Role of Bromothymol Blue pH Indicator in Density Driven Convection of Carbon Dioxide Saturated Water

Gabriela Braganca Costa e Moreira and Bjornar Sandnes
SPEC
College of Engineering
Swansea University
Swansea UK
802118@swansea.ac.uk

Abstract — **In the context of dissolution trapping, presented as one of the promising storage methods of carbon dioxide sequestration in deep saline aquifers, we perform density driven convection of CO_2 in a Hele-shaw cell. The experimental study consists in injecting CO_2 on top of the cell into water with bromothymol blue solution (BTB). The fundamental hypothesis is that the indicator plays a role only to detect the pH changes and has negligible effects on the dynamics. Five experiments within a pH range from 6 to 9 were used to analyze the role of the color indicator in the development of the convective flow. The results showed that all the rate of convective mixing presents a linear area/time gradient, thus the dissolution rate of CO_2 was constant in time. Furthermore, the shapes of the fingers were similar for all experiments and therefore the BTB does not modify the density profile of fingers in the system. In spite of that, the final area measured is smaller the higher is the initial pH. This result is reasonable because in the regions where the fluids are actively mixing (the edges of fingers) the amount of CO2 to dislocate the equilibrium from blue to yellow species and actually detect the change color depends on the initial pH. The properties of BTB were discussed in detail to better understand the behavior of bromothymol blue pH indicator in the system.**

Keywords— carbon dioxide; storage; density driven convection; bromothymol blue, pH

I. INTRODUCTION

Increased emission of carbon dioxide due to human activities is causing global warming and climate change. It is significant and lasting change in terms of environmental issues. The importance of activities that remove greenhouse gas emissions from the atmosphere for mitigating climate changes is considerable and carbon dioxide capture and storage (CCS) is one of the options for reducing emissions of carbon dioxide (CO2) from different sources emitted principally from combustion of fossil fuels. CCS involves the use of technology, first to collect and concentrate the CO_2, transport it to a suitable storage location, and then store it away from the atmosphere for a long period of time. (1)

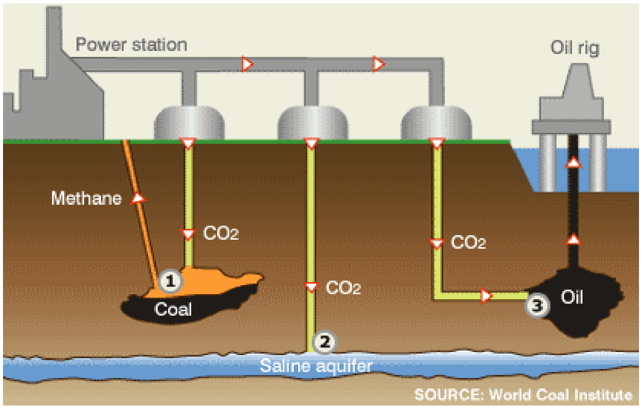

Figure 1. CCS Options
1) CO2 pumped into disused coal fields displaces methane which can be used as fuel 2) CO2 can be pumped into and stored safely in saline aquifers. 3) CO2 pumped into oil fields helps maintain pressure, making extraction easier. (Source: http://www.altenergymag.com/emagazine/2013/04/overview-of-carbon-capture/2068 [Accessed 12 Jul. 2014] (2))

Dissolution trapping, a promising storage method as discussed in (3) consists in inject CO_2 which will dissolve in brine and sinks in the geological formation. In this case is expected an ambient retention with high pressures and temperatures that will result in a liquid CO_2 state. Therefore, a well-sealed cap rock over the selected storage reservoir (at depths below 800 m) is important to ensure that CO_2 remains trapped underground.

