

THE SIGNIFICANCE OF CO₂ SOLUBILITY IN GEOTHERMAL RESERVOIRS

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ABSTRACT

Carbon Dioxide (CO₂) has been considered as a possible working fluid in Engineered Geothermal Systems (EGS). This scenario would have the two-fold advantage of providing renewable electricity generation with simultaneous CO₂ sequestration via subsurface fluid loss. In order to entertain this idea seriously, it is necessary to consider the interactions between CO₂ and the reservoir rock and connate fluid. The laboratory experiments and theoretical work performed to date were designed to investigate thermodynamic effects that may occur when solubility is taken into account. A core-scale experiment measured relative permeabilities in the two-phase system, a micromodel experiment qualitatively observed the dynamic dissolution phenomenon, and theoretical analyses put findings in context and provided a framework to predict results under varied conditions.

The purpose of this research is to analyze and quantify the magnitude of dissolution effects via laboratory and theoretical work. An additional goal is to evaluate the time and length-scales of dissolution and diffusion effects relative to standard hydrodynamic behaviors.

BACKGROUND

It is known that CO₂ is soluble in water, as can be observed in carbonated beverages. Furthermore, you can observe that the CO₂ gas comes out of solution as soon as the container is opened (pressure is lowered) and will go flat sooner when warm (the gas is less soluble at high temperatures). These simple observations illustrate the sensitivity of CO₂ solubility to changes in temperature and pressure.

This research focuses on a two-phase system of CO₂ and water flowing through porous media. The common perception of EGS is fractured rock, however certain researchers have proposed CO₂-EGS in porous reservoirs of produced oil and gas fields (Randolph and Saar, 2010). Nonetheless, production of geothermal energy using CO₂ as the in-situ

working fluid coupled with CO₂ sequestration has been gaining attention (Brown, 2000; Pruess, 2006).

Some previous studies have produced results that help motivate the relevance of studying CO₂-water relative permeabilities. Chang et al. (1998) generated a compositional model for CO₂ floods where the CO₂ solubility had a significant impact on ultimate reservoir performance. During simulation of water-alternating-gas floods, it was found that when CO₂ solubility in water was taken into account up to 10% of the CO₂ dissolved in the water, which delayed total oil production.

In addition, Bennion and Bachu (2008) conducted core flood experiments and observed greater hysteresis in the CO₂-brine case than the H₂S-brine case after primary drainage. Also, the relative permeability of CO₂ was lower than for H₂S. Based on the lower interfacial tension of H₂S, the authors would have predicted that CO₂ relative permeability should have been higher and did not have another explanation for the observed phenomena. Their findings are similar to observations in our core-flood experiments with CO₂-water and nitrogen-water (Stacey et al., 2010). We propose that dynamic dissolution and evolution of CO₂, or “active phase change”, may be responsible for the results of Bennion and Bachu (2008). These effects are described in more detail in the experimental section.

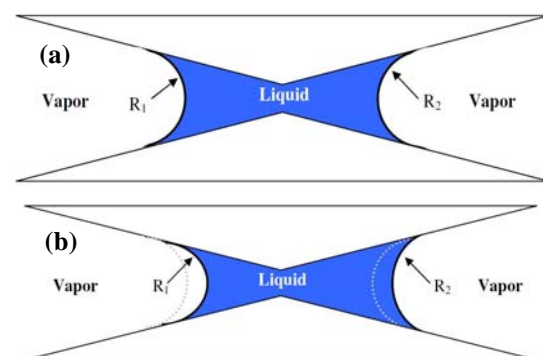


Figure 1 (a) Two-phase system of water and immiscible gas $P_1=P_2$. (b) $P_1>P_2$ causes water lamina to advance $R_1<R_2$.

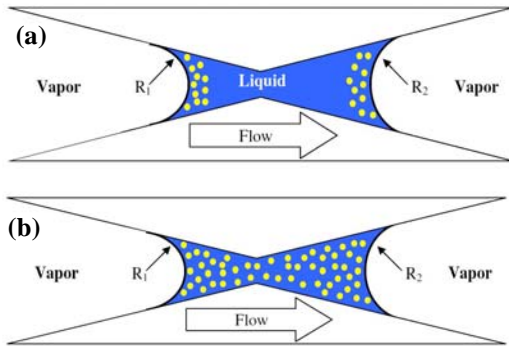


Figure 2 (a) Two-phase system of water and CO₂ gas $P_1 > P_2$ and water lamina advances $R_1 < R_2$. (b) $P_1 > P_2$, but now system is in dynamic equilibrium and CO₂ passes through water lamina by chemical gradient.

