

CONSEQUENCES OF ALKALINE SALT CHOICE FOR PH RAISE DURING CO₂ MINERALIZATION USING ROCK-DERIVED MAGNESIUM SALT

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ABSTRACT

Carbon capture and storage by mineralization (CCSM) is still on the agenda in both research facilities and industry as a method for large-scale storage of CO₂ in stable, solid materials. One interesting path for CCSM is using magnesium as the core of CO₂ capturing. At Åbo Akademi University (ÅAU), a process that involves extraction of magnesium, Mg, from a Mg-silicate based rock resource, followed by removal of (metallic) species and finally the reaction of a magnesium salt with a pure or diluted CO₂ stream, producing a magnesium carbonate has been studied for almost two decades. The magnesium salt produced, magnesium sulfate (MgSO₄), is highly soluble in water, whereas the product, magnesium carbonate (hydrate) is obtained as a precipitate. For the carbonation of the MgSO₄ in aqueous solution a pH raise is needed which in practice involves using a hydroxide of ammonia, sodium, or potassium, NH₄OH, NaOH or KOH. The product can then be filtrated out and the filtrate, a solution of (NH₄)₂SO₄, Na₂SO₄ or K₂SO₄ is then processed, using membrane electrodialysis, and separated into NH₄OH, NaOH or KOH, and sulfuric acid, H₂SO₄. The latter can then again be used for the extraction of Mg from rock, thus closing the process loop. With several motivations for using NH₄OH, NaOH or KOH for the pH raise this has consequences for the reaction with CO₂ as well as the post-processing of (NH₄)₂SO₄, Na₂SO₄ or K₂SO₄ – this is the subject of this paper. It is concluded that it appears feasible to use NaOH or KOH as the pH raise agent instead of aqueous ammonia. The best yield (of Mg converted into carbonate) was found at 35 °C for the NH₄OH experiment and at 40 °C for the NaOH or KOH experiments. The yields were 80.2 %, 56.9 % and 94.0 % respectively for the best NH₄OH, NaOH and KOH experiments. Ongoing work aims at confirming that the BPMED system can produce the needed NaOH and KOH from the Na₂SO₄ or K₂SO₄ solution that remains after removing the magnesium carbonate product. This would close the reagent loop and make the whole process feasible.

1 INTRODUCTION

CO₂ capture and storage by mineralization (CSM) is still on the R&D agenda as a potentially large-scale CO₂ emissions mitigation method and for magnesium-based feedstock materials the step towards industrial – scale use is currently being made (Zevenhoven et al., 2022). Stepwise CO₂ mineral sequestration as developed towards industrial-scale deployment at ÅA, Finland involves extraction of magnesium, Mg, from a Mg-silicate based rock resource, typically a mine tailing, followed by removal of (metallic) species and finally the reaction of a magnesium salt with a pure or diluted CO₂ stream, producing a magnesium carbonate. See Zevenhoven and Häggqvist (2022) for a description of the several (five) ÅA process routes that perform best on serpentinites, i.e. rock containing primarily serpentine, 3MgO·2SiO₂·2H₂O.

For the carbonation of a magnesium salt, here magnesium sulfate (MgSO₄) in aqueous solution a pH raise is needed which in practice implies using a hydroxide of ammonia (NH₄OH), sodium (NaOH) or potassium (KOH). After removing the solid carbonate, an aqueous solution of (NH₄)₂SO₄, Na₂SO₄ or K₂SO₄ is obtained that, using bipolar membrane electrodialysis (BPMED), is separated into NH₄OH,

NaOH or KOH, and sulfuric acid H_2SO_4 . The latter may then be used for the extraction of Mg from rock, thus closing the process loop with the specific electricity consumption (SEC) for membrane electrodialysis as the main energy input requirements for this carbon capture and utilization (CCU) process. (See for our recent work on BMPED: Koivisto et al., 2023.) A schematic of the process procedure is given in Figure 1.

