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Professor Stan Kolaczkowski 10 Dec 2015

Department of Chemical Engineering

University of Bath, Bath, UK

Removal of CO_2 from a submersible atmosphere by scrubbing with water – experiments in a single column

S.T. Kolaczkowski [a], S. Awdry [a], C.D. Le [a], M.L. Nuckols [b], T. Smith [c] and D. Thomas [c]

[a] Department of Chemical Engineering, University of Bath, Bath, BA2 7AY, UK
[b] Department of Mechanical Engineering and Material Science, Duke University, Durham, North Carolina, 27708, US
[c] S & C Thermofluids Ltd, Kelston, Bath, BA1 9AN, UK

Corresponding author: S.T. Kolaczkowski

Abstract

In order to explore methods of removing CO_2 from submersible habitats with sea water, gas scrubbing experiments (using tap water, and tap water with 3.5wt% sea salt) were performed in a 108 mm i.d. pilot-scale column, investigating the removal efficiency of CO_2 (e.g. at 2 vol%) from a gaseous stream. The performance of this column fitted with 5 spray nozzles was compared with a column packed with $1/8^{th}$ inch Dixon rings (packing depth =1480 mm). More detailed experiments were then performed in the column packed with Dixon rings at: liquid flows from 4 to 8 dm^3 min^{-1}; gas flows 18 and 36 Ndm^3 min^{-1}, column pressures = 1 and 4 bar(g); column temperatures approximately 5 and 17 °C. In general, CO_2 removal increased as column operating pressure was increased, or fluid temperature was decreased. When approaching low gas outlet CO_2 levels at the top of the column (e.g. 0.1 vol%), the concentration of carbonate species in the tap water (fed into the column) restricted further improvements in the performance of the column.
In experiments in a short column with Dixon rings (packing depth = 180 mm), using fresh water in each column, the performance of a multi-column 8 chamber compact scrubber was simulated, and shown to be significantly better than a single tall column.

Key Words: CO_2 gas scrubbing; submersible habitat; Dixon rings.

1. Introduction

When personnel need to operate in a submersible atmosphere in the sea, and exhale CO_2 into that atmosphere, then the CO_2 needs to be removed. The guidelines for the concentration of CO_2 in such an atmosphere necessitate that the partial pressure of CO_2 is maintained below 0.005 bar (Nuckols $et\ al.$[1] (p.61)).

In many submersible applications this is achieved by using a variety of chemical techniques, such as (e.g. Nuckols $et\ al.$[1] (pp. 95-114)):

- Example 1: the atmosphere is circulated through a packed bed of calcium hydroxide, $Ca(OH)_2$. This acts as a chemical sorbent, and when it becomes saturated it needs to be taken to the surface to be disposed of (or regenerated at the surface).
- Example 2: the atmosphere is circulated through a gas scrubbing unit, using a solution of amine. Then in a separate operation, CO_2 is stripped from the amine solution and the amine is reused in the gas scrubbing unit. The stripped CO_2 is now available in a more concentrated form, which can be discharged into the sea (or stored).

Despite the fact that such techniques for CO_2 removal already exist, there remains great interest in the potential to use sea water as a scrubbing fluid (e.g. Nuckols $et\ al.$[2,3]), and then to discharge the CO_2 laden fluid back into the sea. This could then:
- simplify the number of unit operations,
- avoid the need to bring and use chemicals for that purpose in a submersible vessel, and
- in Example 1, extend the time that personnel could operate in such a habitat without needing to terminate their activities because of the saturation of the chemical sorbent.

From the literature, although it is well known that water has the capacity to absorb CO_2, investigations into its use in a real application have been limited. Our preliminary thoughts and experiments on this theme were described in Nuckols $et\ al.$[4], which then led to the more rigorous study described in this paper.

In a submersible situation, CO_2 concentrations in the gas can vary, depending on the application, from a partial pressure of:

- 0.04 bar: if the gas stream is from an individual as they exhale, and that gas stream is then fed directly into the CO_2 removal unit (Application 1),

to
- 0.005 bar: in an atmosphere in which the personnel need to live (Nuckols $et\ al$[1]. (p.61)) from which a gas stream is taken which is then fed into the CO_2 removal unit (Application 2).

In this paper, our interest is mainly on Application 1.

At a depth of about 10 m of water, the pressure is 1 bar(g) (~2 bar(a)), so in Application 1, a CO_2 partial pressure of 0.04 bar would correspond to a 2 vol% CO_2 concentration.

Although the use of packed beds for gas scrubbing is well known in the chemical industries, if CO_2 levels at such a low partial pressure (i.e. 0.04 bar) had to be scrubbed with a liquid in a shore-based application (or off-shore above sea), then chemical solutions (e.g. containing amines) would most probably be used to enhance the absorption of CO_2. So even when looking for data on the possible performance of gas scrubbers with water (without chemicals), there is a distinct lack of information on the performance at such low CO_2 concentrations, and even less on how the performance of such a column would be affected by temperature or the presence of salt in the water at these conditions.

In order to explore the viability of using sea water as a CO_2 scrubbing fluid, Nuckols et al.[2], describe the results of trials on a submersible habitat which contained 4 crew members. The air from that habitat was drawn by a centrifugal fan and fed into the base of a 1520 mm high absorption tower (406 mm diameter), into which sea water was sprayed through six nozzles which generated a fine spray. Although in these trials the operational target for CO_2 levels was not reached, the technique was shown to work, and it was suggested that it could be improved further by either:

- increasing the gas pressure within the tower,
- decreasing the tower temperature,
- maximizing the mixing of sea water with cabin gas within the tower,

or a combination of all three. These ideas then led to a patent application (Nuckols et al.[3]).

It is interesting to note, that in general within the process industry simple spray nozzles are now not often used in gas scrubbing applications, as it is generally accepted that a packed column offers more overall benefits. Also, if gas scrubbing with sea water was to be used in a submersible habitat, then it has to be recognized that space for such an additional device would be very limited, and so any device which is contemplated needs to be compact. Likewise, within the process industry, although pH is a variable which could be controlled and enhance gas scrubbing, because of space limitations and complexity in a submersible application, this is not a parameter which would be practicable to consider.

Based on earlier work at the University of Bath, experience had been gained with the use of a high efficiency form of column packing material known as Dixon rings[5,6], so these were selected for the trials that follow. Although the existence of Dixon rings had been known for more than 60 years, it is only relatively recently (over the last 2 years), that manufacturing techniques have improved, and the price of Dixon rings enables them to be considered for many more applications. Therefore data on the performance of such packing material would be useful to investigators contemplating the use of Dixon rings. The Dixon rings were manufactured and supplied by Croft Engineering Services Ltd (Warrington, UK), and are shown in Figure 1.

When looking at the literature, it was not easy to find any actual comparative data in the literature on the performance of a packed bed *versus* a simple spray column

assembly at this scale of operation and concentration of a component that needs to be scrubbed. So our curiosity was aroused to compare the two. This paper therefore consists of three parts. First, the performance of a gas scrubbing column is assessed when the water is fed into the column *via* a number of spray nozzles mounted at different heights in the column. Then the performance of the column with Dixon rings is assessed, and finally experiments are performed on a short column representing a compact multi-path 8-chamber column scrubber.

2. Experimental apparatus

A schematic of the apparatus is illustrated in Figure 2, and the column was specially fabricated by S & C Thermofluids Ltd (Bath, UK) for these experiments. Water was pumped into the top of the column, and the flow of water was set by selecting a suitable speed of rotation of the positive displacement gear pump. The water flow was measured with a rotameter.

A heat exchanger was positioned in the liquid feed line into the column, and for the low temperature experiments this enabled the liquid to be cooled to a desired operating temperature.

The top of the column was made from a 330 mm long section of glass, which enabled the effectiveness of the distribution of liquid at the top of the column to be observed.

The column was constructed from a number of spool-pieces, so that by adding or removing these spool-pieces the overall height of the column could be changed.

The gas was fed into the base of the column, and flowed up through the column.

Above the point at which liquid was fed into the column, the scrubbed gas passed through a demister pad, and then through a flow control valve on a rotameter which measured the flow of gas from the column. This is reported in units of $Ndm^3 \ min^{-1}$ ($\equiv$ normal litre per minute) and was measured at room temperature and pressure.

The gas mixture into the column consisted of air and CO_2. The air was supplied from a compressor and the CO_2 was added into the line from a gas bottle. The pressure in the gas supply line to the column was regulated by a pressure control valve. The desired column operating pressure and gas flow through the column were achieved by making adjustments to the pressure control valve (gas supply line) and also to the valve on the rotameter at the top of the column. This technique was found to work very well.

The concentration of CO_2 in the gas supply line was controlled by setting a CO_2 gas flow on the mass flow controller and then by measuring the actual concentration of CO_2 in a gas sample taken from the gas inlet line to the column. The CO_2 concentration in the gas was measured with a mass spectrometer (MS).

At the base of the column there was a small liquid sump, which maintained a water seal at the base of the column. The liquid level could be set to a desired operating point and this was maintained by a water level detector. This liquid sump consisted of

a glass spool-piece, and therefore the height of the liquid seal could be visually confirmed, and also the extent to which any gas bubbles were entrained into the liquid could also be observed.

The pressure drop across the column was measured with a differential pressure transducer and the temperature of the liquid entering the column was measured with a thermocouple. Experiments were performed using local tap water (supplied by Wessex Water (UK)).

As the equipment would need to operate at different depths in the sea, experiments were performed at a column operating pressure of 1 bar(g), and at a pressure of 4 bar(g). These correspond to two different operating depths below the surface of the sea (i.e. 10 m and 40 m respectively).