CO_2 is injected into the brine-filled porous medium and it initiallyrises to the top of the salty water. Under these conditions, the CO_2 layer becomes denser because of the dissolution of the gas. This conformation will create an unstable flow process of mass transfer of CO_2 into the liquid and density-driven natural convection start to develop. In (4), a similar experiment also has been used a Hele-Shaw cell for visual studies on flow through porous media. Nevertheless, (5) describes a related experiment showing how the permeability affects the dynamics of this latter process, analyzing the behavior of the convection patterns using a Hele-Shaw cell. The relevant dimensionless parameter for this process is the Rayleigh number:

$$R = \frac{H\ K\ \Delta\rho\ g}{\emptyset\ D\ \mu} \qquad [1]$$

Where K= $d^2/12$ is the effective permeability with d the Hele-Shaw gap size, $\emptyset$ is the effective porosity, $\Delta\rho$ is the excess density between CO2-brine and brine, μ is the viscosity, D diffusivity, g gravity, and H the cell height (4, 5).

Rayleigh number associates the rate of buoyancy driven convection, in this case from a density increase, with the rate of diffusive transport. For a constant pressure (and rate) of CO2 injection, Ra number mainly depends on the permeability of the medium, which can be defined as a measure of the ability of a porous material to allow fluids to pass through. If the rate of convection greatly exceeds the system's ability to diffusively distribute the density increase, convection will occur (5, 6). Previous studies show that the formation of fingers is the dominant flow pattern in density driven convection flows in homogeneous media (7.8).

Different techniques can be used to get images of the movements in a Hele-Shaw cell. The patterns can be studied by adding a color indicator as BTB in solution in order to visualize it directly. The main advantage of using color indicators is that it is the easiest way to obtain photographic images of the patterns to analyze, so it is a widespread technique. Of course, the fundamental hypothesis also in this case is that the indicator has negligible effects on the dynamics (9).

We present in this project a further research on patterns obtained by injecting CO_2 in bromothymol blue solution (BTB) applied as an analogy of mass transfer of CO2 in deep saline aquifers. We will take its properties into account that we will discuss further in this project.

The focus of this study is to investigate if distinct started pHs somehow affect dissolution rate and shape of pattern of driven convection of carbon dioxide in saturated water.

II. BROMOTHYMOL BLUE THEORY

BTB is a textile dye derivative commonly deployed as a pH indicator whose protonated and deprotonated forms have two different colors which makes it a good indicator of dissolved CO_2. As a hydrogen ion indicator, it changes color over a pH range from 6.0 (yellow at acid reaction) to 7.6 (blue at alkaline reaction) and within the pH range of 6.5-7.0 has bluish green colour. (10)

$$\underset{\text{yellow}}{HBTB_{(aq)}} + \underset{\text{colorless}}{H2O_{(l)}} \leftrightarrow \underset{\text{blue}}{BTB^-_{(aq)}} + \underset{\text{colorless}}{H3O^+_{(aq)}} \qquad [2]$$

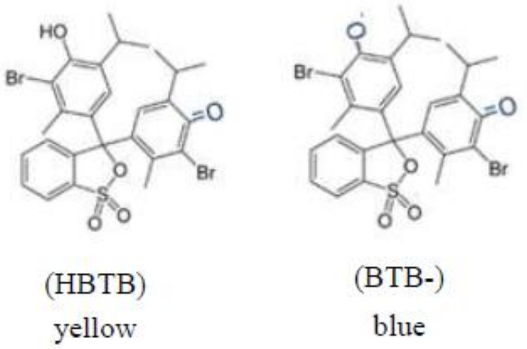

Figure 2. Molecular representation of HBTB and BTB-. (Sourse: i-Lab Student Workbook (11))

The equation [2] represents acid-base reaction of BTB. HBTB correspond to the protonated form and BTB- corresponds to the deprotonated form. When injected CO2 into water it will dissolve and exists in chemical equilibrium producing a week acid: carbonic acid (H2CO3). At equilibrium, only a small fraction (less than 1%) of the dissolved CO_2 is actually converted to H2CO3 (most of the CO_2 remains as solvated molecular form) as in the following equilibrium constant (12).

$$Kh = \frac{[\mathrm{H2CO3}]}{[\mathrm{CO2}]} \approx\ 1.7 \times 10 - 3 \qquad [3]$$

Carbonic acid is a weak acid that dissociates in two steps and will lose protons (H3O+) (13).

$$H_2CO_{3(aq)}\ + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)}\ \ HCO_3{}^+_{(aq)} \qquad [4]$$

$$HCO_3{}^-_{(aq)}\ + H_2O_{(l)} \leftrightarrow H_3O^+_{(aq)}\ \ CO_3{}^{+2}_{(aq)} \qquad [5]$$

