Moving packed beds for cryogenic CO$_2$ capture: analysis of packing material and bed precooling

David Cann$^{a,*}$, Carolina Font-Palma$^b$, Paul Willson$^c$

$^a$ Department of Chemical Engineering, University of Chester, Chester, CH2 4NU, UK

$^b$ Department of Engineering, University of Hull, Hull, HU6 7RX, UK

$^c$ PMW Technology Limited, Thornton Science Park, Ince, Chester, CH2 4NU, UK

Abstract

This work expands upon previous work on a moving bed cryogenic carbon capture (CCC). Cryogenic carbon capture using a fixed packed bed captures CO$_2$ frost deposited on the surface of the bed material; this build-up of frost fouls the heat transfer of the capture column and requires periodic shut down of the process to regenerate the bed material and collect CO$_2$ for further storage. Using a moving bed continuously removes frosted bed material from the capture column preventing the excessive build-up of frost and eliminating the need for a regeneration step within the capture column. This paper sets out two objectives in evaluating an experimental moving bed system with a fixed volume of bed material; i) compare two different types of bed material within the capture column, a high-density ceramic and a steel bed material of similar particle sizes, and ii) combine the precooling step and capture step within the cryogenic capture column to allow the cooling of bed material and CO$_2$ frost formation simultaneously. Frost front velocity results for the two different bed materials show 0.78 mm/s for steel bed material and 1.81 mm/s for ceramic bed material. Introducing a vertical gas injector into the capture column for additional cooling during the capture step allowed the capture step to be extended to approximately 5 minutes of continuous CO$_2$ capture.

Keywords: carbon capture, cryogenic separation, moving bed, desublimation

1. Introduction
The Covid-19 lockdown has interrupted most of human life as we know it for the past year. The lockdown has allowed wildlife to make a return to urban areas such as dolphins reappearing in Venice and has notably reduced CO₂ emissions compared to the previous year. With COP26 expected to be held in November 2021, returning to normal life after lockdown is expected to have made sustainability and climate change a high priority for most governments. The UK still aims to meet its target of 100% reduction in CO₂ emissions from 1990 levels by 2050 [1] and during lockdown has released a Ten Point plan for sustainability, detailing a commitment to capturing 10 million tonnes of CO₂ per annum by 2030 as part of that commitment [2]. Carbon capture and storage (CCS) has been gaining increasing support from governments and is widely accepted to be necessary in order to limit temperature rise to 2°C at the lowest cost [3]. Chemical absorption is the most mature carbon capture technology available for retrofitting onto existing power plants to decarbonise flue gases. However, chemical absorption is less economic for typical smaller scale industrial applications outside the energy sector. Cryogenic carbon capture (CCC) is a method of CCS that appears to be better suited to smaller scale industrial applications, CCC has been gaining interest for applications such as biogas upgrading and marine transport [4, 5].

1.1. Cryogenic carbon capture developments

The most researched methods of CCC include static packed beds [6], anti-sublimation [7] and cryogenic carbon capture with external cooling loop (CCC-ECL) [8]. Each of these methods of CCC takes advantage of the changes of saturated vapour pressure of CO₂ in the gas phase. Cooling gas mixtures containing CO₂ at atmospheric pressure desublimes CO₂ as a frost. When the gas is cooled sufficiently to begin CO₂ desublimation, further cooling causes the saturated vapour pressure of CO₂ to fall rapidly with temperature. A modest additional cooling to the gas can cause a high proportion of CO₂ to be desublimed out.

Static packed bed cryogenic carbon capture passes [6] a gas containing CO₂ through a sufficiently cooled packed bed, so that the CO₂ desublimes onto the surface of the bed material. This method of CCC eventually leads to the build-up of CO₂ frost on the bed surface, and the accumulation of frost
leads to a reduced efficiency of the heat transfer from the packed bed. The packed bed must be periodically regenerated by heating to remove CO₂ frost from the packed bed.

