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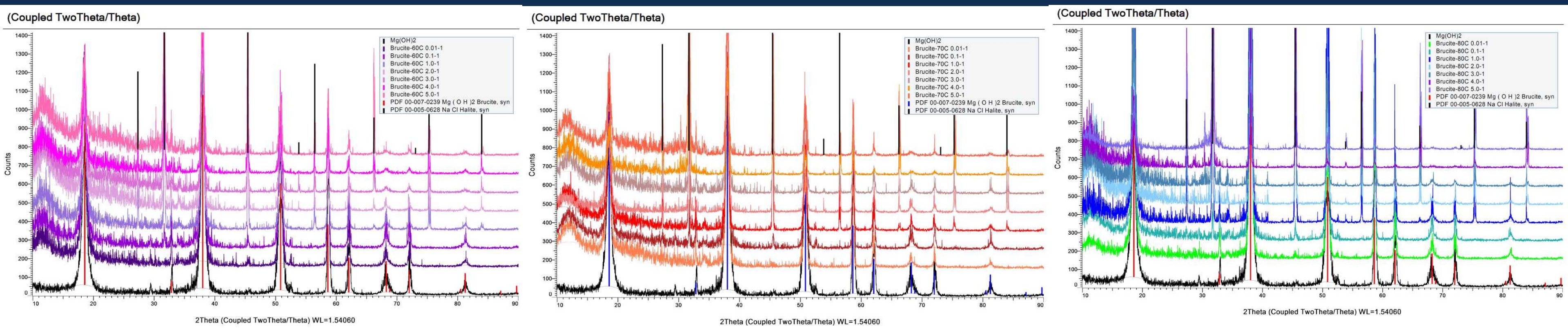


# Experimental Determination of Brucite Solubilities in NaCl Solutions at Elevated Temperatures

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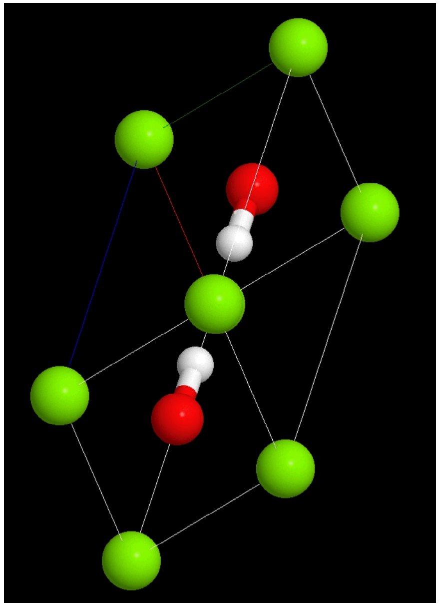
# Introduction- MgO and Mg(OH)2

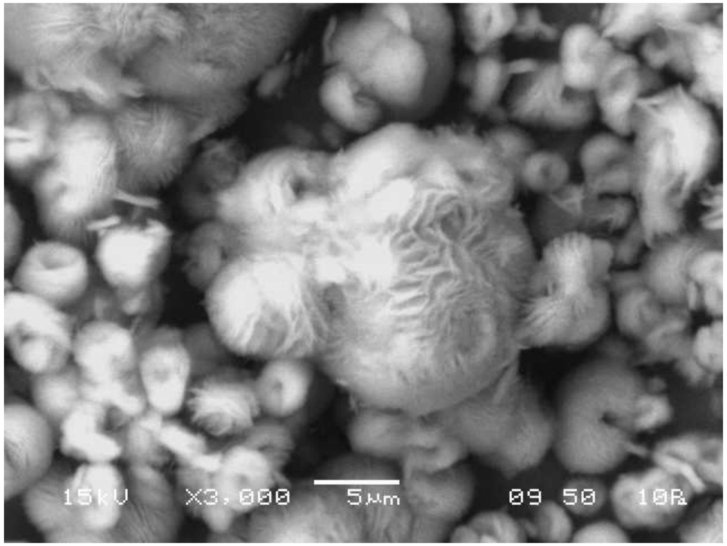
- MgO rapidly hydrates to brucite ($Mg(OH)_2$) upon contact with solution
- The hydrolysis of $Mg^{2+}$ can be expressed as,

$$Mg^{2+}\ H_2O = MgOH^{+} + H^{+}$$

- Brucite will absorb $CO_2$ to form Mg-carbonate species such as hydromagnesite ($Mg_5(CO_3)_4(OH)_2.4H_2O$).



Brucite Structure. PDF4+ software




SNL Synthesized Hydromagnesite

# Introduction-Repository Relevance

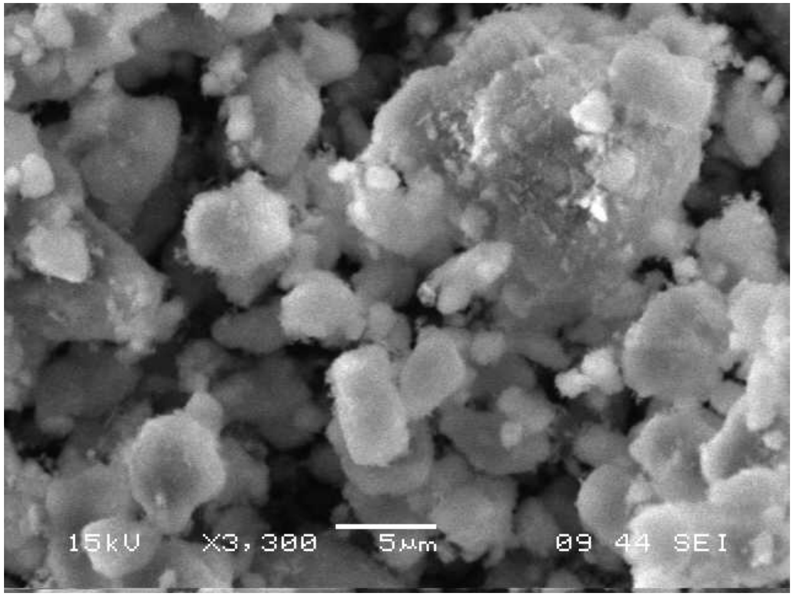

MgO in WIPP

- Periclase (MgO) is currently used as an engineered barrier at the WIPP site and brucite has been considered for use at various other nuclear waste repositories across the world .
- These solids are considered for this role due to their ability to buffer pH and reduce $CO_2$ levels within the repository
- The thermodynamic properties of brucite have been thoroughly characterized at room temperature by recent studies (Altmaier et al., 2003; Xiong, 2003, 2008).