In this case the proton $H_3O^+$is liberated to the water and will react with BTB- (blue specie) from the equation [1]. At the beginning of the experiment the amount of BTB- is highest in the system. By reacting BTB- and H_3O^+ the dynamic equilibrium [2] is disturbed and it will move to the left so that the concentration of BTBH (yellow specie) increases. At high concentration of H_3O^+ (low pH), the concentration of BTB- must be low (and the concentration of HBTB must be high) which result in yellow solution. Similarly, at low concentration of H_3O^+ (high pH), the concentration of BTB- must be high (and the concentration of HBTB must be low) which result in blue solution (11).

This effect is visible and, for a configuration of initial blue porous medium exposed to CO_2 at the top (and impermeable from sides), density-driven natural convection start to develop and the mass transfer rate of CO_2 into the initially stagnant liquid can be traced. Therefore, this changing colour makes BTB ideal to indicate directly fingers in a Hele-Shaw cell.

.

III. EXPERIMENTAL SETUP

This section is a script previously used in (5).

A. Material

The main components are a Hele-Shaw cell which has been constructed using two transparent plates separated by 1.0mm and 5 solutions with follow pHs: 6.0; 6.5; 7.5; 8.0 and 9.0.

The cell was made of 2 plates measuring 25 x 25cm and was sealed on the bottom and vertical sides with a double-sided tape made of silicon. Due to the sealing on sides effective cell volume reduces to 19.4 cm x 22 cm.

The BTB was provided by Sigma-Aldrich (CAS number 34722-90-2 and molecular weight: 646.36 g/mol). The initial bromothymol blue concentration was 230mg/L (pH 5.5). The solution was prepared by dissolving 230mg in 500 ml of deionized water. After solution is effected, sufficient water was added and made up to 1000 ml. This aqueous version of BTB was conveniently made to allow visible contrast during the experiment. In order to achieve the start pH of each solution we separated 5 beaker with 100ml of BTB and 0.1 mol of NaOH was added dropwise while the pH were measured.

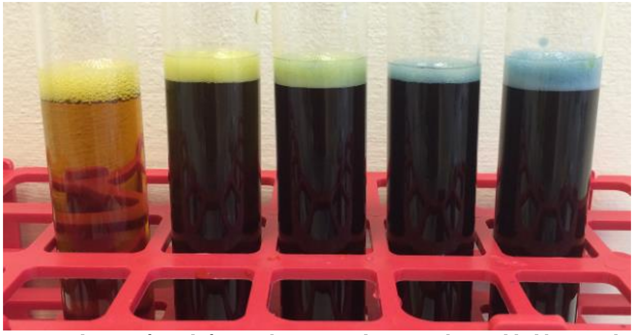

Figure 3. 5 solutions from left to right: BTB solution with no added base and pH: 6.0; 6.5; 8.0 and 9.0.

B. Methods – Set up

It was used a box to set up a dark room to avoid light reflection for the pictures. The Hele-Shaw cell was then filled with the indicator solution and placed over the table fixed with a clamp, which held the cell in a vertical position. The light board was placed behind the cell and the camera was fixed in a support in front of the experiment.

The images were captured using a digital camera Nikon 1 J2 10.1 MP with 10-30mm Lens.

The injection of CO2 into the cell was done using a syringe pump model Alladin-1000, which enabled the flow rate to be adjusted for a desired value.

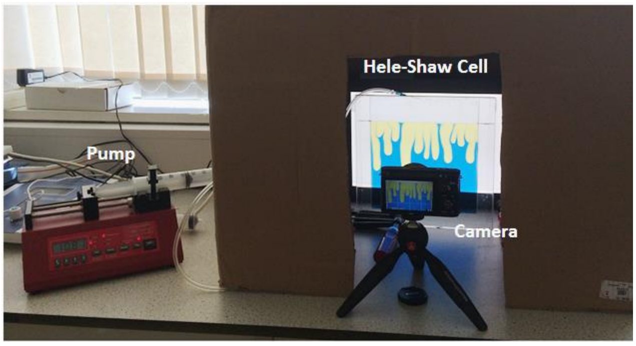

Figure 4. Experimental Set up

C. Experimental Procedures

After the entire environment was set up, the syringe containing gaseous CO_2 was placed into the pump and a tube with a needle in one of the sides was connected from the syringe into the top of the transparent Hele-Shaw cell and the same amount (80ml) of CO_2 was injected. The cell was filled with the same volume of BTB solution every time. Then, the rate was adjusted to be just enough to maintain a stagnant layer of CO_2 over the water and stayed fixed at the same value (1.0 ml/min) for every experiment.