The concept of active phase change was first presented by Chen (2005) during investigation of fundamental flow characteristics in steam-water systems. Consider water and an immiscible gas (e.g. nitrogen) where there is a water lamina in a pinched capillary tube. When a pressure is applied to the left-hand side, the lamina advances slightly downstream (Figure 1). If the system is steam-water a similar effect occurs, however due to pressure differences a small amount of steam condenses on the high-pressure side and a small amount evaporates on the low-pressure (downstream) side. It appears that the steam travels through the water lamina, but in actuality it is a consequence of the thermodynamic effect we have termed "active phase change" (Stacey et al., 2010).

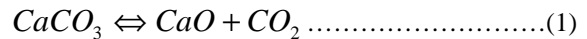
An analogous phenomenon is believed to occur in the CO₂-water systems, but due to gas solubility rather than condensation and evaporation. In this case the CO₂ dissolves on the higher-pressure (upstream) side, and evolves out of solution on the low-pressure (downstream) side (Figure 2).

Thus the condensation and vaporization in the steam-water case are replaced by dissolution and evolution in the CO₂-water case. Chemical diffusion is a much slower physical process than water advection, however at the pore scale a pore throat may be on the order of 100 μm, so the process may not be neglected.

CO₂ INJECTIONS IN THE FIELD

Direct injection of CO₂ into geothermal reservoirs has occurred at a few sites including: Hijiori, Japan; Ogachi, Japan; and Hellisheidi, Iceland. At these sites CO₂ was dissolved in water at very low concentrations (0.01 wt% to 3 wt%) prior to injection. The general chemical equation of concern

is the precipitation or dissolution of carbonate species, primarily calcite (CaCO₃):



At Hijiori, Japan a 3 month long-term circulation test was conducted, in which river water (directly and from a holding pond), and produced reservoir fluid were injected (Yanagisawa, 2010). The authors estimated that about 6.04 tons of CO₂ were injected over the 3 month period. A few noteworthy observations from this study: as calcite precipitates the pH of brine increased, calcite precipitated more readily in the lower temperature zones, anhydrite (CaSO₄) precipitated more in higher temperature zones (Yanagisawa et al., 2008). Massive scaling of mostly calcite (up to 5 cm thick) was observed in production lines of the lower temperature well (HDR-2) (Yanagisawa et al., 2007).

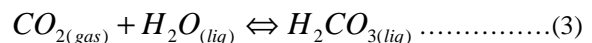
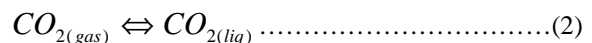
At the Ogachi, Japan site, CO₂ was added to injected water via small blocks of dry ice (Kaieda et al., 2009). In 2006 a 2 week flow test was conducted (0.2 wt% CO₂) where produced fluid detected CO₂ concentration increase which then decreased to background within 3 days. The authors were hesitant to draw conclusions about precipitation rates because of dilution from reservoir fluids. However their results indicate that the CO₂ was staying in the reservoir either by precipitation or solubility effects.

The Hellisheidi, Iceland field features a shallow system (400-800 m), with pH 8.5-9.6, and low temperatures (20-30°C) (Alfredsson and Gislason, 2009). Additional information about water chemistry or CO₂ concentrations of injectant could not be found.

CO₂ solubility plays a key role in the precipitation of minerals. Knowledge of field observations provides a basis, to which theoretical and laboratory results can be compared.