- Brucite thermodynamic data is lacking at elevated temperatures
- Data from this work will be used to establish equilibrium constants for $MgOH^+$ at elevated temperatures to accurately model pH evolution for brines with high concentrations of magnesium at elevated temperatures.

# Experimental Matrix

- 1 gram of ACS grade $Mg(OH)_2$ is placed in various concentrations of NaCl solutions ranging from 0.01 m to 5.6 m
- All samples were prepared in duplicate
- A set of experiments is placed in ovens set to: 40°C, 50°C, 60°C, 70°C and 80°C. (40°C and 50°C data will be presented at a later date).




Brucite ($Mg(OH)_2$) Starting Material

| Sample Matrix | | | | | | |
|---|---|---|---|---|---|---|
| Sample Name | NaCl Concentration | Temperatures °C | | | | |
| Brucite 0.01-1 | 0.01 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 0.01-2 | 0.01 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 0.1-1 | 0.1 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 0.1-2 | 0.1 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 1.0-1 | 1.0 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 1.0-2 | 1.0 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 2.0-1 | 2.1 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 2.0-2 | 2.1 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 3.0-1 | 3.2 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 3.0-2 | 3.2 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 4.0-1 | 4.4 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 4.0-2 | 4.4 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 5.0-1 | 5.6 m | 40 | 50 | 60 | 70 | 80 |
| Brucite 5.0-2 | 5.6 m | 40 | 50 | 60 | 70 | 80 |
| | | | | | Sample Total: | 70 |

# pH Correction at Elevated Temperatures and High Ionic Strength

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- At solution concentrations of ~1 m or greater, the pH values should be corrected. pH correction factors can be determined through plotting data from Gran Titrations.
- 1 m, 2.1 m, 3.2 m, 4.4 m and 5.6 m NaCl solutions were titrated at experimental temperatures (40-80C) in order to obtain pH correction factors
- The relation between the observed pH ($pH_{ob}$) and pcH (corrected pH value) can be expressed as:

$$pC_{H+} = pH_{ob} + A \qquad \text{(eq.1)}$$

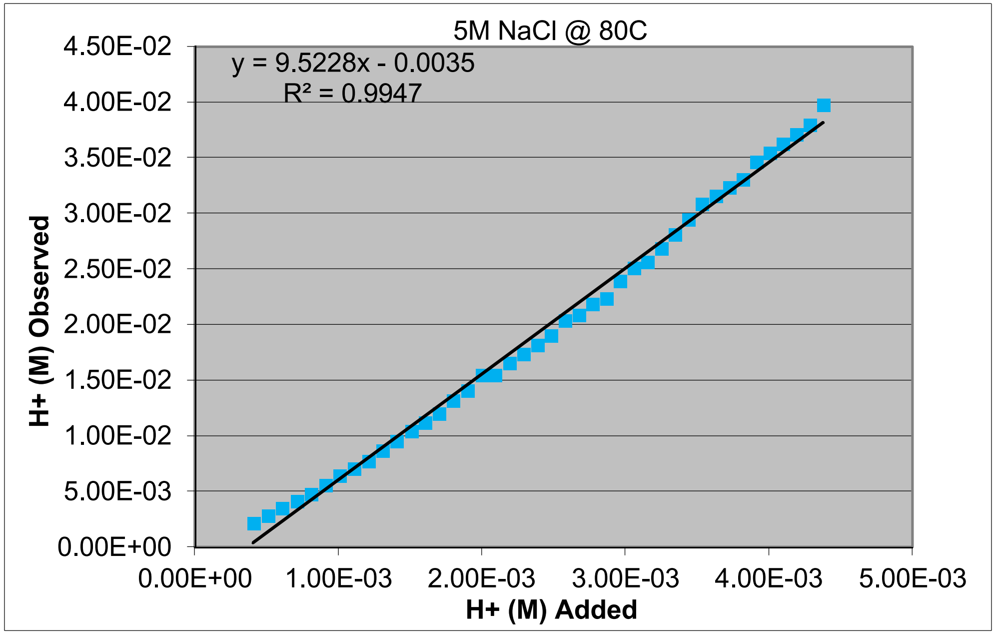
- A is defined as:

$$A = \log \gamma H^{+} + (F/2.303RT)\Delta Ej \qquad \text{(eq.2)}$$

- Where $\gamma H^{+}$ is the molarity-scale activity coefficient of $H^{+}$ and;
- $\Delta Ej$ is the difference in liquid-junction potential between the standards and solutions
- These parameters cannot be independently measured however the combination of the two is measurable . Gran titration is utilized to obtain the necessary parameters.