The time-lapse photography was set to take pictures every 30 seconds and the experiment was carried on until 80ml of CO_2 was injected into the cell. When the syringe got empty it was replaced for another one right after.

All experiments were done under room temperature and pressure conditions.

D. Analysis Procedures

The Image analyses were made using ImageJ software, which is a Java-based image-processing program that is used to display, edit, analyze, process, save and print images.

Initially, all the pictures were imported to the program and they are all set to stack. Then, the desired region was selected and cropped. The scale was set by knowing the length of each cell, which is related to the corresponding pixels in the picture. After that, the threshold in the picture was adjusted in order to isolate the yellow area (finger formation). Then, the images were converted to binary 8-bit images, which makes easier to select and measure the desired area. The measure of the selected area was done using the function "Analyze particles" limiting the minimum size of the area from the starting formation of the layer and approximating the maximum size with the threshold from the last image.

The growth of large amplitude waves at the interface between CO2 and BTB is called "fingers" as shown below.

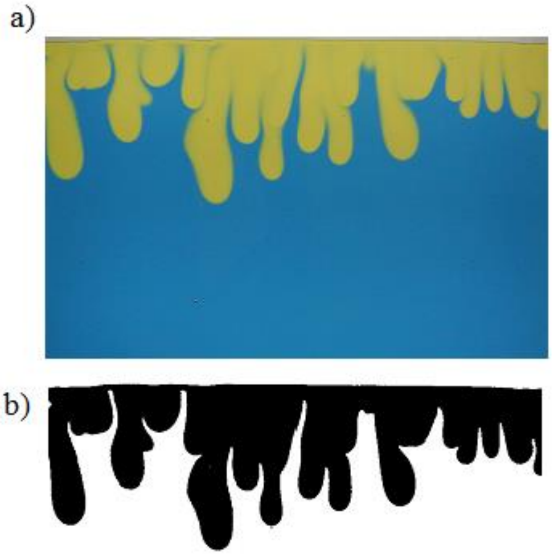

Figure 5. Binary 8-bit image of 'fingers' in a cell of 1.00 mm gap and pH 9, image size length is 19.4cm.

IV. RESULTS AND DISCUSSION

A. Dinamics of Flow

The photographic sequence in Figure 7 gives visual information about the growth behavior using different started pHs from 6 to 9. The experiment takes around 10 minutes to first appear the yellow layer on top and at that point the process is controlled mainly by diffusion (a). After formation of the interface, convective flow takes place through the cell due to the difference of density. Gradually, tiny waves establish, become well defined and continuous to propagate vertically at almost the same speed (b). From point (c) the number of fingers seems to decrease with time due to interaction between neighborhood fingers, and eventually merge into each other (d) and (e).

The shapes of the fingers were similar for all the different started pH indicator used in the experiments.

