Practical experience in post-combustion CO$_2$ capture using reactive solvents in large pilot and demonstration plants

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Abstract

Significant progress on post combustion carbon dioxide (CO$_2$) capture technology using reactive solvents has been reported since the IPCC report of 2005. This has included both the advances in the fundamental knowledge of the technology and practical experience in pilot, demonstration and commercial plants. This second paper looks specifically at the latter aspect. There has been a widespread deployment of pilot and demonstration plants as well as the birth of a commercial size CO$_2$ capture plant. The research and development work being carried out in pilot and demonstration plants have enabled the use of real conditions to study the CO$_2$ capture process and to provide realistic guidance in the design of commercial plants.

The lessons learned from the pilot and demonstration plants have been very varied but have contributed to the continuous improvement of the amine-based CO$_2$ capture technology in terms of off gas emissions, operational issues, solvent management, corrosion, plant size reduction, new and blended amine solvents, and non-amine based solvents. Some of these issues have been resolved through the development and use/experimentation of corrosion inhibitors, degradation inhibitors, non corrosive materials as construction materials, and non thermal reclaiming methods, as well as the application of operating conditions that are compatible with the solvent system used. Since the solvent-based CO$_2$ capture technology constitutes a relatively new industry, measurement standards involving sampling and analysis of the off-gas, and analysis of the solvent system in use were not in place prior to the IPCC 2005 report. Therefore, the emergence of the demonstration plants has thrown light on both the need for these standards and what are currently in place. Specifically, sampling techniques are being introduced which aim to reliably obtain representative samples from the off-gas of an amine based CO$_2$ capture plant. Techniques are also being developed to analyze the current complex amine solvent system itself.

Progress has also been seen on the reporting of the heat duty for solvent regeneration, especially for smaller pilot plants. Bigger demonstration plants have been hesitant to share results on heat duty. However, reports from small pilot plants show that heat duty improvements have been achieved based on two approaches: namely, development of energy efficient solvents and process optimization. Based on these two approaches, the heat duty has been brought down from about 5.0–1.8 GJ/ton CO$_2$ produced. On this issue, it has been noticed that even though the solvent used in conjunction with the process optimization method employed are capable of providing an acceptable heat duty (i.e., close to 1.8 GJ/ton CO$_2$ produced), the actual heat duty obtained in pilot and demonstration plants, in most cases, is higher than design specifications.

Catalysis in amine-based post combustion CO$_2$ capture has become a new trend which may possibly pave the future direction for solvent-based post combustion CO$_2$ capture. Solid mineral catalysts are used in one approach, whereas a biocatalyst is employed in another approach. Both approaches are expected to see extensive research and development work all the way to demonstration plants in order to perfect the respective processes, and to generate reliable data for design of a commercial plant. Thus, future trends could see significantly smaller vessels and heat duties for post-combustion CO$_2$ capture from combustion flue gases using reactive solvents. These would result in significantly lowering the cost for post-combustion CO$_2$ capture. More activity at pilot plant and large demonstration scale plants on the use of amino acid salts and chilled ammonia process have been coming up (CAP), which may help to enhance the performance of these alternative post combustion capture processes.

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1. Introduction

The literature (IPCC, 2005) has shown that there are three basic CO₂ capture strategies: (i) post combustion CO₂ capture (PCC), (ii) precombustion CO₂ capture, and (iii) oxyfuel combustion CO₂ capture. As the name implies, post combustion CO₂ capture refers to the capture of CO₂ after the fossil fuel has been burned and the energy extracted, whereas precombustion capture deals with the decarbonisation of the fuel before the resulting non-carbon fuel is used for energy production. Oxyfuel combustion refers to the strategy of using almost pure oxygen (O₂) to burn the fossil fuel to obtain energy. Since the nitrogen content is negligible, the exhaust gas conceptually contains mainly CO₂, and thus, requires minimum CO₂ separation. This review paper focuses on post combustion carbon dioxide (CO₂) capture using reactive solvents. The preponderance of information in the literature appears to show that significant research, development and deployment work has been performed in CO₂ separation and capture by absorption using chemical solvents, which has led to its more rapid maturity over time compared with other techniques (Feron et al., 2009; Abu-Zahra et al., 2013). The literature (Shi et al., 2014; Idem et al., 2011; Feron et al., 2009; Abu-Zahra et al., 2013) has also shown a comprehensive scope of work ranging from molecular level computational chemistry simulation, to fundamental laboratory scale studies, and then to pilot plant and demonstration plant studies to a full blown commercial scale CO₂ capture plant. Numerous studies on PCC by absorption using chemical solvents were reported prior to 2005, and some of the findings went into the IPCC report on CO₂ capture and storage (CCS) of 2005 (IPCC, 2005). The state of the art at that time included Kerr–McGee/ABB Lummus Crest Process (Barchas and Davis, 1992), the Flour Daniel ECONAMINE process (Sander and Mariz, 1992; Chapel et al., 1999), and the KEPCO/MHI Process by Kansai Electric Power Co., Mitsubishi Heavy Industries (Mimura et al., 2003, 1999). After then, it is clear that PCC by absorption using chemical solvents has blossomed considerably. For example, the solvent technology now includes new MHI solvents (MHI, 2012), Cansolv (2015), HTC Purenergy (2015), Aker (2015), Hitachi (Kikawa et al., 2010), Toshiba (Suzuki et al., 2012), etc. (for conventional amine based solvents), and ionic liquids–based solvents ((a) The US Department of Energy (DOE), (b) The US Department of Energy (DOE)) being developed by Ion Engineering, amino salts (Feron et al., 2009; Siemens, 2011) being developed by TNO/EOn and Siemens, aqueous/chilled ammonia (Feron et al., 2009) being developed by Alstom, etc. (for non-amine based solvents), as well as variants and/or combinations of the listed solvent strategies (Feron et al., 2009). Significant progress has been reported since the IPCC report of 2005. A parallel review paper (Liang et al., 2015) looks at and provides a summary on “Recent progress and
new developments in post-combustion carbon-capture technology with reactive solvents” in terms of fundamental aspects while the current review paper looks at “Practical experience in post-combustion CO₂ capture using reactive solvents in large pilot and demonstration plants”.

2. Pilot, demonstration and commercial PCC CO₂ capture projects

A rapid spread of pilot plant and demonstration plant studies on PCC by absorption using chemical solvents is obvious as seen by the number of pilot plants, demonstration plants and even a full blown commercial CO₂ capture plant having been constructed and commissioned. Some are currently in use for comprehensive studies or for commercial purposes, since 2005. Critically important information has been gathered from these experimental pilot and demonstration plants as well as the commercial scale plant. Work at each scale has provided unique insights which are necessary to enabling growth of a commercially competitive low carbon energy option through CCS. The plants from which data have been obtained and shared to contribute knowledge to the general public are scattered around the globe. In this regard, Abu-Zahra et al. (2013) have compiled a list of small pilot plants (i.e., defined in this paper to mean pilot plants with capacity ≤ 50 ton/day) for CO₂ capture activities using solvents. This is shown in Table 1 with the pilot plants listed by capacity and by region. The table also shows the status of each pilot plant (i.e., completed, ongoing, under construction, planning, and decommissioned, etc.). In regards to large scale post combustion CO₂ capture demonstration plants, Table 2 (Abu-Zahra et al., 2013) shows a compilation of such plants listed by region, with the status for each plant also being provided. In addition, regarding commercial plants, Table 3 shows such plants listed per region with the status of each plant also being provided. Some of these pilot plants, demonstration plants as well as commercial plants from each region (where applicable) have been selected for more detailed discussion based on solvent technology type, uniqueness and lessons learned, especially where information is available, in order to provide the basis for the lessons learned.

3. Pilot plants (≤ 50 ton/day)

3.1. Amine based processes

The amine based pilot plant are presented by region in order to show global distribution as discussed below.

3.2. North America

There are a number of small pilot plants that have been used for post combustion CO₂ capture studies in North America. These include two University of Regina (UofR) pilot plants, namely, 1 ton/day technology development pilot plant and (UofR) consortium 4 ton/day Boundary Dam demonstration plant that was decommissioned in 2012 (Fig. 1), as well as C2P3 University of Texas’ Separations Research Program (SRP), and Hitachi/EERC pilot plant (University of North Dakota). For each of these pilot plants, the focus is on the results obtained with regards to heat duty, absorber efficiency, flue gas source, degradation, corrosion, CO₂ purity and off gas emissions.

3.2.1. Typical process description of a CO₂ capture pilot plant

The processes involved in these plants, and in fact other pilot plants are very similar and typical. Consequently, the CO₂ capture process in pilot plants is described using the University of Regina (UofR) Technology development pilot just as an example, as shown in Fig. 2 (Idem et al., 2006). However, a very brief description is also given for the other pilot plants.

3.2.2. University of Regina CO₂ capture technology development pilot plant

The process flow diagram of the UR pilot plant is shown in Fig. 2 (Idem et al., 2006). Typical of post combustion solvent based CO₂ capture process, this pilot plant consists of three main units connected in series as follows: (i) flue gas generation/pretreatment unit, (ii) absorption-based unit for CO₂ capture, and (iii) post-conditioning unit for product purification. In brief, a steam boiler (250 kW) produces both flue gas and high quality steam for the CO₂ capture unit. A 30 kW micro gas-turbine available in the same unit can help to produce a low CO₂ concentration feed. This unit contains three absorber columns each of which is composed of three 0.3 m-diameter sections for a total height of 10 m packing height, and also equipped with a series of temperature sensors and gas sampling points at a regular interval. The stripper column is also of the same height. The post-conditioning unit has a CO₂ wash scrubber, and a separate chiller to cool the CO₂ gas down to 4°C. From here, the CO₂ product is either released to the atmosphere or is passed through a dryer and purification unit for further treatment to meet food-grade specifications.