Anti-sublimation [7] is a similar method but uses cold evaporator fins rather than packed bed heat exchangers. Anti-sublimation dries flue gas before feeding it through a low temperature frost evaporator (LTFE) to capture CO₂ as a frost on the surface of the evaporator. Multiple LTFEs operating successively allows for a pseudo-continuous process, while one LTFE is being regenerated another LTFE can continue to capture CO₂ frost. This requires the installation of multiple LTFEs which increases capital cost.

CCC-ECL separates CO₂ from a flue gas through heat exchange with a contact liquid. The contact liquid is circulated in a refrigeration loop that desublimes CO₂ as a frost on the surface of cold liquid droplets, forming a slurry with the liquid. Separation of the slurry produces a CO₂ solid stream and a contact liquid stream which is recirculated through the heat exchange loop. The solid CO₂ stream is pressurised and heated to produce a liquid stream of CO₂.

Anti-sublimation and static packed beds both encounter issues with excessive frost build-up. The CO₂ frost must be recovered from the heat exchanger surface, which makes these methods of capture a batch process. Multiple capture units can be used in order to alternate between capture and recovery cycles. Utilising multiple capture units operating cyclically increases capital costs and energy consumption. Furthermore, as frost formation reduces heat transfer efficiency, excessive accumulation of CO₂ frost makes the regeneration cycle more energy intensive [9, 10]. CCC-ECL provides a continuous capture process by allowing a contact liquid to carry CO₂ frost out of the capture unit to be separated downstream. Similar to the circulation of a contact fluid, the solid bed material can circulate creating a moving bed in order to prevent the excessive accumulation of CO₂ frost in the capture column with the added advantages of avoiding gas compression costs by operating close to atmospheric pressure and providing a simple separation stage subliming CO₂ frost present on a moving bed material comparatively to separation of a slurry of CO₂ frost and contact liquid.
1.2. Moving bed for cryogenic carbon capture

Cryogenic carbon capture utilising a moving bed has been developed with both feasibility studies [9] and experimental work [11]. The use of a moving bed addresses the limitation of fixed packed bed CCC by preventing the accumulation of CO₂ frost within the capture column without requiring multiple capture columns or evaporators to operate cyclically, instead the CO₂ frost covered bed material is removed from the capture column to be regenerated and is then recirculated into the capture column. The process also provides an advantage of operating at near atmospheric pressure thus avoiding compression costs. The full operation of this process requires four major stages; the precooling of bed material, desublimation of CO₂ frost on the cold bed material, sublimation of CO₂ frost present on the bed material for recovery and finally recirculation of bed material for precooling. While the moving bed begins to address the limitation of CO₂ frost build up, a continuous CO₂ capture process would be required to perform these individual stages in a combined process and achieve steady-state operation. Feasibility studies have highlighted the potential for the patented advanced cryogenic carbon capture (A3C) system [12], which uses a two-step separation process consisting of cooler-drier and CO₂ separation stages, to be more economically beneficial than amine based absorption in certain smaller scale applications [9]. The cooler-drier stage both removes water content and precools the gas before reaching the CO₂ separation stage. The cooler-drier stage cools the flue gas to 174K by heat exchange with the cold CO₂ lean gas after the CO₂ separation stage. Overall the cooler-drier stage consists of between 11 % to 26 % of the heat exchange duties within the A3C process, where the proportion of heat exchange duty is primarily determined by the total duty required for refrigeration cooling in the CO₂ separation cycle. Therefore, applications that require less overall duty show a higher proportion of heat exchange duty for the cooler-drier stage. The A3C process was found to provide a comparable levelized cost of carbon capture (LCCC) to amine-based capture for large-scale applications and was particularly advantageous for biogas upgrading applications where the LCCC is 120.9 £/tonne CO₂ compared to 395.8 £/tonne CO₂ for an MEA based process of similar scale [9].
The A3C technology is currently at a technological readiness level (TRL) of 3, where the operation of the desublimation column has been demonstrated [11]. The next milestone needed is the completion of the full cryogenic capture cycle for the bed material between desublimation, sublimation and cooling, for a fully continuous process which is currently in progress.