3 Experimental Results

3.1 Performance of column with 5 spray nozzles

As a reminder, the trials reported in Nuckols *et al.*[2], on the use of spray nozzles in a simple sea water absorption tower were the motivation for looking at how a column with spray nozzles might work.

The experimental columns tested are shown in Figure 3. Although there are many variables that could be studied, as this was not the main purpose of our work, five fixed nozzle positions were selected along the length of the column (with fresh water supplied at each point), and experiments were also performed with:
> two different sizes of nozzles (fine and coarse spray), and
> two different nozzle spray angles (120 and 90º).

These results would then be compared with experiments in a packed column. The arrangement of the spray nozzles in the column is shown in Figure 3b, and this can be compared with the position of packing in the column shown in Figure 3a. The spray nozzles were supplied by Lechler Ltd (Sheffield, UK)

To minimize the entrainment of gas bubbles into the liquid phase leaving the column, a liquid seal height of 250 mm was used in the sump at the base of the column.

3.1.1   Experiments at 1 bar(g) with 5 spray nozzles

The results of these experiments are shown in Figure 4. In all of the experiments, at a fixed gas flow of 18 Ndm^3 min^{-1} and a CO_2 inlet concentration of 2 vol%, the gas outlet CO_2 concentration decreases, as the flow of water is increased.
When the nozzle angle is reduced from 120º to 90º, this has the effect of directing more of the spray into the gas phase region in the column, and results in a very slight improvement in CO_2 removal efficiency. Looking through the visual section near the top of the column, this appears to arise from the fact more of the liquid spray is directed into the core of the column through which the gas flows. Whereas, with the 120 º nozzle cone, more of the liquid reached the side walls of the column earlier and then drained down the wall into the sump at the base of the column.

The 90º spray angle was then selected for the subsequent experiments with a different size of nozzle and these results are also shown in Figure 4. With a smaller size of nozzle it is possible to achieve a finer spray, and hence a slightly higher reduction in gas outlet CO_2 concentrations is observed. However, because of the reduction in nozzle size, the pump is unable to provide the higher liquid flows that were possible with the larger size of nozzle.

3.1.2 Experiments at 4 bar(g) with 5 spray nozzles

The results of these experiments are shown in Figure 5. These show a similar trend to the experiments performed at 1 bar(g). At the higher operating pressure of 4 bar(g), the lower CO_2 gas outlet concentrations confirm that the removal of CO_2 is higher.

In the next section, the results of experiments with these spray nozzles will be compared with the experiments in the packed column with Dixon rings.

3.2 Performance of the 1480 mm packed column with Dixon rings

In the experiments with the column packed with Dixon rings (Figure 3a), the liquid was fed into a 'shower-head' type of liquid distributor, at the top of the column. The 'shower-head' liquid distributor at the top of the column had special gas flow-through ports to maintain a uniform gas flow profile across the top of the column. The top of the column was made from a 330 mm long section of glass, which enabled the effectiveness of the distribution of liquid from the shower-head onto the surface of the packing to be observed. This confirmed a uniform liquid distribution across the range of conditions tested.

Near the base of the column, a metal grid supported a 66 mm layer of 1/4 inch Dixon rings, which in turn supported a 1348 mm deep layer of 1/8th inch Dixon rings. Finally at the top of the column, to help with liquid distributions, there was a 66 mm layer of 1/4 inch Dixon rings. So the total height of packing was 1480 mm.

The temperature of the liquid entering the column was measured, and the temperature inside the column near the bottom of the packed section (above the metal support grid) was also measured.

Experiments were performed using local tap water (supplied by Wessex Water (UK)), and also a salt solution of local tap water (salt used was Cornish Sea salt).

To minimize the entrainment of gas bubbles into the liquid phase leaving the column, a liquid seal height of 200 mm was used in the sump at the base of the column. This did not need to be as high as in the earlier spray column experiments.

3.2.1 Start-up of the packed column with Dixon rings

It is important to emphasize that in order to obtain high performance from this type of packing in the column, it is necessary to flood the column with liquid before the

column is put into operational mode. This aspect is emphasized in early work[5,6] on Dixon rings. It is proposed that the packing is completely flooded by temporarily restricting the liquid flow from the column and allowing the liquid to back-up and fill the column, and thereby completely wet the packing. Great emphasis is placed on the need 'to maintain the apertures in the packing sealed with liquid', this means the spaces in the woven wire mesh filled with fluid.

3.2.2 <u>Experiments at 1 bar(g)</u>

As the temperature of the sea can also vary depending on location and depth, experiments were performed at two different fluid temperatures (approximately 17 and 5 ºC). The results of these experiments are shown in Figure 6.

In all of these experiments, a 2 vol% CO_2 gas inlet concentration was used. Over the range of conditions studied, the performance of the column can be seen to increase as the water flow is increased. An increase in the flow of water in the column has a number of important effects. First, a higher flow of water means that the water has a capacity to absorb a larger quantity of CO_2, and this can also enhance liquid phase concentration gradients (hence driving force). Next, because the liquid flow is higher, the liquid film resistance could be reduced, thereby increasing rates of mass transfer. However, as the liquid flow is increased, the liquid film thickness on the packing increases and in the presence of an opposing flow of gas this can lead to a condition known as column flooding. Flooding can also be initiated at the point where the packing is supported on the mesh at the base of the column - caused by a restriction in free area at the interface between the two. A mesh with a high open frontal area is likely to be less prone to flooding, than a mesh with a smaller open frontal area. Experiments were therefore limited to a maximum liquid flow of 8 litre min⁻¹ and this provided plenty of fluid to wet the packing, and a pressure drop measurement across the column confirmed that it was not flooding.

The lower liquid flow of 4 dm³ min⁻¹ was set based on the results of experiments in an earlier project, where it was found that at liquid flows below this value the packing would not remain adequately wetted. This means that for this packing and gas flow conditions, there is a range of liquid flows between 4 to 8 dm³ min⁻¹ over which the column can be operated with confidence.

By reducing the flow of gas into the column from 36 to 18 Ndm³ min⁻¹, the outlet CO_2 levels decrease and the performance of the column is improved. Lower gas flows mean that there is less CO_2 in the gas to be removed, so higher removal efficiency could be expected; however, at a lower gas flow the gas film resistance could be higher, although this does not appear to have a significant effect. For the absorption of CO_2 in water, it is generally accepted (Danckwerts[7]) that the overall mass transfer process is liquid film controlled. So changes to the gas film resistance should not make a big effect.

Comparing the performance of the packed column at a gas flow of 18 Ndm³ min⁻¹ with earlier experiments using the spray nozzles (see Figure 4), it is clear that by using a packing in the column then its overall performance has been improved. However, there is still plenty of scope to improve the performance of the column

further with spray nozzles (e.g. by adding more spray nozzles and reducing their size), however, this was not progressed further.

For the experiments with the packed column (comparing Figures 6a and 6b), it is clear that at the lower operating temperature range (4 to 6 °C), the performance of the column is also increased. The general trend in the effect of temperature was as expected.

The results of the experiments with the 3.5 wt% salt solution are also interesting, illustrating that the presence of the salt affects the capacity for the liquid to absorb CO_2. The general trend is consistent with explanations in the literature (e.g. Al-Anezi et al.[8]) and is known as the 'salting-out effect'. This means, that when water contains dissolved salts, these salts form ionic bonds with water molecules, and this reduces the availability of water molecules to bond with dissociated forms (e.g. carbonate and bicarbonate ions) of the carbon dioxide. Further information on the 'salting-out effect' and possible reaction mechanisms may be found in the literature (e.g.Vorhoz et al.[9]; Al-Anezi and Hilal[10]; Tokumura et al.[11]).

3.2.3 Experiments at 4 bar(g)

A similar set of experiments was then performed at a pressure of 4 bar(g), as shown in Figure 7. Encouraging a similar trend in the results was observed, and the performance of the Dixon rings with the earlier spray nozzle experiments is shown in Fig 5. At this higher operating gas pressure, the performance of the column has clearly improved. This enhancement in performance is interesting, as:

- at the higher operating pressure the driving force for mass transfer in terms of partial pressures is higher, hence an increase in CO_2 removal could be expected, yet
- at the higher pressure of 5 bar(a) *versus* 2 bar(a), the volumetric flow of gas in the column would decrease by a factor of: $5/2 = 2.5$, and so the resistance to mass transfer on the gas phase side would increase.

As mentioned earlier, as the absorption of CO_2 in water is considered to be liquid film controlled, the changes in the gas film resistance should not make a big effect, and for the conditions tested the increase in pressure increases the overall rate of CO_2 mass transfer and the retention of CO_2 in the liquid phase.

However, what is also very interesting about this set of experiments is that in the low gas flow experiments the performance of the column does not appear to improve with liquid flow. It appears that an asymptote has been reached. This then led to some interesting discussions with colleagues and it was only by performing a range of experiments to assess the equilibrium between CO_2 and water in a batch autoclave, that the answer was found. In simple terms, the tap water that was used comes from a water source that is known to consist of hard water, which had been abstracted from a number of different bore holes in the region. This water therefore contains a range of different minerals which include carbonates. When this water is in contact with air, CO_2 is transferred from the liquid to the gas phase until equilibrium is established. In

experiments performed a 1 bar(g) and 16.6 °C in the autoclave, it was shown that the concentration of CO_2 at equilibrium in the gas phase was ~1000 ppm ($\equiv 0.1$ vol%). This now explains why an asymptotic value was approached in the gas scrubbing experiments. The gas leaving the top of the column is in contact with fresh water entering the column, so therefore, the CO_2 level cannot be lower than the gas phase equilibrium concentration at the operating conditions in the column. A brief description of these supplementary experiments in the autoclave is presented in the appendix.