A control system (in this case, a DeltaV process control/instrumentation and data acquisition system) is used to control, monitor, and record a complete spectrum of process operating conditions that include temperature, flow rate, CO₂ removal efficiency, CO₂ production rate, and more importantly, the energy consumption for CO₂ capture. These data can be retrieved from the control system (DeltaV’s) historian database and saved in a spreadsheet format for detailed analysis. There is no flyash in this flue gas since it is obtained by burning natural gas. Consequently, the only conditioning necessary to be performed on the raw flue gas before entering the CO₂ capture unit is to clean and cool it to the desired absorber inlet temperature by passing it through an inlet gas scrubber.

3.2.3. Boundary dam (BD) field demonstration plant (decommissioned 2012)

The BD CO₂ capture unit processes flue gas of 1.4 × 10⁴ m³/day produced from the coal-fired electrical power plant of Saskpower and which has a CO₂ capture capacity of 4 ton/day. The Boundary dam pilot plant consists of three main components that are connected in series as follows: (i) a high-efficiency bag-house unit for flyash removal, (ii) an SO₂ scrubbing unit, and (iii) an amine based CO₂ capture unit. The removal of CO₂ from flue gas is achieved in an 18 inch i.d. absorbent and 16 inch i.d. regenerator using an aqueous solution of amine. An amine reclaimer is also available for amine purification. The following analytical facilities are also included within the plant: (1) continuous on-line SO₂ and O₂ analyzer located downstream of the SO₂ scrubber, (2) on-line analyzer for CO₂ concentration along the side of the CO₂ absorption column, (3) a data logging system installed to retrieve and transmit the data of process temperature and pressure to the control room, (4) local gauges and routine manual logs used for the daily operation of different plant facilities, and (5) corrosometer and electrochemical probes installed to continuously and respectively monitor short-term and long-term corrosion rates at various points in the plant.

The feed to the BD pilot plant normally contains 12–15% of CO₂ as well as some amounts of undesirable flyash, oxygen (O₂), and trace contaminants such as sulfur dioxide (SO₂) and nitrogen oxides (NOₓ). The presence of fly ash in gas stream brings about a number of operational problems such as deposition or caking on process equipment, blocking flow, wrenching pumps and pump seals, and clogging equipment and instrumentation. In the BD power plant, most of the fly ash is removed from the flue gas before discharging to the atmosphere through the flue stack. This plant was decommissioned in 2012. Both plants provide lessons
<table>
<thead>
<tr>
<th>Project</th>
<th>Capacity</th>
<th>Technology/solvent used</th>
<th>Operational status</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C2P3 University of Texas (SRP)</td>
<td>3 ton/day</td>
<td>MEA and 2 variants of PZ-Promoted K₂CO₃</td>
<td>2002–Ongoing</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>UofR (University of Regina)</td>
<td>1 ton/day</td>
<td>MEA and MEA/MDEA</td>
<td>1999–2000</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>UofR-consortium Saskpower power plant Boundary Dam (Saskatchewan)</td>
<td>4 ton/day</td>
<td>Fluor’s Econamine FG™ Technology, MEA, RS-X solvents</td>
<td>2000–Ongoing</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>CESAR/CASTOR (Dong Energy in Denmark)</td>
<td>24 ton/day</td>
<td>30 Wt% MEA, CASTOR-1 and CASTOR-2, CESAR1 and CESAR2</td>
<td>2006–2012</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>CO2CRC/International Power (Hazelwood coal-fired power plant, Australia)</td>
<td>50 ton/day</td>
<td>BASF PuraTreat™ and other new solvents</td>
<td>2009–Ongoing</td>
<td>Wang et al. (2011)</td>
</tr>
<tr>
<td>MHI-KEPCP (MHI Hiroshima R&amp;D Centre)</td>
<td>1 ton/day</td>
<td>KS-1™</td>
<td>2004–Ongoing</td>
<td>Wang et al. (2011) and Mitsubishi Heavy Industries, Ltd. (2012)</td>
</tr>
<tr>
<td>MHI-KEPCP Nanke Pilot Plant</td>
<td>2 ton/day</td>
<td>KS-1™ and other solvents</td>
<td>1991–Ongoing</td>
<td>Imai and Mitchell (2008)</td>
</tr>
<tr>
<td>MHI-KEPCP Kansai power station</td>
<td>10 ton/day</td>
<td>KS-1™</td>
<td>1991–Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td>Alstom/DOW Chemical</td>
<td>15,000 ton/year</td>
<td>Chilled ammonia</td>
<td>2008–Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td>Imperial College London</td>
<td>1.2 ton/day</td>
<td>MEA</td>
<td>2012–Ongoing</td>
<td>London (2012)</td>
</tr>
<tr>
<td>Siemens and LON (Staudinger power station, Germany)</td>
<td>NA</td>
<td>Amino acid salt formation</td>
<td>2009–Ongoing</td>
<td>Siemens (2011)</td>
</tr>
<tr>
<td>Tampa Electric/Siemens Big Bend station project (Florida)</td>
<td>1 ton/day</td>
<td>Amino acid salt</td>
<td>2013–Ongoing</td>
<td>Siemens (2011)</td>
</tr>
<tr>
<td>Tarong Energy/CSIRO/Stanwell corporation Tarong Power Station (QED)</td>
<td>1,000 ton/year</td>
<td>MEA</td>
<td>2010–Ongoing</td>
<td>Stanwell (2012) and CSIRO (2013)</td>
</tr>
<tr>
<td>CSIRO/China Huanceng Group Gaobeidian power station (Beijing)</td>
<td>3,000 ton/year</td>
<td>Amine based solvents</td>
<td>2008–Ongoing</td>
<td>CSIRO (2013) and Wardhaugh (2010)</td>
</tr>
<tr>
<td>CSIRO transportable pilot plant (China)</td>
<td>600 ton/year</td>
<td>Alternative solvent</td>
<td>2008–Ongoing</td>
<td>CSIRO (2013)</td>
</tr>
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<td>CSIRO Loy Yang power station (Victoria)</td>
<td>1,000 ton/year</td>
<td>Amine based solvents including MEA</td>
<td>2008–Ongoing</td>
<td>CSIRO (2013) and Wardhaugh (2010)</td>
</tr>
<tr>
<td>EnBW CHP Plant Heilbronn</td>
<td>7.2 ton/day</td>
<td>Amine solvent</td>
<td>-Ongoing</td>
<td>Wauschkuhn and Unterberger (2011))</td>
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<tr>
<td>SINTEF/NTNU pilot plant (Norway)</td>
<td>1.2 ton/day</td>
<td>New CO₂ capture solvent</td>
<td>-Ongoing</td>
<td>SINTEF (2013)</td>
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<tr>
<td>Hitachi/TEPCO Yokosuka Power Plant</td>
<td>4.5 ton/day</td>
<td>MEA and Proprietary solvents including H3 (Hitachi’s proprietary solvent)</td>
<td>2010</td>
<td>Wu et al. (2010)</td>
</tr>
<tr>
<td>Hitachi/EERC pilot plant (University of North Dakota)</td>
<td>0.05 Nm³/s</td>
<td>MEA and H3-1 Solvent</td>
<td>2010</td>
<td>Kikkawa et al. (2010)</td>
</tr>
<tr>
<td>Project</td>
<td>Capacity</td>
<td>Technology/solvent used</td>
<td>Operational status</td>
<td>Reference</td>
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<tr>
<td>Babcock-Hitachi Kure Research Laboratory (Japan)</td>
<td>0.28 Nm³/s</td>
<td>H3-1 Solvent</td>
<td>2012-Ongoing</td>
<td>Eswaran et al. (2011)</td>
</tr>
<tr>
<td>Hitachi/Electrabel/GCF Suez/E.ON. mobile pilot plant TNO/E.ON. Maasvlakte pilot plant</td>
<td>241 ton/day</td>
<td>Amine solvents developed by Hitachi</td>
<td>2008-Ongoing</td>
<td>Feron et al. (2009) and Eswaran et al. (2011)</td>
</tr>
<tr>
<td>RWE/BASF/Linde RWE Coal Innovation Centre (Niederaussem)</td>
<td>0.69 kg/s</td>
<td>Amine acid salt</td>
<td>2009-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td>RWE/Cansolv Technologies/BOC/IM Skaugen/The Shaw Group Inc./Tullow Oil Plc. (South Wales)</td>
<td>12 ton/day</td>
<td>Amine solvents</td>
<td>2008-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td>RWE Aberthaw pilot plant Fluor/E.ON Power station (Wilhelmshaven, Germany) Cansolv transportable pilot plant E.ON/MHI E.ON/Alstom power (Sweden) Aker Kvaerner Karsto gas terminal facilities (Stavanger) EdF (Le Havre, France) Korean Institute of Energy Research Aker Clean Carbon Scottish power (Longannet) China Huaneng Group Beijing Cogeneration Plant China Huaneng Group (Shanghai) First Energy/Powerspan/Ohio Coal Development office (Ohio) Doosan/Emissions Reduction Test Facility (FRF) ECO2 Burger, Powerspan, Ohio</td>
<td>0.6 ton/day</td>
<td>CANSOLV solvents</td>
<td>Variable</td>
<td>Feron et al. (2009)</td>
</tr>
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<td></td>
<td>1200 ton/day</td>
<td>CANSOLV solvents</td>
<td>2012-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>72 ton/day</td>
<td>MEA solvent using Econamine FG’</td>
<td>2010-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>0.6 ton/day</td>
<td>CANSOLV solvents</td>
<td></td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>96 ton/day</td>
<td>KS-1</td>
<td>2010-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>24 ton/day</td>
<td>Chilled ammonia</td>
<td>2009-Ongoing</td>
<td>Feron et al. (2009) and MIT, (2013a)</td>
</tr>
<tr>
<td></td>
<td>4.3 ton/day</td>
<td>Various solvents</td>
<td>1998-Currently not operational</td>
<td>Feron et al. (2009)</td>
</tr>
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<td></td>
<td>25 ton/day</td>
<td>UCARSOL® FGC 3000 (DOW solvent) using Alstom’s advanced amine process technology 20 wt% EMA using ABB Lumus Technology</td>
<td>2012-Ongoing</td>
<td>Alstom (2012)</td>
</tr>
<tr>
<td></td>
<td>6 ton/day</td>
<td></td>
<td>2004-Currently not operational</td>
<td>Herzog et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>4.8 ton/day</td>
<td>Amine solvents</td>
<td>2009-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>12 ton/day</td>
<td>Amine solvents</td>
<td>2008-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>100,000 ton/year</td>
<td>Amine solvents</td>
<td>2009-Ongoing</td>
<td>Feron et al. (2009)</td>
</tr>
<tr>
<td></td>
<td>20 ton/day</td>
<td>NA</td>
<td>2008-2010</td>
<td>MIT (2013b)</td>
</tr>
<tr>
<td></td>
<td>1 ton/day</td>
<td>MEA solvent, RS-2 solvent</td>
<td>2010</td>
<td>Elgarni and Aboudheir (2011)</td>
</tr>
<tr>
<td></td>
<td>29 ton/day</td>
<td>Proprietary ECO2 solvent</td>
<td>2008-2010</td>
<td></td>
</tr>
</tbody>
</table>
Table 2
Large demonstration PCCC projects – completed & operating (modified from Abu-Zahra et al., 2013).

