

POLITECNICO DI MILANO

Department of Energy

Doctoral program in Energy and Nuclear Science and Technology



POLITECNICO
MILANO 1863

Techno-economic analysis of aqueous ammonia based absorption plant for CO₂ capture supported by experimental data

Doctoral dissertation of:

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XXXI PhD Cycle (2015÷2018)

Extended abstract

Introduction

The consequences of climate change are a major issue in recent years. The rise of Earth's temperatures, due to the ever-increasing anthropogenic emissions, is the major cause of this change. Hence, a collective commitment is needed to lead the reduction of the worldwide carbon dioxide emissions. The Paris Agreement has set a limitation to the raise of temperature at 2 °C by 2050 with respect to pre-industrial level, representing a new step for this challenge.

In order to achieve the 2 °C goal, the reduction of CO₂ emissions is fundamental. For the reduction of CO₂ emissions, the energy production will be changed by increasing the share of energy produced from renewable sources, working on energy efficiency and reducing dependence on fossil fuels. Currently, about 80% of the global primary energy demand is covered by fossil fuels and, hence, significant reductions of the use of fossil fuels appear challenging in an environment of strongly growing energy demand, as the forecast for 2035 shown in Fig. 1. In this context, CO₂ capture technologies are one of the mitigation actions that need to be taken.

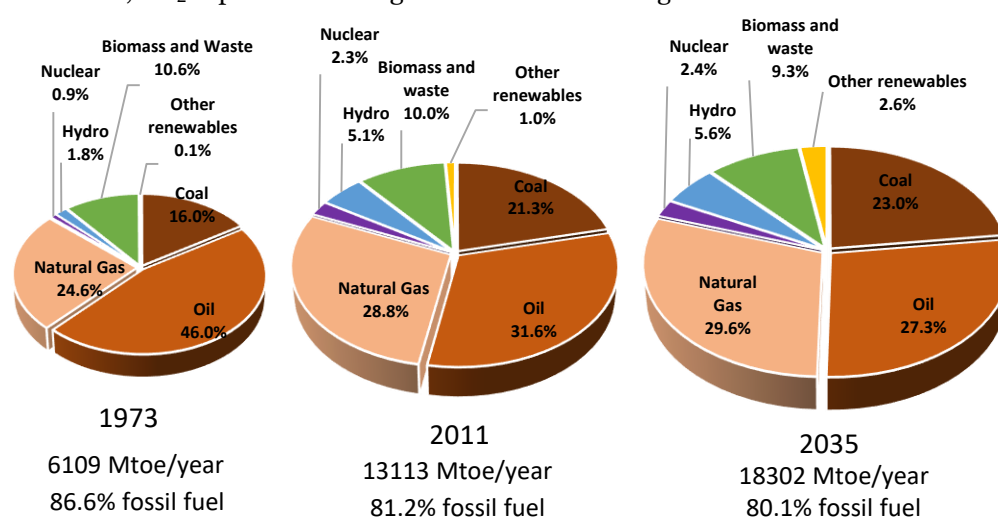


Fig. 1. Global primary energy consumption by source given in tons of oil equivalents (toe), based on data from International Energy Agency (IEA)

Goal and methodology

The aim of this thesis is the experimental characterization of the solvents, the process modelling and the evaluation of the techno-economic performance of two absorption post-combustion technologies applied to a USC (Ultra Super Critic) coal-fired steam plant. The capture plant is positioned after the SCR (Selective Catalytic Reactor), the baghouse and the FGD (Flue Gas Desulfurization) and takes the heat for the solvent regeneration by the steam extracted from the turbine. The Two absorption technologies studied are the Cooled Ammonia and the Mixed-Salt Technology.

The thermodynamic model used for the simulation of the chemistry of absorption is the Extended-UNIQUAC. This thermodynamic model is calibrated for the calculation of the properties of the system CO₂-NH₃-H₂O used in the cooled ammonia, and the system CO₂-NH₃-K₂CO₃-H₂O used in the Mixed-Salt technology with more than 8000 data taken from the literature. After the model validation, the solvents are characterized in both the thermodynamic properties, using the thermodynamic model, and the kinetics of absorption using Wetted Wall Column experimental apparatus.

The Cooled ammonia technology is then analyzed with a sensitivity analysis with an equilibrium-based approach and the plant layout is designed in order to minimize the energetic consumption. After, a rate-based model is developed in Aspen Plus and validated with experimental data from pilot plants found in the literature. The rate-based model is used for the component sizing of the cooled ammonia and the techno-economic analysis is assessed comparing the results with the reference cases of the EBTF and the NETL report.

For the mixed-salt technology, a similar approach is adopted. The plant is designed and studied with sensitivity analysis in order to optimize the energetic consumption with an equilibrium-based approach. Since in literature there are no data available from pilot plants, the columns are sized with the experimental data on the kinetics of absorption available from the wetted wall column. Estimated the component sizing and the

performance of the overall plant integrated with the power section, the techno-economic analysis is assessed comparing the results with the reference case of NETL report.

Novelty and impact

The novelties of the work are (i) a new calibration of the Extended-UNIQUAC thermodynamic model, (ii) a new characterization of the kinetic of the absorption reactions in liquid phase for the system $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$, (iii) a rate-based model in Aspen Plus of the absorber of the ternary system $\text{CO}_2\text{-NH}_3\text{-H}_2\text{O}$, (iv) a plant simulation and a sensitivity analysis of the Mixed-Salt Technology, (v) a techno-economic analysis for both the Cooled Ammonia and the Mixed-Salt Technology.

The impact of the thesis on the Ammonia technology will be the interest in the pilot test of different operative conditions avoiding the salt precipitation. Moreover, since the ammonia technology has a good level of maturity, the rate-based model can study the behavior of the capture plant applied to power plant at off-design and dynamic conditions in order to increase the readiness of the technology on the market.

The impact on the Mixed-Salt Technology will be a higher interest of this technology due to the promising results in terms of costs and energy efficiency. Indeed, on this topic a team led by SRI International with Politecnico di Milano as a partner has won a project founded by the American Department Of Energy (DOE). The project will have the aim to test the technology in the pilot plant of the Technic Center of Mongstad to study the performance in-design, off-design and start-up.

Thermodynamic model validation

The thermodynamic model applied for the calculations and the analysis of this thesis is the Extended UNIQUAC. The current model is based on a completely new framework of model parameters updated in 2014. All the model parameters have been determined on the basis of experimental data in the temperature range from the freezing point of the solutions to 200°C with more than 8000 experimental data.