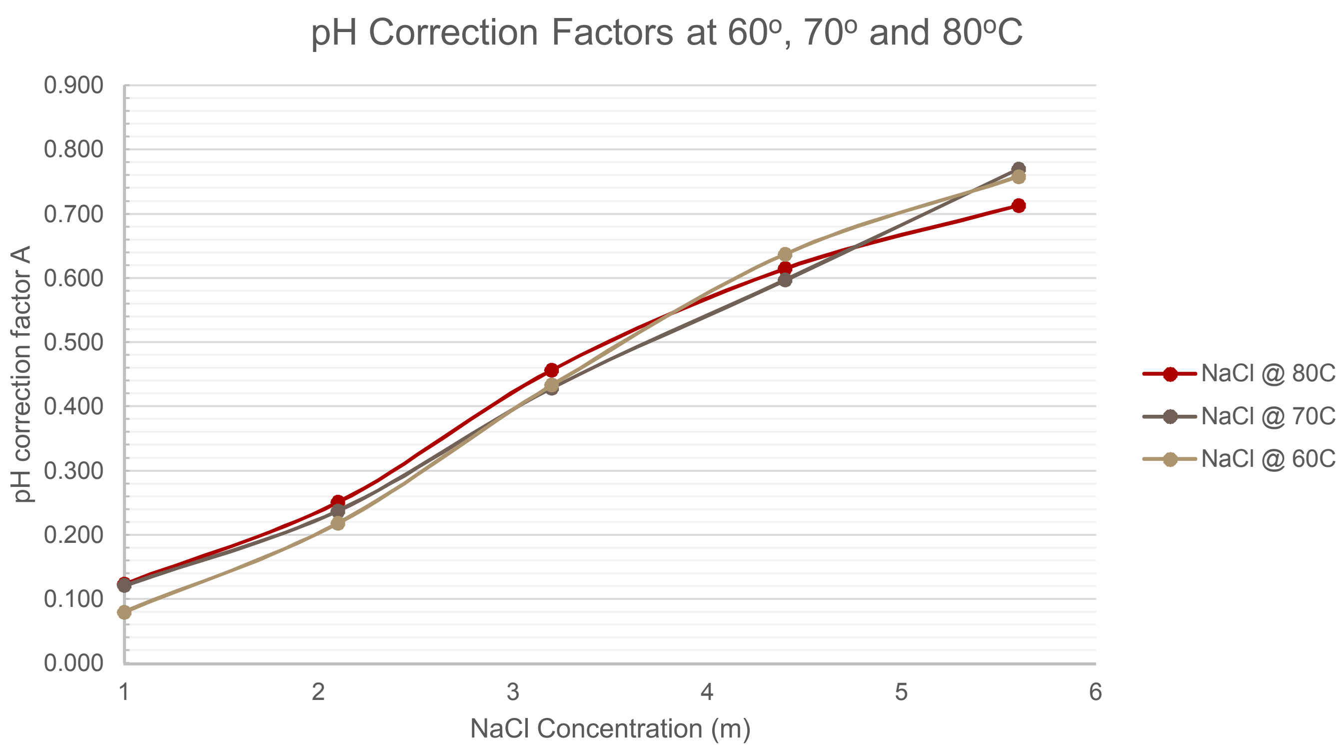
# pH Correction at Elevated Temperatures

- Rewriting Eq. (2) as a logarithmic expression yields:
  - $-\log(C_{H+}) = -\log(H^+_{obs}) + A$ (eq.3)
- The $pC_{H+}$ correction factor, A, can then be obtained from the Gran titration data by plotting the $H^+_{add}$ (moles of H+ added) against the $H^+_{obs}$.
  - $H^+_{obs} = 10^{-pHobs}$ (eq.4)
  - $H^+_{add} = mL\ HCl\ added \left(\frac{N\ of\ HCl}{mL\ HCl + mL\ of\ Sample}\right)$ (eq.5)
- The logarithm of the slope of this curve is the correction factor A needed to convert the measured pH reading to $pC_{H+}$.



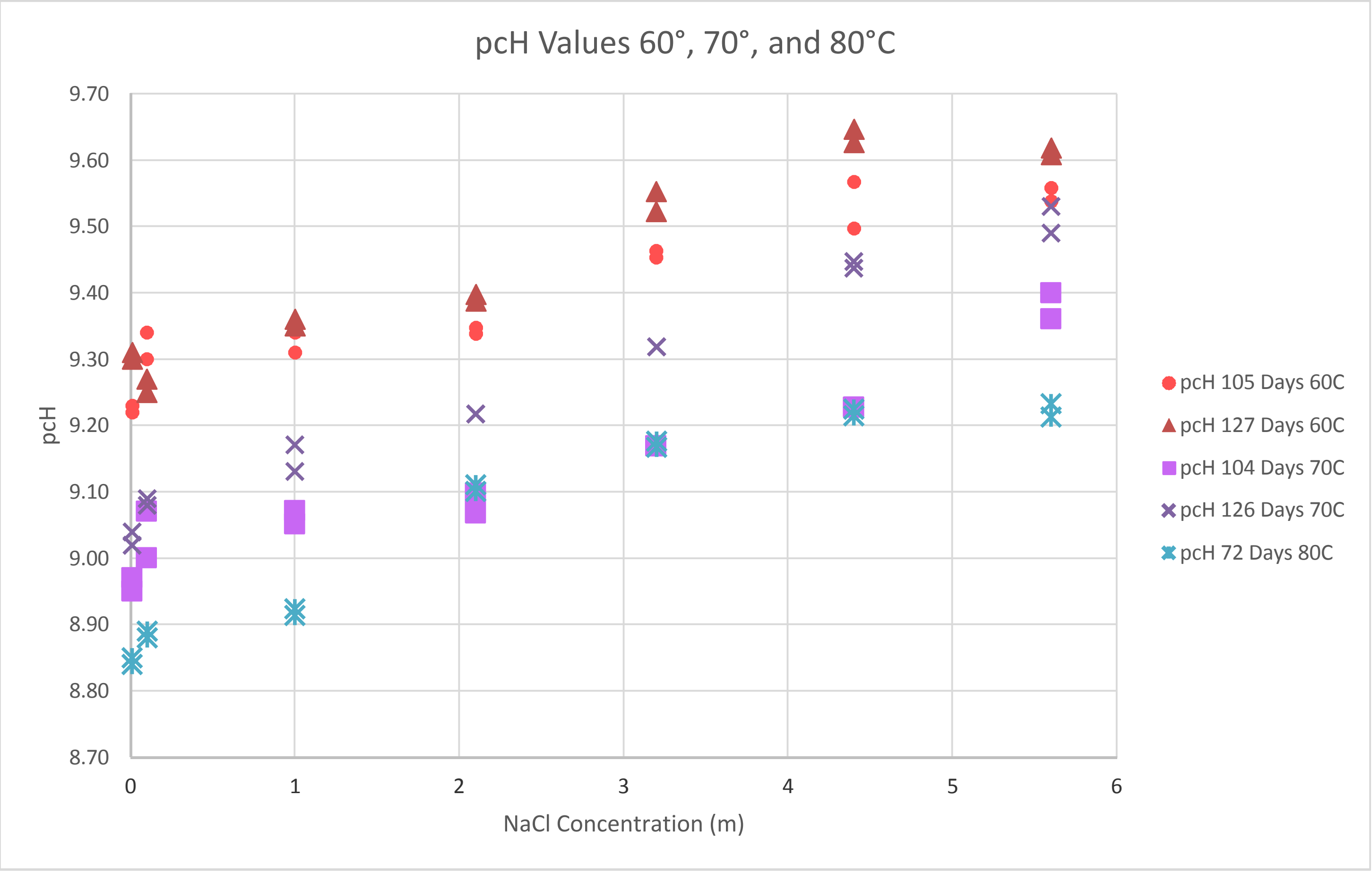
# pH correction factors (pcH) for 60°,70° and 80°C