PHYSICAL PROPERTIES CO₂

In order to calculate diffusion rates, it is necessary first to determine initial concentrations via CO₂ solubilities. CO₂ solubility in water is quite complex because it is dependent on a variety of conditions including temperature, pressure, pH, and salinity (Konrad and Bird, 1995). A CO₂-water system seeks to achieve equilibrium between the following equations:



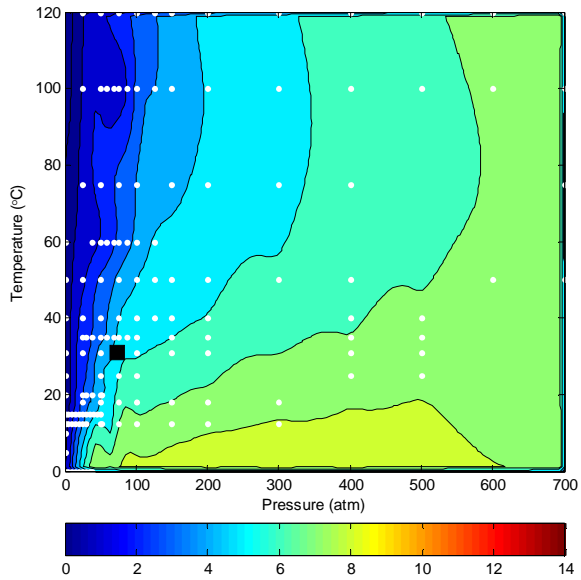


Figure 3 Experimental data from Dodds et al. (1956); contours of CO₂ Solubility (kg CO₂/100 kg water) as a function of Temperature and Pressure. Black square is critical point of CO₂.

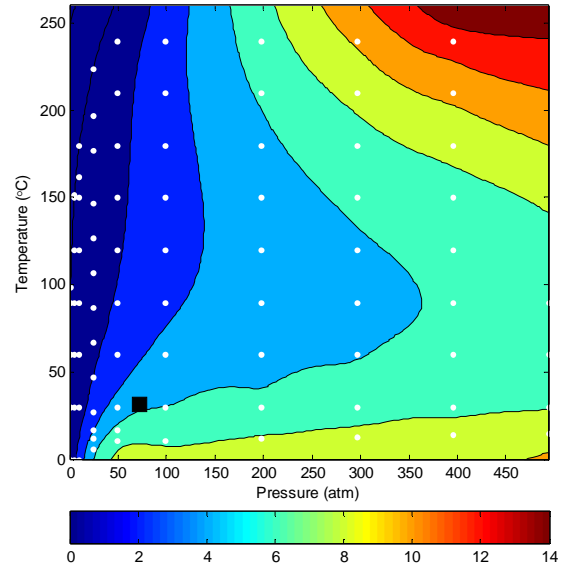


Figure 4 Data from thermodynamic model (Duan and Sun, 1956); contours of CO₂ Solubility (kg CO₂/100 kg water) as a function of Temperature and Pressure. Black square is critical point of CO₂.

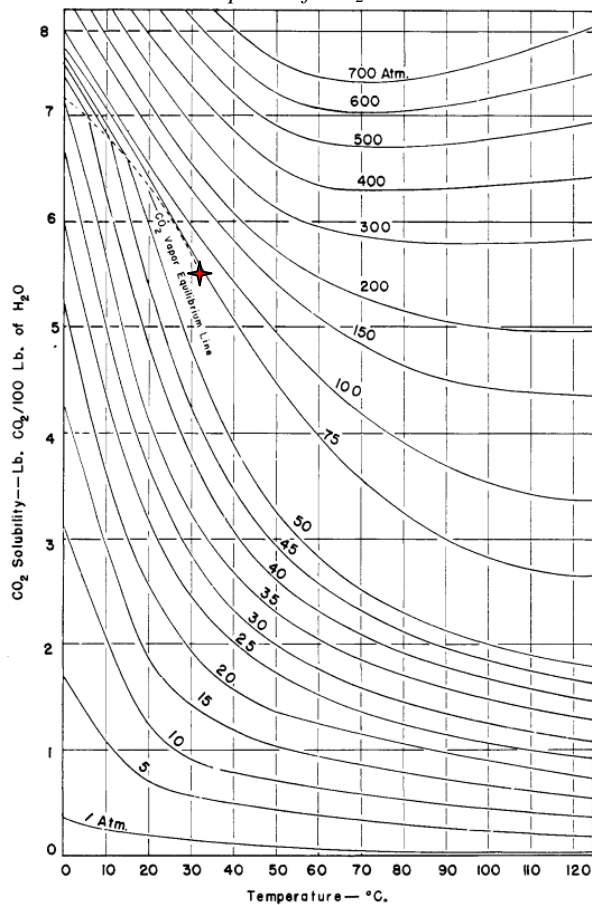


Figure 5 Interpretation of experimental data (Dodds et al., 1956); solubility of CO₂ in water as a function of Temperature and Pressure; red star is critical point CO₂.

