Experimental study of carbon dioxide desublimation and sublimation process on low temperature surface

Y N Wang¹, J M Pfotenhauer², L M Qiu¹-*, X Q Zhi¹, X B Jiang¹

¹Institute of Refrigeration and Cryogenics, Zhejiang University, Hangzhou 310027, China
²Department of Mechanical Engineering, University of Wisconsin, Madison, Wisconsin 53706, USA
*E-mail address: limin.qiu@zju.edu.cn (L.M. Qiu)

Abstract. Cryogenic carbon dioxide capture by the desublimation method has the advantage of being contamination free and energy efficient under high concentration. Due to the difficulty of collecting solid CO₂ after desublimation, this method has not been applied. In this paper, a visual experimental setup for carbon dioxide desublimation and sublimation on a low temperature surface is introduced in detail. The core part of the experimental set-up is a visual tube-in-tube counterflow heat exchanger consisting of a Pyrex glass tube with a larger diameter and a stainless-steel tube with a smaller diameter. The crystal growth and dissipation occur on the precooled outer surface of the inner tube, which is recorded by a camera. When carbon dioxide desublimates under different working conditions, such as temperature and supersaturation, the growth shape and growth rate of the solid are different. The thermal properties of the solid such as porosity, thermal conductivity and density are also different, leading to variations in the sublimation process and speed. Three distinct sublimation processes are discussed in this paper to provide guidance on the actual carbon capture process.

1. Introduction
It is a worldwide concern to develop carbon capture and storage technology with high efficiency [1-3]. Cryogenic carbon dioxide (CO₂) capture using a desublimation method separates CO₂ from other flue gases by utilizing the difference in their desublimation temperatures. It can be seen from the three-phase diagram of CO₂ that desublimation can occur under 195K and normal pressure [4], but there is still no efficient method for collecting solid CO₂, which restricts the application of the desublimation method. Recently many researchers have focused on the process design and energy consumption [4], but there are few studies on the actual growth process of CO₂ crystals. In this paper, findings from a series of experimental studies on CO₂ desublimation and sublimation characteristics are reported.

Unlike CO₂, the growth of ice (H₂O) crystals has been a research hotspot since the last century and can provide direction for the study of CO₂ crystals. In the field of ice crystal morphology, research has been going on for more than a century. In 1903, Nature published a series of photographs of different forms of snowflakes formed under natural conditions [5]. In 1954, Nakaya U. systematically and quantitatively described the effects of temperature and water vapor supersaturation on the morphology of ice crystals for the first time. [6] It is found that stellar plates and dendrites are formed at around -15°C, and high supersaturation promotes the growth of the branches. Since the 1990s, K. Libbrecht has carried out a significant amount of research regarding the growth law of ice crystals and including experiments to precisely control the growth conditions [7]. The observation technology of ice crystals has gradually
grown becoming mature and varied. In 2003, X. Wu studied the microscopic process of frost on a cold surface and found the frost formation on a cold surface generally begins with the formation and growth of condensate droplets [8]. In 2016, W. Shimada used Michelson interferometer to reveal the three-dimensional structure of a plate growth crystal and measured the thickness of different positions of the crystal [9].

In the field of crystal growth models, in 1989, E. Yokoyama and T. Kuroda built a model to simulate the growth process considering not only temperature and supersaturation but also the dimensionless crystal size with reference to the mean free path of a water molecule [10]. In 2005, P. Chidyagwai and C. Reiter proposed a two-dimensional growth model of dendritic crystals. [11] In 2016, J. Li et al. proposed a new geometric model considering interface control based on this. By defining two new variables, growth delay and growth inertia, J. Li and others improved models to simulate the growth of both tree and plate structures more accurately. [12]

Based on the above studies, it can be found that the growth process of the crystal is closely related to the conditions of growth temperature and supersaturation. In this study, the CO₂ desublimation and sublimation process and mechanism are analyzed based on a series of visual experiments, which lays the foundation for further exploration of the thermal properties of solid CO₂ and the application of cryogenic carbon capture.

2. Experimental set-up

An experimental set-up was designed and constructed to quantitatively study the mechanism of CO₂ crystallization on a cold surface and to explore the method of controlling CO₂ crystal growth under low temperatures [4,13,14]. The principle of the CO₂ desublimation visualization experiment is to use low temperature N₂ as a cold fluid in the horizontal countercurrent tube-type heat exchanger, and to control the temperature of the outer surface of the inner tube as the growth surface by adjusting the flow rate of the low-temperature N₂. When the desublimation saturation pressure corresponding to the wall temperature is lower than the partial pressure of CO₂ in the flowing gas stream, the CO₂ gas molecules diffuse toward the wall surface and desublimation onto the wall surface. After desublimation, the gas supply to the inner and outer tubes is stopped, and a vacuum pump is connected with the outer tube where the pressure is rapidly lowered to 200-300Pa, in order to accelerate the sublimation process of the solid CO₂. Visualization research methods were introduced in the experimental set up. With the combination of a vacuum-compatible stepping motor and endoscope, the CO₂ crystal growth characteristics under different flow and cooling conditions are observed and recorded.

