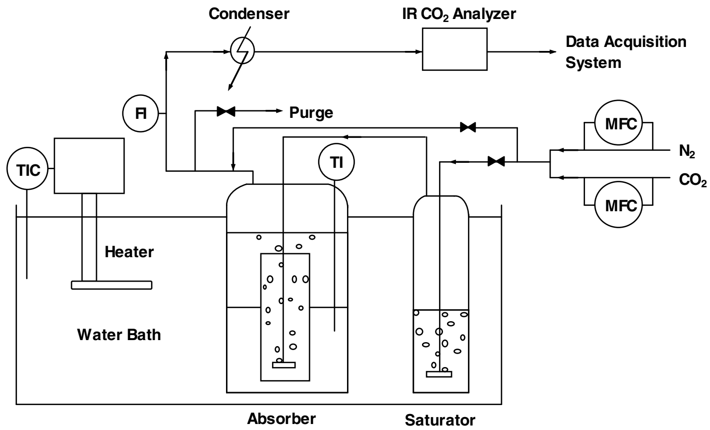
Fig. 1. Illustration of contents of SOLVit subprojects and how they are interlinked.

3. Highlights and main achievements

In the following subsections selected highlights from the SOLVit programme are presented.

3.1. Solvent developing and characterization

Solvent developing and characterization have been key activities in the SOLVit programme. The objective of this activity is to identify new promising solvents and qualify them for pilot plant testing. The work with solvent development has followed two different paths. Along the first path, the activities have focused on screening and characterization of solvent systems that can be commercially deployed within a relatively short timeframe and in conventional amine absorption-desorption processes. The solvents investigated in this category are termed 1st generation solvents and represent solvents such as blended amines, amino acid salt solutions or combinations thereof. The aim has been to identify solvent systems with significantly improved performance relative to reference solvent 30% MEA.



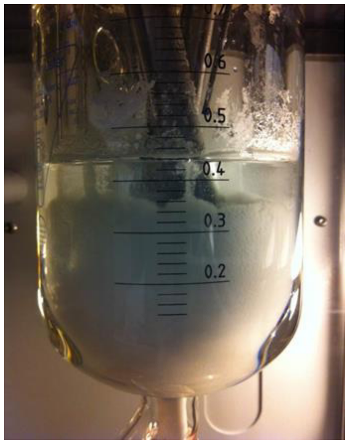


Figure 2. Left) Schematic illustration of screening apparatus used to assess CO_2 absorption rate and absorption capacity. Right) Picture of screening apparatus loaded with novel precipitating solvent system.

In the second path, the focus has been on developing radically new solvent systems (termed 3rd generation solvents) which have potential of providing a step reduction in energy consumption but are less mature and may require substantial modifications to the CO_2 capture process. Examples of 3rd generation solvents that have been investigated are precipitating salt systems and systems forming two liquid phases.

In order to screen a great number of chemical compounds for use as CO_2 capture solvents, a screening methodology was developed which addressed key solvent properties such as [2]:

- CO_2 absorption rate and absorption capacity
- CO_2 desorption rate and heat of absorption
- Solubility and volatility in solution
- Toxicity, biodegradability and other HSE properties
- Thermal and oxidative degradation rate
- Corrosiveness
- CO_2 solubility and equilibrium measurements (VLE)
- Misc. physical properties

In the initial stage of screening, molecular modelling was used to locate chemical structures that had favourable properties with respect to CO_2 absorption. The most promising of these compounds and mixtures thereof were subsequently tested experimentally in a stirred cell setup or screening apparatus as illustrated in Figure 2. Following the initial screening tests, the more promising solvent candidates underwent further testing and characterisation to determine some of the other key properties listed above [2]. The solvent candidates that fulfilled all screening criteria and achieved highest score were selected for pilot plant testing. Clearly trade-offs exist between some of the properties above, hence selecting the right solvent is often a compromise between the various properties. During the SOLVit project increased focus on formation of harmful degradation products from amine solvents e.g. nitrosamines, etc., resulted in abandonment of some of the solvent candidates proposed in the early stage of the project. As a result of this shift in direction, environmentally friendly solvents or green solvent have been developed which show only miniscule formation of nitrosamine when applied on real NO_x containing industrial flue gas (see Figure 5).