The equilibrium measurements in the autoclave enabled the apparent mole fraction of CO_2 in the aqueous phase to be determined. The term apparent is used, as the CO_2 is in a number of different forms and not just in the dissolved form. Therefore the apparent mole fraction of CO_2 in the aqueous phase at the inlet to the column could now be assigned a value of:

$$x_{CO_{2\,in}} = 2.6 \times 10^{-6} \tag{1}$$

Looking at the top of the column, if the liquid was to be in equilibrium with the gas phase, then Henry's law could be applied, and:

$$y_{CO_2,e} = \frac{H\ x_{CO_2,e}}{P_T} \tag{2}$$

For CO_2 in water, the following expression (Perry and Green.[12]) for Henry's constant, H, was used:

$$\ln\left(\frac{1}{H}\right) = -159.854 + \frac{8741.68}{T} + 21.6694\ln(T) - 1.10261.10^{-3}T \tag{3}$$

Substituting into equation (2) for the two different pressures at which experiments were done, at a column operating temperature of 17 °C (290.15 K), then H = 1302 bar (mol fraction)$^{-1}$, and:

at $P_T = 2$ bar(a), then $y_{CO_2,e} = 0.001690$ (~ 0.17 vol%),

at $P_T = 5$ bar(a), then $y_{CO_2,e} = 0.000677$ (~ 0.068 vol%).

At an operating temperature of 5 °C (278.15 K), then H = 874.71 bar (mol fraction)$^{-1}$, and:

at $P_T = 2$ bar(a), then $y_{CO_2,e} = 0.001137$ (~ 0.11 vol%)

at $P_T = 5$ bar(a), then $y_{CO_2,e} = 0.000455$ (~ 0.046 vol%).

This now helps to explain why in Figures 6 and 7, asymptotic values were being approached.

This then led to the performance of some additional experiments on the column, in which CO_2 was not intentionally added into the air supply. However, one should be aware that the background levels of CO_2 in the air were approximately 350 ppm, so this level of CO_2 would still have been present in the gas fed into the column. These results are shown in the earlier Figures 4 and 5, and are labelled as 'blank runs'. From these it is also clear that even with fresh tap water the gas leaving the absorption column has actually gained CO_2 from the water which had been supplied to the column, so this provides more evidence of why an asymptote in removal efficiency is being approached with this source of water supply.

3.3 Performance of the short 180 mm packed bed

In the chemical (process) industry, gas absorption columns are used in a range of different applications, and there are fewer limitations on the height of such a column than would be encountered in a submersible vessel. So in this new application, it was important to think more broadly about possible solutions to the problem. Looking at the literature, Kurata and Abe[13] describe the development of a cross-flow type of stripping-absorption apparatus of a multi-stage design, which consisted of a multiple number of short columns, thereby avoiding the need for a single tall column. In their design the liquid flowed into the top of the gas-liquid contacting zone and then out from the bottom, while the gas flowed in a horizontal direction (cross-flow) from one side to the other of the contacting zone. Depending on the design, liquid was also re-circulated from the sump of individual scrubbing stages.

In this paper, it was decided to explore the viability of installing a number of very short columns, with each column having its own supply of fresh liquid which would then be discharged. The gas and liquid were to be fed in counter-current flow mode across the gas-liquid contacting zones, thereby maximizing the driving force for mass transfer. An outline schematic of such a concept scrubber, consisting of eight chambers, is illustrated in Figure 8. The side view in Figure 8(a) shows how the gas flows through four chambers from left to right. At the top of each chamber a fresh supply of liquid is provided, which trickles through the packing. The top view of the scrubber is shown in Figure 8(b) which indicates the location of the liquid supply nozzles, and shows how the gas flows in from left to right through the chambers (bottom row), and then flows in the opposite direction from right to left (top row).

Using this approach, the scrubbing system could be designed to fit the available volume in the submersible vessel. The use of a fresh supply of liquid to each column meant that the driving force for mass transfer (and capacity to absorb) was higher; hence the total bed volume should be lower. As there was no need to re-use the liquid from any of the segments this simplified the process, and in the submersible application the water could be discharged into the sea. Although there is plenty of water around a vessel, the main disadvantage in this approach was that a larger volume of fresh water would need to be pumped into the scrubber.

To explore the viability of this method, spool pieces were removed from the column described in Section 3.2, such that the total bed height was 180 mm. In this shorted bed, the layers of ¼ inch Dixon rings at the top and bottom of the column were

reduced from 66 to just 10 mm. So the packed bed consisted of: 10 mm (1/4 inch Dixon rings), 160 mm (1/8 inch Dixon rings), and then 10 mm (1/4 inch Dixon rings).

Therefore, in order to make use of one short experimental column to simulate how eight short columns might perform in the configuration illustrated in Figure 8, it is necessary to perform experiments in a sequential manner. So if we start with the first column at the point of gas entry, this would have a fixed inlet concentration (e.g. 2 vol% CO_2) and a fresh feed of liquid. As the gas passed through this 1st column, the concentration of CO_2 would decrease and the gas outlet CO_2 concentration would be measured. Then to represent the performance of the 2nd column, it would be necessary to set the inlet CO_2 concentration to match the value measured at the exit of the 1st column, and to use a fresh supply of liquid. The procedure could then be repeated for the remaining six columns in this particular scheme.

For the sequence of experiments that followed:
- the gas flow into the column = 18 Ndm^3 min^{-1},
- the liquid flow = 7 dm^3 min^{-1}, and
- the height of the liquid level in the sump = 200 mm.

3.3.1 Start-up of the packed column with Dixon rings

The same procedure was followed as described earlier in Section 3.2.1.

3.3.2 Experiments at 1 bar(g) on short column

This set of experiments was performed at a liquid temperature of 16 ºC. To represent how a multi-path scrubber may function, a number of experiments were performed using this short column, and the CO_2 gas inlet concentration for each individual experiment was set as follows:
In Experiment 1: CO_2 gas inlet = 2 vol%.
In Experiment 2: CO_2 gas inlet = CO_2 gas outlet from Experiment 1.
In Experiment 3: CO_2 gas inlet = CO_2 gas outlet from Experiment 2.
In Experiment 4: CO_2 gas inlet = CO_2 gas outlet from Experiment 3.
etc.

The results of these experiments for tap water and salt water are shown in Figure 9, from which it is interesting to note:

(a) that the difference between the performance with tap-water, and salty-tap-water is now relatively small, and
(b) from the shape of the curve, there is a clear indication that an asymptote is being approached.

If these results are compared with data in Figure 6a (gas flow = 18 Ndm^3 min^{-1}, liquid flow = 7 dm^3 min^{-1}), then:

(a) for a single column with a total length of 1480 mm, the gas outlet $CO_2 = 0.59$ vol% for tap-water, and 0.75 vol% for salty-tap-water.

whereas,

(b) in a multi-path 8 chamber scrubber, for a total bed length of 8 x 180 mm = 1440 mm, the gas outlet CO_2 was 0.2 vol% for tap-water, and 0.23 vol% for salty-tap-water.

This shows a significant improvement in performance, and the presence of sea salt in the water now has a smaller effect on CO_2 removal. This enhanced performance is a result of the use of a fresh supply of liquid at the top of each of the short columns which creates a higher driving force for mass transfer, in combination with a greater total volume of gas scrubbing liquid which provides a higher capacity to absorb CO_2.

3.3.3 Experiments on short column exploring salt concentration

Depending on the geographical location, as the concentration of salt in the sea can vary, a short set of experiments was performed to assess the effect of salt concentration on the performance of the column. These experiments were performed on the short column (gas flow = 18 Ndm^3 min^{-1}, liquid flow 7 dm^3 min^{-1}), at an operating pressure of 1 bar(g), and with sea salt concentrations of 0, 2.0, 3.5, and 6.0 wt%. Experiments were also performed at a liquid temperature of 15 ºC and also at 4.5 ºC.

The results of these experiments are presented in Figure 10, from which it is clear that over the range of conditions tested (0 to 6 wt% sea salt) the performance of the column at both temperatures decreases as the concentration of sea salt increases.

4. Concluding remarks

(a) Column with spray nozzles: Although the performance of the column with the spray nozzles was not as good at the column that was packed with Dixon rings, there was still room to improve the performance of the column with the spray nozzles (e.g. by increasing number of nozzles, decreasing nozzle size, choice of nozzle spray cone angle and direction). For some applications, spray nozzles may be adequate. However, the limitation of spray nozzles needs to be recognized, for example:

- particulates may deposit in the nozzles – thereby affecting their spray characteristics;
- if the diameter of a nozzle is fixed, then this tends to correspond to a narrow range of flows, so this limits the turn-down or turn–up ratios for that nozzle;
- the nozzles may corrode or foul – thereby affecting their spray characteristics.

(b) Column with Dixon rings: Over the range of conditions tested, the 108 mm i.d. column, can be operated over a liquid flow range of 4 to 8 dm^3 min^{-1}.

Above a liquid flow of 8 dm^3 min^{-1}, conditions start to be approached at which the column may flood.

(c) The local tap water that was fed into the column contained an apparent mole fraction of CO_2 corresponding to x $_{CO2}$ = 2.6 x 10 $^{-6}$. This limits the scrubbing efficiency of the column. After discussions with the water provider (Wessex Water), the source of this water was confirmed to contain water which also came from local bore holes, and this water is known to be hard, containing minerals and carbonates. In the planned end-use application of this technology, the effect of the local concentration of CO_2 in the water used from the sea will need to be factored into the design.