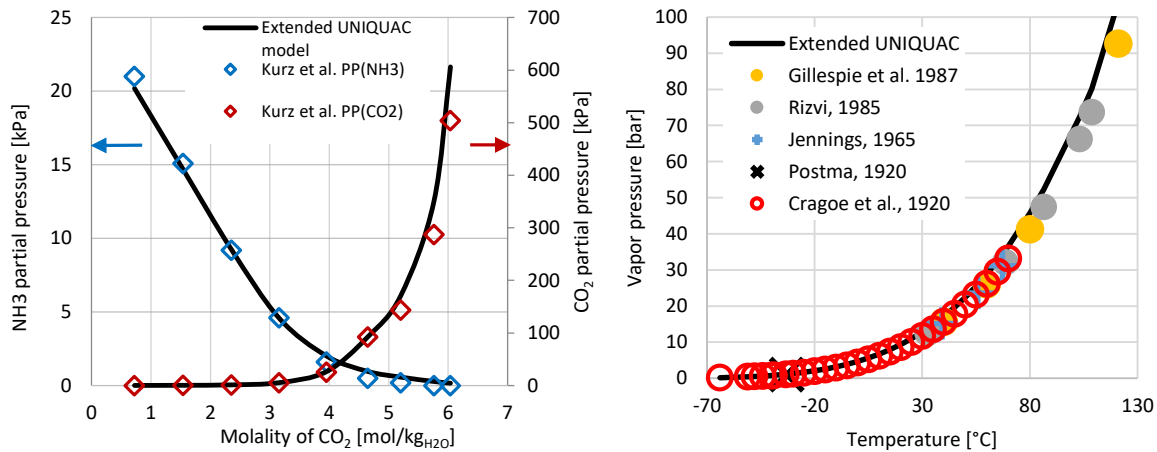


Fig. 2. Validation of the thermodynamic model Extended UNIQUAC with experimental data

Experimental characterization of the Cooled Ammonia solvent

The study of the rate of absorption is fundamental to determine the required contact area between liquid and gas. The experimental apparatus chosen for the measurement of the CO_2 absorption rate is the Wetted Wall Column (WWC). The configuration of the WWC (Fig. 3) is very simple and can reproduce in a good scale the simulation of the mass transfer of a real packed column. The results permit an understanding of the overall phenomenon measuring the overall mass transfer coefficient of the CO_2 absorption K_{ov} for different operational parameters (Fig. 4). Moreover, after the reactor modeling, the experimental data allows the calibration of the Arrhenius parameters for the kinetic of the reaction between CO_2 and NH_3 in the liquid phase. The data fitting returns the following Arrhenius equation for the forward reaction while Fig. 5 shows the agreement between the data and the calculated values.

$$r_{\text{CO}_2\text{-NH}_3} = k_{\text{NH}_3} C_{\text{CO}_2} C_{\text{NH}_3}^{1.89} \quad \text{with} \quad k_{\text{NH}_3} = 1.41 * 10^8 \frac{\text{mol}}{\text{m}^3 \text{ s}} \exp\left(-\frac{60680 \frac{\text{J}}{\text{mol}}}{RT}\right)$$

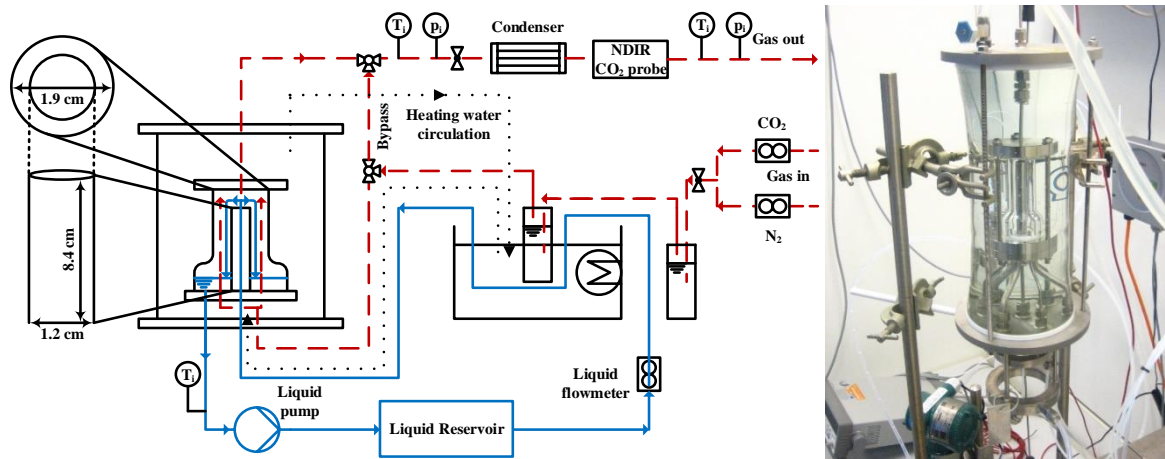


Fig. 3. (Left) Wetted Wall Column layout where: (i) solid blue line is the solvent, (ii) dashed red line is the gas mixture and (iii) dotted black line the cooling water from the thermostatic bath. (Right) Picture of the reactor

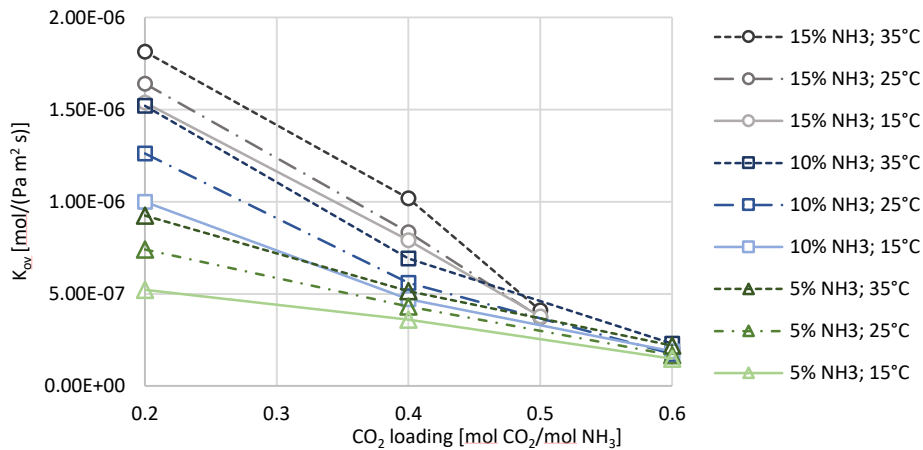


Fig. 4. Overall mass transfer coefficient as a function of the CO₂ loading for 5%, 10% 15% of NH₃ concentration at 15°C, 25°C and 35°C.