<table>
<thead>
<tr>
<th>Large demonstration PCCC projects – completed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project</td>
</tr>
<tr>
<td>Pleasant Prairie, Alstom, WI, USA</td>
</tr>
<tr>
<td>AEP Mountaineer, AEP, WV, USA</td>
</tr>
<tr>
<td>Karlshamn, E.ON, Sweden</td>
</tr>
<tr>
<td>Ferrybridge CCS Pilot 100³, SSE, UK</td>
</tr>
<tr>
<td>Aberthaw, RWE, Wales, UK</td>
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</tbody>
</table>

Table 3
Commercial size PCCC projects worldwide.

<table>
<thead>
<tr>
<th>Commercial size PCCC projects worldwide</th>
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<tbody>
<tr>
<td>Project</td>
</tr>
<tr>
<td>Jilin, PetroChina, China</td>
</tr>
<tr>
<td>Shidongkou, Huaneng, China</td>
</tr>
<tr>
<td>IFP Energies nouvelles/EnEL Brindisi</td>
</tr>
<tr>
<td>Wilhelmshaven, E.ON, Germany</td>
</tr>
<tr>
<td>Mongsund, Statoil, Norway</td>
</tr>
<tr>
<td>Plant Barry, Southern Energy / MHI / AL, USA</td>
</tr>
<tr>
<td>South Energy / MHI / SCS / SECARB / EPR Plant Barry Power Station (Alabama) E.W.Brown, University of Kentucky, KY, USA</td>
</tr>
<tr>
<td>E.W.Brown, University of Kentucky, KY, USA</td>
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</table>

that can be derived from coal power plant and a natural gas power plant.

3.2.4. University of Texas CO₂ capture pilot plant
The University of Texas, Austin, United States has a pilot plant which provides quantitative screening of contactor alternatives and demonstrates important process concepts. It is located in a facility at the Pickle Research Center, and permits testing with artificial gas consisting of an air/CO₂ mixture in a 16.8-inch absorber/stripper. The stripper is tested at 0.2–4 atm. A wide variety of chemical solvents including promoted potassium carbonate, piperazine, etc., have been tested in the pilot plant (Dugas, 2006; Rochelle et al., 2014).

3.2.5. Hitachi/Energy and Environmental Research Center (EERC) pilot plant (University of North Dakota)
The Energy and Environmental Research Center (EERC), University of North Dakota in collaboration with Hitachi operates a 200 Nm³/h (130 scfm) CO₂ capture pilot plant. An average of 90% of the CO₂ fed to the absorber is removed at steady state during a typical test period.

3.2.6. Heat duty, absorber efficiency and CO₂ purity
Most of the pilot plants, in general operate at an absorber efficiency of 90%. Typical heat duty results reported for studies performed experimentally and by modeling/simulation for a CO₂ recovery (absorber efficiency) of 90% from the two University of Regina pilot plants are shown in Fig. 3 (UoR Consortium Final Report, 2010). As shown in the figure, these studies reported a reduction in the heat duty from about 5.0 GJ/ton to about 2.0 GJ/ton by both experiments and simulation runs, and further down to 1.5 GJ/ton by only simulation runs for various case scenarios. Experimental studies covering the reduction down to 1.5 GJ/ton were yet to be performed. According to Idem et al. (2006) (UoR Consortium Final Report 2010), the scenarios used consisted of different combinations of solvent, process configuration, and operating parameters as indicated in the figure legend. In all cases, the CO₂ product purity was measured to be >99.99% (UoR Consortium Final Report, 2010).
In the case of Hitachi/Energy and Environmental Research Center (EERC) pilot plant, Ref shows that for 90% CO₂ capture, the solvent recirculation rate needed was about 45% lower and the energy required to regenerate the Hitachi (H3-1) solvent was about 30% lower than that for 30% aqueous MEA solution. In absolute terms, recent tests conducted in this pilot facilities using coal-fired flue gas showed that for H3-1 solvent with about 90% absorber efficiency, the regeneration energy/heat duty was in the range of 2.4–2.8 GJ/t-CO₂.

Fig. 1. UoR technology development pilot plant (left) and Boundary Dam demonstration plant (right) (University of Regina Consortium, 2010).

Fig. 2. Process flow diagram of technology development pilot plant at the University of Regina (Idem et al., 2006).
3.2.7. Degradation, heat stable salts (HSS) and off gas emissions

Studies using the two UofR pilot plants (Idem et al., 2006) showed that degradation of solvent and off gas emissions depended on the flue gas contaminants (composition and concentration), severity of operating conditions (i.e., temperature and pressure), type of solvent, whether or not inhibitors (degradation and corrosion) are added in the solvent. It was reported (Idem et al., 2006) that with an operating strategy involving relatively lower temperatures and pressures, low levels of contaminants in the flue gas, as well as the addition of appropriate corrosion/degradation inhibitors where applicable, a stable operation and very low degradation of the amine used were achieved. On the other hand, with severe operating environments, a more pronounced degradation was obtained. For example, in the tests done to compare the Boundary dam demonstration plant operating environment with the UR technology development plant operating environment for aqueous MEA and blended MEA-MDEA solvents each with a total concentration of 5 mol/l, the results from analysis of the lean amine stream showed that degradation occurred in the BD plant but not in the UofR campus plant. The major compounds observed included straight chain amines such as 1-propanamine, cyclic compounds such as 1,2,3,6-tetrahydro-1-nit-pyridine and 2-pyridilidinone, dialcohols such as 1,2-ethanediol, as well as sulfur compounds such as isothiocyanato-ethane and 1,1-dioxidotetrahydro-thiophene. The presence of sulfur compounds were attributed to contact of aqueous MEA and MDEA with trace amounts of sulfur dioxide (SO2) that survived the scrubbing process in the SO2 unit. As pointed out by Idem et al. (2006), the major difference between the Boundary Dam pilot plant and the UoR technology development plant was primarily that the former was fed with flue gas from a coal-fired power plant (which is composed of CO2, O2, SO2, N2, particulates, Hg, etc.) whereas the latter is fed with flue gas derived from the combustion of natural gas (composed mainly of CO2, O2 and N2). This difference in flue gas feed components was considered to be the major factor responsible for the difference in the degradation product slate between the two plants. The other factor may have involved the inhibitor. According to Idem et al. (2006), it was possible that the inhibitor acted as catalyst to facilitate degradation. In the Boundary dam pilot plant off gas analyzed qualitatively using Draeger tubes, components observed included volatile aldehydes, ketones formats, and ammonia. Another parameter which impacted operation in the Boundary dam CO2 capture plant was the presence of flyash in the flue gas to the pilot plant process system. This impacted solvent degradation adversely. In studies at UT Separations Research Program (SRP) pilot plant and Pilot Plant 2 (PP2), Texas, USA using a Piperazine-based solvent process, degradation was reported and the degradation products were compared with those from CSIRO’s Tarong pilot plant of Australia. These products were: total formate, 2-piperazineOH, nitrosopiperazine, nitrate, sulfate, and iron in different concentrations (Rochelle et al., 2014).

3.2.8. Corrosion

Corrosion studies were performed and reported in the UofR Boundary dam pilot plant (UofR Consortium Final Report, 2010) as well as in the Technology Development pilot plant (Kittel et al., 2009). In the Boundary Dam pilot plant, the major contribution to corrosion, conducted using corrosometer probes and carbon steel metal coupons, was the presence of SO2 and SO3 in the flue gas stream, high total amine concentration, high CO2 loading and high temperature. Additional studies in the UofR Boundary dam pilot plant in which coupons were strategically placed in certain locations in the plant over a six months period of operation revealed that the locations with significant corrosion were: flue gas stream to the absorber, SO2 scrubber solution, absorber bottom vapor, and CO2 product as shown in Fig. 4. In the case of SO2 scrubber solution, there was complete dissolution of the coupon due to severe corrosion. These corroborated the earlier results that used online measurements which showed the detrimental effect of the presence of certain compounds in the process streams. In 2009, under the framework of CAPRICE project, evaluation of corrosion was performed on the University of Regina (U of R) pilot plant using an online electrochemical probe (Kittel et al., 2009). The tests used MEA and evaluated corrosion in the process system. Corrosion measurement identified temperature as being a significant parameter in increasing the rate of corrosion. MEA concentration also contributed to an increase in the corrosion rate.