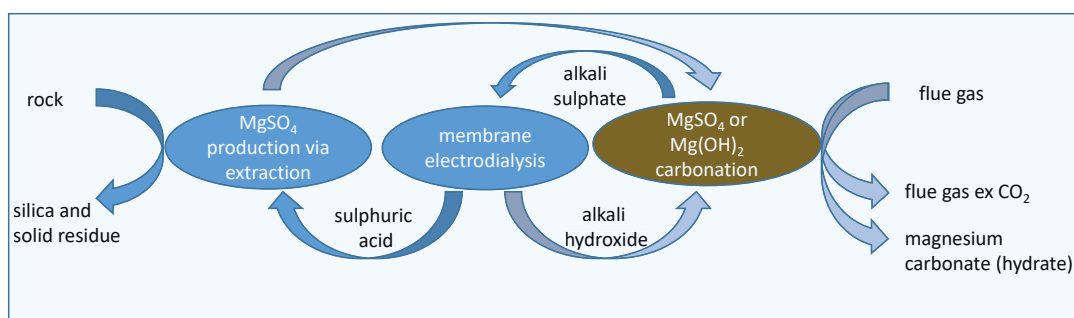


Figure 1: Schematic of the ÅA process route for Mg silicate-based rock CO_2 mineralization. This paper focuses on the carbonation step and the alkali salt used.

The novelty of what is presented here is the process that produces nesquehonite (NQ) as part of a CCSM process, with the carbonation step being critical one when it comes to yield and conversion rate for NQ at temperatures where it does not decompose (release crystal water).

There are several motivations for using NH_4OH , NaOH or KOH for the pH raise:

1. bringing the pH to a suitable level of around 10 for reaction of aqueous MgSO_4 with CO_2 requires a significant amount of aqueous ammonia which brings down the concentration of the MgSO_4 which preferably is around 0.75 M (moles/litre). (See Back and Zevenhoven, 2024, for details.)
2. using aqueous ammonia results in formation of small amounts of carbamate NH_2COO^- ions, which won't occur with NaOH or KOH for the pH raise
3. some magnesium silicate – based rock types suitable for CO_2 mineralization via the ÅA routes contain significant amounts of potassium, K, for example flogopite type mine tailings. These will bring K as a side stream to the process, with valuable K_2SO_4 as a side product.
4. during the carbonation, a vapor phase of NH_3 may leave the process with the flue gas from which CO_2 has been converted into carbonate, requiring an additional gas cleaning step for NH_3 recovery. (Note that for the work reported here, the gas used was 100% CO_2 .)

On the other hand, the use of aqueous ammonia gives rise to pH buffering effects that are beneficial for the carbonation process. Important is also that this process step integrates well with the rest of the process, with acceptable residence time of, say, 1 h, and acceptable energy input requirements. Aiming at the production of magnesium carbonate trihydrate, i.e. nesquehonite $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (NQ), which can be used for cyclic thermal energy storage, TES, via $\text{MgCO}_3 \cdot 3\text{H}_2\text{O} + \text{heat} \rightarrow \text{MgCO}_3 + 3\text{H}_2\text{O} (\text{g})$, see Erlund and Zevenhoven, (2019) this dictates temperatures $< 45 \dots 50 \text{ }^\circ\text{C}$.

All this has consequences for the reaction with CO_2 as well as the post-processing of $(\text{NH}_4)_2\text{SO}_4$, Na_2SO_4 or K_2SO_4 – this is the subject of this paper. Limited solubilities of sulfate salts as well as of possible carbonates or bicarbonates may lead to co-precipitation of salts with the magnesium carbonate that make extensive washing necessary or allowed concentrations to become too low for effective processing. As another issue, the membrane electrodialysis SEC, mass throughput rate or performance in general may become problematic. This paper will report, for a given starting concentration of MgSO_4 , on how raising the pH to allow for carbonate formation using any of these three salts affects the carbonation process and the quality of the solid product, and the processing of the filtrate after carbonate removal. Earlier work done shows that the temperature is the parameter that most affects the yield of NQ and the rate of conversion. For a comparable data set, the CO_2 flow, stirring speed, stirring time and initial MgSO_4 concentrations were kept equal between tests.