During Phases 1 and 2 of the SOLVit programme more than 80 different 1st generation solvents were characterised in laboratory test rigs at SINTEF and NTNU of which 8 solvent candidates (and MEA) were qualified for testing in pilot plants. The third generation solvents were primarily developed during Phases 2 and 3 of SOLVit. More than 10 different 3rd generation solvents and concepts were investigated resulting in 3 systems being selected for pilot plant testing in Phase 3. The outcome of the pilot plant testing is described in Section 3.5.

3.2. Investigation of degradation chemistry and development of analytical methodology

From the work with solvent development in SOLVit it was soon learned than it is essential to characterise the degradation behaviour of new solvent candidates in the early stage of the screening process as degradation may become inhibitive high for many amines. This is particularly true when the solvent mixtures are exposed to some of the impurities that may be present in real industrial processes e.g. corrosion products, fly ash and flue gas pollutants. In SOLVit a degradation screening test procedure was applied where the oxidative and thermal degradation rates were benchmarked against a reference solvent (MEA) in the presence of iron salts (degradation catalyst). This procedure resulted in good predictability of relative degradation rate of solvents [3]. For some of the more promising 1st generation solvents as well as for MEA, comprehensive work has been undertaken to identify degradation mechanisms and the main degradation products. Knowing the main degradation products it is possible to document the fate of the solvent amines and assess if problematic compounds are formed. To evaluate to what extent the major degradation products have been identified, the total nitrogen content of the solvent is compared with the summarised nitrogen content of all specific solvent compounds and degradation products. Typically closure of this nitrogen balance within 1-2% has been achieved.

The detective work with identification of degradation products goes hand in hand with development of sensitive and accurate analytical techniques. In SOLVit, significant effort has been used in developing highly sensitive LC-MS (Liquid Chromatography Mass Spectroscopy) methods for accurate quantification of degradation products in a solvent matrix. Sensitivities below 1 ng/ml have been achieved and methods for many different amines and degradation products have been developed [3].

Below is listed the number of analytical methods which have been developed for specific groups of compounds:

- Amines (>50 compounds)
- Alkylamines (7 compounds)
- Nitrosamines (20 compounds)
- Nitramines (7 compounds)
- Degradation products (26 compounds)

The build-up of analytical expertise and lab facilities in SOLVit has made it possible to analyse nearly 10 000 solvent samples from the different laboratory tests and pilot plant campaigns in the project. Further details on development of analytical methodology in SOLVit is described in [3].

3.3. Modelling and simulation

As part of the modelling work in SOLVit, SINTEF has developed a full flowsheet process simulator "CO2SIM" for solvent based CO_2 capture processes. Initially CO2SIM was primarily equipped with "soft models" derived from simple equilibrium measurements and data fitting to test campaigns at the Tiller pilot plant, however the level of sophistication has been expanded during the project. In Phase 3 of SOLVit, rigorous eNRTL thermodynamic models with full speciation have been implemented for the more promising 1st generation solvents, resulting in a simulator with excellent predictive capability. CO2SIM has been widely used in the project to validate data from test campaigns and to investigate potential gains from process optimisations. Examples of the predictive capability of CO2SIM are shown in Figure 3 where simulated results are compared to pilot plant data obtained from TCM.

The developed simulation tool, CO2SIM, is a valuable tool for scale-up, process optimisation and design of full-scale carbon capture plants