3.3. Europe

The listing in Table 2 shows the following small CO2 capture pilot plant projects in Europe in terms of name of project, location, CO2 capture capacity and solvent technology used: SINTEF/NTNU pilot plant (Norway, 0.05 ton/h, new CO2 capture solvent), EnBW CHP Plant (Heilbronn, 0.3 ton/h, amine solvent), CESAR/CASTOR – Dong Energy (Denmark, 24 ton/day, 30 wt% MEA), CASTOR-1 and CASTOR-2, CESAR1 and CESAR2; Imperial College (London, 1.2 ton/day, MEA), IFP Energies nouvelles/ENEL Brindisi power plant (Italy, HiCapt™ process, 2.25 ton/hr, different solvents including MEA (20–40 wt%)), RWE/BASF/Linde RWE Coal Innovation Centre
MEA, AMP, PZ as well as NH₃ emissions were observed by Martens (2015). Also, online measurement of water-wash section. Due to volatility, MEA was also detected in DEA, formaldehyde, methylamine, acetamide, and ammonia which ceased was observed and the degradation products slate included EU Project CESAR. Degradation based on the MEA solvent process CO₂ Capture. In a comparative degradation study by Stoffregen capture plant capable of removing 7.2 ton/day of CO₂ from a slip-structure material evaluation was carried out in a pilot scale CO₂ capture plant. According to De Vroey et al. (2013), additional investigation on corrosion using coupons, on-line monitoring using electrochemical probe, and pilot plant inspection were also performed with MEA solvent separately in both the Dong Energy’s pilot plant at Esbjerg (Denmark), and TNO’s Maasvlakte pilot plant (The Netherlands). De Vroey et al. (2013) reported that the weight loss measurement of coupons (placed in strategic locations throughout the process) correlated well with on-line measurement using the electrochemical techniques. Corrosion resistance in most zones in the pilot plants using carbon and Stainless steels in the tests was generally good. However, De Vroey et al. (2013) identified the stripper sump, high temperature lean solvent pipe, reboiler and reclaimer as critical zones which should be carefully monitored. Studies on the inter-relationship between corrosion rate, solvent degradation and NH₃ emissions based on MEA solvent process has recently been reported (Khakharia et al., 2015) using the 6 ton/day TNO’s Maasvlakte CO₂ capture pilot plant in the Netherlands. Measurement of corrosion was done using both on-line electrochemical probe and off-line coupon weight loss. Based on this test, corrosion was found to generally increase with flue gas oxygen concentration and length of operation but reduce only temporarily with the addition of amine make-up. Corrosion was also found to be in a direct relationship to NH₃ emission and metal content (more degradation). This work has suggested the use of online corrosion monitoring to help detect both early degradation and increased emissions.

3.4. Australia

In Australia, the listing in Table 2 shows the following small CO₂ capture pilot plant projects in terms of name of project, location, CO₂ capture capacity and solvent technology used: CO2CRC/International Power (Hazelwood coal-fired power plant, Australia), 50 ton/day, BASF Puratreat™ and other new solvents, Tarong Energy/CSIRO/Stanwell corporation (Tarong Power Station (QLD), 1000 ton/year, MEA), CSIRO Loy Yang power station (Victoria, 1000 ton/year, amine based solvents including MEA).

No studies have been reported on corrosion and heat duty obtained from each specific pilot plant. On the other hand, degradation in solvents used in CO₂ capture pilot plants in Australia was reported by Azzi et al. (2014), in which various emissions components including amines (e.g., MEA and DEA and alkyamine products), NH₃, nitrosamines, aldehydes (e.g., formaldehyde and acetaldehyde), heat stable salts (e.g., formate, acetate, and propionate) were observed from the absorber outlet, water-wash liquor, water-wash outlet, solvent liquor, and inlet-gas streams.

3.5. Asia

Table 2 also shows the small post combustion CO₂ capture pilot plants in Asia. These are: MHI-KEPCP (MHI Hiroshima R&D Centre), 1 ton/day, KS-™; MHI-KEPCP Nanko pilot plant; 2 ton/day, KS-™ and other solvents; MHI-KEPCP Kansai power, KS-™; MHI-KEPCP/J-Power Matsushima Thermal Power Station of Electric Power Development Co. (Nagasaki), 10 ton/day, KM-CDR Process (Denmark), and TNO’s Maasvlakte pilot plant (The Netherlands). In Australia, the listing in Table 2 shows the following small CO₂ capture pilot plant projects in terms of name of project, location, CO₂ capture capacity and solvent technology used: CO2CRC/International Power (Hazelwood coal-fired power plant, Australia), 50 ton/day, BASF Puratreat™ and other new solvents, Tarong Energy/CSIRO/Stanwell corporation (Tarong Power Station (QLD), 1000 ton/year, MEA), CSIRO Loy Yang power station (Victoria, 1000 ton/year, amine based solvents including MEA).

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This was claimed to generate a higher CO₂ loading, thus reducing the driving force for the absorption process even at increased loading. To the best of our knowledge, Siemens and desorption of CO₂ as well as being as energy efficient as the least perform as effectively in terms of the ability in absorption the operational issues, the new type of absorbents must also at related operational problems. However, in addition to addressing types of absorbents with the goal of correcting these amine-solvent related operational problems. Due to these reasons, efforts have been put into developing different types of absorbents with the goal of correcting these amine-solvent absorbent system. Only a few tests of amino acid based technology have to improve in order to compete with the amine based technology. On the other hand, Sanchez-Fernandez et al. (2014) have reported on studies of the patented process validation in a pilot scale in 2009 using a 1 ton/day CO₂ capture pilot plant set up at unit 5 of E.ON’s Staudinger steam power plant in Germany. With more than 4000 h in operation by March 2011, the PostCap process was claimed to reach 90% CO₂ capture rate with low energy consumption, nearly zero solvent loss and high stability (with less than 1% degradation). A more recent work has reported a pilot scale test of aqueous sodium glycinate (NaGly) for CO₂ capture ability from real power plant flue gases extracted from EVN Dürrnrohr coal based power plant in Austria (Rabensteiner et al., 2014). An absorber and desorber of respective heights of 12 and 8 m (as shown in Fig. 5) were used to treat flue gas containing 11–13% CO₂ so that the results could reflect industrial conditions. By varying test parameters including NaGly concentration, flue gas flow rate, liquid to gas ratio, desorber pressure, and absorber height, NaGly used 40% energy requirement higher than that of a typical 30 wt% MEA tested for comparison. As pointed out by Rabensteiner et al. (2014), this is an indication that energy consumption will be one of the areas where amino acid based absorption process might have to improve in order to compete with the amine based technology. On the other hand, Sanchez-Fernandez et al. (2014) have reported on simulation work done by The Netherlands’ TNO, as well as TU Delft and the UK’s Process Monkey for the use of potassium taurate based precipitating amino acid salts processes called DECAP and DECAP plus in terms of energy requirement saving within the CO₂ removal unit. The simulation results were claimed to reduce energy requirement for the DECAP processes by 15% as compared with that for the MEA baseline case (Sanchez-Fernandez et al., 2014). However, actual pilot plant test must be used to validate the modeling data, which no information is available up to the present date. Although, as recently published in the literature (Abu-Zahra et al., 2013), TNO/EON Maasvlakte pilot plant is listed as a project based on the use of amino acid salts as being in operation since 2008. There is still no information available as to confirm if this TNO related project is the same DECAP process mentioned earlier.

3.6. Amino acid salts

Although amine-based solvents are effective to capture CO₂ from a low pressure flue gases produced from fossil fuel combustion based power plant process, the compounds have been shown to suffer gradually from chemical breakdowns and other operational related problems as have been mentioned previously. Due to these reasons, efforts have been put into developing different types of absorbents with the goal of correcting these amine-solvent related operational problems. However, in addition to addressing the operational issues, the new type of absorbents must also at least perform as effectively in terms of the ability in absorption and desorption of CO₂ as well as being as energy efficient as the amine-based absorbents. Amino acid has been proposed as a potential alternative to the conventional amines. Structurally, amino acid contains a CO₂ absorbing amino group (–NH₂) similar to that of the amine. At the other end of the molecule, amino acid also features a carboxylic functional group which is often converted to a salt to help reduce the volatility of the solution during the absorption-regeneration process. These acids were tested specifically for the potential use as lower toxic air scrubbing solution (compared to MEA solvent) for a navy based submarine. Hook (1997) evaluated potassium salts of various propanoic acid based amino acids in terms of CO₂ absorption and desorption rates compared to MEA and hindered AMP solvents. Although a few were found to be comparable to MEA and AMP solvents, carbonate salt crystallization became the problem as this specifically prohibited the use of many of these amines as a direct replacement for MEA. However, Majchrowicz et al. (2009) and Aronu et al. (2013) have highlighted the occurrence of salt precipitation during the absorption process as being an advantage in that it helped to maintain the CO₂ partial pressure driving force for the absorption process even at increased loading. This was claimed to generate a higher CO₂ loading, thus reducing the energy usage during solvent regeneration. In order to fully benefit from this precipitation system, the existing CO₂ capture plants or pilot plant must be modified in terms of the absorber, regenerator, pumps, and other associated equipment for testing with amino acids so that they can handle solid/slurry formation during the reaction. This can be a big burden unless a completely new pilot plant is designed and built specifically for this precipitating solvent. This review paper focuses only on pilot scale testing of this new absorbent system. Only a few tests of amino acid based technology for CO₂ capture have been evaluated at pilot plant scale (i.e., CO₂ capture size of >1 ton/day). To the best of our knowledge, Siemens AG from Germany is one of the technology developers who has been able to test its amino acid based proprietary solvent and process configuration known as PostCap™ process at this operational scale.