2 EXPERIMENTAL PROCEDURE

Three test series were conducted, one with aqueous ammonia, NH_4OH (aq), (VWR Chemicals, Conc. 25 % w/w in water, assay 29 %), a second with sodium hydroxide (NaOH) (Fisher Scientific, assay 99.1 %) and a third with potassium hydroxide (KOH) (VWR Chemicals, 47 %, assay 46.0 – 48.0 %) as pH raise agent.

Tests were done in a one litre four-neck round-bottom glass flask reactor where the temperature and pH could be observed. The experiments in the different series were conducted at 20, 30, 35, 40 and 45 °C. To ensure a stable temperature, the glass reactor was kept in a water bath. The stirring was done with a 50 mm × 8 mm magnetic stirrer at 400 rpm. One of the necks of the reactor was used for gas inlet with a gas diffuser at the end of the tube to ensure a high level of diffusion of the CO_2 (g) (Woikoski, ≥99.8 % purity) used. This CO_2 forms as NQ when reacting with the dissolved free magnesium ions (Mg^{2+}) coming from the dissolved MgSO_4 (VWR Chemicals, assay on anhydrous chemicals 100.0 %. LOI 450 ± 25 °C = 27 %). Earlier experiments conducted at the lab showed that the ideal concentration of MgSO_4 for best NQ precipitation is around 0.75 M. The solvent used was water cleaned via reverse osmosis combined with electrode ionization, EDI. 500 ml of water was used in all the experiments. This water also acted as feedstock for the crystal water needed to form the NQ crystals.

The MgSO_4 was first dissolved into the water for up to 10 minutes. After this CO_2 was introduced via the diffuser into the mix. The CO_2 was bubbling into the solution at a rate of 0.16 liters/min to ensure sufficient CO_2 is present for carbonation while also the bubbling contributes to mixing. The CO_2 reacts in water to form carbonic acid (H_2CO_3). At equilibrium, the ions hydrogen carbonate (HCO_3^-) and carbonate (CO_3^{2-}) are present in amounts that depend on pH. After 10 minutes of diffusing CO_2 into the solution equilibrium is obtained at a pH of 4.4. This is done to ensure the maximum amount of CO_3^{2-} -ions possible to be ready to react with the Mg^{2+} -ions to form NQ when the pH rise is done. Earlier experiments have shown that the pH rise had to be done in intervals not to elevate the pH too much. At a too high pH, Mg starts to precipitate as undesired magnesium hydroxide ($\text{Mg}(\text{OH})_2$), brucite.

NQ precipitates at around pH 9. Earlier conducted experiments showed that it is not viable to first rise the pH before the start of the CO_2 diffusion. One challenge with this would be the risk of magnesium precipitating as hydroxides and the other being that the total amount of pH raiser would be higher adding excess amount of other ions, in this case ammonia ions (NH_4^+), Sodium ions (Na^+) or potassium ions (K^+) that might in turn precipitate as unwanted salts. Earlier experiments showed that ammonia should not exceed the concentration of 1.6 M (Back and Zevenhoven, 2024).

The full procedure can be depicted in 9 steps, with a total reaction time of 100 minutes:

1. Dissolve 0.75 mol MgSO_4 in 500 ml of water
2. Diffuse CO_2 into the mix for 10 minutes
3. Continue the CO_2 flow, add pH raise solution
4. Stir for 20 minutes with continued CO_2 flow, add pH raise solution, second dose
5. Stir for 20 minutes with continued CO_2 flow
6. Stir for 45 minutes without CO_2 flow
7. Rinse the product out of the flask with 300 ml of water
8. Filter the product with vacuum filtration
9. Let air dry at room temperature.