The results of previous experimental work has demonstrated the potential of the A3C process with the moving bed able to control the excessive accumulation of CO$_2$ on the frosted bed material [11], therefore showing the potential for the process to continuously capture CO$_2$. It also highlighted the requirement of combining the cooling step and the capture step within the capture column, allowing both to occur simultaneously. Allowing both the cooling and mixed gas streams to flow through the capture column without interfering with one another under moving bed conditions would extend the length of the capture step and be a positive step towards the development of a fully continuous process.

The previous work used steel bed material as the heat transfer surface within the capture column, with experimental results and theoretical predictions for frost front velocity aligning well together [11]. Frost front velocity determines the rate at which the accumulation of frost inside the capture column advances through the column. Testing a greater range of bed material types for CCC has not been explored previously. Glass beads have been typically used as the packing material for cryogenic columns [13, 14]. Testing a wider range of bed materials can both assess the optimal choice of bed material for the capture column and can be compared with simulated results from theoretical models to determine accuracy of theoretical predictions on suitability of different bed materials.

This paper addresses two aims; firstly, a comparison of two types of bed materials as the heat transfer surface within the capture column, steel and high-density ceramic. High-density ceramic was chosen as a high density and high specific heat capacity are expected to improve the loading of CO$_2$ frost on the packed bed material compared to lower density materials. Secondly, the novelty of this paper is presenting the first attempt at performing the precooling step and capture step simultaneously in a moving bed through the addition of a second vertical gas injector into the
capture column. Addressing the need to perform the multiple stages of the CCC cycle simultaneously, this work performs the precooling step of the bed material and the capture step simultaneously as a first step towards a continuous process.

2. Materials and Methods

The cryogenic capture rig is a modified version of the design described in detail in previous work [11], this modification includes the introduction of a vertical injector into the capture column, the newly introduced injector has been highlighted in red in figure 1. The cryogenic capture column is a 1m tall column made from PTFE in order to withstand the near cryogenic temperatures, the capture column is fitted with two copper pipe gas injectors, one placed horizontally inside the injector and one placed vertically inside the injector. Both gas injectors are perforated with 1 mm width slits across opposite sides of the copper pipe to allow gas to flow into the capture column. The 100 mm gap between the horizontal and vertical gas injectors is CO₂ frost is formed inside the capture column.

![Figure 1. Sketch of moving bed experimental set up. (colour)](image)

The capture column was filled with two different sets of bed material for comparison of frost front velocities. Table 1 shows the bed materials that were selected for their high density, low density bed materials risk fluidisation under high gas flow rates that can occur within the capture column.
### Table 1. Comparison between steel and ceramic bed material

|                          | Steel   | Ceramic |
|--------------------------|---------|---------|
| Density (kg/m³)          | 7850    | 5900    |
| Specific Heat Capacity during capture step (J/kg K) | 400 | 420 |
| Particle Diameter (mm)   | 1.4-1.7 | 1.4-1.7 |
| Supplier                 | Pometon particles | Chemco beads [15] |

As shown in figure 1, the capture column was injected with two separate gas lines. The nitrogen cooling gas stream (blue) and the nitrogen and CO₂ mixed gas stream (orange) are both cooled using copper pipes submerged in a liquid nitrogen (LN2) bath to -140 °C and -75 °C respectively. The cooling gas stream (blue) is fed to provide cooling duty to the capture column until the bed material in the column reached -120 °C, then the cooling gas flow is reduced to continue cooling bed material while the mixed gas line (orange) is fed into the capture column through the horizontal gas injector. This experimental work focuses on assessing the CO₂ separation stage of the A3C process, therefore water is not included in the gas mixture as the gas would be dried before reaching the CO₂ separation stage. The bed material cools to the mixed gas causing CO₂ to desublime and form a frost on the bed material. The flow rate of the mixed gas is controlled using Bronkhorst El-Flow control valves which are used to set the volumetric concentration of CO₂. An in line GSS gas sensor and rotameter measure the CO₂ concentration and flow rate of the mixed gas.

Fixed bed experiments measure the frost front velocity (FFV) from a feed gas flowing through the horizontal injector at 0.23 m/s and 18 % v/v CO₂. The packed bed FFVs for steel and ceramic bed material are compared with simulated results estimated as in [11].