(d) Multi-column 8 chamber compact scrubber: The use of fresh water at the top of each short column experiment provided a significant benefit in terms of the overall removal of CO_2 in column. However, this was at the expense of using a greater amount of fresh water – which may be readily available in this application.

(e) The presence of a 3.5 wt% sea salt was shown to reduce the efficiency of the single tall column packed with Dixon rings, however, when experiments were performed on the short column (simulating the multi-column compact scrubber) the presence of salt had less of an effect. This was because a supply of fresh water was used at each stage.

(f) In general, an increase in the operating pressure of the column, or a decrease in the fluid temperature, increases the removal of CO_2.

(g) The supplementary equilibrium experiments that were performed in the autoclave worked well and provide a useful method of checking equilibrium values between gas and liquid phases. Using this technique, the apparent concentration of CO_2 in the local tap water was determined, and Henry's constant was also checked.

(h) Having performed these trials, it will now be possible to make use of these experimental techniques and data to back-calculate the overall mass transfer coefficients in such a column with Dixon rings, which will enable alternative design configurations for the end-use application to be explored.

Acknowledgements

Nomenclature

H	Henry's constant, bar (mol fraction)$^{-1}$.
P_T	absolute pressure of the system, bar(a).

T	temperature, K.
x_{CO_2}	mole fraction of CO_2 in the water.
$x_{CO_2 in}$	mole fraction of CO_2 in the water fed into the column.
$x_{CO_2,e}$	mole fraction of CO_2 in the liquid phase in equilibrium for the gas.
$y_{CO_2,e}$	mole fraction of CO_2 in the gas phase in equilibrium with the liquid.
$y_{CO_2,t=0}$	mole fraction of CO_2 in the gas in the autoclave at t = 0.
$y_{CO_2,in air}$	mole fraction of CO_2 in air = 0.00035($\equiv$ 0.035 vol% ; 350ppm).

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APPENDIX **An investigation of CO$_2$ equilibrium in water**

A1.1 Experimental technique

Experiments were performed, using a stainless steel autoclave, which was adapted to enable vapour liquid equilibrium studies to be performed. This involved placing a known quantity of liquid (e.g. water) into the autoclave, and then adding a known amount of gas at a fixed starting pressure (e.g. 1 bar(g) $\equiv$ 2 bar(a)). Then the system was closed. The liquid was stirred (with a magnetic stirrer) and the gas and liquid where given time to come to equilibrium. Then the concentration of CO$_2$ in the gas phase was measured.

A schematic of the apparatus is illustrated in Figure A1. Gas of a known composition is supplied from a cylinder. This is fed into the autoclave and pressurized to the desired set point. A differential pressure transducer is then used to measure the change in pressure in the autoclave with time – a decrease in pressure indicating that the gas was being dissolved into the water phase. When equilibrium is established, valve V4 is opened, and the concentration of CO$_2$ in the gas phase is measured using a Mass Spectrometer (MS). The experimental procedure was as follows:

(a) First, gas from an air cylinder was used to purge the gas lines and the inside of the autoclave.

(b) The top of the autoclave was removed and 200 ml of fluid was added (e.g. 200 ml of water). The water used in this experiment was from the tap, and for the salty tap water experiments sea salt was added to tap water (concentration 3.5 wt%). The top of the autoclave was then replaced.

(c) At the start of an experiment, valves V_1 and V_4 were closed, and valves V_2 and V_3 were kept open. The air cylinder was replaced with a gas cylinder containing a known concentration of CO$_2$ in air.

(d) Valve V_1 was then opened slowly and the gas flowed through and into the system, which was pressurized to a set value (measured on the pressure gauge). When the set pressure was reached, valve V_1 was closed, and then valve V_3 was also closed (this fixed the pressure on one side of the differential pressure transducer).

(e) The magnetic stirrer in the liquid phase was then turned on. Any change in the differential pressure was displayed on the PC (transducer connected to PC). In general, after a period of about 5 minutes there was no more change in pressure, as equilibrium between the vapour and liquid had been reached. However, the stirring action was maintained for 10 minutes to ensure equilibrium had been achieved.

(f) Finally, valve V_4 was opened very slowly to make the gas flow to the mass spectrometer. V_4 was adjusted carefully to make sure the pressure inside the

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autoclave only changed very slowly, and that the gas flow to the mass spectrometer (MS) was adequate to achieve a stable reading on the MS.

The volume of the whole system, including the autoclave and the lines when valves V_1, V_3, V_4 are closed, while V_2 is open, was determined to be 435 ml. This was determined from an experiment in which the system was pressurized to 3 bar(g), and then as the pressure was reduced to 2 bar(g) the quantity of gas that was discharged was measured (by displacing water with gas, in an inverted measuring cylinder that was filled with water). This was then repeated for a change in pressure from 2 to 1 bar(g).

A1.2 Experimental conditions

Experimental conditions were selected to support the test performed on the column packed with Dixon rings. Such experiments were therefore performed mainly at 2 bar(a) and some were also performed at 5 bar(a) - both tap water and tap water with 3.5 wt% sea salt were used.

A1.3 Estimate the initial concentration of CO_2 in the gas phase

At the start of an experiment, if the autoclave was pressurized with a gas containing CO_2, then at time t = 0 when the autoclave was at its set-point pressure, the initial concentration of CO_2 in the autoclave, could be calculated from:

$$y_{CO_2, t=0} = \frac{y_{CO_2, \text{in air}} + (P_T - 1) \times y_{CO_2, \text{in cylinder}}}{P_T} \tag{A1}$$

where:

$y_{CO_2, t=0}$ is the mole fraction of CO_2 in the gas in the autoclave at t = 0.

$y_{CO_2, \text{in air}}$ is the mole fraction of CO_2 in the air = 0.00035 ($\equiv$ 0.035 vol%; 350ppm).

P_T is the absolute pressure of the system, bar(a).

This equation was used to check on the actual measured values obtained from preliminary experiments without water in the autoclave.

A1.4 Experiments with tap water and air from a gas bottle (with 350 ppm CO_2)

To check on the presence of CO_2 in the tap water, 3 runs were performed with air (which contained a background level of 350 ppm of CO_2), at 2 bara and 16.6 ℃. The measured CO_2 levels in the outlet stream were: 0.098; 0.1; and 0.098 vol.% These results are consistent with one another and are significantly higher than the

background level of 350 ppm of CO_2 in the air. These confirm that transfer of CO_2 from the liquid (200 ml of fluid) to the gas phase had occurred.

Additional experiments were then performed to assess if boiled water and de-ionized water would have different levels of CO_2 in them. The results are presented in Table A1. After boiling the water it was expected that any CO_2 which may be in a dissolved form as gas, would be readily displaced and a lower reading of 0.084 vol% was obtained - but this is still relatively high. This indicates that the form in which CO_2 is retained in the liquid phase is more complex.

Additional experiments with deionized water yield a significant reduction in CO_2 levels in the gas phase (now 0.046 vol%), and when the deionized water was boiled a further reduction in levels was obtained.

By performing a material balance over the closed system in the autoclave it should now be possible to determine the apparent mole fraction of CO_2 in the water at the start of the experiment. The term apparent mole fraction is used to recognize that the CO_2 is in a more complex form and not just as a dissolved gas. As the composition of the CO_2 in the liquid phase at the end of the equilibrium experiment is not known, the material balance is therefore solved with the aid of information using Henry's equilibrium constant.

This involves, using a method based on trial and error, and a technique known as a Hypothetical Flash Calculation was performed over the system using Aspen Plus V7.2. A schematic of the system is illustrated in Figure A2. As the composition of CO_2 in the gas when t = 0 is known (equivalent to a feed into a hypothetical flash), and the initial volume of water is also known (that is fed into the system), then by adjusting the mole fraction of CO_2 in the water fed into the system, a solution is found which enables a match to be obtained with the CO_2 level in the gas at the end of the experiment (equivalent to gas CO_2 concentration in gas phase from the flash-drum).

This enabled the concentration of CO_2 in the tap water to be back-calculated and estimated. Based on such a simulation (at 2 bar(a), and a 0.098 vol% CO_2 at t = 0), the CO_2 concentration in tap water was found to be 2.61 ppm (on a molar basis in tap water) resulting in a mole fraction, $x_{CO2} = 2.6 \times 10^{-6}$.

A1.5 Additional equilibrium experiments using CO_2 at different concentrations

A1.5.1 Experiments with tap water

Addition equilibrium experiments were then performed in which the concentration of CO_2 in the gas cylinder that was used to pressurize the autoclave was: 4 vol%, 4000 ppm and 1000 ppm.

Then, using the apparent mole fraction, $x_{CO2} = 2.6 \times 10^{-6}$, for CO_2 in the tap water, these experiments were then simulated in Aspen to calculate the composition of CO_2 in the gas outlet stream, and these values were then compared with the measured

values in the experiments, see data on tap water in Table A2. From these values, it is clear that a good match has been obtained. Also, the values of Henry's constant which were evaluated at each experimental point are also listed in Table A2. When these are compared with published data, they provide a good match, providing confidence in the value used within the Aspen simulation.

It is important to remember, that at each initial gas cylinder CO_2 concentration there would be a dilution effect as the autoclave was pressurized with gas. For example, when the 1,000 ppm CO_2 cylinder was used, the initial value of CO_2 concentration was 0.065 vol.% (as expected). However, the gas outlet CO_2 concentration was found to have increased reaching a value = 0.11 vol%, indicating that CO_2 was being degassed from the water into the gas phase.