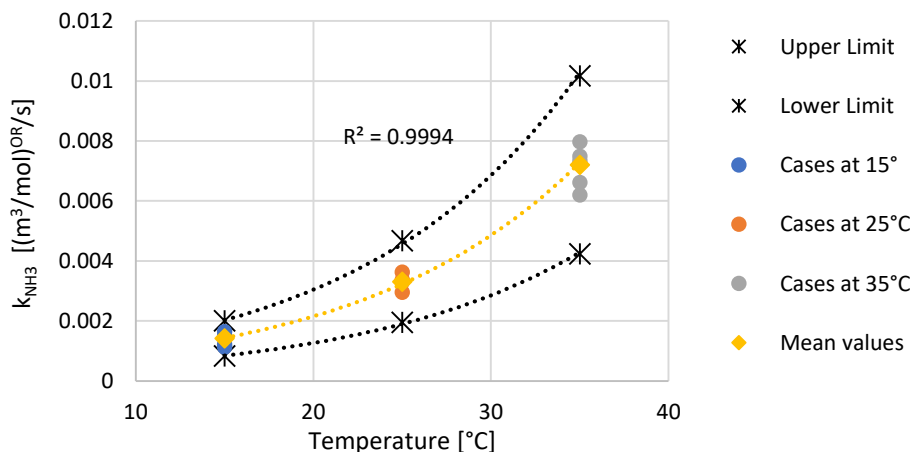


Fig. 5. The filled circles are the experimental values of the k_{NH_3} at every and with the filled diamonds the mean value at every temperature. The dotted yellow line is the regression with the Arrhenius law expressed in equation. The black dotted lines are the upper and the lower limit of the mean value of k_{NH_3} due to the absolute errors of the measurement.

Techno-economic analysis of the Cooled Ammonia process

The kinetics of absorption has been studied experimentally with the Wetted Wall Column. Implemented the kinetic in Aspen Plus, the rate-based model of the absorption is calibrated with the experimental data of the Munmorah pilot plant. The model calibrated is used for the full-scale plant columns sizing and the overall

capture plant simulation. Known the size of the plant and the energy consumptions, the capture plant is integrated with the coal power plant with the economic analysis of a retrofitted and a green-field case. With this kind of tool, the simulation of the ammonia capture process with a rate-based approach allows a more accurate evaluation of the energetic performances and an accurate sizing of the components which can be exploited for the economic analysis of the component costs.

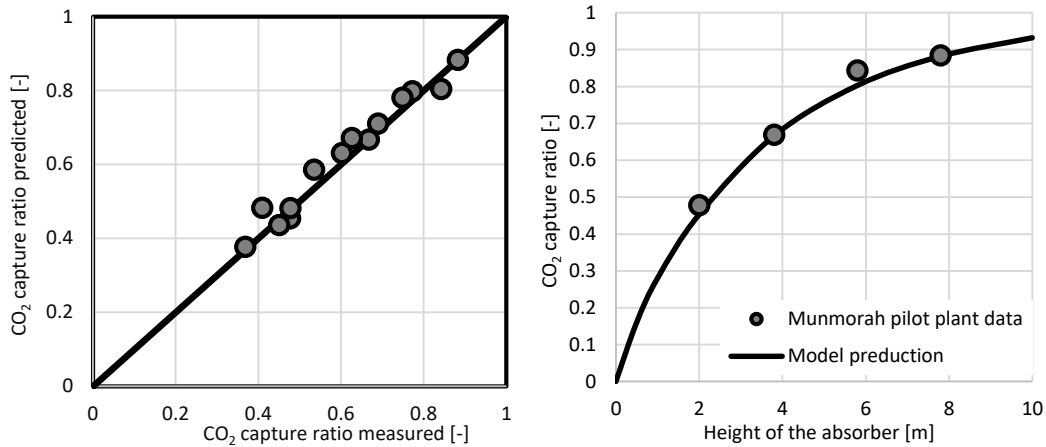


Fig. 6. Left: comparison of the carbon capture ratio measured with experimental data of the pilot plant and the predicted values. Right: comparison between experimental data and the model results of the CO₂ capture ratio as a function of the column height with the solvent temperature of 22°C and a CO₂ lean loading of 0.24.

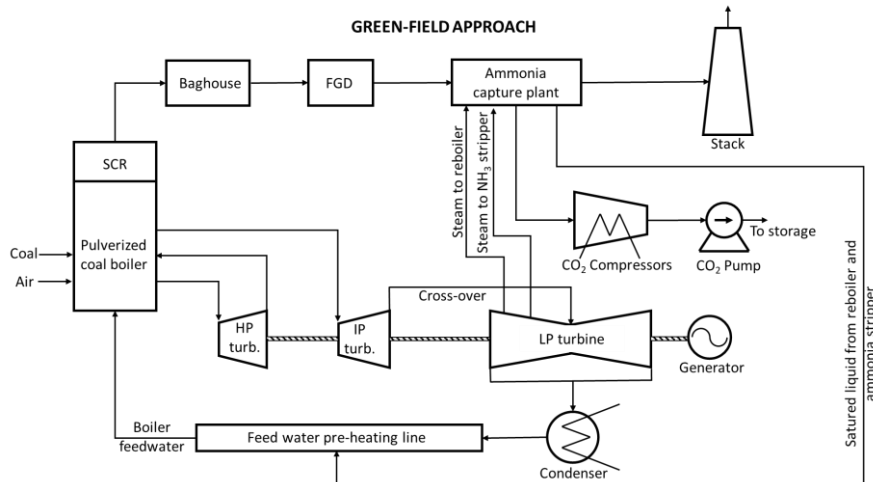


Fig. 7. The layout of the coal plant integrated with the ammonia capture plant with a green-field approach.

Fig. 7 shows the layout of the power plant integrated with the carbon capture plant while Tab. 1 shows the results of the energetic performance for the reference case without capture, the Cooled Ammonia and the reference case with Capture presented in the NETL report assuming a green-field integration. The results highlight a *SPECCA* (Specific Primary Energy Consumption for CO₂ Avoided) of 3.23 MJ/kg_{CO₂} captured for the Cooled Ammonia against 3.30 MJ/kg_{CO₂} with the Cansolv capture plant. The benefit of the Cooled Ammonia with respect to Cansolv derive from a reduction of the reboiler temperature and a higher regeneration pressure while Cansolv has the benefit of a lower heat duty. The higher regeneration pressure brings a lower CO₂ compression consumption due to a lower compression ratio required to send the CO₂ to storage, while the effect of the steam extraction is the sum of both the effect of the heat duty and the regeneration pressure. Indeed, with a green-field approach, the steam bled increase with the heat duty but its pressure decrease with the reboiler temperature with a consequent higher expansion in the turbine and a higher electric production. In the Cansolv case the steam is bled at 5.1 bar (corresponding to a saturation temperature of 152°C) while in the Cooled Ammonia is bled at 2.4 bar (corresponding to a saturation temperature of 126°C) for the reboiler and at 1.4 bar (corresponding to a saturation temperature of 109°C) for the ammonia stripper. Despite the Cansolv technology steam bleeding has a lower mass flow, the lower extraction pressure produces an increase in electric efficiency.