Once the fixed bed experiments were completed for different bed material types, moving bed experiments were conducted using a screw conveyor to control the column outlet bed flow. The screw conveyor was used to set the flow rate of bed material to match the FFV. The capture column was designed for mass flow conditions where the bed material at the centre of the column and near the column wall travelled at a uniform speed.
The superficial gas velocity and CO₂ concentration of the mixed gas was set at 0.23 m/s and 4% v/v. The bed flow rate was set at 0.016 kg/s in order to closely match the bed material superficial velocity to the FFV.

Moving bed experiments precooled the ceramic beads to -140 °C. The cooling gas flow rate was reduced once the ceramic bed was sufficiently cooled. The screw conveyor was then activated shortly afterward to set the bed material flow rate before introducing the mixed gas. Once the bed flow rate was set, the mixed gas was fed into the column via the horizontal mixed gas injector. Thermocouples placed 5 mm and 30 mm above the horizontal injector measured the bed material temperature over time to detect frost formation. Thermocouple temperatures would plateau at approximately -110 °C when the frost front had fully developed. Thermocouples placed further away from the horizontal injector helped to check the temperature of the ceramic bed material being precooled by the vertical gas injector.

3. Results and discussion

3.1 Evaluation of steel and ceramic bed material in static bed mode

The steel and high-density ceramic bed materials are both materials with a high density and comparable specific heat capacities. Evaluation of these two separate bed materials will help to determine which bed material is more suitable to be used in the capture column based on frost front velocity. A slightly higher frost front velocity is expected from the ceramic bed material due to the lower density of ceramic compared to steel. Slower frost front velocities would mean that a greater mass of CO₂ frost can be collected in a given depth of bed material in comparison. Resulting in higher levels of CO₂ loading.

The results in figure 2 compare the difference in FFV between the ceramic and steel bed materials under fixed bed operation. The frost front velocity is calculated by measuring the distance covered by the frost within the capture column over time, meaning the frost front velocity is represented by the gradient of the graphs.
Figure 2. Frost front velocity measurements for steel bed material and ceramic bed material under similar gas flows (0.23 m/s, 18 % v/v CO$_2$) (colour)

The frost front travels at a slower velocity on the steel bed material than on the ceramic, this is due to the higher density of the steel bed material. The greater density of steel means there is a greater available cooling duty within the bed material, therefore the steel bed material can frost a greater volume of CO$_2$ before becoming saturated with frost. Both sets of results have an associated uncertainty with them from repeated experiments, the ceramic bed material shows a lower level of uncertainty of 9 % at 370 mm and more repeatable results with the exception of a large percentage uncertainty of 42 % error for 30 mm recordings, whereas the steel bed material tends to initially show a high percentage error of 46 % for 5 mm recordings and eventually settling to 13 % uncertainty at 250 mm. It appears to be the case that recording frost front advance at the initial stages introduces a large amount of error which is reduced as the frost front continues to develop through the capture column. The more uniform shape and size distribution of ceramic bed material in comparison to the steel bed material could factor into the reduced error in results.

From figure 2, it is clear that the theoretical model and experimental results align well. The main discrepancy is from experimental results displaying a lag time, requiring up to 50 seconds before CO$_2$
frost is detected by the thermocouples placed 5mm above the mixed gas injector. This discrepancy likely indicates that the frost front takes longer to develop at the initial stages. The 5 mm thermocouple is placed 5 mm above the top of the horizontal gas injector, it is possible that the frost formation initially travels horizontally as well as vertically until the frost front fully develops past the gas injector. The experimental results both intercept the y axis close to -33 mm, which would indicate that the initial frosting location is not affected by the change of bed material.

The comparison of frost front velocities for two different bed materials with theoretical predictions has shown that the theoretical model is able to accurately predict the rate of frost formation within the capture column for different bed materials. The theoretical modelling work has the potential to reliably predict frost front velocities for a further range of different materials with confidence that the theoretical predictions are accurate. CO$_2$ must be able to readily form a frost on the bed material surface and not be disturbed by the transport of bed material through the capture column. Reducing the lag time between feeding a CO$_2$ mixed gas into the capture column and CO$_2$ frost being formed on the bed material surface will result in a more stable CO$_2$ frost. The effect of supercooling from the bed materials is currently not able to be predicted by the theoretical model, therefore testing of individual materials for suitability of CO$_2$ frost formation is still necessary.