A1.5.2 Experiments with tap water containing sea salt

For the set of experiments involving sea-salt (3.5 wt%) in the water, as the CO_2 concentration in the tap water to which sea salt was added was now known, then from a material balance, the apparent concentration of CO_2 in the liquid phase at equilibrium could be calculated, and then Henry's constant determined. These results are presented in Table A3.

A1.6   Concluding remarks

From this supplementary work, there are a number of important conclusions which support the paper:

(a) It is shown that when performing CO_2 gas scrubbing experiments with water, especially when low gas exit CO_2 concentrations are being considered (e.g. < 2,000 ppm), it is important to quantify the background level of CO_2 in the water used.

(b) The value of the CO_2 concentration in the tap water was determined to be, x_{CO2} = 2.6 x 10^{-6}, which at low gas phase concentrations would limit the amount of CO_2 that can be scrubbed from the gas phase. This now helps to explain the asymptotic shape observed in some of the runs in Figures 6 and 7.

(c) Confidence has also been gained in the selected form of expression for Henry's constant, which will be used in modelling work that follows this paper. Also, information has also been obtained on Henry's constant when the tap water contains 3.5 wt% sea-salt.

Table A1   Experiments performed with different fluids.

Col. 1 Pressure, and (CO₂ conc. in gas cylinder)	Col. 2 Liquid temp. °C	Col. 3 CO₂ initial gas phase conc. [1] at t = 0 vol.%	Col. 4 Measured CO₂ gas phase conc. at equilibrium vol.%
Fresh water 2 bar(a) (350 ppm)	16.6	0.035	0.098
Boiled fresh water 2 bar(a) (350 ppm)	17.0	0.035	0.084
Deion. water 2 bar(a) (350 ppm)	15.9	0.035	0.046
Boiled deion. water 2 bar(a) (350 ppm)	16.1	0.035	0.036

Note [1]: In preliminary experiments without water in the autoclave, the initial gas composition in the autoclave was also measured, and this is reported as the CO_2 concentration, at t = 0.
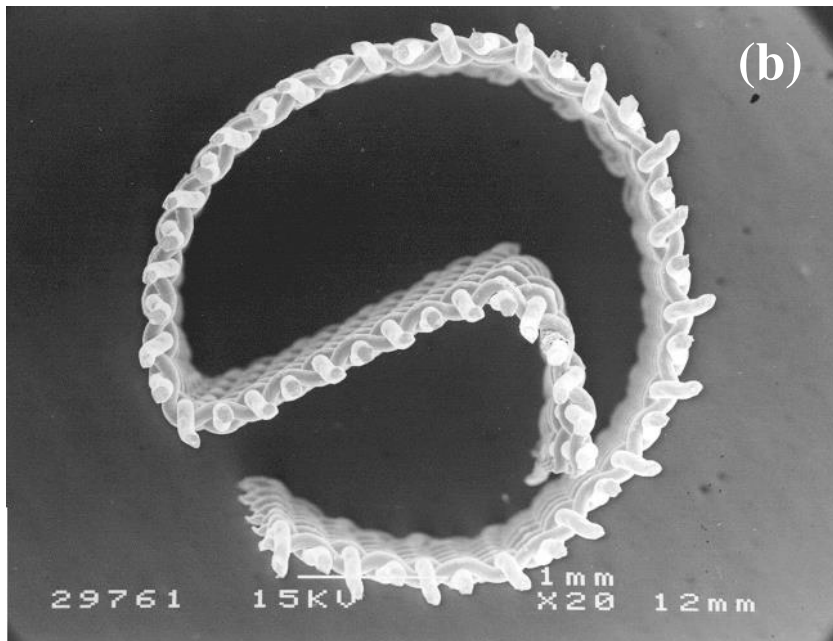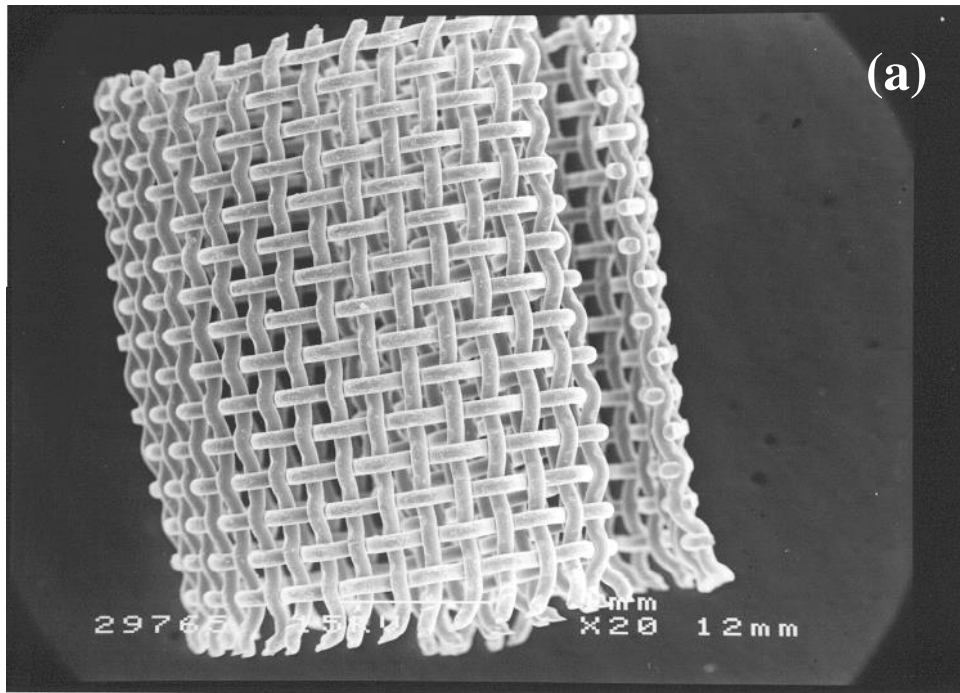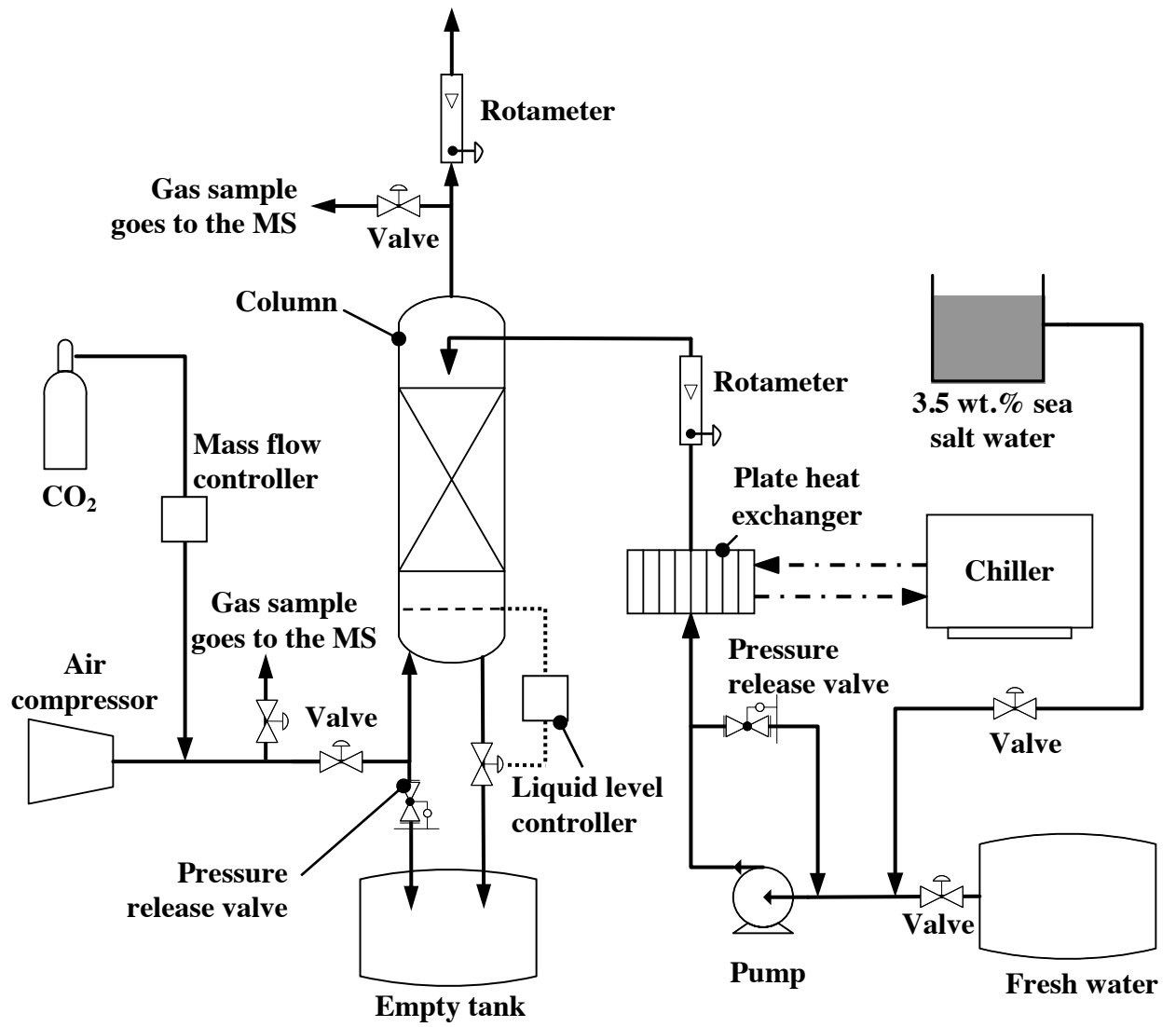
Table A2 Comparison between experiment and modelling for Tap Water.