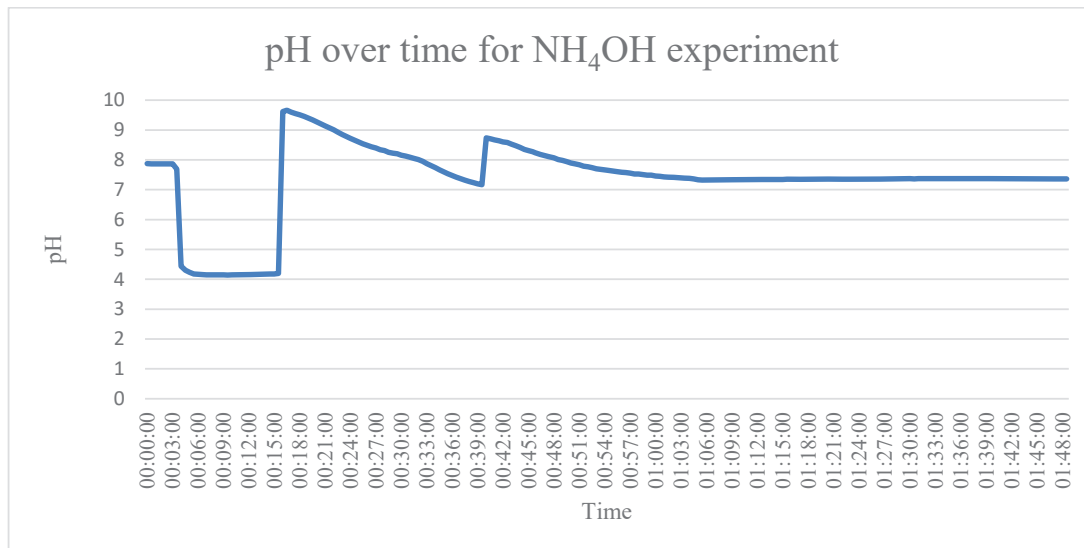
3 EXPERIMENTAL RESULTS: CARBONATE PRECIPITATION

3.1 Aqueous ammonia for pH raise

The results for the aqueous ammonia experiments are given in Table 1. The NH_4OH was added in 25 ml doses totalling to 50 ml used per experiment. The 25 %-wt in water aqueous ammonia is equivalent to a 14.7 M NH_3 solution. The pH versus time was plotted for the 35 °C experiment in Figure 2.

Table 1: Results from the first experiment series with aqueous ammonia for pH raise

No.	Temperature (°C)	Mass of product (g)	Theoretical yield (%)
1-1	20	20.9	40.2
1-2	30	35.1	67.7
1-3	35	41.6	80.2
1-4	40	32.6	62.8

**Figure 2:** Plot of the pH over time in the 35 °C NH₄OH experiment

3.2 Aqueous NaOH for pH raise

The results for the NaOH experiments are given in Table 2. In the 20 °C experiment a 1 M solution of NaOH was used. The total volume used for the pH raise was 430 ml (100 ml + 330 ml). As can be seen from Table 2 this did not yield a good result, with a yield hardly exceeding 10%. For the rest of the experiments in this series a 5 M NaOH solution was prepared and then used for the pH raise. A total of 100 ml of 5 M NaOH was used, 25 ml in the first adding and 75 ml in the second. The pH versus time was plotted for the 35 °C experiment and is given in Figure 3.

Table 2: Results from the second experiment series with aqueous NaOH for pH raise

No.	Temperature (°C)	Mass of product (g)	Theoretical yield (%)
2-1	20	1.4	12.6
2-2	30	26.9	51.8
2-3	35	23.7	45.7
2-4	40	29.5	56.9
2-5	45	25	48.1

