



## Effect of limestone and buffer solution in the aqueous speciation and pH of brines for CO<sub>2</sub> sequestration

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### Abstract

Carbon dioxide (CO<sub>2</sub>) geological sequestration in saline aquifers is a complex process, where multiple physical and geochemical trapping mechanisms are responsible for the ultimate fate of CO<sub>2</sub> in the storage formation. Geochemical trapping would occur when CO<sub>2</sub> gets dissolved into the brine formation and, subsequently and depending on the brine pH, H<sub>2</sub>CO<sub>3</sub> will dissociate to HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> and ultimately react with metal cations in the brine, such as Ca<sup>2+</sup> and Mg<sup>2+</sup>, to form stable carbonate minerals. This process is known as mineral trapping and it is the most permanent mechanism for CO<sub>2</sub> sequestration [1]. Brine pH is the key parameter for the mineral trapping process [2, 3], as precipitation of carbonate minerals is favoured over a basic pH of 9.0 because of the availability of carbonate ions [4]. However, brine pH will drop to acidic values once CO<sub>2</sub> is injected into the storage formation. Therefore, there is a need to understand how brine pH can be buffered and stabilized at basic pH values, which would then enhance mineral trapping of CO<sub>2</sub>. Biocatalysts, buffer solutions and host rocks have been previously studied as buffer alternatives to enhance initial brine pH. Amongst the different buffer solutions reported in the literature for their high buffer capacity [5, 6], tris buffer (C<sub>4</sub>H<sub>11</sub>NO<sub>3</sub>) has been identified as the most optimal one in terms of pH enhancement [5].

In this work, pH stability studies were conducted to understand how two different brines behave in the presence of either a natural limestone buffer rock or a synthetic tris buffer solution in order to evaluate the efficiency of the two different buffers for increasing pH and enhancing CO<sub>2</sub> mineral trapping. Two different synthetic brines, namely B1 and B2, were prepared as an analogue to a natural brine from a natural gas well in Youngstown, Ohio. The main difference between B1 and B2 composition was the absence of SO<sub>4</sub><sup>2-</sup> ions in the B1 brine. The pH stability of B1 and B2 was studied at ambient temperature and pressure with the natural and synthetic buffers in both closed and open atmospheres. A total of four experiments were conducted, including two sets of duplicates: one for the rock-brine studies, and one for the synthetic buffer-brine studies. Additionally, an aqueous and solid speciation model (built with the PHREEQC code (version 2.0)) was used to investigate the effect of either the limestone host rock or the tris buffer solution in the pH along with the aqueous and solid speciation of the two synthetic brines. Modelling calculations were conducted by using experimental conditions as well as the chemical composition and pH values of the two brines as input data. The results from the model were then compared to experimentally derived results on the same system.

The results indicate that brines containing SO<sub>4</sub><sup>2-</sup> would be suitable for CO<sub>2</sub> sequestration as no SO<sub>4</sub><sup>2-</sup> containing solid phases were identified by XRD in brines when the host rock and/or buffer was

added, which is in agreement with the geochemical modelling. This finding is quite significant as for those brines, the formation of  $\text{CaSO}_4$  could inhibit the limestone dissolution by coating the host rock surface. The comparison of B1 and B2 to an open atmosphere indicates that both brines are stable under open atmosphere regardless of the buffer used.

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