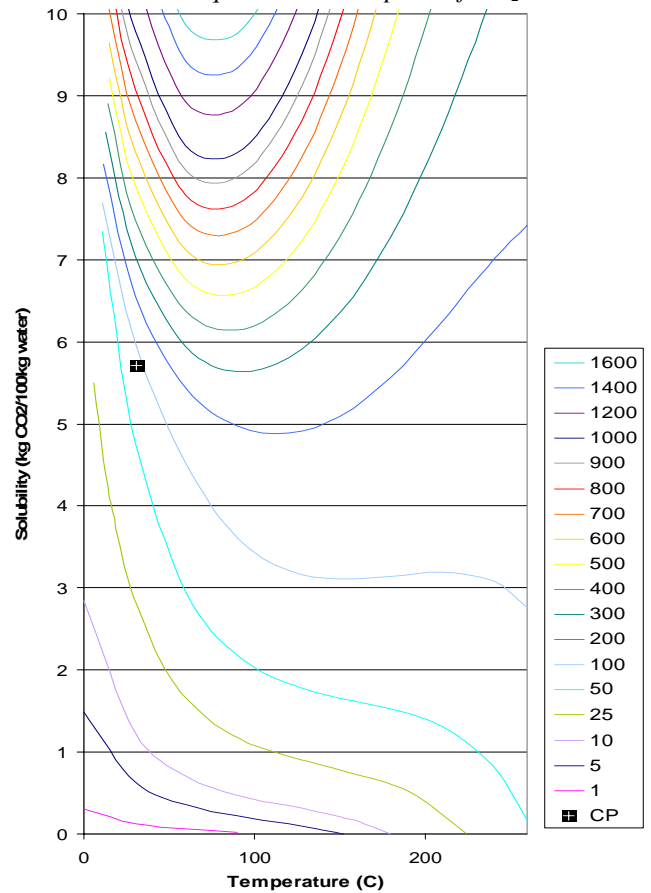


Figure 6 Data from thermodynamic model (Duan and Sun, 1956); solubility of CO₂ in water as a function of Temperature and Pressure; black square is critical point CO₂.

At atmospheric conditions the rate of Equation 3 is quite slow with only about 10^{-5} *m* (i.e. mol H₂CO₃(aq) per kg water) at equilibrium while the rest of the CO₂ remains as CO₂(aq) (Konrad and Bird, 1995).

Experimental data from Dodds et al. (1956) was used to visualize the effects of temperature and pressure of CO₂ solubility in water (Figure 3). Figure 4 shows similar data that was generated using a thermodynamic model for CO₂ solubility created by The Duan Group, (Duan, 2003 and 2005). The colorbars have identical scales so the experimental and computational data may be compared directly.

Dodds et al. (1956) also drew a set of smooth curves as their best interpretation of the same data (reproduced here as Figure 5). The Duan Group's model was used to generate a similar figure based upon their CO₂ equation of state (Figure 6). The theoretical data (Figures 4 and 6) seem to match the experimental data quite well. These data give us confidence to trust the model's predictions for higher temperatures and pressures where experimental data is not available.

From these data, it is clear that solubility is highly sensitive to changes in pressure and temperature. Both experimental and theoretical data show that, at any given temperature, increasing pressure will universally increase solubility. Temperature is less straightforward. At low temperatures (generally less than 100°C), a decrease in temperature raises CO₂ solubility. At higher temperatures solubility seems to be less sensitive to temperature changes. Above about 200 atm and 100°C, the model shows that a temperature increase leads to an increase in solubility (Figure 6).

So, for higher pressure, low temperature reservoirs, higher concentrations may be expected thus the effect of active phase change may be expected to be greater. Current understanding of a viable EGS source would require a high pressure, high temperature. Under these conditions CO₂ would be supercritical and CO₂ solubility is predicted to be high. For example a 200°C reservoir at 500 atm would have a calculated solubility of about 10 kg CO₂/100 kg water, or about 10% of fluid mass.