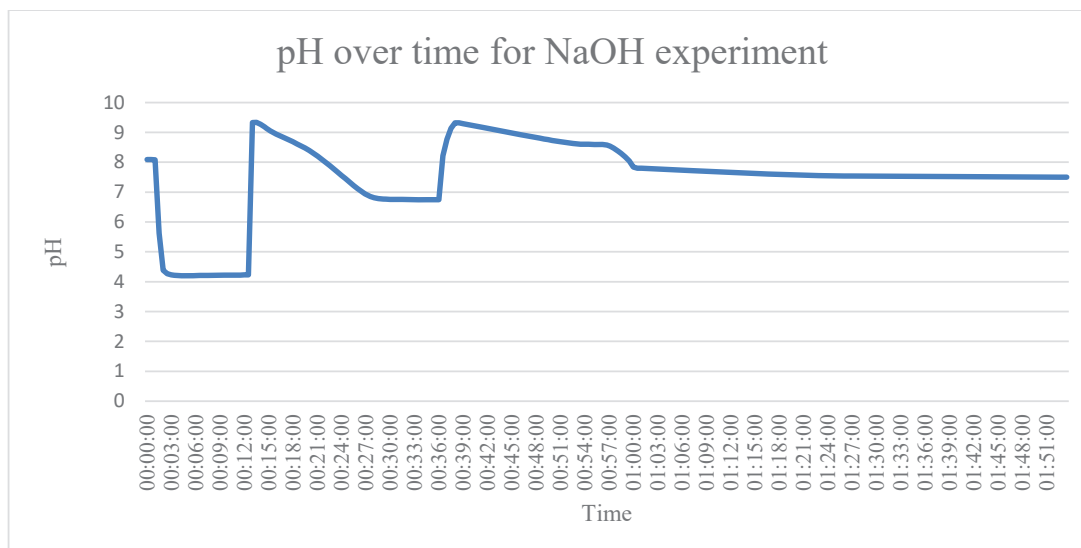


Figure 3: Plot of the pH over time in the 35 °C aqueous NaOH experiment

3.3 Aqueous KOH for pH raise

The results for the KOH experiments are given in Table 3. In the 20 °C experiment a total of 80 ml of KOH 47 %, which is equal to a 12.4 M solution, was used, 20 ml in first adding and 60 ml in the second. However, it was noted that this was too much KOH for the pH rise with the pH rising up to 13.1. Far above the ideal 9-10 pH for NQ precipitation. For the other temperatures a total of 55 ml was used (20 ml + 35 ml). The pH over time was plotted for the 35 °C experiment in Figure 4.

Table 3: Results from the third experiment series with aqueous KOH for pH raise

No.	Temperature (°C)	Mass of product (g)	Theoretical yield (%)
3-1	20	60.1	115.8
3-2	30	42.8	82.5
3-3	35	44.7	86.2
3-4	40	48.8	94.0
3-5	45	45.8	88.3

From the pH plots, comparing the use of KOH with the use of NH_4OH or NaOH, it can be concluded that the KOH keeps the pH at desired level the best while with the NH_4OH it dropped to under 8 in about 15 minutes.

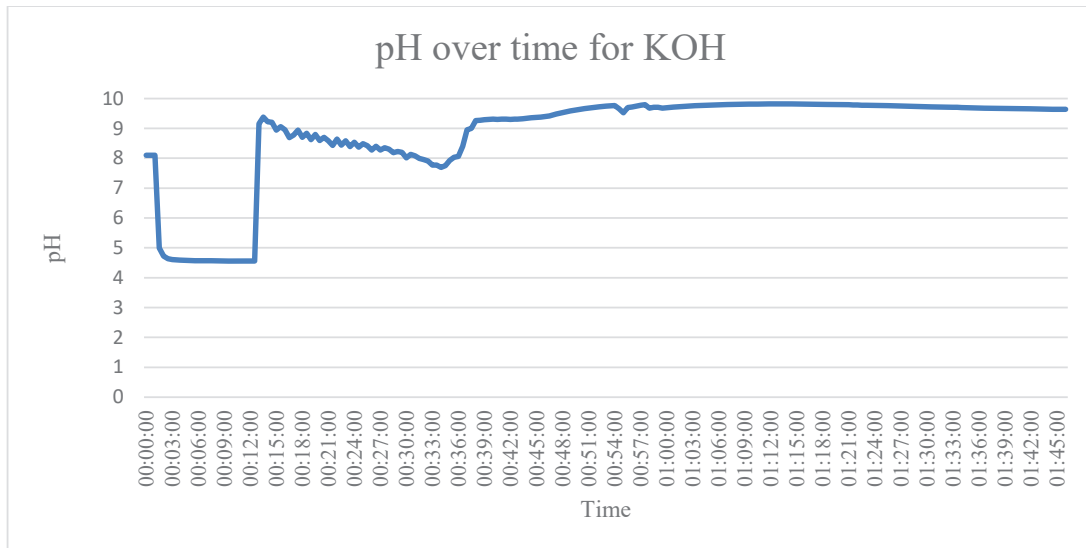


Figure 4: Plot of the pH over time in the 35 °C aqueous KOH experiment

4 EXPERIMENTAL RESULTS: ANALYSIS OF CARBONATE PRODUCT

4.1 SEM-EDS analysis

SEM-EDS was applied to the solid products for 1) getting an image of the material, confirming its fibrous structure and its suitability as a TES material and 2) measuring levels of contamination with for example sulfur or alkali salts.