Tab. 1. Performance of the NETL reference case without CO₂ capture (Case 12A) and the NETL power plant with the Cooled Ammonia CO₂ capture and the Cansolv CO₂ capture with a green-field approach.

| Parameter | Unit | Reference case without Capture | Case with Ammonia | Case with Cansolv |
|--|-------------------------------------|--------------------------------|-------------------|-------------------|
| Thermal Input | MW _{th} HHV | 1351.4 | 1663.5 | 1694.4 |
| Gross Electric Power | MW _e | 580.0 | 629.4 | 642.0 |
| Power Plant Auxiliaries | MW _e | 30.0 | 39.0 | 36.6 |
| CO ₂ Capture Consumptions | MW _e | - | 13.1 | 16.0 |
| CO ₂ Compression Consumptions | MW _e | - | 27.3 | 35.7 |
| Net Electric Power | MW _e | 550 | 550 | 550 |
| Heat Duty Reboiler | MJ/kg _{CO2} | - | 2.89 | 2.48 |
| Heat Duty Stripper | MJ/kg _{CO2} | - | 0.61 | - |
| Heat Duty Reclaimer | MJ/kg _{CO2} | - | - | 0.01 |
| Net Electric Efficiency, η_{el} | % | 40.70 | 33.06 | 32.50 |
| CO ₂ capture ratio | % | - | 85.0 | 90.0 |
| Specific CO ₂ emission, E | kg _{CO2} /MWh _e | 773.5 | 142.0 | 97.1 |
| SPECCA | MJ/kg _{CO2} | - | 3.23 | 3.30 |

Tab. 2. Economic analysis summary results for the case with a retrofitted approach expressed in \$-2011.

| Parameter | Unit | ECONOMIC ANALYSIS | | |
|--|-------------------------------------|---------------------|----------------------|----------------------|
| | | NETL w/o Capture | NETL with Ammonia | NETL with Cansolv |
| <u>Power performances</u> | | | | |
| Thermal input (HHV) | MW _{th} | 1351.4 | 1663.5 | 1694.4 |
| Net electric power | MW _e | 550 | 550 | 550 |
| Net electric efficiency | % | 40.70 | 33.06 | 32.50 |
| CO ₂ emissions | kg _{CO2} /MWh _e | 773.5 | 142.0 | 97.1 |
| Capture efficiency | % | - | 85 | 90 |
| Capacity factor | % | 85 | 85 | 85 |
| <u>Capital Costs</u> | | | | |
| Equipment cost power section | M\$ | 549 | 630 | 638 |
| Equipment cost capture section | M\$ | - | 113 | 218 |
| Bare erected cost power section | M\$ | 905 | 1036 | 1061 |
| Bare erected cost capture section | M\$ | - | <u>154.2</u> | 434 |
| Total plant cost power section | M\$ | 1114 | <u>1277</u> | 1307 |
| Total plant cost capture section | M\$ | - | 227 | 632 |
| <i>Total plant cost (TPC)</i> | M\$ | <u>1114</u> | <u>1504</u> | <u>1939</u> |
| <u>Operating and Maintenance Costs</u> | | | | |
| <i>Total fixed O&M</i> | M\$/year | 39.3 | 62.5 | 63.1 |
| <i>Total variable O&M</i> | M\$/year | 37.1 | 82.5 | 60.4 |
| <i>Fuel cost</i> | M\$/year | 100.8 | 124.2 | 126.5 |
| <u>Owner's Costs</u> | | | | |
| Inventory capital | M\$ | 29.2 | <u>43.0</u> | <u>41.1</u> |
| Other costs | M\$ | 198.1 | <u>267.2</u> | <u>344.1</u> |
| <i>Total overnight costs (Owner's+TPC)</i> | M\$ | <u>1378.6</u> | <u>1866.7</u> | <u>2384.4</u> |
| <i>Total as spent cost (high risk, 35 years)</i> | M\$ | <u>1563.4</u> | <u>2128.0</u> | <u>2718.2</u> |
| <u>Cost index</u> | | | | |
| Parameter | Unit | NETL w/o Capture | NETL with Ammonia | NETL with Cansolv |
| COE | \$/MWh _e | <u>82.30</u> | <u>124.30</u> | <u>133.20</u> |
| Cost of CO₂ avoided | \$/t _{CO2} | - | <u>66.50</u> | <u>75.25</u> |

Tab. 2 reports the values of the techno-economic analysis for the same cases previously analyzed. The results highlight both a lower Cost Of Electricity (COE) and a lower cost of CO₂ avoided for the ammonia capture technology. The result is mainly due to a lower capital cost on both the capture and the CO₂ compression section. The thermodynamic efficiency of the ammonia solvent integrated with a green-field approach is slightly higher, and consequently, the size of the power section is slightly lower as well as the costs. The drawback of the ammonia technology is the costs consumables. This cost is high because the ammonia slip

control requires a large amount of water that needs to be purged. The purge contains both water and ammonia, hence also a large amount of ammonia has to be refilled. Considering a cost of the ammonia of 0.33 \$/kg and a cost of clean water of 1.67 \$/m³, the cost of consumable is almost one third higher than the Cansolv case. The second comparison shows that the efficiency of the plant is similar, but lower investment cost for the carbon section leads to a lower cost COE.

Experimental characterization of the Mixed-Salt Technology solvent

Technology based on ammonia is capable of capturing CO₂ at high loadings compared to amine-based technology. In addition, ammonia-based technology can strip CO₂ at high pressure, reducing the CO₂ compression costs. However, the technology requires cooling the flue gas and the absorber solvent as well as washing the treated gas to reduce the ammonia emissions. In comparison to ammonia technology, potassium-carbonate-based technology has no emission issues. However, it has a low CO₂ absorption efficiency, very low loading capacity, and cannot be regenerated at high pressure. As such, new approaches for improved potassium carbonate-based CO₂ capture technology has been in development for decades.