3.6.1. North America

The US DOE awarded this project in July 2010 with a $8.9 million grant. This pilot plant was one of 10 selected by the DOE aimed at developing advanced technologies for capturing carbon dioxide from coal combustion. This pilot plant project is demonstrating Siemens POSTCAP technology which utilizes an amino acid salt formulation as a solvent for CO₂ absorption. It was expected to be operational in 2013. So far, no results from this project have been reported in the open literature.

3.6.2. Europe

Schneider and Schramm (2011) have reported on studies of the patented process validation in a pilot scale in 2009 using a 1 ton/day CO₂ capture pilot plant set up at unit 5 of E.ON’s Staudinger steam power plant in Germany. With more than 4000 h in operation by March 2011, the PostCap process was claimed to reach 90% CO₂ capture rate with low energy consumption, nearly zero solvent loss and high stability (with less than 1% degradation). A more recent work has reported a pilot scale test of aqueous sodium glycinate (NaGly) for CO₂ capture ability from real power plant flue gases extracted from EVN Dürrnrohr coal based power plant in Austria (Rabensteiner et al., 2014). An absorber and desorber of respective heights of 12 and 8 m (as shown in Fig. 5) were used to treat flue gas containing 11–13% CO₂ so that the results could reflect industrial conditions. By varying test parameters including NaGly concentration, flue gas flow rate, liquid to gas ratio, desorber pressure, and absorber height, NaGly used 40% energy requirement higher than that of a typical 30 wt% MEA tested for comparison. As pointed out by Rabensteiner et al. (2014), this is an indication that energy consumption will be one of the areas where amino acid based absorption process might have to improve in order to compete with the amine based technology. On the other hand, Sanchez-Fernandez et al. (2014) have reported on simulation work done by The Netherlands’ TNO, as well as TU Delft and the UK’s Process Monkey for the use of potassium taurate based precipitating amino acid salts processes called DECAP and DECAP plus in terms of energy requirement saving within the CO₂ removal unit. The simulation results were claimed to reduce energy requirement for the DECAP processes by 15% as compared with that for the MEA baseline case (Sanchez-Fernandez et al., 2014). However, actual pilot plant test must be used to validate the modeling data, which no information is available up to the present date. Although, as recently published in the literature (Abu-Zahra et al., 2013), TNO/EON Maasvlakte pilot plant is listed as a project based on the use of amino acid salts as being in operation since 2008. There is still no information available as to confirm if this TNO related project is the same DECAP process mentioned earlier.
Thus, pilot plant results are still needed as proof for such claim of energy reduction discussed earlier.

3.7. Aqueous/chilled ammonia process

Alstom is one of the few leading technology developers in the field of chilled ammonia based carbon capture process (CAP). Alstom’s CAP was licensed in 2006 and showed success during multi stages of laboratory scaled testing with Electric Power Research Institute (EPRI) and industrial funders (Telikapalli et al., 2011). It was based on these lab results that two pilot plant tests at We Energies Pleasant Prairie Power in Pleasant Prairie, Wisconsin, US (shown in Fig. 6) and E.ON’s Karlshamm in Sweden shown was later performed in parallel to prove the concept of the CAP process. Both pilot plants could reach 90% CO2 capture efficiency with less than 10 ppm emission of NH3. A CSIRO report published in 2009 also mentioned the start up of an aqueous ammonia based CO2 capture plant at Delta Electricity Munmorah power station in Australia (Feron et al., 2009). This pilot plant with the process flow diagram shown in Fig. 7 (Yu et al., 2011) is based on the use of aqueous ammonia for CO2 capture from the power station without the flue gas desulfurization (FGD) or denOx unit. According to the same report (Yu et al., 2011), various pilot plant trial conditions were tested using up to 6% aqueous NH3 solution. Although the process still consumed higher regeneration energy than the conventional MEA process, it was suggested that this aspect could be improved by increasing the concentration of NH3 even though the testing at higher NH3 concentrations was not performed. Besides Alstom, and CSIRO and Delta Electricity, it was only mentioned that South Energy, MHI, SCS, SECARB, and EPR Plant Barry Power station in Alabama, USA have had an on-going CO2 capture pilot test using chilled ammonia based solvent (Abu-Zahra et al., 2013). The results however, are not publicly available, to our present knowledge.

3.8. Ionic Liquids

Information is very scanty regarding testing of ionic liquids for CO2 capture at the pilot plant scale. In North America, according to the Office of Fossil Energy (FE), US Department of Energy (DOE) website (http://energy.gov/fe/articles/ten-projects-selected-doe-advance-state-art-carbon-capture-coal), DOE announced its funding support for the use of ionic liquids for CO2 capture from coal combustion as one of the 10 projects in the U.S. that aimed to reduce the energy and efficiency penalties to existing and new power plants. However, this project was only awarded to Ion Engineering, LLC to conduct bench-scale development and testing studies. Though, the current information on the DOE website (http://energy.gov/energy-department-investments-innovative-carbon-capture-projects) still describes this project as one of DOE’s investments, the project status is unknown and listed only as “will test an advanced CO2 capture solvent under realistic slipstream conditions during continuous long-term operation.”

3.9. Summary of lessons learned from small pilot plant operations

Pilot plant operations generally have been used to evaluate solvents, operating strategies, and process configurations as well as process integration and process optimization strategies for CO2 capture in terms of heat requirement for solvent regeneration, type of heat medium, source, moisture content and temperature of flue gas stream to absorber, packing or column internals, concentration of CO2 in the flue gas, flue gas conditioning, lean and rich loadings, ease of operation, CO2 production, emissions, type of solvent and solvent stability (Idem et al., 2006). Pilot plant operations are also used not only to compare results from different pilot plants, but also for capacity building as well as to evaluate the degree of correlation of different simulation software with experimental data from different pilot plants such as reported by Luo et al. (2009). Finally, as has been mentioned earlier, pilot plant operations can be used to obtain engineering data for design of larger demonstration plants, which would then be used to design commercial CO2 capture plants. According to Gelowitz et al. (2013b), some pilot plant operation results are proprietary, but there are others where results have been made available in the open literature. Nevertheless, there are indications that some results have shown some of the design flaws and assumptions usually made in designing absorption based CO2 capture plants. Gelowitz et al. (2013b) points to an example which attempts to transpose the design philosophy in natural gas processing to amine based CO2 capture from flue gas. The notable differences are that natural gas is at high pressure while flues gas is generally at low pressure; also, natural gas may contain hydrogen H2S, COS but no O2 (i.e., in a reducing atmosphere), flue gas contains SO2, O2, NOx, etc. (in an oxidizing atmosphere). According to Gelowitz et al. (2013b), pilot plant operations have highlighted optimum ranges of operating variables such as flue gas feed temperature, solvent circulation rates, absorber size compared with the stripper size, stripper pressure, heat exchanger sizes, type of solvent, etc. that need to be used for optimum plant performance while minimizing capital costs. The use of these operating variables in addition to the use of field flue gas such as in the Regina pilot plant (natural gas generated flue gas) and Boundary dam pilot plant (coal fired flue gas) have also shown the impact of flue gas impurities on solvent stability, the need to condition the flue gas stream before it is introduced into the absorber unit, off gas emissions, waste disposal and overall plant performance. Gelowitz et al. (2013b) also indicates that there is an optimum plant size that is suitable for pilot plant studies, even though the current authors note that “optimum size” depends upon the information for which the experiment is undertaken. Generally, commercial technologies are evaluated first at smaller scale, moving towards larger scale as uncertainty boundaries are reduced. Gelowitz et al. (2013b) suggest that the pilot plant should be big enough so that reliable engineering data can be obtained for plant design. At the same time, it should be small enough to allow for changes in the plant configuration at a reasonable cost. As has been demonstrated, there are a lot of pilot plants located in different parts of the world, the ones discussed in further detail in this review paper were selected on two bases: (1) some of their operation results are available in the open literature, and (2) the pilot plants span the CO2 capture capacity spectrum.
of (a) <1.0 ton/day, (b) = 1.0 ton/day, (c) 1.0 < CO2 capture capacity < 10 ton/day, and (d) >10 ton/day. Based on the experience by Gelowitz et al. (2013b), pilot plant sizes or capacities in the range of 1.0–10.0 ton/day are most suitable to provide this optimum size. For example, on the low end, gas/liquid distribution is sufficient to represent large scale plant operation. Additionally, the level of control, types of instrumentation, measurement equipment, etc., is typical to a large scale facility. If it is smaller than 1.0 ton/day, it will generally tend to use lab scale type instrumentation and measuring devices. Alternative means are used to ensure column liquid distribution and there are issues with liquid wall effects on small diameter columns. If it is above 10.0 ton/day, it requires a significant amount of resources such as volume of amine solvent, disposal, electricity, heat, cooling, and other utility related items to achieve similar results from a unit less than 10.0 ton/day but with a higher cost. Additionally, configuration changes may require cranes and other heavy equipment to change piping, replacement of pumps, valves, etc., and require a large facility footprint to accommodate the plant and use of this heavy equipment.

Operational issues have been encountered in the amine-based pilot plants including degradation, corrosion, aerosol formation, off gas emissions, as mentioned previously. The occurrence of these issues has allowed remedies to be put in place in subsequent or larger demonstration plants. For example, amine solvents now have amines that are less prone to degradation and less volatile, while the plants are constructed with materials that are less prone to corrosion. Also, in order to minimize degradation as well as aerosol formation, some solvent technologies adopt a more enhanced polishing of the inlet flue gas in order to remove degradation and aerosol forming compounds. Furthermore, in order to minimize both degradation and corrosion, some solvent technologies adopt the strategy of adding degradation and corrosion inhibitor additives in their solvent formulation. More extensive pilot plant activity is needed regarding the use of amino acid salt, chilled ammonia and ionic liquids for CO2 capture in order to generate adequate results that can be used in subsequent improved design for these alternative solvent-based post combustion capture technologies.