The process design of the test bench system is shown in Figure 1, which mainly includes three parts: a) the gas supply and cooling system, b) the vacuum system, and c) the data measurement and control system [13]. The gas supply and cooling system comprises two channels of high purity nitrogen gas (99.999%), one channel of high-purity carbon dioxide gas (99.999%) and a liquid nitrogen dewar for cooling the two nitrogen gas streams. The N₂ and CO₂ pipelines for preparing the mixed gas are set with a normal temperature gas flow controller which can control the flow rate (regulation range between 25-2000 ml/s) before the gas is precooled and is used for regulating the volume fraction of CO₂. The vacuum system includes a vacuum chamber, a nitrogen heater, N₂-CO₂ gas mixers, precooling heat exchangers, visual flow channels and image acquisition systems. The measurement and control systems include the temperature measurement and control systems, the flow measurement and control systems, the pressure measurement systems, and the stepper motor control systems. A photo of the set-up is shown in Figure 2.

The visual flow channel as shown in Figure 3 is the core part of the system. Considering the comprehensive process and the observation purpose, the visible flow channel is designed as a tube-in-tube structure, consisting of a Pyrex glass tube with a larger diameter and a 304 stainless steel tube with a smaller diameter. Cold gaseous N₂ flows through the stainless-steel tube, while a N₂– CO₂ mixture (or pure CO₂) flows through the annular space between the glass tube and the stainless-steel tube. The connection between the glass and the metal is performed by Kovar welding. In addition, considering the shrinkage property of the materials at a low temperature, a stainless-steel corrugated tube is added.
between the glass and the stainless steel to prevent shrinkage and cracking of the glass at low
temperatures. A screen is added at the outlet of the outer pipe for filtering small particles of solid CO\(_2\)
flowing with the gas stream, in order to prevent the solid particles from entering the air outlet pipe and
causing blockage. The 4 gas ports of the visible flow channel are connected to the pipes in the system
using VCR fittings. Ten calibrated thermometers in the inner tube and six in the annular tube measure
the temperature of the flow. The thermometers are fixed on two separate fiberglass rods which have
poor thermal conductivity and therefore have minimal effect on the temperature measurements. Three
thermometers are attached to the outer wall of the inner tube. However, a layer of insulating material
exists between the thermometer and the wall, causing a slight temperature difference (less than 2K)
between the wall and the temperature measurement.

![Figure 1 Schematic of the experimental set-up for CO\(_2\) desublimation\(^\text{[4]}\)](image)

![Figure 2 The experimental set-up.](image)
Since the length of the visible channel is 0.7 m, it is difficult to collect the CO$_2$ desublimation image along the path using a conventional external high-speed camera. Therefore, the desublimation process of CO$_2$ in the channel is recorded by a camera on a slide rail driven by a stepping motor. This method is used to acquire images of CO$_2$ desublimation at different locations. Since both the visual channel and the camera are in the vacuum chamber and there is no window on the wall of the vacuum chamber, a LED light strip is also mounted in the vacuum chamber. Notice that the camera and the LED strip cannot convectively dissipate any of the heat that they generate due to the vacuum environment (which can reach $10^{-5}$ Pa during the experiment). Therefore, various copper mesh and copper braids are connected between the camera, the LED strip and the wall of the vacuum chamber to dissipate heat through conduction, so as to prevent the camera and the LED strip from failure due to over-heating.

The basic operations after evacuating the system are provided elsewhere [4]. The temperature of the nitrogen flowing into the mixer must be carefully controlled in order to avoid CO$_2$ desublimation and blockage in the gas mixer. Additionally, the flow rate of the cold nitrogen flowing through the precooler heat exchanger should also be carefully controlled to avoid CO$_2$ desublimation and blockage in the precooler heat exchanger. For both cases, even when no blockage occurs, any desublimation before the gas enters the visible flow channel will reduce the actual flow into the visible flow channel, affecting the accuracy of the analysis.

3. Results and discussion

In the following experiments, the volume flow rate of CO$_2$ was 25 ml/s, and the different volume concentrations were achieved by changing the flow rate of N$_2$ in the mixture. At different temperatures and concentrations, the growth rate of solid carbon dioxide is different. Consequently, the morphology, porosity and density of the solid are also different. These differences in thermal physical properties have a large impact on the sublimation process under low pressure (200–300Pa).

Figure 4 shows the formation and sublimation process of a kind of ice-like CO$_2$ solid near the saturation point. After a long time for ice-like growth, a dense and thick solid CO$_2$ layer forms, which sublimes slowly under low pressure. This is mainly caused by two factors. Firstly, the CO$_2$ molecule is closely attached to the solid surface. Secondly, the surface temperature is low after a long time of cooling, and the temperature increases slowly under low pressure. Under this condition, the time ratio of desublimation and sublimation is about 1:2.