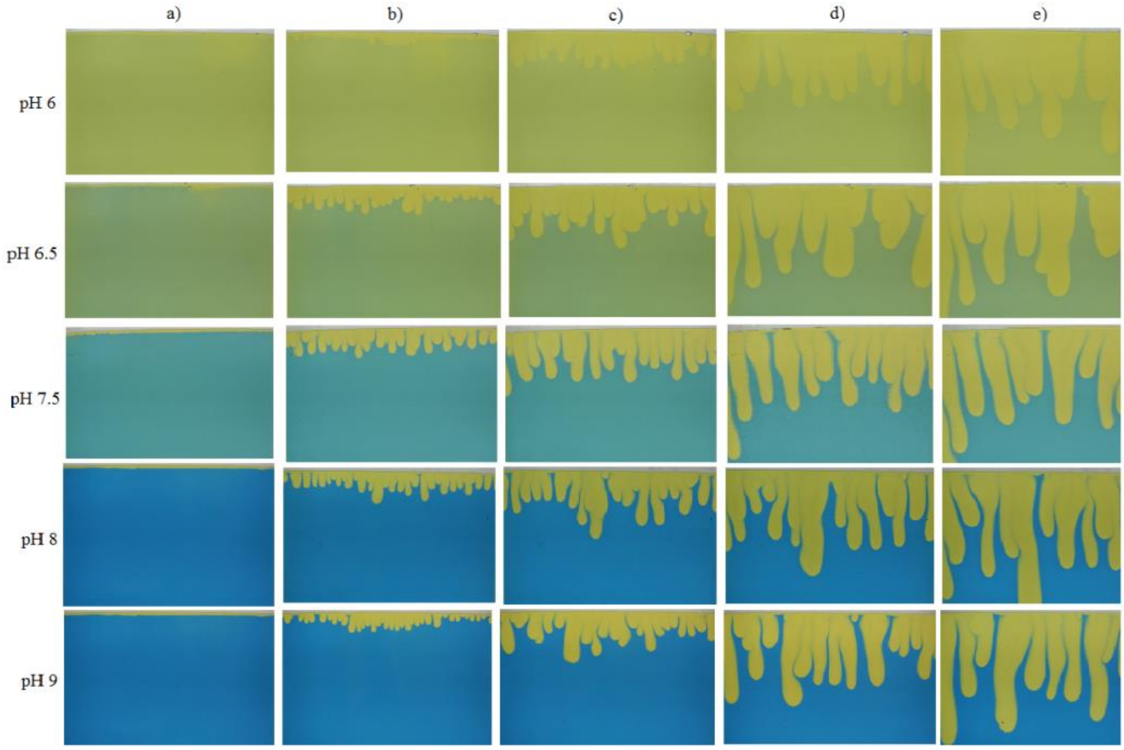

Figure 6. Time evolution of fingers using a Hele-Shaw cell with 1.0 mm gap and 5 different pHs; Images size width are 19.4 cm; Images from a) to e) was taken at 14min intevals.

B. Gap Size

The spacing between the plates of 1.00mm was chosen to limit three-dimensional effects and to have a sufficiently long diffusive regime before convection starts.

If perform the analysis using smaller gap size (e.g. 0.50mm or 0.25mm) the needle used (0.6mm diameter) would not fit on top of the cell and it would not be possible to set it up and seal it properly which could lead to leaking of CO_2. If increasing gap size higher than 1.0mm it was more evident the formation of convection rolls and the fingers were pushed towards the sides of the cell.

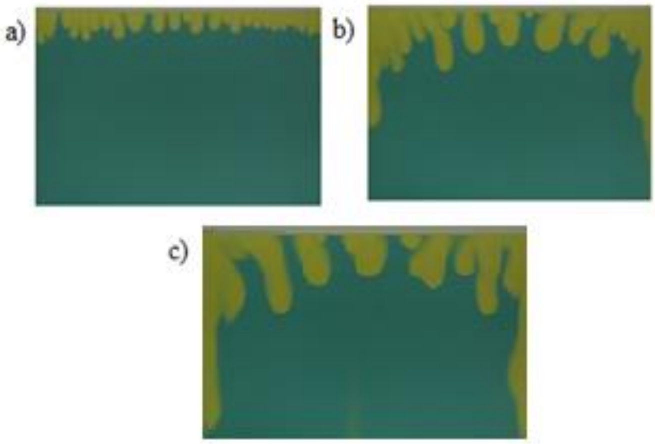

Figure 7. Large convection rolls starting to form in the 1.5mm cell. Images size length are 19.4cm. a) Fingers start to getting apart in the middle of the cell. b) and c) Rolls forming.

Therefore, for practical handling it was used 1.0mm gap to guarantee the same patterns of convective roll in every experiment and complete injection of 80ml of CO_2 into the cell.