| Sample Name | pH Correction Factor (A) 80°C | pH Correction Factor (A) 70°C | pH Correction Factor (A) 60°C |
|---|---|---|---|
| 1.0 m NaCl | 0.124 | 0.121 | 0.080 |
| 2.1 m NaCl | 0.251 | 0.238 | 0.218 |
| 3.2 m NaCl | 0.457 | 0.429 | 0.433 |
| 4.4 m NaCl | 0.615 | 0.597 | 0.637 |
| 5.6 m NaCl | 0.713 | 0.770 | 0.758 |

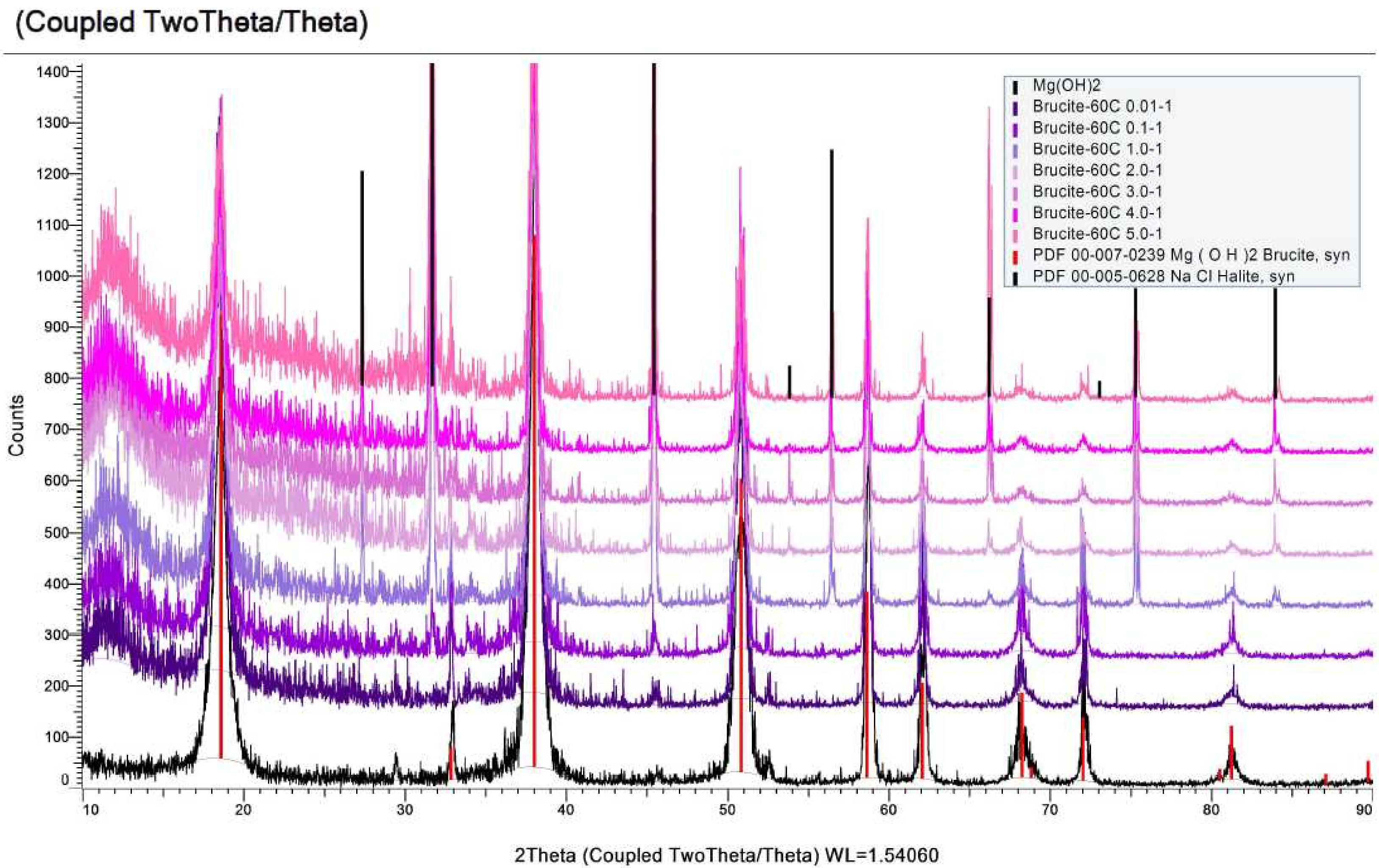