4. Large demonstration plants

4.1. Amine based process

Fig. 8 is a picture representing different sections of TCM, which is a joint venture set up by the Norwegian state (75.12%), Statoil (20%), Shell (2.44%) and Sasol (2.44%). TCM aims to increase knowledge on carbon capture technologies, in order to reduce technical and financial risk, and accelerate the development of qualified technologies capable of wide scale international deployment. According to de Koeijer et al. (2011), TCM consists of two large post-combustion CO2 capture demonstration plants near the Statoil operated Mongstad refinery, located at the Norwegian west coast north of Bergen. Also, according to de Koeijer et al. (2011), the amine plant was designed and constructed based on the CO2 capture technology provided by Aker Clean Carbon (ACC). TCM defined further specifications and additional generic functionalities. New technology elements that were included in the testing and verification matrix included improved solvents. The initial 16 months of operations involved the testing of monoethanolamine and a new ACC solvent after which tests were run by the TCM partners. de Koeijer et al. (2011) indicate that for TCM, the quality and quantity of emissions from the absorber to air became top priority, which represented a health and environmental uncertainty, mainly due to the lack of reliable and accessible experimental data. Some results from this demonstration plant were presented during GHGT-12 in Austin, Texas (Maxson et al., 2014; Hamborg et al., 2014a,b; Falk-Pedersen et al., 2014; Brigman et al., 2014; Morken et al., 2014a,b; Gorset et al., 2014a,b). Also, Knudsen (2015) validated solvents S21 and S26 for degradation and emissions in TCM. The degradation of both solvents was found to be much less than MEA. The same trend was found for total nitrosamine emissions.

Another large CO2 capture demonstration plant that has operated recently is the SSE Ferrybridge Carbon Capture Pilot (CCPilot100+) plant in the United Kingdom. It has a capacity of 100 ton of CO2 produced per day. It was launched on 30 November 2011 as a collaborative project between government and industry after the completion of its construction phase. The objective...
of the project was to test amine based post combustion capture (PCC) technology on a real working power station. According to Fitzgerald et al., (2014a), the test program was to run from 2012 to 2013 during which period the process and components would be optimized, and performance models developed. The 100 ton of CO₂ per day are captured from a flue gas slipstream corresponding to approximately 5 MW of electric power (Fitzgerald et al., 2014a). This slipstream is extracted after the newly commissioned flue gas desulphurisation unit at the Ferrybridge power station. The retrofit, with the super critical boiler and turbine, are intended to capture, through an efficiency increase from 36% to 45%, 0.5 Mt/year CO₂. According to Fitzgerald et al. (2014a), Ferrybridge represented the largest carbon capture plant of any type in the UK. Therefore, it also represented a significant step forward in the world of CCS as a critical bridge between research and commercialisation. The Doosan Babcock, SSE and Vattenfall consortium successfully completed the two year test programme on the CCPilot100° post combustion carbon capture (PCC) pilot plant at SSE's Ferrybridge Power Station in December 2013. Some results from this demonstration plant were presented during GHGT-12 in Austin, Texas. These were on Ferrybridge CCPilot100° operating experience and final test results (Fitzgerald et al., 2014a,b).

There are other large demonstration plants worldwide. These include E.ON/MHI (4 ton/h, KS-1), RWE Aberthaw pilot plant (50 ton/h, Cansolv solvent), Fluor/E.ON power station (Wilhelmshaven, Germany, 3 t/day, Fluor Econamine FG Plus); E.ON/MHI (4 ton/h, KS-1), IFP Energies nouvelles/EnEL Brindisi power plant (Italy (HiCapt° process), 2.25 ton/h, different solvents including MEA (20–40 wt%), South Energy/MHI/SCS/SECARB/EPR Plant Barry power station (Alabama, 500 ton/day, KS-1 solvents (MHI) technology), and China Huaneng Group (Shanghai, 100,000 ton/year, amine solvents).

4.2. Aqueous/chilled ammonia process

4.2.1. North America

Validation using a larger power plant with the capture unit designed to remove 100,000 ton/year was done in 2009 at AEP Mountaineer Power Plant in New Haven, USA, also shown in Fig. 9. This pilot plant test was able to generate 78–85% CO₂ capture efficiency with 50,000 t/year capacity as of year 2011 (Kozak et al., 2011).

4.2.2. Europe

A paper has reported more results of Alstom’s CAP process runs conducted at Technology Centre Mongstad (TCM) chilled ammonia pilot plant in Norway (Lombardo et al., 2014). The pilot plant shown in Fig. 10 designed back in 2008 and commissioned in 2012 is able to treat both refinery off-gas from an oil residue cracker unit as well as the exhaust from a gas turbine based combined heat and power plant at a CO₂ capture rate in the range of 22,000–82,000 ton/year. The CAP process carried out at TCM was reported to produce a similar results to those obtained earlier at the Mountaineer plant with the capture rate between 75 and 85%. Low emission of NH₃ was still observed in the TCM based test.

5. Commercial plants

5.1. Amine based Process

The only operating commercial CO₂ capture plant in the world constructed and commissioned after the IPCC report is the SaskPower BD3 plant in Estevan near Regina in Canada. An overall view of this plant is given in Fig. 11. The estimated capacity is 1 Mt/year of CO₂ produced. The BD3CO₂ capture process uses the CANSOLV technology. According to Rochelle (GHGT-12, 2014), this is regarded as a second generation CO₂ capture technology which has improvements over the first generation CO₂ capture technologies. Prior to the IPCC report, there were three commercially available absorption processes for CO₂ capture in post combustion systems. These were: Kerr–McGee/ABB Lummus Crest Process (Barchas and Davis, 1992), the Flour Daniel ECONAMINE process (Chapel et al., 1999; Sander and Mariz, 1992), and the KEPCO/MHI Process by Kansai Electric Power Co., Mitsubishi Heavy Industries (Mimura et al., 2003, 1999). The lessons learned and experienced acquired through the project (Monea, 2014), as well as the technology description of the process (Cansolv, 2014) of the BD3CO₂ capture plant were highlighted during GHGT-12. So far, news regarding the operation of this plant reveals interesting flyash chemistry and waste water chemistry. Also, the design team,
There is one commercial size CO₂ capture plant that has been reported to be under construction. This is the WA Parish Petra Nova, NRG, Texas for which the source of flue gas is coal, capacity is 250 MW, solvent technology is MHI (KS-1), and is presently under construction. In addition, there are other commercial CO₂ capture plants that are still in the planning stage. These include the following with their respective source of flue gas, capacity and solvent technology: Bow City, BCPL, Alberta (coal, 1000 MW, and Cansolv), ROAD, E.ON, Netherlands (250 MW), Peterhead, Shell and SSE, UK (gas, 385 MW, and Cansolv), Shengli Oil Field EOR, Sinopec, China (coal, 101–250 MW, and amines), and PG Elektrownia Belchatow, Poland (N/A, 1.8 M ton/day, Alstom amine technology).

6. Experience with practical implementation

Based on the available reports of studies on pilot plants, demonstration plants, and commercial plants, most amine solvents are claimed to be better than the benchmark MEA solvent (30 wt% aqueous MEA) in most performance criteria such as heat duty, degradation characteristics, volatility, corrosion, etc. In contrast, the toxicity characteristics of MEA appear to be much less than these other solvents. On the other hand, amino acid salts is said to be more stable than the amines but its performance characteristics in terms of heat duty has not yet been verified practically to be equal to, or let alone surpass that for amines. Chilled ammonia has not yet been compared to amine solvents on the same basis while ionic liquids has not yet fully gone into pilot scale studies at this point in time. On the whole, the operation of many of these pilot plants, demonstration plants and commercial plant have contributed to the wealth of knowledge on PCC by absorption using reactive solvents. It has created awareness on the need for optimization strategies that could be used to minimize heat duty for solvent regeneration, design to minimize plant size, effective and economic flue gas polishing strategies, development of online analytical methods (van der Ham et al., 2014; Pouryousefi, 2015; Pouryousefi and Idem, 2008), effective reclaiming methods (Elmoudir et al., 2014), etc. Operational experience has also brought to light the need for a thorough understanding of environmental and safety implications in amine processes. In particular, the

Fig. 9. AEP Mountaineer Power Plant in New Haven, USA (Lombardo et al., 2014).

Fig. 10. Technology Centre Mongstad (TCM) chilled ammonia pilot plant in Norway (Lombardo et al., 2014).
Health, Safety and Environmental characteristics, the formation mechanisms and the management, of nitrosamines and aerosols has been seen critical to maintaining a safe and environmentally acceptable operation. Much of the needed science in this area has been established or is in progress.

6.1. Degradation and degradation products

As has been shown earlier, most amine solvents do degrade to varying extents depending on the operating conditions. The degradation products are also varied because of the varying operating conditions. These include ammonia, aldehydes, ketones, organic acids, other amines, etc. For secondary amines, nitrosamine is formed as an additional degradation product. These products are typically found in the liquid stream in the process and in the absorber offgas stream (for volatile amines and degradation products). Also, depending on the operating conditions, aerosols are formed and released in offgas stream. In order to ensure that the Health, Safety and Environmental characteristics of PCCC plant using reactive solvents are maintained, appropriate sampling, monitoring and measurement techniques must be put in place for the offgas as well as liquid in process and liquid effluents to ensure an environmentally acceptable operation. It must be emphasized that a clear distinction should be made between coal, gas and industrial pilots each of them focusing on separate challenges.