Col. 1 Pressure, and (CO_2 conc. in gas cylinder)	Col. 2 Liquid temp.	Col. 3 CO_2 initial gas phase conc. [1] at t = 0	Col. 4 Measured CO_2 gas phase conc. at equilibrium	Col.5 Calculated CO_2 liquid phase conc. at equilibrium from material balance	Col.6 Calculated CO_2 gas phase conc. at equilibrium from Aspen simulation	Col.7 H, calculated & used inside Aspen model	Col.8 H, calculated from values in Col. 4 and Col. 5.	Col.9 H, calculated at liquid temp. in Col.3, from equation (3)
	°C	vol.%	vol.%	mol fraction	vol.%	bar.mol fract^{-1}	bar.mol fract^{-1}	bar.mol fract^{-1}
2 bar(a) (4 vol%)	21.0	1.89	1.09	(1.677×10^{-5})	1.16	1474	1300	1464
2 bar(a) (4,000 ppm)	17.8	0.228	0.198	(0.316×10^{-5})	0.205	1343	1254	1334
2 bar(a) (1,000 ppm)	19.6	0.065	0.11	(0.177×10^{-5})	0.118	1416	1240	1406
2 bar(a) (350 ppm)	16.6	0.035	0.098	(0.151×10^{-5})	0.098	1296	1296	1286
5 bar(a) (4,000 ppm)	15.9	0.321	0.194	(0.82×10^{-5})	0.202	1273	1183	1259

Note [1]: In preliminary experiments without water in the autoclave, the initial gas composition in the autoclave was also measured, and this is reported as the CO_2 concentration, at t = 0.

Table A3 Experiments using tap water with 3.5 wt% sea salt.

Col. 1 Pressure, and (CO_2 conc. in gas cylinder)	Col. 2 Liquid temp. °C	Col. 3 CO_2 initial gas phase conc. [1] at t = 0 vol.%	Col. 4 Measured CO_2 gas phase conc. at equilibrium vol.% and (mol frac.)	Col.5 Calculated CO_2 liquid phase conc. at equilibrium from material balance (mol fract.)	Col.6 H, calculated from values in Col. 4 and Col. 5. bar/mol fract.
2 bara (4 vol%)	21.0	1.89	1.15 (0.0015)	(1.575×10^{-5})	1460
2 bara (4,000 ppm)	17.8	0.228	0.205 (0.00205)	(0.3053×10^{-5})	1343
5 bara (4,000 ppm)	15.8	0.321	0.203 (0.00203)	(0.790×10^{-5})	1285

Note [1]: In preliminary experiments without water in the autoclave, the initial gas composition in the autoclave was also measured, and this is reported as the CO_2 concentration, at t = 0.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Water in

Gas in

Gas to
the next
chamber

Water
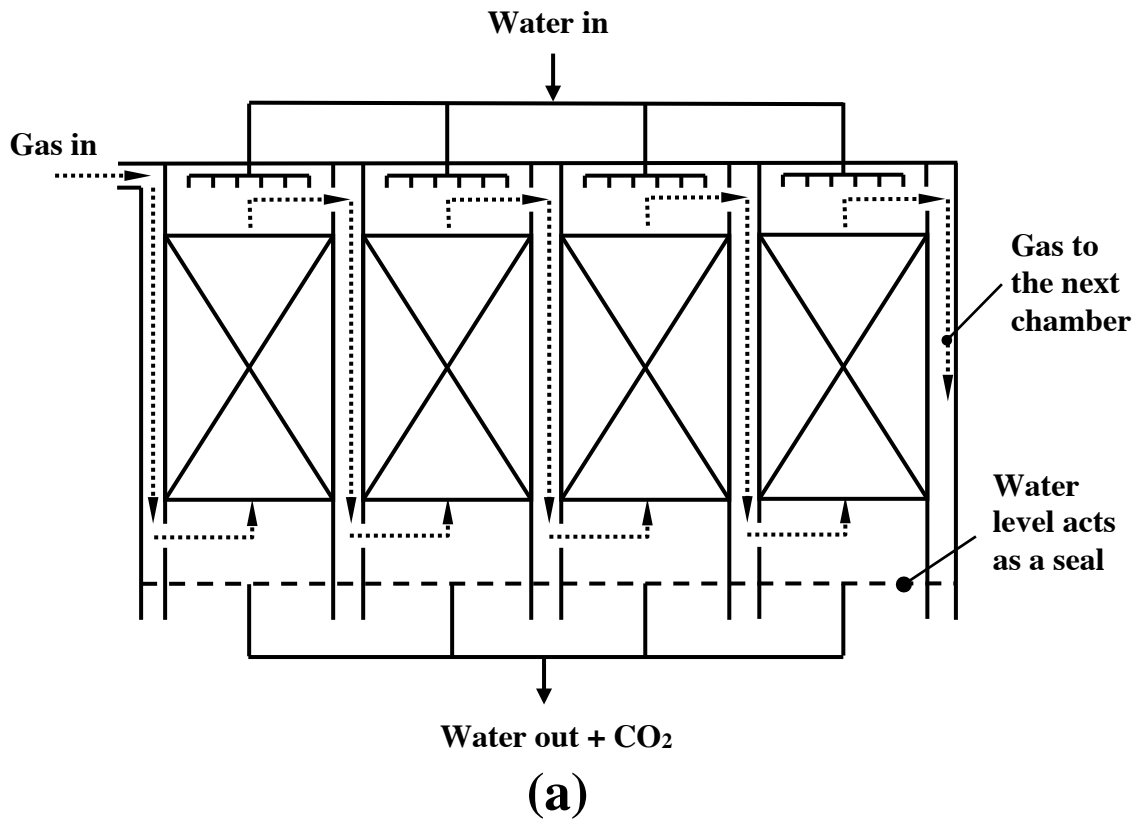level acts
as a seal

Water out + CO₂

(a)