# Experimental Data- pcH

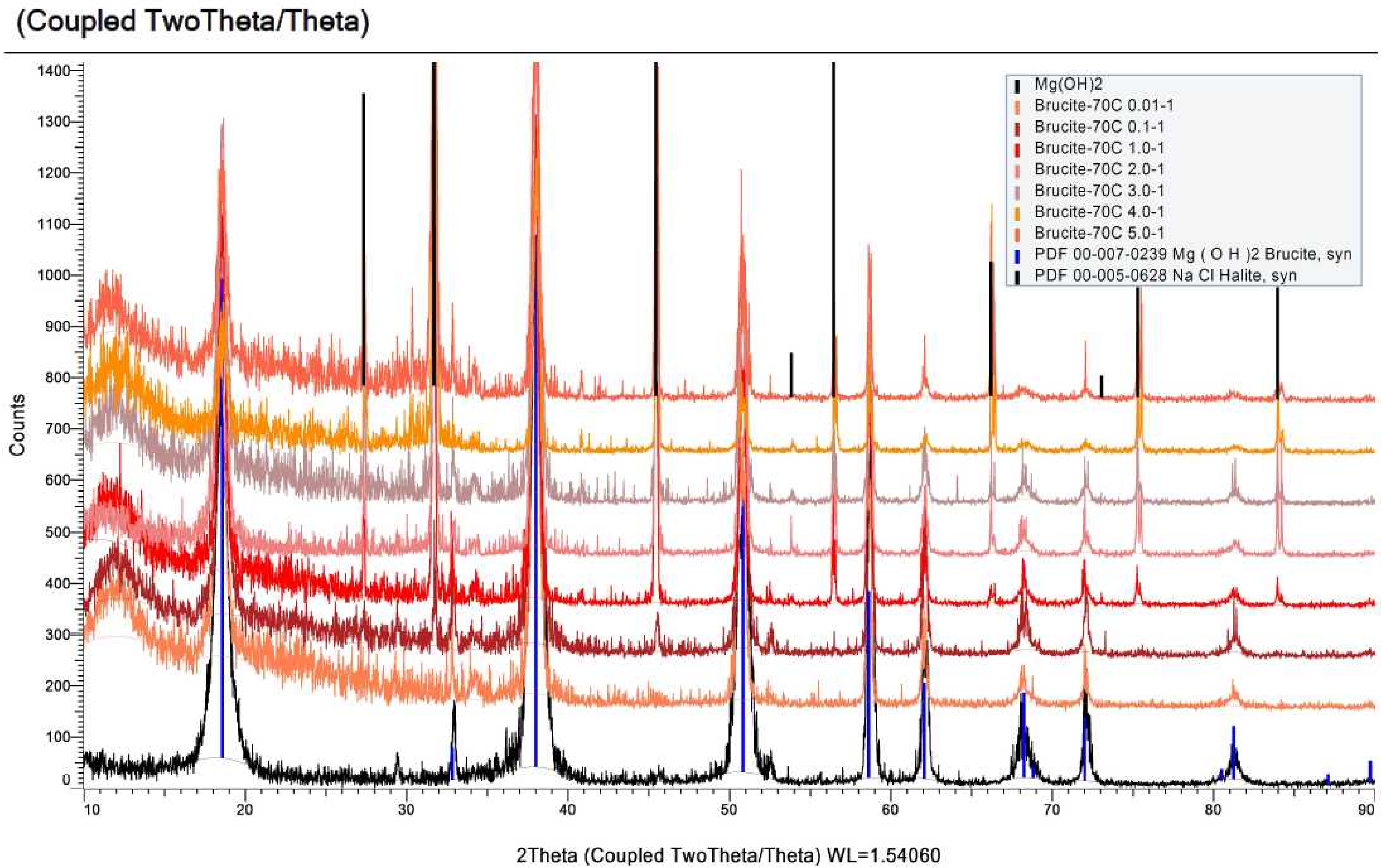
- Experimental pcH values were higher with lower temperatures.
- Brucite is believed to have a retrograde solubility (lower temperature higher solubility).
- The higher pH values at lower temperature would support this idea.



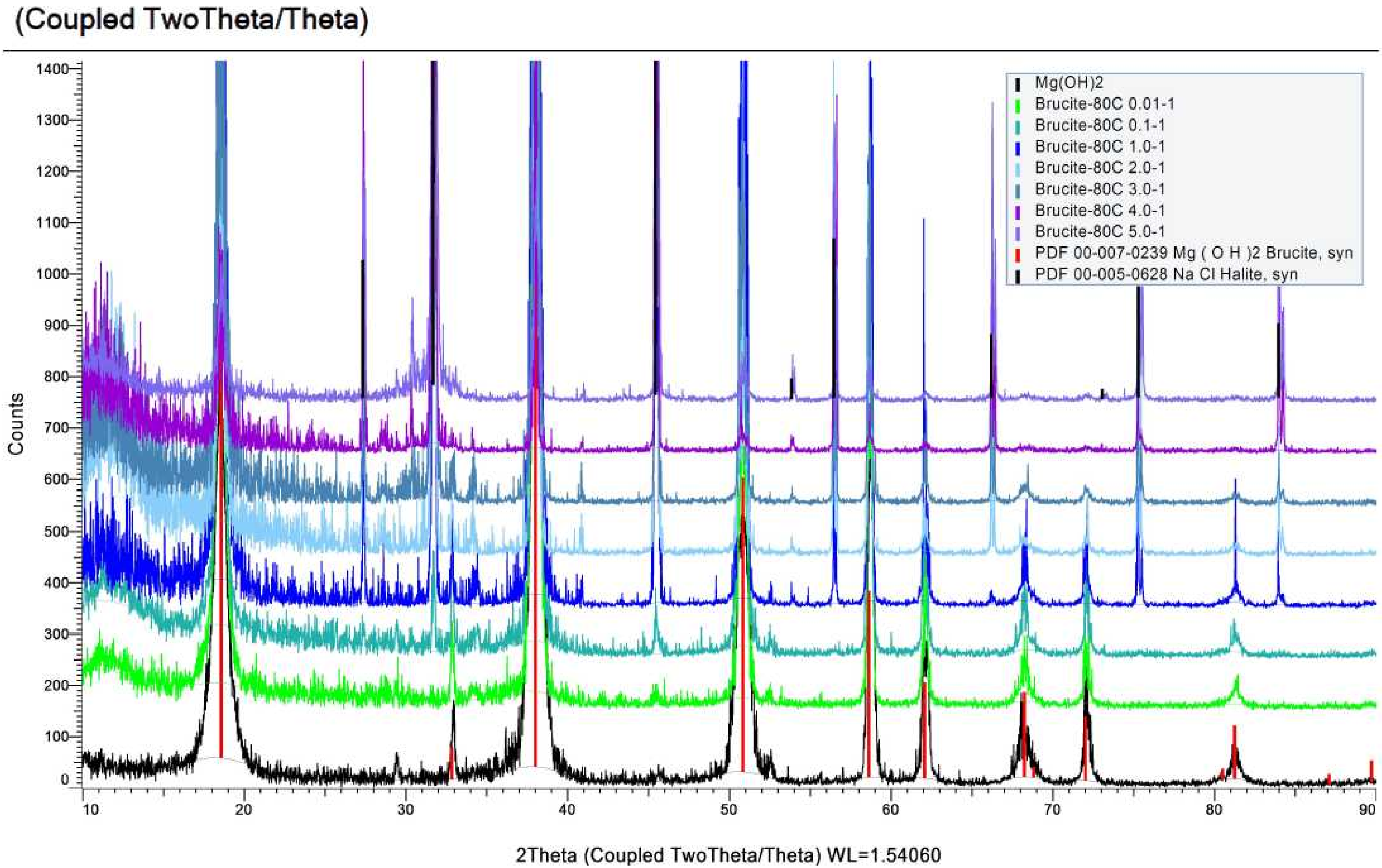
# Experimental Data-
# Solid Characterization by XRD 60°C-218 Days