6.2. Off gas: sampling and analytical techniques

6.2.1. Sampling

Typical offgas emissions also likely carry aerosols that can contain trace amounts of amine, degradation products, nitrosamine, and a number of other formed products, depending on the solvent and operating conditions. Part of the challenges of practical implementation is that, as part of an operating permit, it is required that these chemical compounds be identified, quantified and monitored to ensure they fall within the allowable exposure limits as set by regulatory bodies. The challenge is that currently there are no standardized methods developed to recover these vapors and aerosols from amine based carbon capture facilities. Basically, an extractive sampling system is required similar to that developed by USEPA Methods 1-8 (USEPA, 2015a; USEPA, 2015b; USEPA, 2015c; USEPA, 2015d; USEPA, 2015e; USEPA, 2015f; USEPA, 2015g; USEPA, 2015h; USEPA, 2015h; USEPA, 2015a; 2015h). However, in order to accurately quantify aerosols and their compounds, certain modifications must be made on the typical sampling setup. For example, since there is no particulate matter, the heated filter box and filter assembly can be removed. Several organizations and institutes in various parts of the world (including TNO, SINTEF and SaskPower/UoR from The Netherlands, Norway, and Canada, respectively) are currently working on isokinetic sampling methods to effectively obtain representative samples. These methods include either one or any combination of a heated probe, cold probe, high velocity, high volume, and use of Phase Doppler Interferometer (PDI) to measure size, concentration, and velocity of aerosols, use of sorbent tubes, and filtration methods. For the most part, impinger bottles immersed in an ice bath are used to contain the sample along with the use of a pitot tube, manometer, temperature probes, dry gas meter, and sample pump.

6.2.2. Analysis of off-gas emissions including amines, volatile degradation products, and nitrosamines. A major problem related to the analysis of off-gas emissions is that their measurement is extremely difficult due to the ultra low concentration and complicated matrix effect in the samples. Unlike bulk liquids, off-gas always contains amines and other emitted pollutants in extremely small concentrations of which can be as low as part per billion (ppb) level. In addition, the off-gas samples need to be collected properly to preserve the species in the emission at such low concentrations before being sent to the laboratory for detailed analysis. As suggested by most of the method developers listed earlier, the procedure required to collect the emitted species in off-gas streams is nor-
mally through the use of an effective isokinetic probe system for sampling the off-gas from the vent stack. An impinger system containing a series of impinger bottles filled with appropriate chemical solutions is then used to trap the compounds emitted in the off-gas stream. A dilute acid solution is normally used to trap not only the amines but also nitrosamines and other emission components. The National Institute for Occupational Safety and Health (NIOSH) recommends the use of hexanesulfonic acid diluted with water to obtain a 2 mM solution to trap MEA, DEA, and TEA from air sample (NIOSH, 1994). A combination of cold probe, condenser, and liquid absorption system using impingers has been recommended by SINTEF.

According to SINTEF report (SINTEF Materials and Chemicals, 2012), the impinger solution used was 0.1 N sulfuric acid (H₂SO₄) to trap the amine, ammonia, and also nitrosamines and other compounds. A similar concentration of sulfamic acid was also used specifically for nitrosamines to help prevent an artifact being formed during sample collection. A separate work evaluated the amine emissions from its proprietary amine solvent used in pilot plant run in Japan (Fujita et al., 2013). This work also used a probe sampling system to sample the off-gas and send to an on-line proton transfer reaction-mass spectrometry (PTR-MS) for amine emission analysis. The technique sensitivity was reported to be less than 10 ppbv. Off-line off-gas samples were also collected using 2 impinger bottles containing an unidentified reagent to trap the emitted amines for GC–MS and LC–MS analysis. This off-line technique was reported to have a detection sensitivity of less than 2 ppmv. A similar sampling system was used more recently to measure MEA and nitrosamine emissions related to aerosol formation. Three impingers bottles with the first 2 containing 0.1 N sulfuric or sulphamic acids and the last one being left empty were used. In addition to MEA, N-nitrosodimethylamine (NDMA), N-morpholine (NMOR), N-nitrosodiethanolamine (NDELA) and MEA-nitramine were analyzed from the impinger solution mixture (after sample pretreatment using liquid–liquid or solid phase extraction) using tandem liquid chromatography triple quadruple mass spectrometry (LC–MS–MS–QQQ) (Khakharia et al., 2014a,b). SINTEF (2012) also recommended sample pretreatment of off-gas samples in its study to minimize the interference of high concentration of MEA in the samples prior to the analysis of trace components including nitrosamines, alkylamines, and ammonia.

The discussion so far has been centered on off-line analysis. On-line monitoring and measurement of off-gas emissions is also becoming more common as the technique is capable of giving real-time data, thus allowing any process anomalies to be immediately detected. Analytical tools used to measure the CO₂ plant emissions on-line normally rely on spectrotechnical procedure for Fourier transform infrared analyzer (FTIR). A field test was conducted at the Danish Esbjerg CO₂ capture pilot plant to show capability of an online FTIR in measuring inorganic and organic emissions in the process off-gas (Mertens et al., 2012). The FTIR system tested at Esbjerg plant was installed downstream of the absorber top having the entire system including probe, probe filter, sampling line, and the analyzer heated constantly at 180 °C to avoid condensation problem from water saturated off-gas stream. The same FTIR setup was later used to measure the emissions of MEA and NH₃ also from Esbjerg pilot plant. The real-time monitoring data generated by the FTIR helped understand the emission behaviors of NH₃ and MEA and the effect of water wash section used to reduce the emissions (Mertens et al., 2013). Other works have demonstrated the use of a different on-line monitoring technique in measuring the emissions of amines. This is based on a pilot plant test of the Japanese Mikawa Power Plant of Sigma Power Co., Ltd. (Fujita et al., 2013). This work incorporated an on-line amine measurement of their pilot plant off-gas using a proton transfer reaction mass spectrometry (PTR-MS). Unlike the FTIR technique discussed previously, the off-gas sampled from the stack was required to be cooled down before injecting into the instrument. Amine emissions measured from this on-line instrument was found to be less than that obtained using the off-line analysis. This trend, which was also observed in the previous FTIR technique, was thought to be due to the loss of sample while attaching the sample probe. More investigation of these on-line measurements is needed in order to confirm the accuracy of the data.

6.3. Main body of liquid
6.3.1. Offline analysis of amines and degradation products. Amine analysis is an essential element required during the carbon dioxide (CO₂) capture process. The amine concentration, which is an important process parameter in controlling the CO₂ absorption performance, must be accurately determined prior to running the capture plant. Gas and liquid chromatographic techniques (GC and LC) are often used to analyze amine components and their degradation products in the solvent mixture. This allows the solvent blend ratio, largely influencing the CO₂ absorption behavior, to be accurately monitored. Some recent works on GC method development for liquid analysis are available. According to a report (Rey et al., 2013), glycol based high polar column of DB-Wax and non polar CP-SIL 8CB-ms column were used to analyze MEA and its pyrazine based degradation products. Although GC–MS is a powerful tool for amine analysis, the technique still poses a problem as it cannot effectively analyze all amines due to the highly polar nature typical of many CO₂ capture solvents. One study did not recommend GC–MS analysis for 2-(methylamino)-ethanol (MMEA) and 2-(dimethylamino)-ethanol (DMMEA) in their oxidative degradation investigation due to noise interference in the resulting chromatogram (Vevelstad et al., 2013a). Other studies suggested the use of GC–MS for analysis of ammonia (NH₃), volatile alkylamines, and degradation products generated from amine oxidation (Vevelstad et al., 2013b, 2014). The LC technique has also become an alternative to the GC especially with liquid solvent containing highly polar amines. Tailoring problems associated with GC analysis of these amines can be managed more easily with LC by fine tuning the liquid mobile phase using an appropriate additive such as triethylamine.

Recent work in the thermal and oxidative degradation work to quantify 5 single amines of MEA, PZ, 2-amino-2-methyl-1-propanol (AMP), 2-amino-2-hydroxymethyl-1,3-propanediol (AHPD), 2-amino-1,3-propanediol (Serinol), and one mixed amine solvent containing AHPD and PZ made use of an ion exchange method (Bougie and Ilitu, 2014). The LC based technique was also used to quantify PZ degradation in pilot plant (Nielsen et al., 2013).

6.3.2. Online analysis
In terms of online measurement of amines, though limited, some work associated with the online technique is available. We have demonstrated the use of a couple of physical properties of density and refractive index to predict concentration of MEA, MDEA, and CO₂ in their blended system (Pouryousefi, 2015; Pouryousefi and Idem, 2008). This technique correlated density and refractive index data with different concentration ratios of MEA-MDEA-CO₂–H₂O mixture into a useful mathematical equation which was used to accurately determine concentration ratio of all 4 components. The technique was aimed to replace chromatographic techniques such as the HPLC for an easier and quicker online analytical tool for amine composition analysis. Similar work has been recently done using density, conductivity, refractive index, and sonic speed data to develop a model in predicting concentrations of MEA and CO₂ in the liquid phase used in a mini-pilot plant (van Eckeveld et al., 2014). The model was also built based on the presence of some major degradation products, namely, ammonia, formaldehyde, formic acid, acetic acid, and oxalic acid to ensure its use is
also applicable to real-life amine samples containing these products. One more study related to on-line measurement of amine uses a spectroscopic FTIR by attenuated total reflectance (ATR) to carry out an on-line analysis of MEA solution in a pilot plant (Einbu et al., 2012). The accuracy measured in terms of relative uncertainty was comparable with the physical property based on on-line prediction described earlier.

7. Minimizing heat duty

7.1. Current approach

A major drawback of amine-based post-combustion CO₂ capture as well as any other CO₂ capture technology is that the energy required for the process is still too high. In the case of amine-based post-combustion CO₂ capture, about 70% of the energy is expended during solvent regeneration for CO₂ stripping (Idem et al., 2006). Rochelle (2009) has recently proposed approaches that could be used to minimize the heat required for regeneration. According to Rochelle (2009), the theoretical minimum energy of CO₂ separation and compression is estimated to be (0.11 MWh/ton CO₂)/(353.6 kJ/kg CO₂) which remains a challenge to be attained. Accordingly, the two methods that could significantly cut heat duty to achieve the expected value are solvent optimization and process integration.