C. *Rate of convection*

In order to calculate the dissolution flux and subsequent mixing of CO_2 into water, the yellow area was calculated in each image using Imagej and plotted as shown in figure 8. For all pH evaluated, there are a regime of constant rate of mixing i.e. there is a linear area/time gradient. It also provides evidence that the dissolution rate (gradient) is similar, and, therefore the variation of pH does not affect the movement that is generated by density-driven convection.

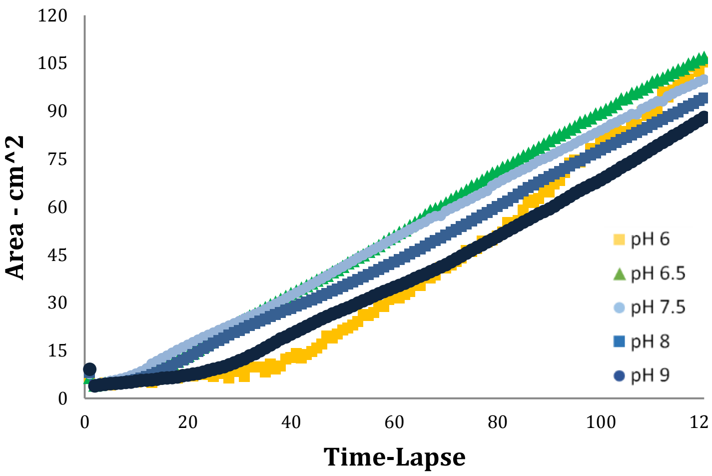

Figure 8. Area rate of each pH through time with time-lapse of 30sec.

D. *Initial pH and Growth rate of fingers*

The initial pH plays a role in the regions where the fluids are actively mixing, which coincide with the edges of the density-driven fingers. The boundary region between water and CO_2 can be represented by the equilibrium shown in equation [2]. Higher pH, in this case, represents the equilibrium in which products (blue color) dominate the mixture. As the CO_2 dissolve into water, the equilibrium will move so the concentration of the blue specie will decrease.

In all experiment were injected the same amount of CO_2 (80mL). Figure 10 and 11 show the average width of fingers and final measured area according to each pH as can be seen below. The width of finger becomes narrower as we increase the pH. In addition, the final area measured for pH 6.0, 6.5, 7.5, 8 and 9 were, respectively 107.05, 110.85, 102.87, 97.27, 90.99 cm^2. Here, let us note that the final area measured is smaller the higher the initial pH. These data and figure 8 also suggest that on the boundary of fingers in solutions with higher pH will be needed more concentration of CO_2 to actually change the initial blue color to yellow (i.e. moves the position of equilibrium to the right) and consequently cause the color change required for visual observation.

The rates of growth plotted in figure 12 were similar for all cases. It has just a slight difference because at higher pH, a higher dissolution of CO_2 is produced.

From these graphs we can suggest that the fingers do not develop faster or slower due to different started pH. Therefore, the role of the color indicator is negligible in the density driven convection of CO_2.