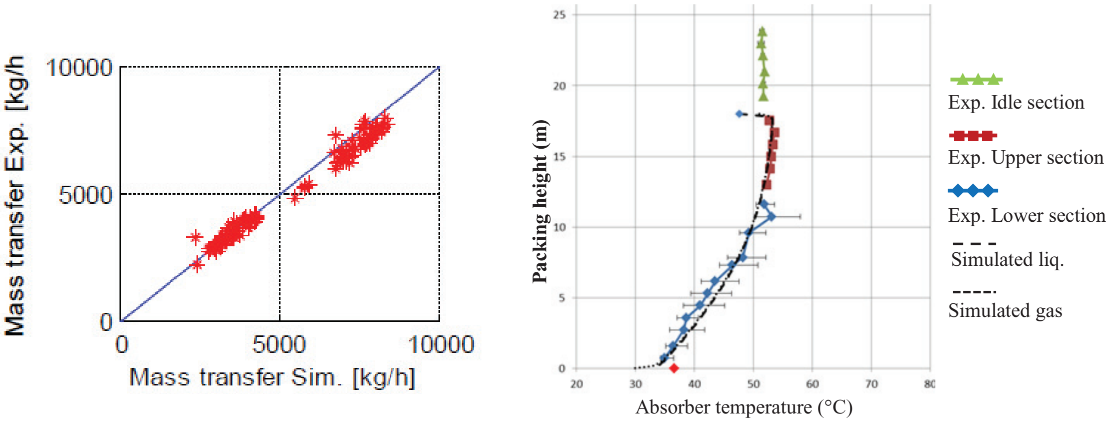


Figure 3. Left) Parity plot of measured vs. simulated absorber mass transfer rate for multiple operating points with S26 solvent at TCM. Right) Example of predicted absorber temperature profile during operation with S26 at TCM.

3.4. Establishment of pilot plant facilities

During Phase 1 of SOLVit, the research pilot plant at SINTEF Tiller was established (Figure 4). The Tiller plant has provided the SOLVit project with a unique opportunity to test new solvent candidates in an early stage of development at realistic operating conditions, but in a well-controlled test environment.

The Tiller pilot plant has been upgraded and modified a number of times during SOLVit. In 2014, the Tiller was modified to include an acid wash system in order to allow for testing of more volatile solvent systems. Later the same year Tiller was also modified to allow for testing of 3rd generation solvents forming two liquid phases. Key design data and specifications for the Tiller pilot is shown in Figure 4.

Tiller research pilot plant:

- Completed April 2010
- Flue gas from 270 kW propane burner
- Flexible and large operating range
- CO_2 content: 2-20 vol%
- CO_2 capture capacity: 60kg/h
- Absorber diameter: 0.2 m
- Extensive monitoring throughout the process
- Access via 11 floors
- Access to laboratory facilities

Figure 4. Tiller research pilot plant at SINTEF and main specifications.

3.5. Pilot plant validation and demonstration

To demonstrate the performance of the SOLVit solvents under operating conditions as close as possible to future commercial plants, testing with real industrial flue gases have been key priority. Aker Solutions Mobile Test Unit (MTU, flue gas capacity 1000 Nm^3/h) has been used since the start of the SOLVit programme to test new solvents at various industrial sites. In SOLVit, the MTU has been operated at two different coal-fired power stations, two gas-fired power stations, a cement plant and a refinery catalytic cracker unit. Also MEA and SOLVit solvents have been tested in a pilot plant (flue gas capacity 1500 Nm^3/h) with coal flue gas at SOLVit partner EnBW's coal-fired power plant in Heilbronn Germany. Finally, also MEA and two of the more promising SOLVit solvents (S21 and S26) have been tested in larger scale at the large amine plant at TCM (flue gas capacity is 55.000 Nm^3/h, about 2-10% of full-scale power plant). During the entire SOLVit programme 31 individual pilot plant test campaigns have been completed with about 40.000 operating hours in total. 11 different SOLVit solvents as well as "standard" solvent MEA have been tested.

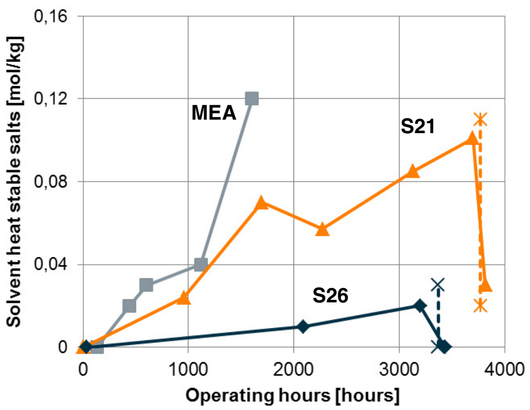
In addition to the gain of general operating experience and the demonstration of reliable operation of the SOLVit solvents, the pilot plant test campaigns have also served as a routine to quantify key performance parameters such as:

- CO_2 capture rate
- Specific energy consumption
- Solvent consumption rate
- Solvent stability and degradation rate
- Emissions to air
- Corrosion

As an example, the reduced regeneration energy requirement of the SOLVit solvents has been demonstrated in the pilot plant test campaigns. The achievements can be summarised as follows:

- Compared to reference solvent 30% MEA a reduction of the energy consumption with 10-25% has been demonstrated in pilot plants with 1st generation solvents using a "standard" amine plant flowsheet
- Applying an advanced process flowsheet e.g. vapour compression, stripper inter-heating, etc. increases energy saving of 1st generation solvents with up to 35% compared to reference solvent
- Pilot plant tests at Tiller with 3rd generation solvent, indicate nearly 30% saving with relatively simple flowsheet, further improvement plausible with advanced flowsheet

With respect to degradation and environmental performance also significant progress have been demonstrated with the SOLVit solvents during pilot plant testing. In Figure 5 data is shown from test campaigns at TCM with two SOLVit solvents S21 and S26 as well as MEA. It is clear from Figure 5 that much lower build-up rates of heat stable salts and nitrosamines are achieved with SOLVit solvents, in particular with S26 where the rates are 10 times lower compared to MEA when tested at similar conditions (same flue gas, same plant, etc.). Despite MEA showed much higher formation of nitrosamines compared to S21 and S26, many other solvents containing components with secondary amine functionality such as piperazine show much higher formation of nitrosamine. The solvent consumption during the campaign was also quantified as approx. 2.6 kg/ton CO_2 for MEA, 0.5-0.6 kg/ton CO_2 with S21 and 0.2-0.3 kg/ton CO_2 with S26 [4]. Long term testing of S26 (almost 1.5 years) with the MTU at a cement plant confirms solvent consumption below 0.15 kg/ton CO_2 [5]. The great improvement in degradation rate of SOLVit solvents results in significantly reduces costs related to make-up, reclaiming, corrosion and waste disposal. Moreover the environmental impact of the capture process is greatly reduced as emissions and wastes will be reduced.



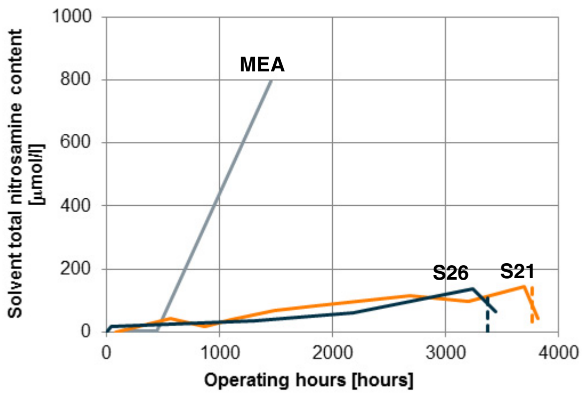


Figure 5. Build-up of heat stable salts (Left) and total nitrosamine content (Right) in MEA and SOLVit S21 and S26 solvents during test campaigns at the large amine plant at TCM. [4]

Aker Solutions has used significant effort in developing efficient emission control technology for amine based CO_2 capture processes. This has resulted in proprietary technology for avoiding amine mist emission and the reduction of volatile alkaline emissions (amines, ammonia, etc.). As described in [6] and [7], the MTU has been modified to include these novel emission control technologies. The SOLVit MTU test campaigns have been used to quantify emissions from different industrial exhaust gases and evaluate the performance of the emission control systems. In Table 1, emission results from operating the MTU on flue gas from gas turbine exhaust at TCM is shown. It appears that very low emissions of solvent amines and degradation products can be achieved with the S26 solvent. It is furthermore seen, that if Aker Solutions' acid wash system is applied emissions can virtually be eliminated. A prerequisite for this work has been access to reliable emission measuring technology. Emission measurement procedures and sampling techniques have been developed and validated as part of the SOLVit project.