3.2 Combining the capture and cooling step in moving bed mode

The vertical injector was added to the capture column to provide cooling gas to the bed material while the horizontal mixed gas injector feeds CO$_2$ mixed gas into the capture column. However, feeding two separate gas streams into the capture column increases the complexity of the capture step. The ceramic bed material was chosen for these cryogenic experiments due to the shorter lag time experienced for CO$_2$ frost formation.

The operation of the vertical cooling gas injector was tested to evaluate how uniformly the bed material is cooled by the gas flowing through the injector. These early tests revealed that the vertical gas injector did not uniformly cool down the bed material in the vertical direction. Within the 100 mm bed depth between the vertical and horizontal gas injectors, there is a small band of relatively
warmer bed material; this band is detected by thermocouples at 5 mm and 30 mm when the moving bed is in operation as a temperature peak. This peak representing the warmer band of bed material moving down the column can be observed in figure 3.

The temperature profiles recorded when both gas streams are feeding into the capture column was dependent on which gas flow was dominant. If the feed pressure of the cooling gas flow was too high then the mixed gas stream appeared to be flushed out of the capture column, flowing in the incorrect direction through the column. Balancing the two gas streams is required to ensure that the CO$_2$ frost formation is not disturbed.

![Image](image.png)

**Figure 3.** Double gas injector moving bed experimental results (0.23 m/s, 4 % v/v CO$_2$, ceramic bed material). A - Temperature peak from undercooled section of bed material, B - Possible temperature peak from undercooled section of bed material, C - Stable temperature showing desublimation, D - Stable temperature achieved from bed precooling.

Figure 3 shows an example of a moving bed experiment with both gas injectors feeding into the capture column with the frost front successfully developed and controlled. Introducing the vertical cooling gas injector into the capture column resulted in an extended capture step compared to a single gas injector set up used in previous work [11]. The 5 mm and 30 mm thermocouples recorded a steady temperature for the bed material at the expected desublimation temperature of the CO$_2$ frost after the initial temperature peak has passed and the relatively warm band of bed material has passed through the capture column.
The stable period of CO$_2$ capture extended to approximately 5 minutes in length which is double the length of time of previous experimental runs using a single horizontal gas injector, shown in figure 4. This extended capture time represents the length of time that CO$_2$ frost is being formed on the bed material. When the temperature profiles begin to increase in temperature, the bed material is no longer cold enough to desublime CO$_2$ and this rising temperature results in undesirable sublimation of CO$_2$ frost off of the bed material surface.

Figure 4 shows temperature profiles from the capture step utilising a single horizontal gas injector setup with steel bed material. Comparing temperature profiles between figures 3 and 4 shows that the double injector setup leads to an improved cooling of bed material throughout the column. In figure 3, the 350 mm and 500 mm thermocouples maintain temperatures between -100 to -140 °C, and in figure 4a for 150 mm and 250 mm thermocouples, temperatures rise from -120 °C to -60 °C, which leads to increased capture time from the double gas injector set up. Maintaining temperature profiles through the use of the double gas injector set up is critical for a continuous capture step.
The second gas injector used to precool bed material maintains bed temperature more stable within the capture column throughout the capture step, which makes balancing flow rates for a continuous capture cycle more manageable. The precooling stage is still required to initially cool the bed material to -140 °C. However, the continuous cycle including a frost regeneration unit to regenerate the frosted bed material would only require to be sufficiently heated to sublime the CO₂ frost rather than heating back to ambient temperature. The reduced cooling gas flow rate from the vertical gas injector would need to be sufficient to cool regenerated bed material from these temperatures back to -140 °C.

Follow-on work has focused on the design of the frost regeneration unit and recirculation of regenerated bed material to the capture column, balancing the three-unit operations of cooling, desubliming and subliming to create a fully connected continuous process.