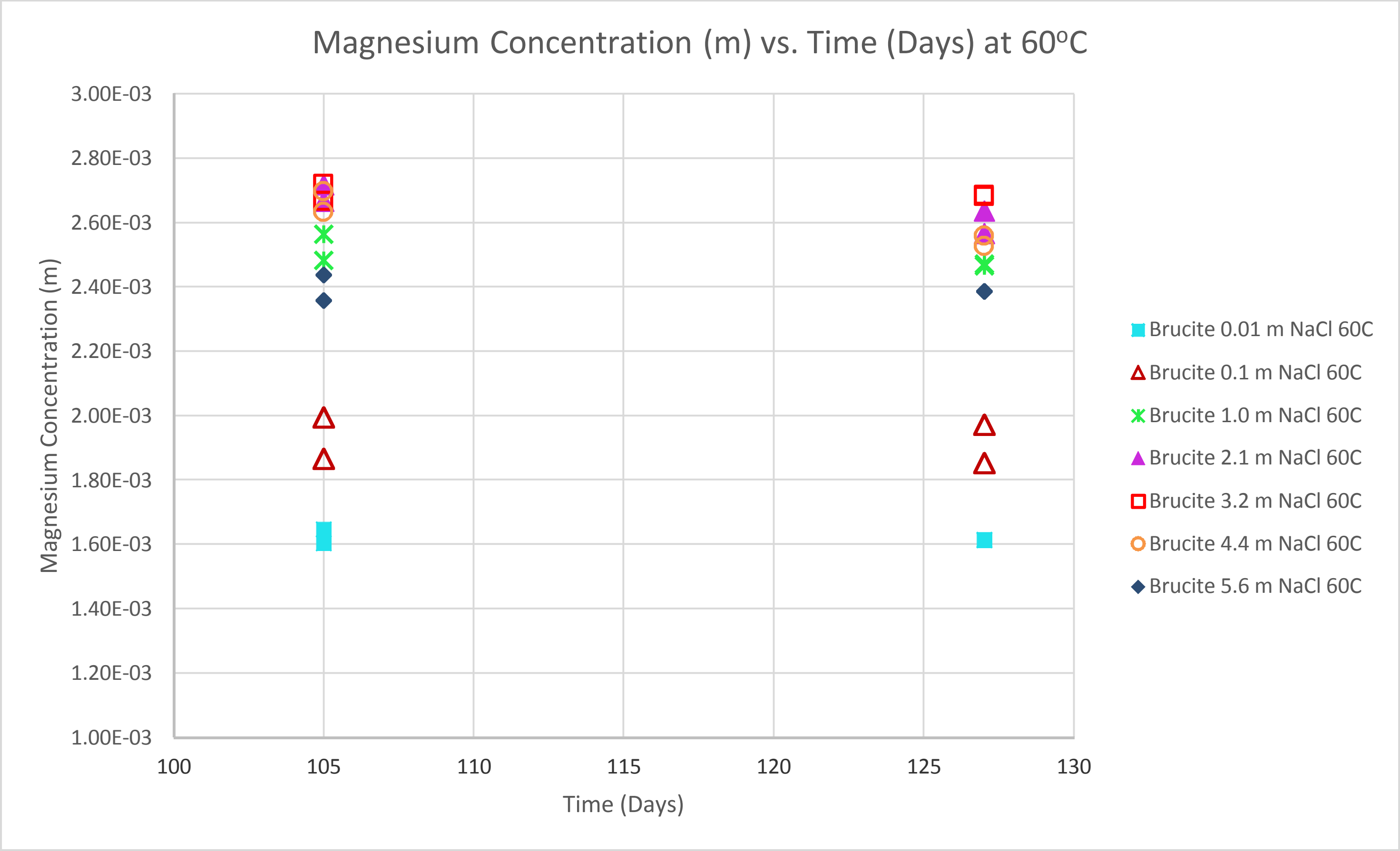
# Experimental Data-
# Solid Characterization by XRD 70°C-216 Days