Table 1. Results from emission measurements at MTU with SOLVit S26 solvent on natural gas flue gas

Compound	Unit	Emissions without Acid wash	Emissions with acid wash
Solvent amines	mg/Nm^3	0.6	0.09
Other volatile amines	mg/Nm^3	0.025	0.0005
Ammonia	mg/Nm^3	5	0.01
Nitrosamines*	$\mu g/Nm^3$	< 0.2	< 0.2
Nitramines*	$\mu g/Nm^3$	< 0.15	< 0.15

*Below limit of detection

The main conclusions from the pilot plant test campaigns above are that the SOLVit solvents are robust and energy efficient as well as exhibit excellent environmental performance. Up to 35% improvement in energy consumption relative to MEA has been demonstrated with novel solvents and process upgrades. Furthermore, 10 times lower solvent consumption rate compared to MEA has been demonstrated and much lower degradation rate (Figure 3). Emissions of amine and degradation products could be maintained at very low values, reducing the uncertainties related to environmental impact of amine processes.

3.6. Educational Programme

As explained in section 2, an Educational Programme at NTNU has been linked to the SOLVit project for the whole eight year period. The Educational Programme is an integral part of the SOLVit project and is conducted concurrently with and fully integrated into the various tasks of SOLVit. The know-how and results obtained in the Educational Programme are used directly towards the rest of the project. The overall scientific goal of the Educational Programme is to create knowledge and a theoretical basis that will allow the subsequent development and design of substantially improved process technologies for CO_2 capture and to educate top qualified personnel for the Norwegian industrial and research sector.

The Educational Programme has in particular contributed to the developments of SOLVit within the areas of molecular modelling, mechanistic understanding of solvent degradation and development of 3rd generation solvent systems forming two liquid phases.

Several PhD and MSc candidates have graduated through the Educational Programme contributing greatly to the general education of qualified scientist within CO_2 capture technologies:

- 4 PhD graduated (Solvent degradation mechanisms, Molecular modelling, Thermodynamic models for CO_2 absorption systems, Degradation and corrosion link)
- 1 PhD in the pipeline (Liquid-liquid solvents)
- 2 Associated PhD's (Aerosol formation and abatement and Biological treatment of reclaimer waste)
- 3 Post doc.
- 12 MSc degrees

4. Conclusion

In summary, the eight year SOLVit programme with the aim of developing energy efficient and environmental friendly post combustion carbon capture systems for large-scale industrial CO_2 emissions have been concluded. The programme has increased the understanding of solvent based capture processes on both fundamental and industrial levels. Several new post combustion capture solvents have been developed in the project offering up to 35% improvement in energy consumption relative to MEA along with significantly improved degradation and environmental performances. The programme has also demonstrated that emissions of amine and amine degradation products can be maintained at very low values, reducing the uncertainties related to environmental impact of amine processes.

All in all the pilot plant activity in SOLVit has contributed significantly to mature the CO_2 capture technology of Aker Solutions and to mitigate risks related to scale-up and large-scale deployment.

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References

[1] http://www.climit.no/no/prosjektene
[2] KA Hoff, EF da Silva, I Kim, A Grimstvedt, S Ma'mun. Solvent development in post combustion CO_2 capture – Selection criteria and optimization of solvent performance, cost and environmental impact. Energy Procedia 37 (2013) 292 – 299.
[3] A Grimstvedt, K Zahlsen, SJ Vevelstad, K Vernstad, T Holten, A Brunsvik. Exploration of degradation chemistry by advanced analytical methodology. Energy Procedia 00 (2017) 000–000 (in press)
[4] O Gorset, JN Knudsen, OM Bade, I Askestad. Results from testing of Aker Solutions advanced amine solvents at CO_2 Technology Centre Mongstad. Energy Procedia 63 (2014), 6267-6280.
[5] JN Knudsen, OM Bade, I Askestad, T. Mejdell. Pilot Plant Demonstration of CO_2 Capture from Cement Plant with Advanced Amine Technology. Energy Procedia 63 (2014) 6464-6475.
[6] JN Knudsen, OM Bade, M Anheden, R Bjorklund, O Gorset, S Woodhouse: Novel Concept for Emission Control in Post Combustion Capture. Energy Procedia 37 (2013), 1804–1813.
[7] OM Bade, JN Knudsen, O Gorset, I Askestad. Controlling Amine Mist Formation in CO_2 Capture from Residual Catalytic Cracker (RCC) Flue Gas. Energy Procedia 63 (2014) 884-892.