4. Conclusion

To advance the low-TRL cryogenic capture process, assessment of CO₂ frosting characteristics is needed. This work compared two separate bed materials as heat transfer surfaces for a cryogenic CO₂ capture column. The frost front velocity was measured for both steel and high-density ceramic
bed materials under a gas flow of 0.23 m/s and 18 % v/v CO$_2$, producing frost front velocities of 1.81 mm/s for the high-density ceramic and 0.78 mm/s for the steel bed material. The two bed materials show that theoretical estimates can accurately predict the frost front velocity of the CO$_2$ frost within the capture. The experimental frost front velocities were compared with theoretical predictions, which matched well with the experimental data.

This work also advances the design of the capture column to feed in cooling gas and CO$_2$ mixed gas to conduct the bed precooling and CO$_2$ capture stages simultaneously, using the ceramic bed material as the heat transfer surface. Allowing the cooling gas to continue to precool bed material in the capture column while CO$_2$ mixed gas is injected into the capture column increased the capture time for experimental work to approximately 5 minutes.

**CRediT authorship contribution statement**

David Cann: Validation, Formal analysis, Investigation, Writing – original draft, Writing – review and editing. Carolina Font-Palma: Resources, Writing – review and editing, Visualization, Supervision, Project administration, Funding acquisition. Paul Willson: Conceptualization, Resources, Writing – review and editing, Visualization, Supervision, Funding acquisition.

**Declaration of interests**

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. There are no competing interests in this work.

☒ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
Acknowledgements

This project is sponsored by PMW Research in conjunction with The University of Chester. The University of Chester is a proud delivery partner of the Eco-Innovation Cheshire and Warrington project which is part-funded by the European Regional Development Fund.

Funding: This work was supported by the European Regional Development Fund [03R16PO1048]; and PMW Research.

References

1. HM Government., The Climate Change Act 2008 (2050 amendment) order 2019. 2019.
2. HM Government., The Ten Point Plan for a Green Industrial Revolution. 2020.
3. Global CCS Institute, Global status of CCS 2019. 2019.
4. Spitoni, M., et al., Theoretical evaluation and optimization of a cryogenic technology for carbon dioxide separation and methane liquefaction from biogas. Journal of Natural Gas Science and Engineering. 2019. 62: p. 132-143.
5. Font-Palma, C., D. Cann, and C. Udemu, Review of Cryogenic Carbon Capture Innovations and Their Potential Applications. C, 2021. 7(3): p. 58.
6. Tuinier, M.J., M.V. Annaland, and J.A.M. Kuipers, A novel process for cryogenic CO2 capture using dynamically operated packed beds-An experimental and numerical study. International Journal of Greenhouse Gas Control, 2011. 5(4): p. 694-701.
7. Clodic, D., et al. CO2 capture by anti-sublimation Thermo-economic process evaluation. 2005.
8. Baxter, L., A. Baxter, and S. Burt, Cryogenic CO2 Capture as a Cost-Effective CO2 Capture Process. 2009.
9. Willson, P., et al., Evaluation of the performance and economic viability of a novel low temperature carbon capture process. International Journal of Greenhouse Gas Control, 2019. 86: p. 1-9.
10. Tuinier, M.J., H.P. Hamers, and M. van Sint Annaland, Techno-economic evaluation of cryogenic CO2 capture—A comparison with absorption and membrane technology. International Journal of Greenhouse Gas Control, 2011. 5(6): p. 1559-1565.
11. Cann, D., C. Font-Palma, and P. Willson, Experimental analysis of CO2 frost front behaviour in moving packed beds for cryogenic CO2 capture. International Journal of Greenhouse Gas Control, 2021. 107: p. 103291.
12. Willson, P., Apparatus. 2016: UK.
13. Ali, A., et al., Energy Minimization in Cryogenic Packed Beds during Purification of Natural Gas with High CO2 Content. Chemical Engineering & Technology, 2014. 37(10): p. 1675-1685.
14. Tuinier, M.J., et al., Cryogenic CO2 capture using dynamically operated packed beds. Chemical Engineering Science, 2010. 65(1): p. 114-119.
15. Tojo, T., et al., Heat capacity and thermodynamic functions of zirconia and yttria-stabilized zirconia. The Journal of Chemical Thermodynamics, 1999. 31(7): p. 831-845.