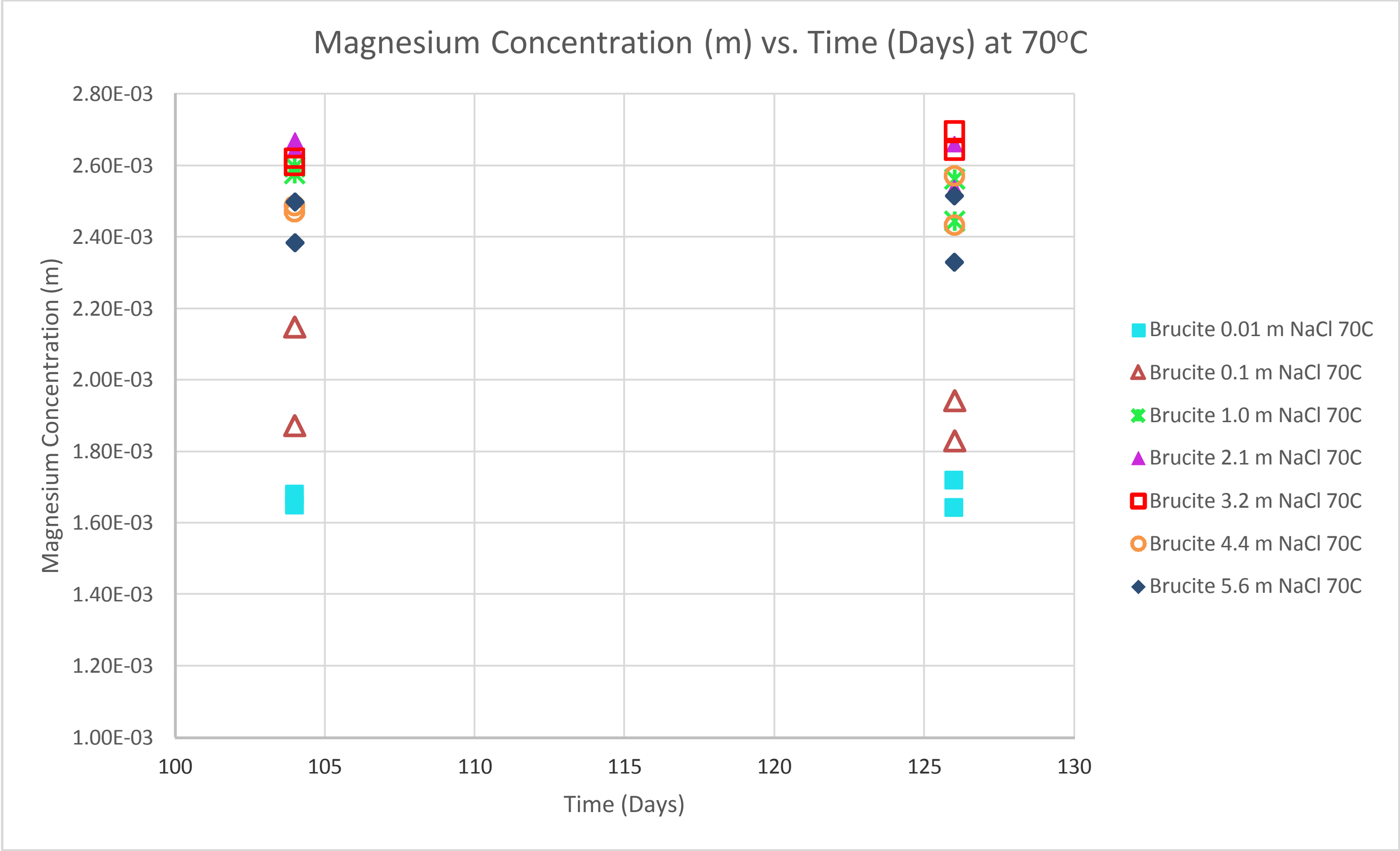
# Experimental Data-
# Solid Characterization by XRD 80ºC-216 Days



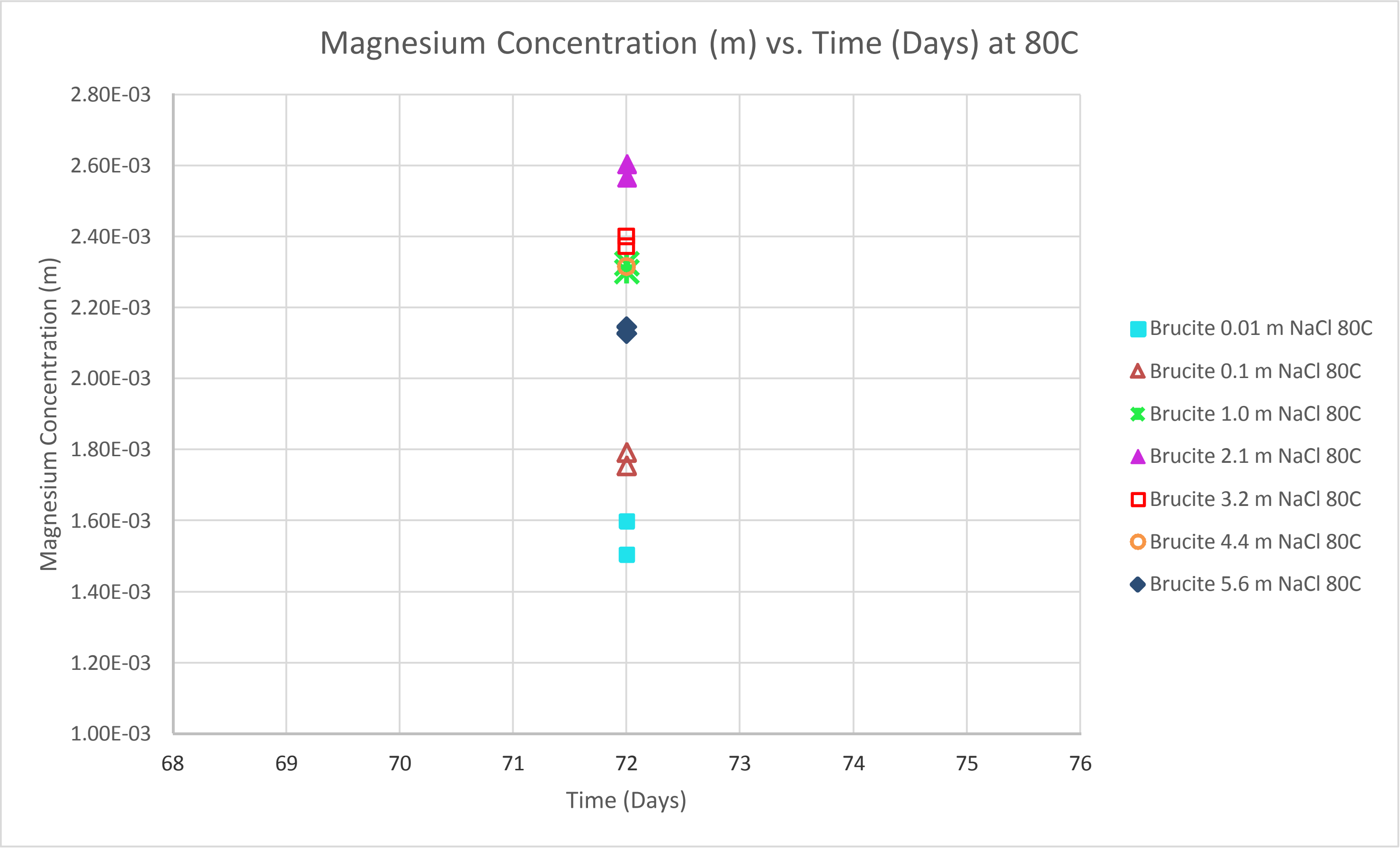
# Experimental Data- Magnesium (m) vs. Time 60°C