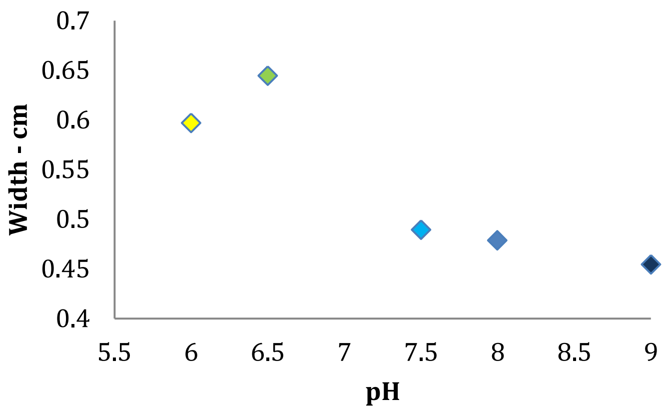

Figure 9. Average finger width according to each pH

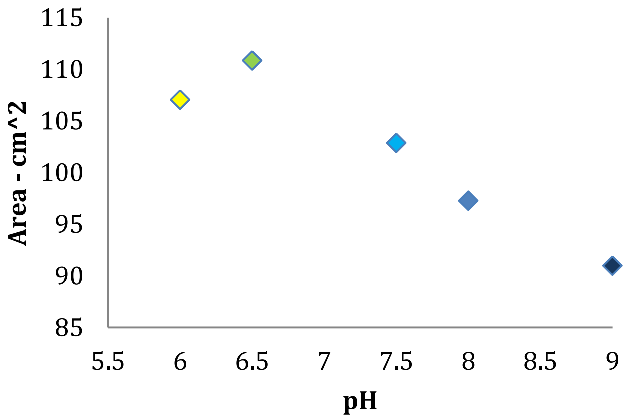

Figure 10. Final measured area according to each pH

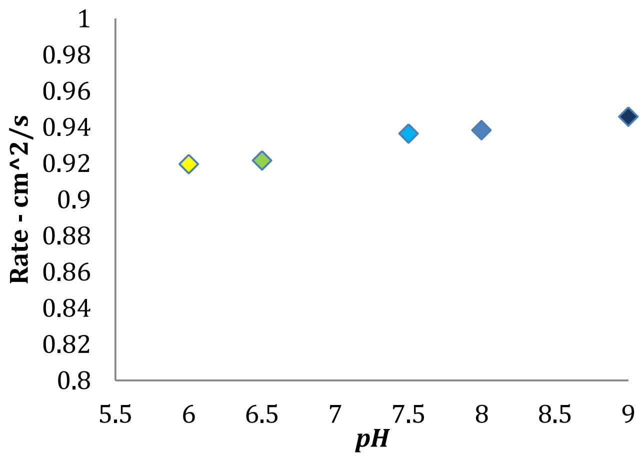

Figure 11. Area rate according to each pH

E. *Width of fingers*

To calculate the average finger width, was followed the script suggested in (5). It was measured approximating the fingers to a rectangle, according to: A= w*S/2, isolating w, w= A*2/S. Where w is the width of the fingers, A is the yellow area, and S is the perimeter of the yellow area. Fig. 9 shows the width variation through time.

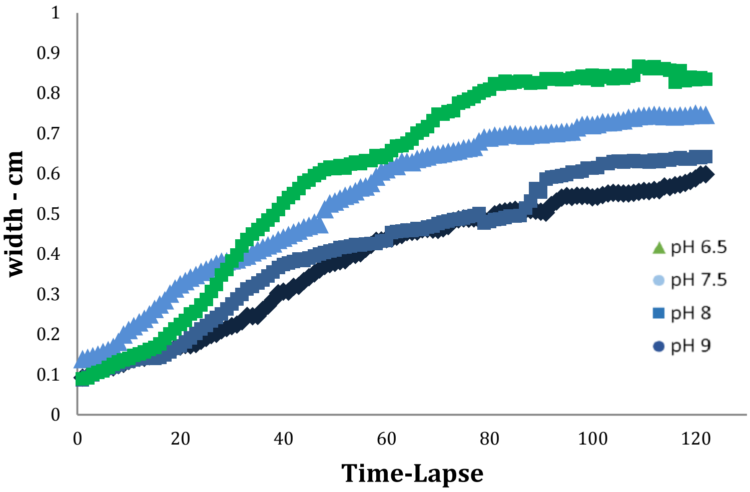

Figure 12.Width of fingers of each pH throug time with time-lapse of 30sec.

As may be expected, the estimation of the width improves as the number of fingers increases. Despite that, each experiment has its own irregularities in the pattern of growing fingers which leads to lack of standard on the curve. Let us note that pH 6.0 was not plotted on figure 9 due to lack of contrast, thus it was not possible to threshold the image.

F. *Limitations*

The experiment in which we used pH 6.5 has a distinct pattern from all cases. In figure 6, the merging of fingers take place from point c) so we can notice the decrease in the wave number at the interface between the gaseous CO_2 and the aqueous solution which gives us higher width of fingers. This visual observation also can be seen in figure 10 and 11.

Also, due to lack of contrast between yellow and green it was not possible to plot pH 6 in figure 9.

It is important to note that all these graphs above is a result of only one experiment. In this case, it was just to guide the eye and help to identify trends if varying pH of the BTB color indicator.