Figure 5 shows that ice-like CO$_2$ solid growth still occurs under a growth temperature range of 165-174K. The solid is almost transparent, with a diameter of 2-3mm after growing for 3 minutes. When the pressure inside the outer tube drops rapidly, sublimation begins and the area of each single crystal gradually shrinks and eventually disappears. The fact that the desublimation process spreads from the top to bottom of the cylinder may be caused by an uneven distribution of temperature and volume fraction caused by gravity. Under the conditions in Figure 5, the time ratio of desublimation and sublimation is about 3:2.

In figure 6, where the temperature is lower than the case in figure 5, the growth rate of the ice-like solid is accelerated, the crystals continuously grow and join together, and the thickness also noticeably increases. During the sublimation process, the solid gradually changes from transparent ice to a white frost layer, and the large piece of frost is even more likely to fall off from the wall surface. Under this condition, the time ratio of desublimation and sublimation is about 3:2.
Figure 4 Thick ice which is extremely difficult to remove, 175-188K, x=80%

Figure 5 Formation and sublimation of ice-like CO$_2$ solid, 165-174K, x=20%

Figure 6 Formation and sublimation of ice-like CO$_2$ solid, 157-163K, x=10%

Figure 7 shows the formation and sublimation process of a kind of snowflake-like CO$_2$ solid under the growth temperature range of 133-153K. The transition from ice-like to snowflake-like solids is still unclear. These white and small snowflake particles fall off one by one during sublimation, and the ratio of desublimation to sublimation time is about 3:4.
Figure 7 Formation and sublimation of snowflake particles CO$_2$ solid, 133-153K, x=5%

In figure 8, due to the low precooling temperature of the wall, the CO$_2$ molecules quickly and evenly cover the entire surface once they enter the tube. This kind of solid is the most loosely attached to the wall, and it is easy for the whole piece to fall off when the pressure decreases. The ratio of desublimation to sublimation time is about 12:5.

Figure 8 Formation and sublimation of uniform cover CO$_2$ solid, 125-130K, x=5%

4. Conclusion
A series of experiments on the desublimation and sublimation of CO$_2$ at different temperatures and volume concentrations were carried out, and the relationship between working conditions, solid formation and sublimation was initially explored. In the actual carbon capture process, in order to collect solid CO$_2$ efficiently, the loosely formed snow layer associated with the condition of a low precooling temperature would be preferred, while the formation of a dense thick ice layer under saturated conditions should be avoided. The relationship between porosity, thermal conductivity of the carbon dioxide solids, operating conditions, and the rate of formation will be further investigated to provide experimental data for efficient carbon capture.

References
[1] Bahlke M E, Mendoza H A, Ashall D T, Yin A S and Baldo M A 2012 Dry lithography of large-area, thin-film organic semiconductors using frozen CO$_2$ resists Adv. Mater. 24(46) 6136-40
[2] Boot-Handford M E, Abanades J C, Anthony E J, Blunt M J, Brandani S, Mac Dowell N, Fernández J R, Ferrari M C, Gross R, Hallett J P and Haszeldine R S 2014 Carbon capture and storage update Energy Environ. Sci. 7(1) 130-89

[3] Yue L and Lipiński W 2015 A numerical model of transient thermal transport phenomena in a high-temperature solid–gas reacting system for CO₂ capture applications Int. J. Heat Mass Transf. 85 1058-68

[4] Wang Y N, Pfotenhauer J M, Zhi X Q, Qiu L M and Li J F 2018 Transient model of carbon dioxide desublimation from nitrogen-carbon dioxide gas mixture Int. J. Heat Mass Transf. 127 339-47

[5] Photographs of snow crystals Nature 1903 68 129-132

[6] Nakaya U and Marshall J S 1954 Snow crystals American Journal of Physics 22 573

[7] Libbrecht K G 2005 The physics of snow crystals Rep. Prog. Phys. 68(4) 855

[8] Wu X, Dai W, Xu W and Tang L 2007 Mesoscale investigation of frost formation on a cold surface Exp. Therm. Fluid Sci. 31(8) 1043-48

[9] Shimada W and Ohtake K 2016 Three-dimensional morphology of natural snow crystals Cryst. Growth Des. 16(10) 5603-05

[10] Yokoyama E and Kuroda T 1990 Pattern formation in growth of snow crystals occurring in the surface kinetic process and the diffusion process Phys. Rev. A 41(4) 2038

[11] Reiter C A 2005 A local cellular model for snow crystal growth Chaos Solitons Fractals 23(4) 1111-19

[12] Li J and Schaposnik L P 2016 Interface control and snow crystal growth Phys. Rev. E 93(2) 023302

[13] Yuan L C 2015 Theoretical and Experimental Investigation of Cryogenic CO₂ Capture by Desublimaiton[D] Zhejiang University (Chinese)

[14] Yuan L C, Jiang X B 2015 Design of CO₂ low temperature desublimation visualization experimental device Cryogenics 2015 (3) 30-36 (Chinese)

Acknowledgements
This work was supported by the Nation Key R&D Program of China (2017YFB0603701), and the National Natural Science Foundation of China (Key program, No. 51636007). We are grateful to Mr. Lingcheng Yuan and Mr. Xiaobo Jiang for help building the experimental set-up.