The aim of this section is the study of the thermodynamic properties and the kinetics of CO₂ absorption of mixtures of NH₃ and K₂CO₃ in the same solvent. Compared to the aqueous ammonia solvent analyzed in the previous parts, this mixture is expected to be characterized by a lower heat duty of regeneration, a reduced ammonia slip, and maintaining a high regeneration pressure, combining the best properties of the two solvents. This solvent has been termed the Mixed-Salt Technology solvent.

This section presented the thermodynamic and kinetic properties of CO₂ absorption in the NH₃-K₂CO₃-CO₂-H₂O solvent system. The thermodynamic properties and the speciation of the solvent were calculated with the Extended UNIQUAC thermodynamic model, while the kinetics of absorption were measured experimentally using a WWC setup. Fig. 8 describes the heat of desorption and the ammonia slip as a function of the K₂CO₃ molality at different iso-capacities where the iso-capacities is defined as

$$iso - capacity = \frac{n_{NH_3} + n_{K_2CO_3}}{m_{H_2O}}$$

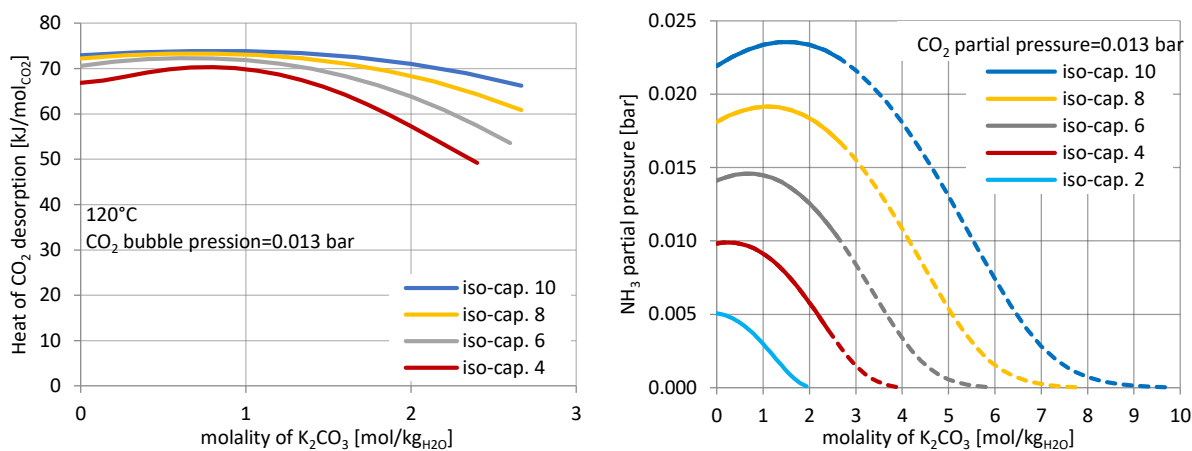


Fig. 8. Left: the heat of CO₂ desorption at 120 °C as a function of the solvent composition at different values of iso-capacity express as the definition in [mol/kg_{H₂O}]. The curves are continued until salt deposition occurs. Right: ammonia partial pressure as a function of the K₂CO₃ initial molality for different iso-capacities of the solvent. The partial pressure of CO₂ is constant, 0.013 bar and the temperature is 25 °C. The solid lines are the conditions without salt precipitation while the dashed line are the points where salt precipitation occurs

The heat of desorption decreased with increased regeneration temperature. For instance, the heat of desorption of the solvent comprised of 2 molal NH₃ and 2 molal K₂CO₃ decreased from 58 kJ/mol_{CO₂} at 120 °C to 40 kJ/mol_{CO₂} at 130 °C. The heat of desorption also decreased when the fraction of K₂CO₃ in the solvent was increased, and this effect overshadowed the effect of increasing the regeneration temperature. For instance, at 120 °C, the heat of desorption decreased from 70 kJ/mol_{CO₂} (for a mixture of 3 molal NH₃ and 1 molal K₂CO₃) to 55 kJ/mol_{CO₂} (for a mixture of 2 molal NH₃ and 2 molal K₂CO₃). The ammonia slip decreased with increasing fraction of K₂CO₃ in the solvent due to the decrease of free ammonia in the liquid phase. Increasing the concentration of K₂CO₃ in the solvent resulted in reduced solubility. Consequently, salt precipitation occurred at a lower CO₂ loading.

Fig. 9 shows the measurement of the overall mass transfer coefficient with the wetted wall column. The overall mass transfer coefficient increased with increasing temperature and decreased with increasing CO₂

loading, following the kinetic description of the Arrhenius equation. On the other hand, it decreased with an increased fraction of K_2CO_3 in the solvent due to the reduction in the amount of free ammonia in the reactive layer. For instance, between the solution of 4 molal NH_3 and the solution of 1.5 molal NH_3 and 2.5 molal K_2CO_3 (both at 35 °C), the overall mass transfer coefficient decreased from 7.34×10^{-7} [mol/(Pa m² s)] to 3.14×10^{-7} [mol/(Pa m² s)].

The kinetics of absorption were mainly influenced by the reaction between free ammonia and CO_2 . The overall mass transfer coefficient decreased with increasing K_2CO_3 fraction in the solvent. The carrying capacity increased with increasing fraction of K_2CO_3 in the solvent, from 158.44 [g $_{CO_2}$ /L $_{H_2O}$] for the solvent with 4 molal NH_3 to 224.45 [g $_{CO_2}$ /L $_{H_2O}$] for the solvent with 1.5 molal NH_3 and 2.5 molal K_2CO_3 . The Mixed-Salt solvent had an overall mass transfer coefficient 1.5-2 times smaller than that of MEA.

Globally, the solvent has interesting properties for CO_2 capture applications. As a first analysis, the solvent compositions considered in this evaluation have good thermodynamic properties (low ammonia slip and low heat of desorption), with the drawback of slower absorption kinetics compared to those in an aqueous ammonia solvent.