Gas out

Water
supply
nozzle

Gas in

(b)
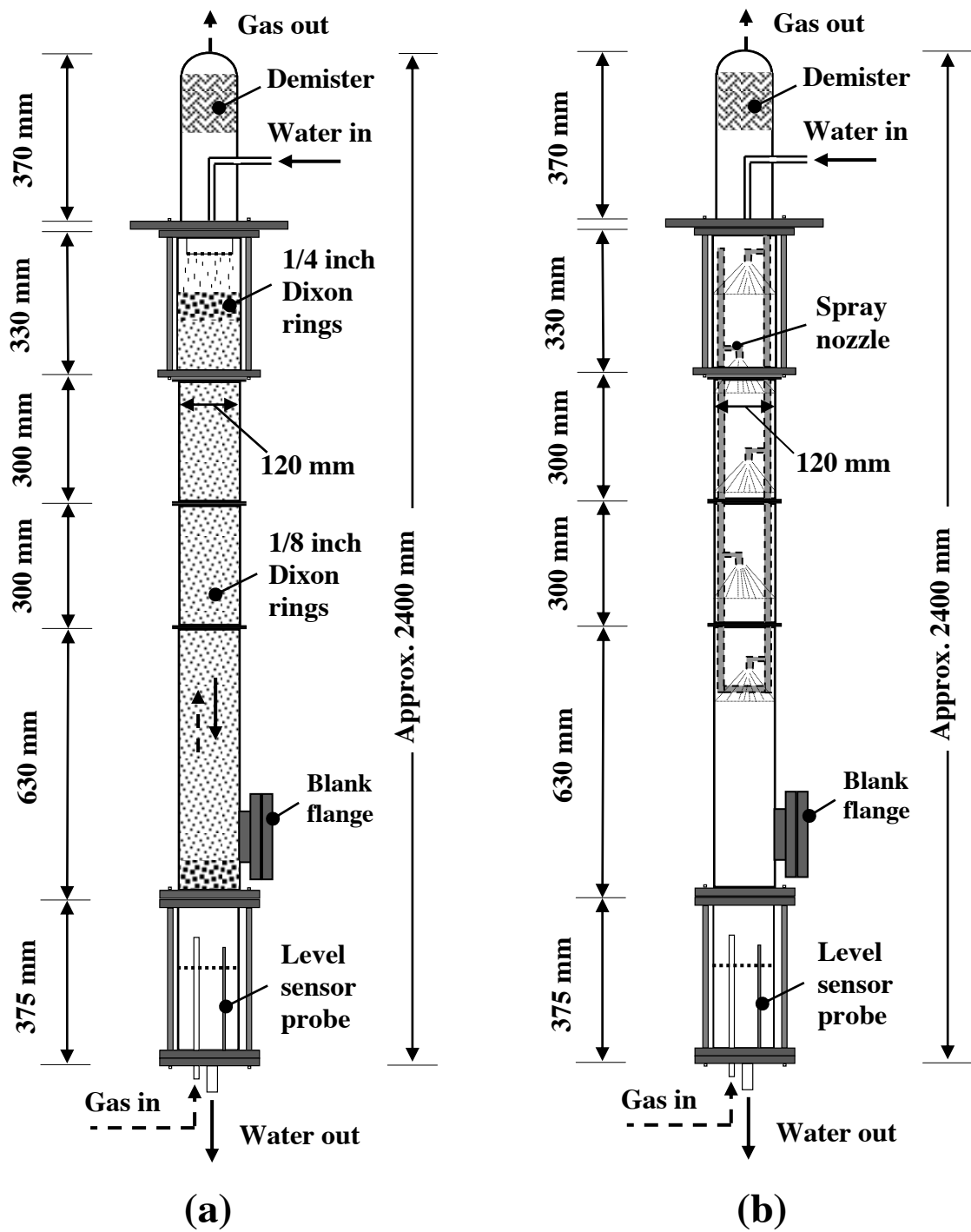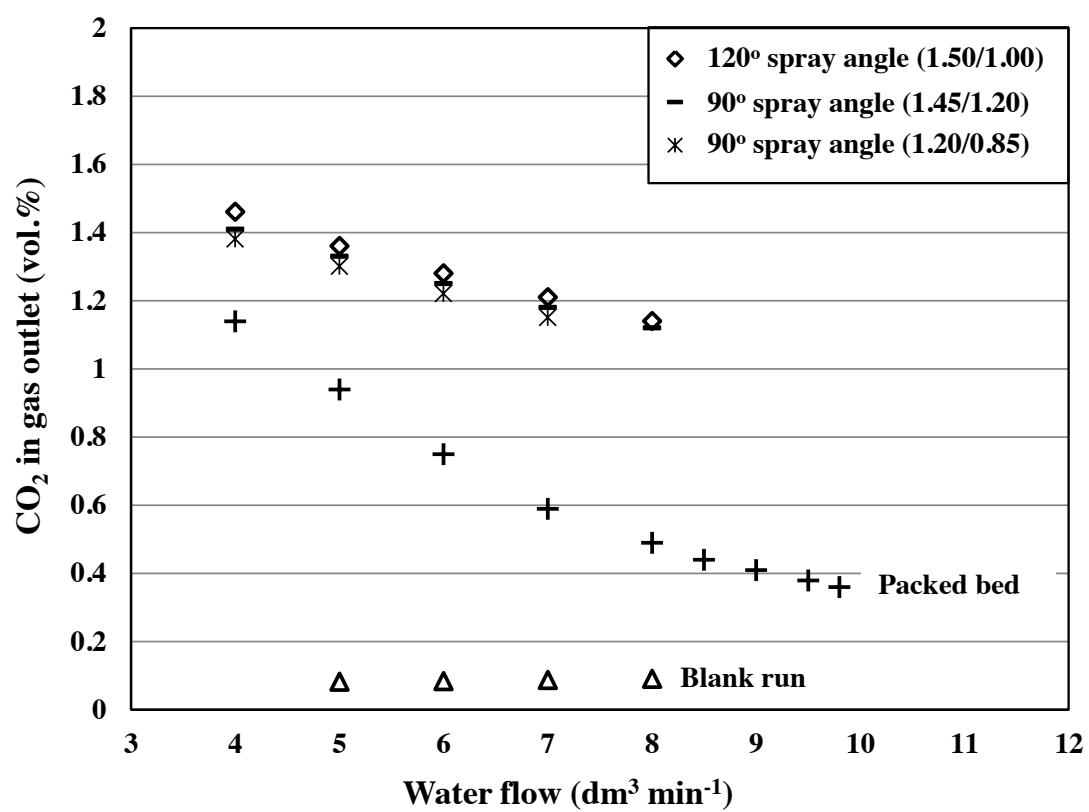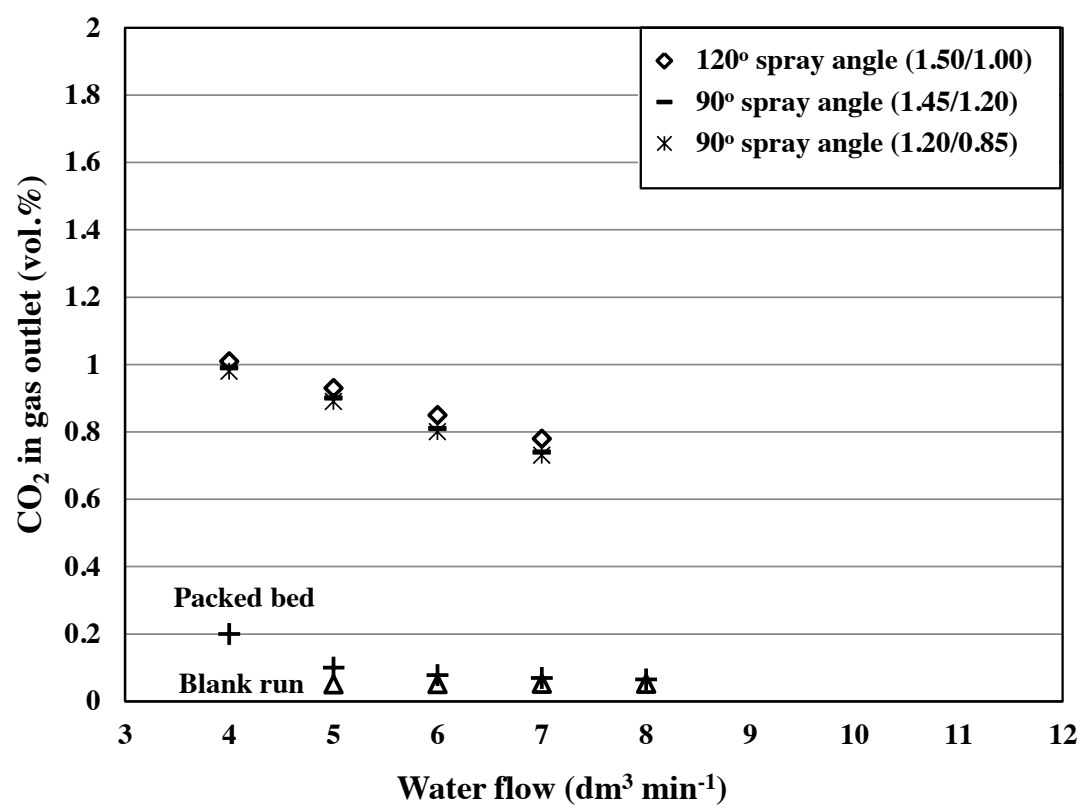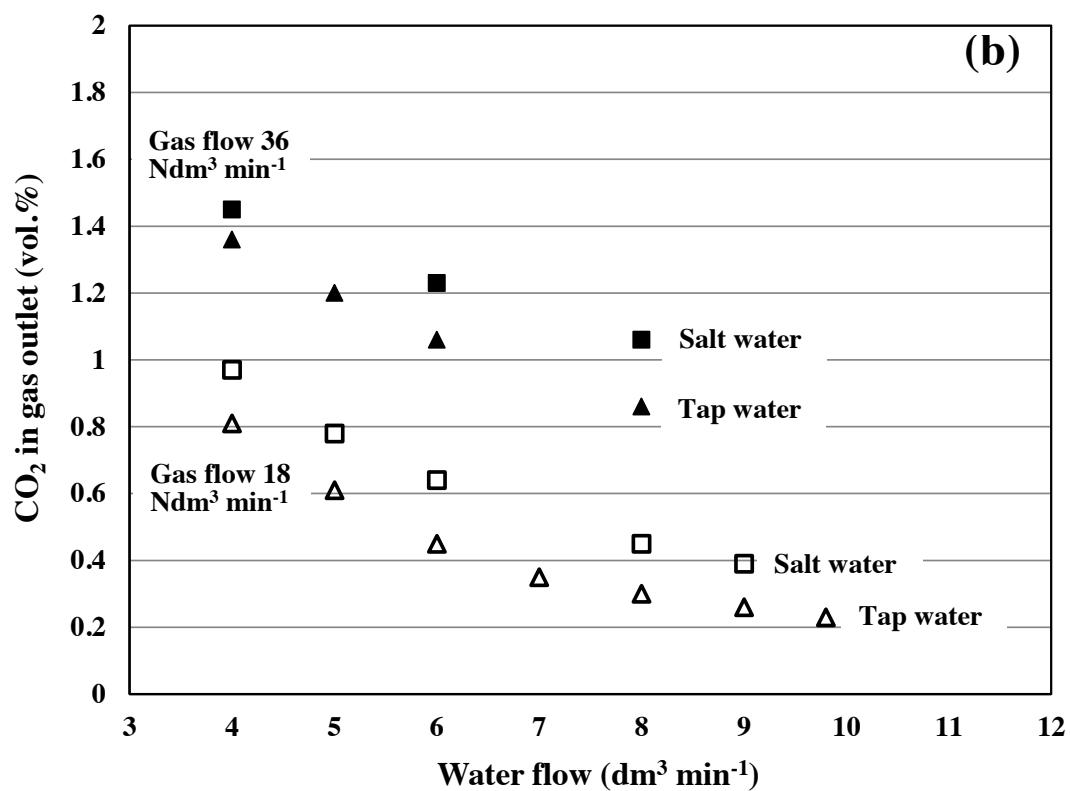