It has been reported that the heat duty is more dependent on operating conditions such as temperature (T) and pressure (P), and less dependent on process configurations, except process integration and heat optimization (Sakwattanapong et al., 2005). Consistent with the suggestion by Rochelle (2009), a number of researchers have reported measures that have been used to effectively reduce heat duty (Aroonwilas and Veawab, 2007; Idem et al., 2006; Rochelle, 2009; Sakwattanapong et al., 2005; Zhang et al., 2012). These include the development of a series of different novel solvents, which can reduce the heat duty from 1.738 to 0.409 MWh/ton CO₂ (i.e., 6256.8 – 1742.4 steam kg/kg CO₂) and reflux ratio of H₂O/CO₂ from 0.7 to 0.1 (Feron, 2010). Recently, efforts have been made to improve Heat Exchanger Network (HEN) optimization, which exhibits a good potential to improve energy efficiency of an overall power plant with a reduction in the energy penalty for CO₂ capture from 19.4% to 15.9% (Khalilpour and Abbas, 2011).

In the case of solvents, other methods include the blending of amines to reduce the regeneration energy compared to MEA (Idem et al., 2006). According to Sakwattanapong et al. (2005), a large amount of heat (>80% of heat) is used for water vaporization for MEA solutions, and only approximately 50% of heat is used for vaporization for blended MEA:MDEA (1:1) solution. Also, CO₂ regeneration was improved significantly by Agar’s group with specific blended amines such as dipropylamine (DPA) and improved FCC processes such as a combined improvement for the capture process and power generation process (Feron, 2010; Zhang et al., 2012). These measures still have not achieved regeneration energy of acceptable or theoretical levels (Aroonwilas and Veawab, 2007; Feron, 2010; Idem et al., 2006; Sakwattanapong et al., 2005; Zhang et al., 2012). In the case of process configuration optimization, a number of novel approaches have emerged since 2005 (Aroonwilas and Veawab, 2007; Gao et al., 2014; Gelowitz et al., 2013a; Rochelle, 2009). These are all aimed at utilizing as much of the external energy input as possible.

Since high heat duty could also be due to adoption of a design approach that may lead to inadequate plant size, either in terms of column height or column diameter or both or the size of packing element relative to the diameter of the column, attention should be focused on design assumptions, even of a conventional plant. In general, most designers focus on the height of column and the size of packing element relative to column diameter. Very little attention seems to be directed to the right or effective diameter of column. The reason appears to be that a flooding percentage of between 60 and 70% seems to be the acceptable norm to most designers. However, based on our internal experimental work, it appears that an appropriate flooding percentage also depends on the type of solvent used and the CO₂ concentration in the inlet gas stream (University of Regina (UofR) Consortium, 2010). A flooding percentage less than 50% could be the appropriate value to use for design. The inappropriate flooding percentage specification may be the reason why a large number of pilot plant studies do not achieve the designed heat duty. As such, the observed heat duties relative to the designed heat duties that should be obtained from the solvent used are generally not reported. In general, in most of the studies, the capacity of the columns (especially, the absorber column) is smaller than necessary thereby making it inadequate to achieve the desired or designed absorber efficiency for the designed heat duty. The implication of inadequate column size is that either the absorber efficiency or heat duty or both will be compromised.

7.2. Novel approaches and future trends

As mentioned previously, significant progress has been made in reducing heat duty based on solvent improvement or process optimization or both. However, these measures have still not achieved regeneration energy that is close to the theoretical level. Heat duty consists of three parts; namely, chemical energy for CO₂ stripping from the amine, sensible heat, and heat of vaporization of water/amine. Recently, another approach has been reported (Idem et al., 2011) that has significantly reduced heat duty. This approach is based on the use of a solid alkaline catalyst to act as packing in the absorber and a solid acid catalyst to act as packing in the stripper (Shi et al., 2014). This approach of using a solid acid catalyst in the stripper has achieved a breakthrough of performing solvent regeneration at a temperature less than the boiling point of water. This obviates the need to use steam for solvent regeneration. The implication is that the heat of evaporation, which constitutes a very large fraction of the heat of regeneration, is eliminated. According to Idem et al. (2011), the alkaline catalyst in the absorber accelerates the rate of CO₂ absorption in the amine solvent. Thus, the catalytic amine scrubbing process reduces both the heat duty and plant size. This catalytic amine-based CO₂ capture approach can be used together with an energy efficient solvent (Shi et al., 2014) as well as an optimized process configuration. The catalytic approach could therefore be regarded as the “third generation” of amine-based post-combustion CO₂ capture technology.

Another novel approach in post combustion CO₂ capture is based on the use of enzymes called carbonic anhydrase (Chu, 2009; Tripp et al., 2001). According to Tashian (1989), carbonic anhydrase is a fast enzyme that can catalyze the hydration of CO₂ into bicarbonate ions and proton at turnover numbers that approach 10⁶/s. Chu (2009) and Savile and Lalonde (2011) have demonstrated the potential for enzymatic acceleration of carbon dioxide capture from combustion flue gas. However, Savile and Lalonde (2011) have indicated that available carbonic anhydrases are inadequate for the harsh environment of the post combustion CO₂ capture process. In their review, Savile and Lalonde (2011) summarized recent approaches to improve carbonic anhydrase as well as the processes that employ the enzyme with the objective of exploiting carbonic anhydrase as an extremely fast biocatalyst to their maximum the benefits. According to Savile and Lalonde (2011), these approaches include using thermophilic organisms as the source of CAs, application of protein engineering to produce thermo-tolerant enzymes, immobilizing the enzyme to stabilize and confine to cooler regions, and modification of the CO₂ capture process such that the thermal and solvent-stress on the enzyme are minimized. Extensive work is
being carried out by a number of groups aimed at perfecting some of these approaches. Both these heat duty reduction approaches employ catalysts in order to accelerate both the absorption of CO₂ into the solvent and desorption of CO₂ from the solvent. The use of catalyst thus appears to be the new trend in amine-based post-combustion CO₂ capture process. The application of catalysis in any process is usually intended to accelerate the rate as well as decrease the activation energy of the process, the latter of which could result in the use of a lower process operating temperature. Both approaches are expected to see extensive research and development work all the way to demonstration plants in order to perfect the respective processes, and to generate reliable data for design of a commercial plant. Thus, future trends could see significantly smaller vessels and heat duties for post-combustion CO₂ capture from combustion flues using amine-based solvents. These would result in significantly lowering the cost for post-combustion CO₂ capture.

Another approach that could be used to reduce heat duty is in the use of alternative solvent-based post combustion CO₂ capture processes such as amino acid salt, chilled ammonia process (CAP), phase change solvents, biphasic solvents (for low temperature regeneration), and ionic liquids. All these processes work at the bench scale, and both CAP and amino acid salts have been tested at large pilot plant scales. These processes are expected to still do extensive research and development work all the way to demonstration plants in order to perfect the respective processes, and to generate reliable data for design of a commercial plant.

8. Conclusions

In this review paper, we have seen the widespread deployment of pilot and demonstration plants. We have also seen the birth of a commercial size CO₂ capture plant. The research and development work being carried out in these plants have enabled the use of real conditions and to study their effects on the CO₂ capture process. The lessons learned from the pilot and demonstration plants have been very beneficial and have contributed to the continuous improvement of the amine-based CO₂ capture technology. Most of the lessons are related to emissions, heat duty, plant size, new solvents, and solvent management. Because the amine-based CO₂ capture in power plant is a relatively new industry, measurement standards involving sampling and analysis of the off-gas, as well as analysis of the solvent system in use were not in place prior to the IPCC report. Therefore, the emergence of the demonstration plants has thrown light on the need for these standards. We have started to see methods developing that would allow some sort of standards to evolve. Specifically, sampling techniques are being introduced aimed at reliably obtaining representative samples from the off-gas of an amine based CO₂ capture plant. Techniques are also evolving aimed at analysing the obtained samples qualitatively and quantitatively.

The other area that has seen tremendous progress is the heat duty for solvent regeneration. A number of approaches have been suggested. Currently, these approaches have focused on the development of energy efficient solvents and process optimization. Based on these approaches, the heat duty has been brought down from about 5.0–1.8 GJ/ton CO₂ produced. On this issue, it has been noticed that even though the solvent used in conjunction with the process optimization method employed is capable of providing an acceptable heat duty (i.e., close to 1.8 GJ/ton CO₂ produced), the actual heat duty obtained in pilot and demonstration plants, in most cases, is higher than expected. It is suggested that more attention be given to the assumption made in the design, especially as it relates to the flooding percentage.

Catalysis in amine-based post combustion CO₂ capture has become a new trend which may possibly pave the future direction for amine-based post combustion CO₂ capture. Solid mineral catalysts are used in the approach suggested by Idem et al. (2011) whereas a biocatalyst is employed in the approach by Chiu (2009). The use of catalyst thus appears to be the new trend in amine-based post-combustion CO₂ capture process. The application of catalysis in any process is usually intended to accelerate the rate as well as decrease the activation energy of the process, the latter of which could result in the use of a lower process operating temperature. Both approaches are expected to see extensive research and development work all the way to demonstration plants in order to perfect the respective processes, and to generate reliable data for design of a commercial plant. Thus, future trends could see significantly smaller vessels and heat duties for post-combustion CO₂ capture. More activity at pilot plant and large demonstration scale plants on the use of amino acid salts, chilled ammonia process (CAP), phase change solvents, biphasic solvents and ionic liquids are expected, which may help enhance the performance of these alternative post combustion capture processes.

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