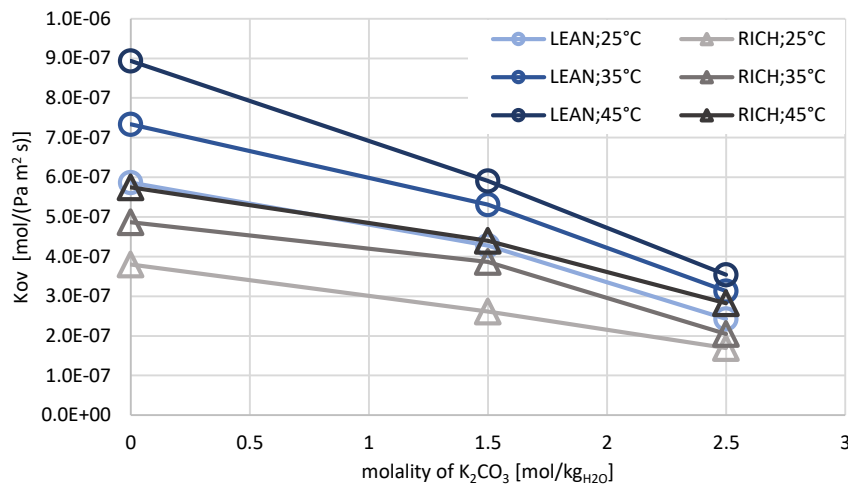


Fig. 9. Overall mass transfer coefficient K_{ov} as a function of the K_2CO_3 molality for solvents with iso-capacity 4 mol/kg $_{H_2O}$. The data are measured at 3 different temperatures (25 °C, 35 °C, 45 °C) and 2 different CO_2 loadings (LEAN and RICH).

Techno-economic analysis of the Mixed-Salt Technology

The section explains the core of the research that has been pursued on Mixed-Salt Technology. It exposes the parametric analysis that is carried out to investigate the optimum working point of the capture plant. The parametric analysis was conducted in Aspen Plus with the Extended UNIQUAC thermodynamic model with an equilibrium based approach. Found the optimum working of the capture plant, the performance of the power plant integrated with the capture plant (Fig. 7) was calculated.

Tab. 3 shows the values of the energetic performance for the reference case without capture, the Cooled Ammonia and the reference case with Capture presented in the NETL report. The results highlight a *SPECCA* of 2.13 MJ/kg $_{CO_2}$ for the Mixed-Salt Technology against 3.30 MJ/kg $_{CO_2}$ with the Cansolv capture plant. The benefit of Mixed-Salt Technology with respect to Cansolv derive from a reduction of the heat duty and a reduction of the reboiler temperature. The lower heat duty requires a lower amount of steam extracted from the steam turbine with consequently a higher electric production of the low pressure steam turbine. Moreover, the lower regeneration temperature allows the steam bleeding at a lower pressure increasing the expansion in the steam turbine with consequently a higher electric production of the low pressure steam turbine. These two effects reduce a lot the electric losses at the steam turbine rising the net electric efficiency the power plant. Indeed, the Cansolv case the steam is bled at 5.1 bar (corresponding to a saturation temperature of 152°C) while in the Mixed-Salt Technology is bled at 0.97 bar (corresponding to a saturation temperature of 98°C) for the reboiler and at 1.4 bar (corresponding to a saturation temperature of 109°C) for the ammonia stripper. These two effects reduce a lot the electric losses at the steam turbine rising the net electric efficiency of the power plant from 32.5% to 35.0% and reducing the *SPECCA* from 2.13 MJ/kg $_{CO_2}$ to 3.30 MJ/kg $_{CO_2}$.

Tab. 3. Performance of the NETL reference case without CO₂ capture (Case 12A) and the NETL power plant with the Mixed-Salt Technology (MST) CO₂ capture and the Cansolv CO₂ capture with a green-field approach.

| Parameter | Unit | Reference case without Capture | Case with MST | Case with Cansolv |
|--|-------------------------------------|--------------------------------|---------------|-------------------|
| Thermal Input | MW _{th} HHV | 1351.4 | 1573.4 | 1694.4 |
| Gross Electric Power | MW _e | 580.0 | 632.9 | 642.0 |
| Power Plant Auxiliaries | MW _e | 30.0 | 36.1 | 36.6 |
| CO ₂ Capture Consumptions | MW _e | - | 8.7 | 16.0 |
| CO ₂ Compression Consumptions | MW _e | - | 38.1 | 35.7 |
| Net Electric Power | MW _e | 550 | 550 | 550 |
| Heat Duty Reboiler | MJ/kg _{CO2} | - | 1.91 | 2.48 |
| Heat Duty Stripper | MJ/kg _{CO2} | - | 0.33 | - |
| Heat Duty Reclaimer | MJ/kg _{CO2} | - | - | 0.01 |
| Net Electric Efficiency HHV, η_{el} | % | 40.70 | 35.00 | 32.50 |
| CO ₂ capture ratio | % | - | 90.0 | 90.0 |
| Specific CO ₂ emission, E | kg _{CO2} /MWh _e | 773.5 | 90.1 | 97.1 |
| SPECCA | MJ/kg _{CO2} | - | 2.13 | 3.30 |

Tab. 4. Economic analysis summary results for the case with a green-field approach.

| ECONOMIC ANALYSIS | | | | |
|--|-------------------------------------|------------------|---------------|-------------------|
| Parameter | Unit | NETL w/o Capture | NETL with MST | NETL with Cansolv |
| Power performances | | | | |
| Thermal input (HHV) | MW _{th} | 1351.4 | 1573.4 | 1694.4 |
| Net electric power | MW _e | 550 | 550 | 550 |
| Net electric efficiency | % | 40.70 | 35.00 | 32.50 |
| CO ₂ emissions | kg _{CO2} /MWh _e | 773.5 | 90.1 | 97.1 |
| Capture efficiency | % | - | 90 | 90 |
| Capacity factor | % | 85 | 85 | 85 |
| Capital Costs | | | | |
| Equipment cost power section | M\$ | 549 | 609 | 638 |
| Equipment cost capture section | M\$ | - | 120 | 218 |
| Bare erected cost power section | M\$ | 905 | 1004 | 1061 |
| Bare erected cost capture section | M\$ | - | 165 | 434 |
| Total plant cost power section | M\$ | 1114 | 1239 | 1307 |
| Total plant cost capture section | M\$ | - | 239 | 632 |
| Total plant cost (TPC) | M\$ | 1114 | 1478 | 1939 |
| Operating and Maintenance Costs | | | | |
| Total fixed O&M | M\$/year | 39.3 | 63.1 | 63.1 |
| Total variable O&M | M\$/year | 37.1 | 74.0 | 60.4 |
| Fuel cost | M\$/year | 100.8 | 117.5 | 126.5 |
| Owner's Costs | | | | |
| Inventory capital | M\$ | 29.2 | 50.7 | 41.1 |
| Other costs | M\$ | 198.1 | 302.4 | 344.1 |
| Total overnight costs (Owner's+TPC) | M\$ | 1378.6 | 1831 | 2384.4 |
| Total as spent cost (high risk, 35 years) | M\$ | 1563.4 | 2088 | 2718.2 |
| Cost index | | | | |
| Parameter | Unit | NETL w/o Capture | NETL with MST | NETL with Cansolv |
| COE | \$/MWh _e | 82.30 | 117.55 | 133.20 |
| Cost of CO₂ avoided | \$/t _{CO2} | - | 51.58 | 75.25 |

The reduction of the reboiler temperature can be a benefit for the partial load operation of the power plant. Indeed, at partial load with the steam turbine controlled in sliding pressure, the cross-over pressure decreases and consequently decreases also the steam saturation temperature and the reboiler temperature. In this case, a lower regeneration temperature guarantees the total regeneration of the solvent also at partial load without the addition of a valve in order to maintain a high the cross-over pressure, which would introduce another power loss in the power plant.