V. CONCLUSION

Our experiments was guided by a few key objectives: (i) carry out the experiment in the Hele-Shaw cell with the same environment as earlier studies (ii) finding lowest pH, which means green colour solution as close as possible to first transition (green to yellow) that can still be traced without interference in the results; (iii) finding if the convective rate is independent on initial pH and (iv) if distinct initial pH present difference in measured area.

Through this experiment we confirmed the dynamics of growth behavior of fingers in the Hele-Shaw cell described previously in (4) and (5). We took further approach within the use of BTB in experimental works devoted to analyze density driven convection of carbon dioxide. In conclusion, the ideal pH in order to properly detect the fingers is above 7.5. By modifying the pH of the system the main difference was the tint of blue in each experiment and it did not cause unusual instabilities (no significant differences in the mixing zone) or has changed the density profile which means that the patterns of fingers and convective rate is independent on initial pH, and, most important, does not affect the density driven convection of CO_2.

We have seen that even basic laboratory scale research is important to understand and predict the behavior of density driven convection of CO_2 in the dissolution trapping context. Thus, as we expected, Bromothymol blue solution should continue to be used in further experimental works.

VI. ACKNOWLEGMENTS

I would like to thank my tutor and professor at Swansea University, Dr. Bjornar Sandnes, for his supervision and help throughout this project. Also, I wish to thank Dr. Benjy Marks who have given me great suggestions while I was working on the experimental part.

Particularly, I wish to thank my parents and my brother, Pedro Moreira, for their undivided support and interest who encouraged me to go my own way. At last but not the least I want to thank my friends who go hand in hand with me no matter how far from each other we are and finally to God who made all the things possible.

VII. REFERENCES

1. Rubin, E. and De Coninck, H. (2005). IPCC special report on carbon dioxide capture and storage. UK: Cambridge University Press.
2. The Alternative Energy eMagazine. (2014). [online] Available at: http://www.altenergymag.com/emagazine/2013/04/overview-of-carbon-capture/2068 [Accessed 12 Jul. 2014].
3. Iglauer, S. (2011). Dissolution trapping of carbon dioxide in reservoir formation brine--a carbon storage mechanism. Mass Transfer (ed.: Nakajima H).
4. Slim, A., Bandi, M., Miller, J. and Mahadevan, L. (2013). Dissolution-driven convection in a Hele--Shaw cell. Physics of Fluids, vol 25.
5. Michel, I. and Sandnes, B. (2013). Density Driven Convection of Carbon Dioxide Saturated Water.
6. Kneafsey, T. and Pruess, K. (2010). Laboratory flow experiments for visualizing carbon dioxide-induced, density-driven brine convection. Transport in Porous Media, pp.123--139.
7. Hassanzadeh, H., Pooladi-Darvish, M. and Keith, D. (2007). Scaling behavior of convective mixing, with application to geological storage of CO2. AIChE journal, 53(5), pp.1121--1131.
8. Farajzadeh, R., Ranganathan, P., Zitha, P. and Bruining, J. (2011). The effect of heterogeneity on the character of density-driven natural convection of CO2 overlying a brine layer. Advances in Water Resources, 34, pp.327-339.
9. Outeda, R., El Hasi, C., D'Onofrio, A. and Zalts, A. (2014). Experimental study of linear and nonlinear regimes of density-driven instabilities induced by CO2 dissolution in water. Chaos: An Interdisciplinary Journal of Nonlinear Science, 24(1), p.013135.
10. Sciencecompany.com, (2014). Bromothymol Blue pH Indicator, 30mL (1 oz.). [online] Available at: http://www.sciencecompany.com/Bromothymol-Blue-pH-Indicator-30mL-1-oz-P6363.aspx [Accessed 5 Jul. 2014].
11. i-Lab Student Workbook. (2014). [online] Available at: http://www.microspectralanalysis.com/TechnicalDownloads/MSA%20Academic%20Brochure-Student%20Manual.pdf [Accessed 24 Jul. 2014].
12. Housecroft, C. and Sharpe, A. (2008). Inorganic chemistry. 1st ed. Harlow: Prentice Hall.
13. Lide, D. (1994). CRC handbook of chemistry and physics. 1st ed. Boca Raton, FL: CRC Press.