Other parameters affect the solubility of CO₂ in water. Salinity was shown to decrease CO₂ solubility (Figure 7, reproduced from Chang et al., 1998). Introduction of a basic solution would neutralize the weak acid, H₂CO₃, forcing Equation (3) to the right allowing more CO₂ (gas) to dissolve into solution (Konrad and Bird, 1995). Similarly, if the partial pressure of CO₂(gas) is increased the forward reaction is favored and more CO₂ will dissolve.

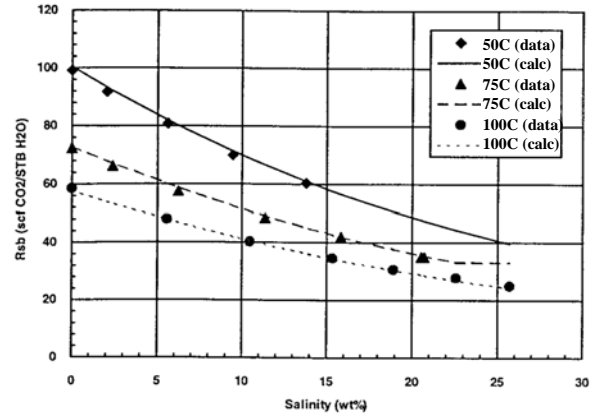


Figure 7 CO₂ solubility as a function of salinity (Chang et al., 1998).

EXPERIMENTAL WORK

Details of experimental work were reported previously in Stacey et al. (2010). The core-scale experiment consisted of a titanium core holder loaded with a Berea sandstone core. A series of drainage (gas injection) and imbibition (water injection) cycles were performed to evaluate relative permeabilities of the respective fluids.

Nitrogen was used in a control experiment because solubility of nitrogen in water was assumed to be negligible. After primary drainage, the residual water saturation stays approximately constant with continued cycles of drainage and imbibition (Figure 8). For CO₂, a gas highly soluble in water, the residual water saturation decreases with every cycle of drainage and imbibition (Figure 9). As CO₂ dissolves it is able to diffuse into the smallest pore spaces without overcoming capillary entry pressure. When CO₂ evolves out of solution it displaces the water that was previously immobile into higher-permeability pathways. The additional mobile water also impedes the flow of CO₂, thus the relative permeability of CO₂ is less than nitrogen.

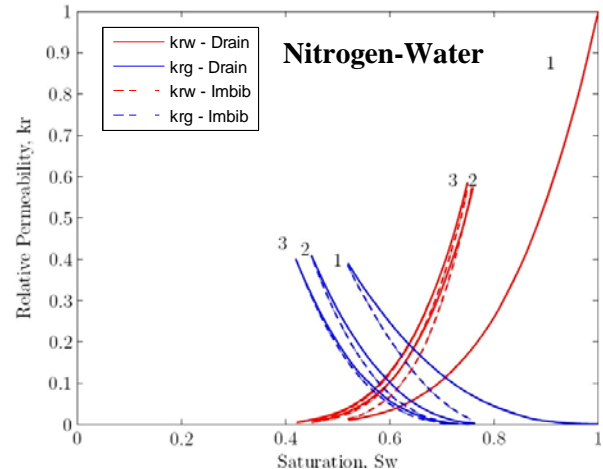


Figure 8 Relative Permeability curves for nitrogen (blue) and water (red).

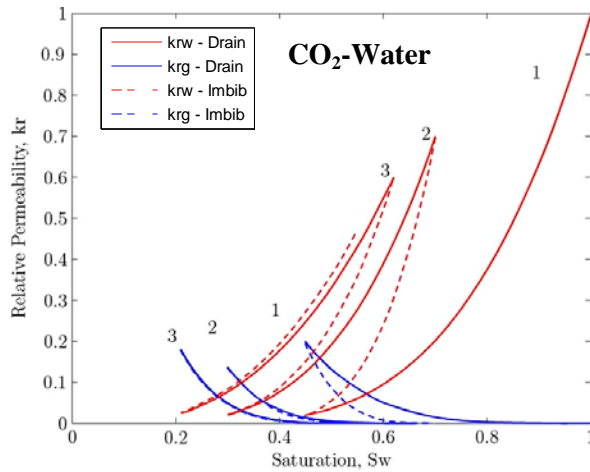


Figure 9 Relative Permeability curves for CO₂ (blue) and water (red).