Reading the results, it is important to take in mind that the Mixed-Salt Technology is simulated with an equilibrium based approach, so the results are more optimistic than what might result from a simulation with a rate-based approach. Anyway, the SPECCA difference between the two cases is very high, so the results are really promising and the Mixed-Salt Technology would result more efficient also with a rate-based approach since the penalization with respect to the equilibrium-based approach is usually expected no more than 20%.

Tab. 4 shows the values of the energetic performance for the same cases previously presented. The results highlight both a lower Cost Of Electricity (COE) and a lower cost of CO₂ avoided for Mixed-Salt Technology. The result is due to a lower capital cost on both the capture and the power section. The net electric efficiency of the Mixed-Salt Technology integrated with a green-field approach is higher (35.0% vs. 32.5%), and consequently, the size of the power section is lower as well as the costs. The drawback of Mixed-Salt Technology is the costs for the consumables. This cost is high because the ammonia slip control requires a large amount of water that needs to be purged in order to maintain the water balance. The purge contains both water ammonia and potassium carbonate, hence also a large amount of ammonia and potassium carbonate has to be refilled. Considering an ammonia cost of 0.33 \$/kg, a potassium carbonate cost of 0.75 \$/kg and a cost of clean water of 1.67 \$/m³, the cost for consumables is almost 20% higher than the Cansolv case.

General considerations about CO₂ capture integration in coal fired plants and partial loads

The integration between coal fired steam plant and absorption technologies for carbon capture. Absorption technologies for carbon capture introduce different power losses in the coal plant which are mainly due to the steam extraction at the power plant cross-over for the solvent regeneration, the CO₂ compression, the solvent cooling and the auxiliaries of the capture plant itself. Fig. 10 shows the electric power loss for every contribute in percentage for three different technologies. The power losses are distributed almost in the same way where almost two thirds of the power losses are due to the steam extraction and one forth to the CO₂ compression. In light of this preliminary analysis, the section is focused mainly on the steam extraction and the different integration between the power plant and the capture plant with a final part looking at the impact of the CO₂ compression.

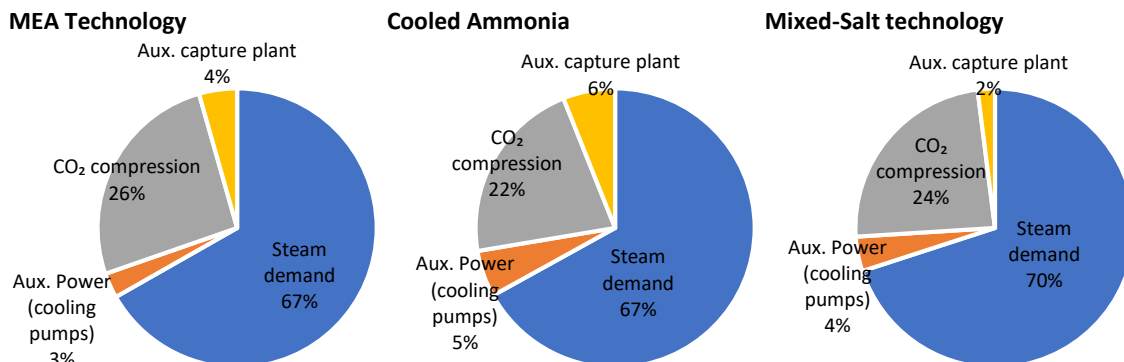


Fig. 10. Left: percentage of electric power losses due to every contribute for an MEA capture plant. Center: percentage of electric power losses due to every contribute for a Cooled Ammonia plant. Right: percentage of electric power losses due to every contribute for a Mixed-Salt Technology plant.

In summary, the results showed deal with the following considerations:

- The contributes on the power losses of the post-combustion absorption carbon capture plant with a coal fired steam plant are distributed almost in the same way for different kind of technologies and solvents. In detail, almost two thirds of the power losses are due to the steam extraction and one forth to the CO₂ compression while the solvent cooling and the auxiliaries of the capture plant are around 5% each one.
- The power loss factor, which is the ratio between electric power loss and the heat duty, rises when the cross-over pressure is lower than the required pressure at the solvent regenerator. This happens because a pressure maintaining valve is needed which introduce an entropy generation. Hence, at the same heat duty, a low regeneration temperature reduces the electric power loss especially for retrofit integrations since it reduces the steam pressure required by the regenerator and consequently the loss due to the pressure maintaining valve.
- The higher is the pressure of the regenerator, the lower are the CO₂ compression electric power loss since it is the only variable that influences this parameter. However, high regeneration pressures lead to high regeneration temperatures with the penalization for the steam extraction already discussed in the previous point. This brings to a trade off with an optimum compromise.

- Inorganic solvents based technologies such as Cooled Ammonia and Mixed-Salt Technology combine low regeneration temperature with the opportunity to rise in a wide range the regeneration pressure maintaining the heat duty comparable with the amines technologies.

Life cycle assessment of solvent based carbon capture technologies

The environmental impacts of different technologies for separating CO₂ from the flue gas stream of a coal-fired power station have been compared. In particular, two comparisons taken from the literature between amine based solvents and inorganic based solvents are presented. The benefits of the inorganic solvents (such as NH₃ and K₂CO₃) compared with amines (such as MEA and MDEA) are principally due to avoided of carbon dioxide emissions from amine degradation along with a cleaner footprint during the production and transport process of the solvent. For what concerns the energy saving and the specific carbon dioxide emission, the benefits of the inorganic solvents are less evident.