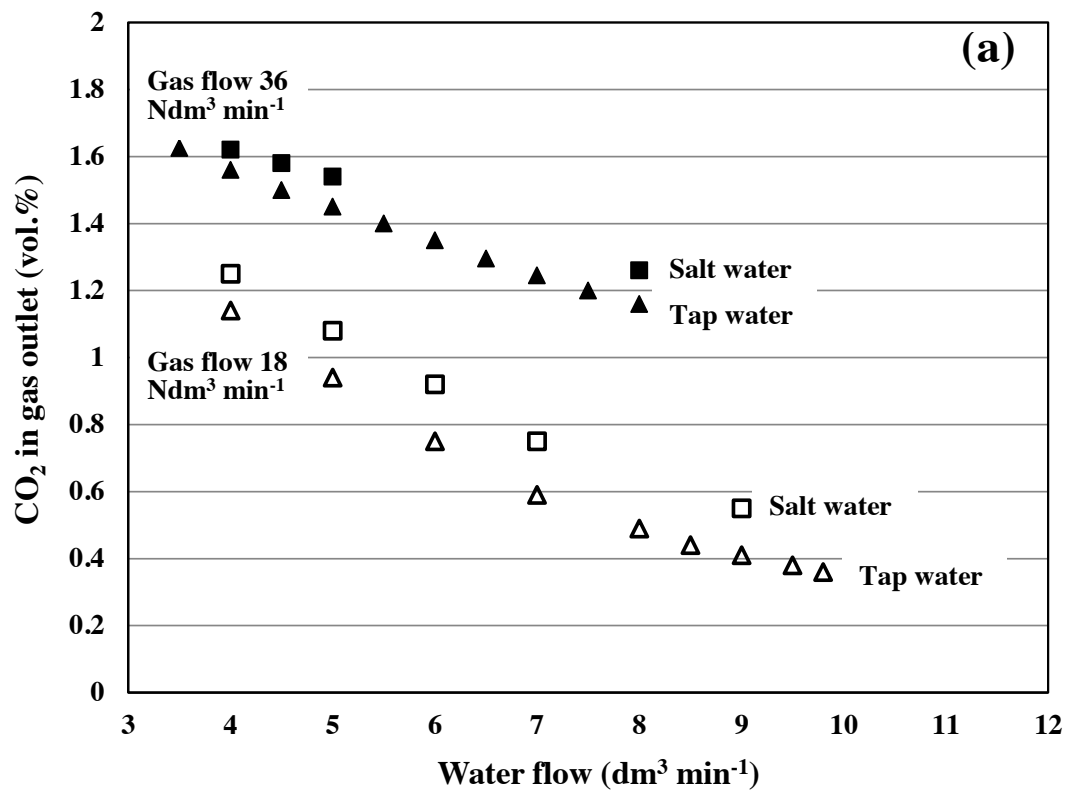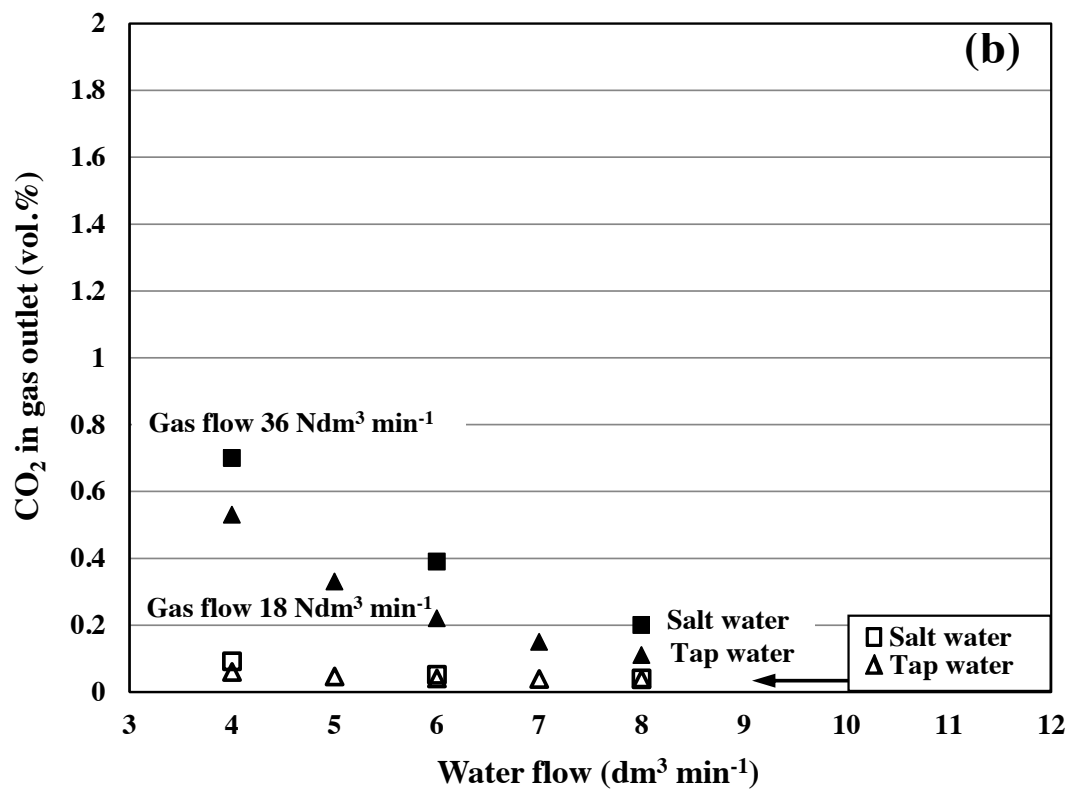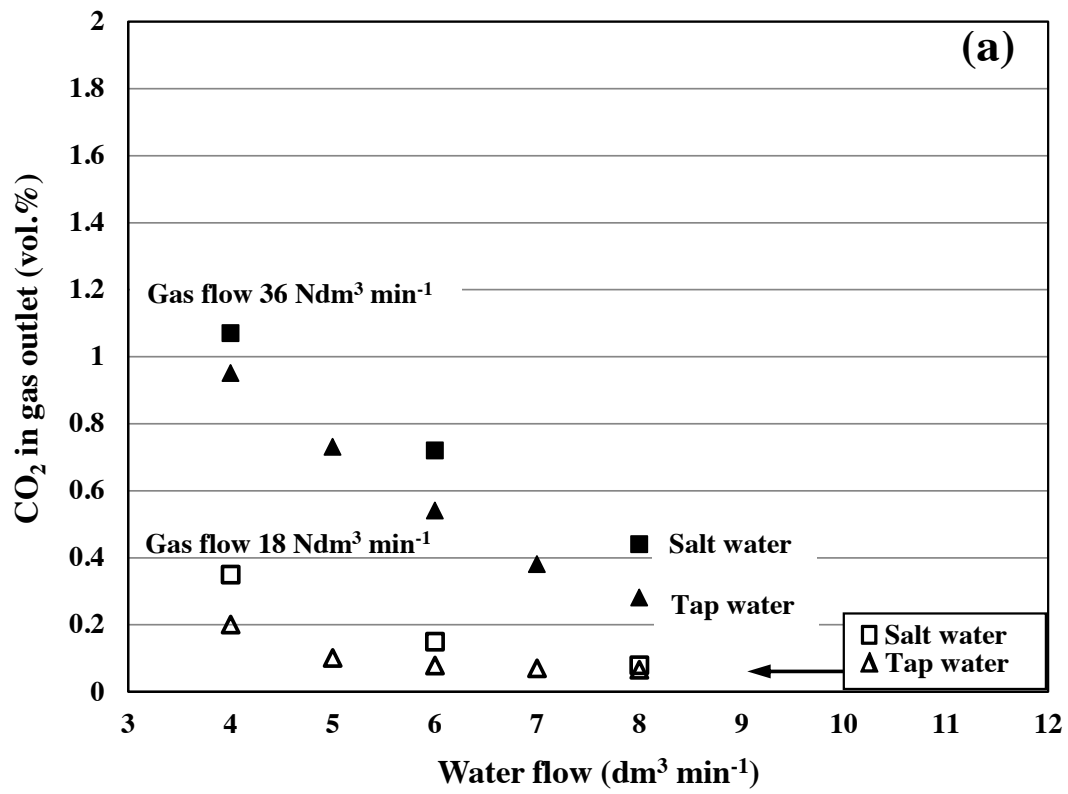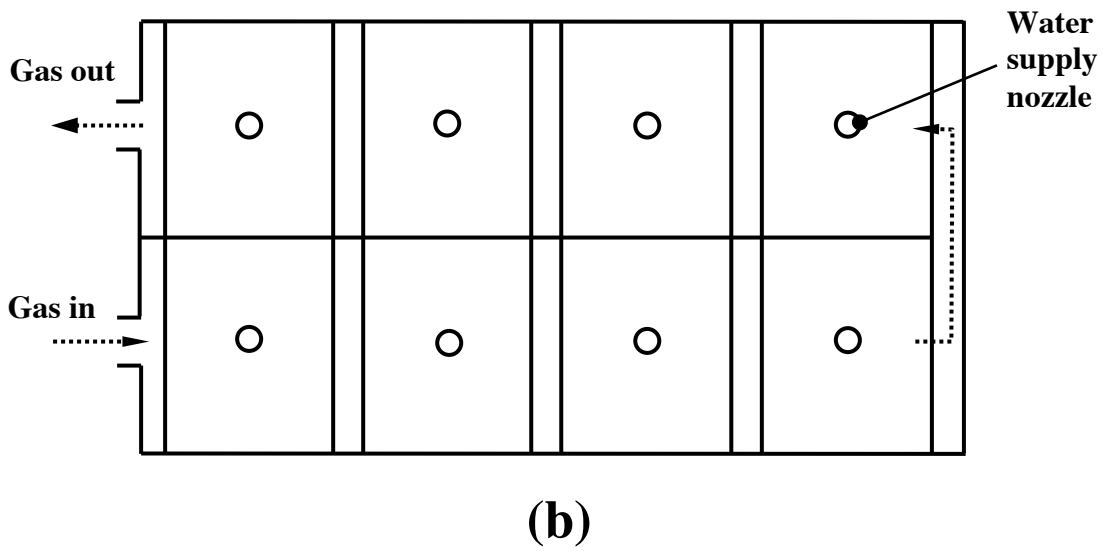
Fig. 8

Fig. 9

Fig. 10

Fig. A1

Fig. A2