A micromodel experiment was conducted to observe the phenomenon of active phase change qualitatively. A silicon micromodel was etched to mimic the pore structure of Berea sandstone, saturated with water, and drained with CO₂. The CO₂-water displacement front was recorded with digital photographs wherein the active phase change phenomenon was recorded visually (Figure 10).

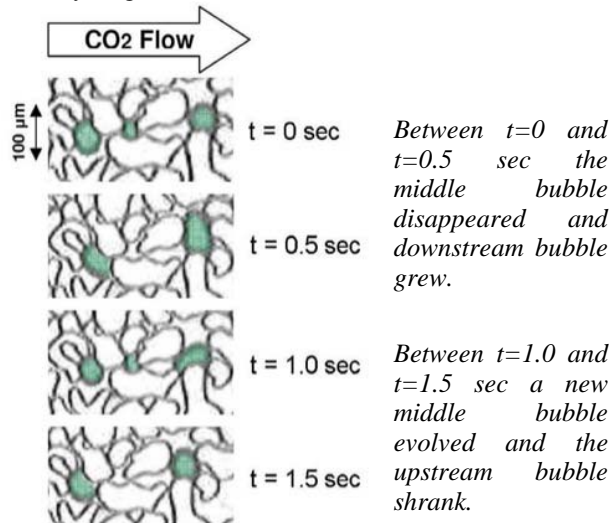


Figure 10 As CO₂ flows from left to right you can see bubble growth and nucleation that occurred as a result of active phase change (Stacey et al., 2010).

This process is illustrated further in Figure 11a where a supersaturated CO₂ front is depicted that precedes the actual gas-liquid interface. It is in this supersaturated region that bubbles may nucleate in advance of the front itself. In contrast, Figure 11b shows a cartoon of a nitrogen-water system where no supersaturated zone occurs. In this case the gas is only mobile in regions where it is connected.

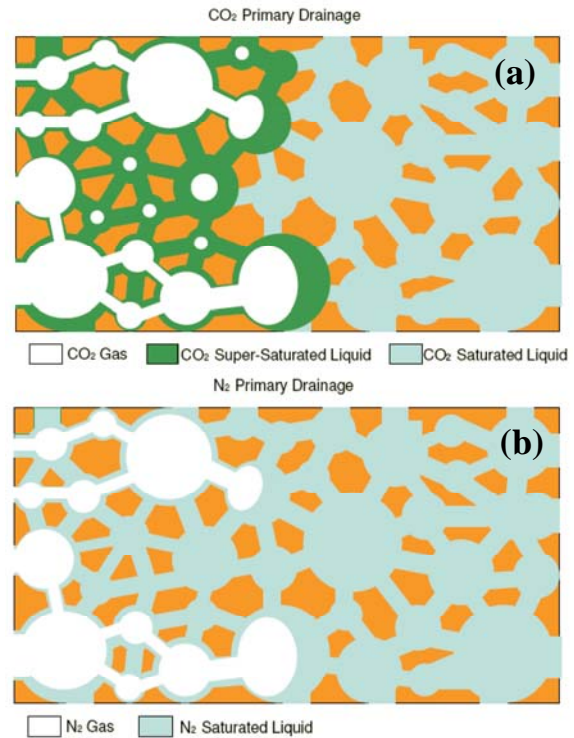


Figure 11 Schematics of multiphase flow with (a) CO₂-water and (b) nitrogen-water.

CONCLUSIONS AND FUTURE WORK

Work presented here as well as previous studies (Bennion and Bachu, 2008; Chang et al., 1998) has shown that CO₂ solubility has a significant impact on the two-phase flow behavior of CO₂ and water. In core experiments residual water saturation decreased with successive imbibition and drainage cycles and active phase change was confirmed visually using the silicon micromodel.

Currently our experimental work considers active phase change in a CO₂-water system at atmospheric conditions. However, we recognize that CO₂ solubility is a function of temperature, pressure, pH, and salinity. Bennion and Bachu (1998) observed a similar phenomenon under saline conditions, which is known to reduce solubility of CO₂. Continued work on this project plans to analyze the effect of pressure and temperature changes on active phase change. CO₂ will still be soluble even at the supercritical phase so it is not clear if the phenomenon observed at atmospheric conditions will persist.

ACKNOWLEDGEMENT

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