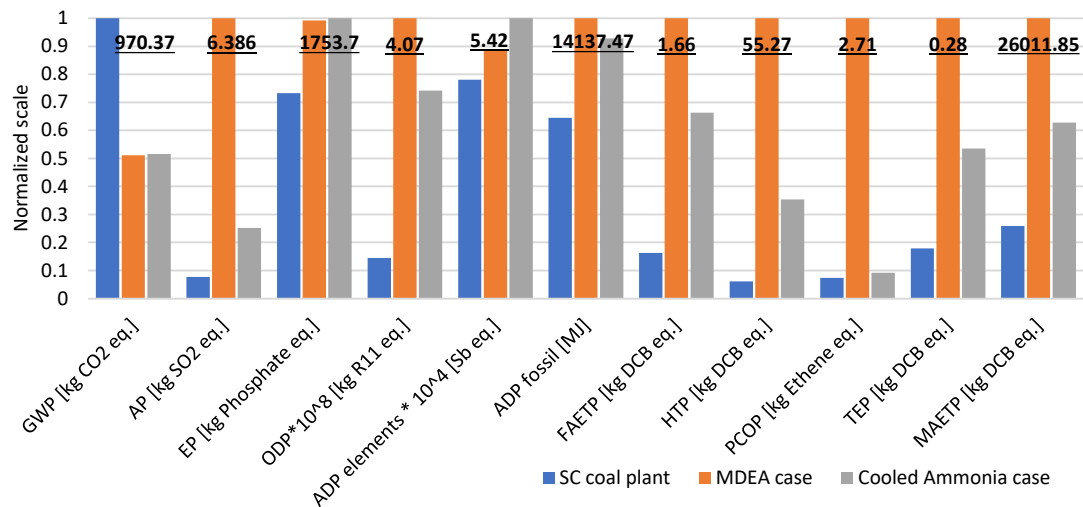


Fig. 11. LCA indicators values for the three cases analysed by Petrescu et al. specifics on the MWh of electric power produced. The results are normalized on the higher value of each indicator, which value is reported with the number on the top of the columns.

Conclusion and future works

The study about the Cooled Ammonia technology can lead the following conclusions:

- The rate-based model in Aspen Plus is calibrated against a large number of experimental data with a very good agreement between predictions and measured values with an error lower than 20% and an average error lower than 5%.
- The parameter Specific Primary Energy Consumption for CO₂ Captured (SPECCA) of the Cooled Ammonia applied to a retrofitted power plant is 3.21 against 4.35 MJ/kg_{CO₂} of the EBTF MEA case and this is mainly due to the lower heat duty of regeneration. Similarly, the SPECCA of the Cooled Ammonia applied to a green-field power plant is 3.23 against 3.30 MJ/kg_{CO₂} of the NETL Cansolv case 12B; this is mainly due to the lower regeneration temperature and the consequent reduction of the pressure of the vapor bleeding.
- The green-field approach can always better integrate the capture plant with the power plant since the tailored design of the steam turbine allows the steam extraction at the lowest pressure as possible with a higher expansion of the steam in the turbine and less power losses.
- The levelized cost of electricity (LCOE) and the cost of CO₂ avoided of the Cooled Ammonia are 87.66 €/MWh_{el} and 47.03 €/ton_{CO₂} against 92.27 €/MWh_{el} and 51.62 €/ton_{CO₂} for the EBTF MEA, mainly due to the higher thermodynamic efficiency despite the investment costs are the same and the consumables cost are almost doubled. Similarly, the LCOE and the cost of CO₂ avoided of the Cooled Ammonia are 124.3 \$/MWh_{el} and 66.5 \$/ton_{CO₂} against 133.2 the \$/MWh_{el} and 75.25 \$/ton_{CO₂} of the NETL Cansolv case, mainly due to the lower capital cost and the higher thermodynamic efficiency despite the consumables cost are almost 30% higher.
- Ammonia carbon capture is a valid alternative to the amines technology since it has a better energy performance, a lower the plant cost as well as a lower environmental impact and toxicity of the solvent.

Future works on this topic are the pilot plant test of different operative temperature in the absorber in order to avoid the salt precipitation and verify the performance of the overall plant on an industrial scale. Moreover, further improvements in the rate-based model and the simulation can be achieved with more experimental data. The ammonia technology has already a good level of maturity, so other interesting studies will be focused on the rate-based simulation of the behavior of the capture plant applied to the power plant at off-design and dynamic conditions in order to increase the readiness of the technology on the market. Finally, improved the know-how on the component of the capture plant, future works will be on the economic analysis focusing on the cost detail of every component giving a better cost estimation.

The study about the Mixed-Salt Technology can lead the following conclusions:

- Analyzing the thermodynamic properties of the solvent, the results show that the heat of desorption decreases with rising temperature of regeneration and the ammonia slip decreases with increasing the K_2CO_3 fraction in the solvent due to the reduction of free ammonia in the liquid phase.
- Increasing the concentration of K_2CO_3 in the solvent results in reduced solubility and consequently, salt precipitation occurs at a lower CO_2 loading.
- The experimental measurement of the overall mass transfer coefficient shows that the rate of absorption rises with temperature and decreases with rising CO_2 loading following the kinetic description of the Arrhenius equation. Moreover, the overall mass transfer coefficient decreases with rising K_2CO_3 fraction in the solvent due to the reduced amount of free ammonia in the reactive layer.
- The plant simulation with an equilibrium-based approach presented shows that the SPECCA of the Mixed-Salt Technology applied green-field to the power plant is 2.19 MJ/kg CO_2 against 3.30 MJ/kg CO_2 of the NETL Cansolv case 12B and this is mainly due to the lower regeneration temperature and lower heat duty of regeneration with the consequent reduction of the pressure and the mass flow of the vapor bleeding.
- The COE and the cost of CO_2 avoided of the Mixed-Salt Technology are 117.55 \$/MWh $_{el}$ and 51.58 \$/ton CO_2 against 133.20 \$/MWh $_{el}$ and 75.25 \$/ton CO_2 of the NETL Cansolv case mainly due to the lower capital cost and the higher net electric efficiency despite the consumables cost are almost 20% higher.
- Mixed-Salt Technology capture is a valid alternative to the amines technology since it has a better energy efficiency of the process, lower the plant costs and the lower environmental impact and toxicity of the solvent.

Future works on the Mixed-Salt Technology are a pilot plant test of the technology, the development of a rate-based model to improve the plant simulation validated with the experimental data, the study of the off-design and dynamic operation of the capture plant integrated with a power plant and a more detailed techno-economic analysis in view of the new results. All of these studies will be achieved since SRI International as the project coordinator with a partner the Politecnico di Milano has won a project funded by the American Department Of Energy (DOE). The project will have the aim to test the technology in the pilot plant of the Technic Center of Mongstad to study the performance in design, off-design, start-up, and shut-down. Finally, in light of the test results, the techno-economic analysis, the technology gas analysis, and the technology maturation gap will be assessed.