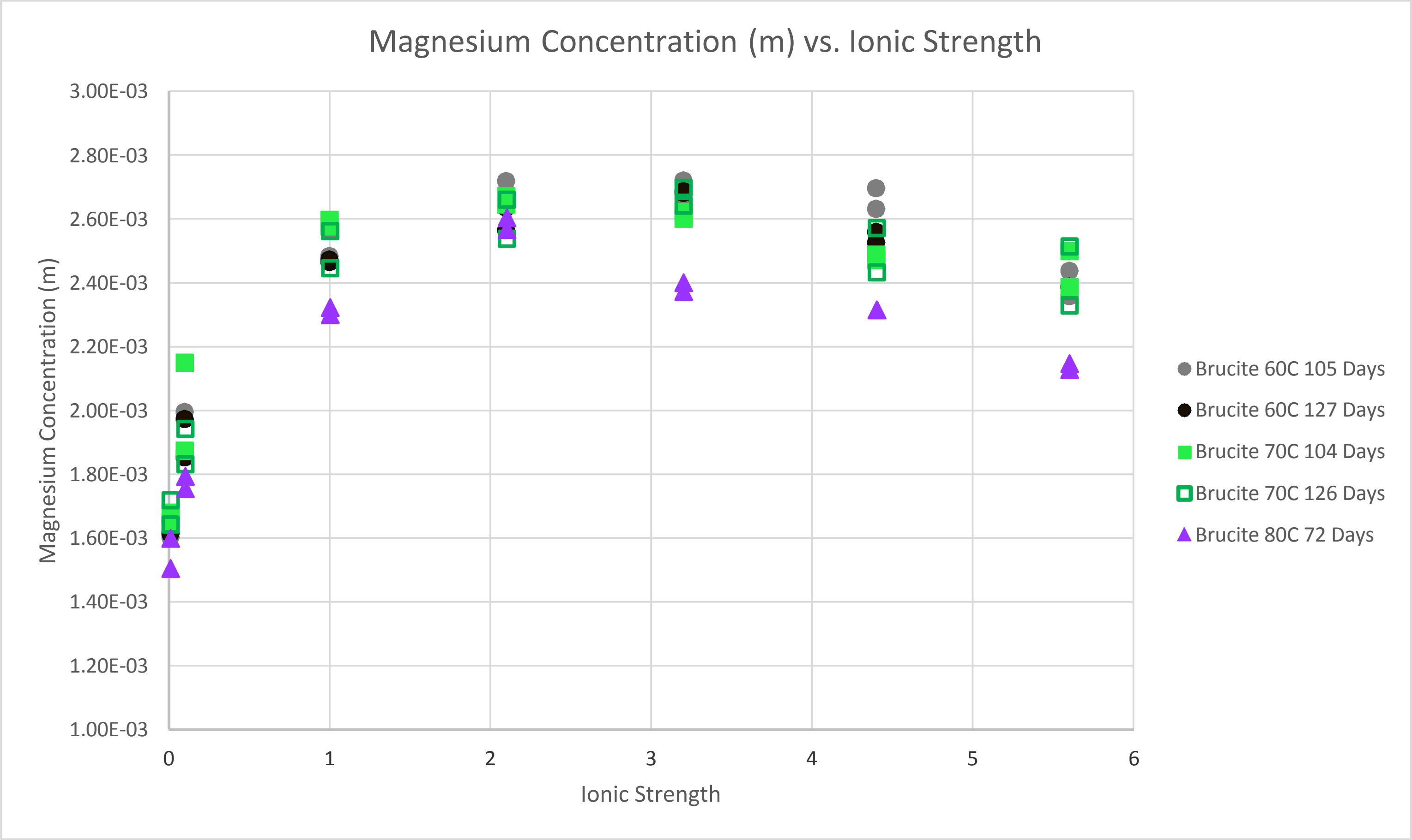
# Experimental Data- Magnesium (m) vs. Time 70°C



# Experimental Data- Magnesium (m) vs. Time 80$^{o}$C



# Experimental Data- Magnesium (m) vs. Ionic Strength



# Work in Progress

- Experiments will continue to be monitored
- pH and Mg concentrations will continue to be measured
- Brucite solubility data will be obtained for 40°C, 50°C, 60°C, 70°C and 80°C
- pcH correction factors will be determined for 40°C, 50°C, 60°C, 70°C and 80°C at NaCl concentrations from 1 m to 5.6 m.
- Equilibrium constants for $MgOH^+$ will be determined for elevated temperatures and a range of NaCl concentrations
- Thermodynamic calculations will be performed regarding brucite solubilities in NaCl solutions ranging from 0.01 m to 5.6 m at elevated temperatures from 40°C to 80°C.

# Questions?