SEM pictures for aqueous ammonia experiment can be seen in Figure 5. SEM pictures for NaOH experiment can be seen in Figure 6. The pictures for KOH experiment can be seen in Figure 7. Shown are the three products from the 20, 30, 35 and 40 °C experiments respectively.

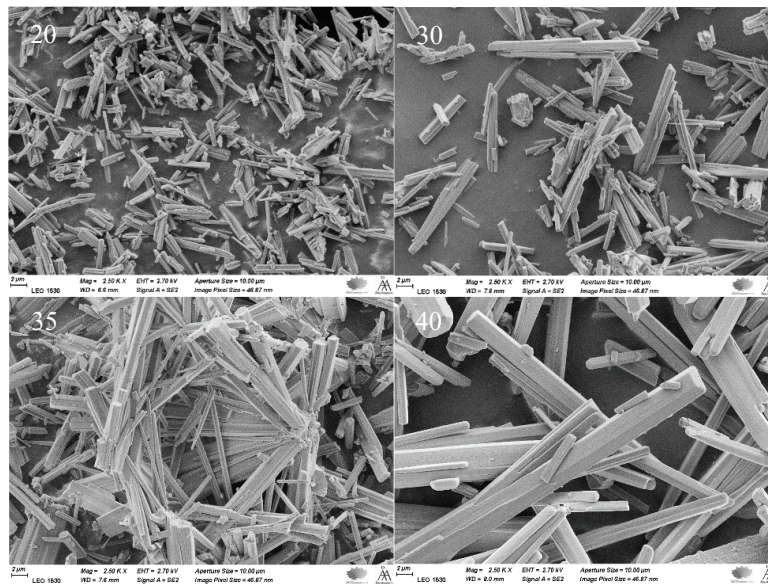


Figure 5: SEM images of NQ formed using NH₄OH at 20, 30, 35 and 40 °C

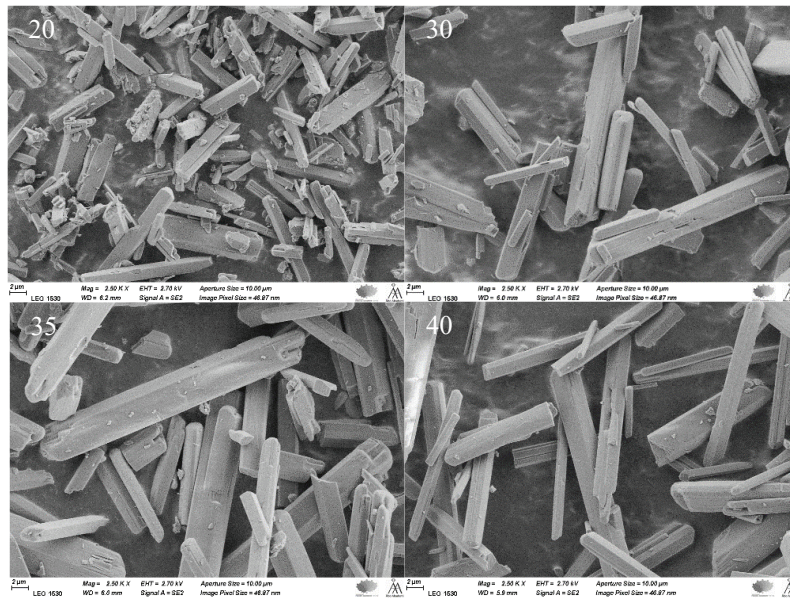


Figure 6: SEM images of NQ formed using NaOH at 20, 30, 35 and 40 °C

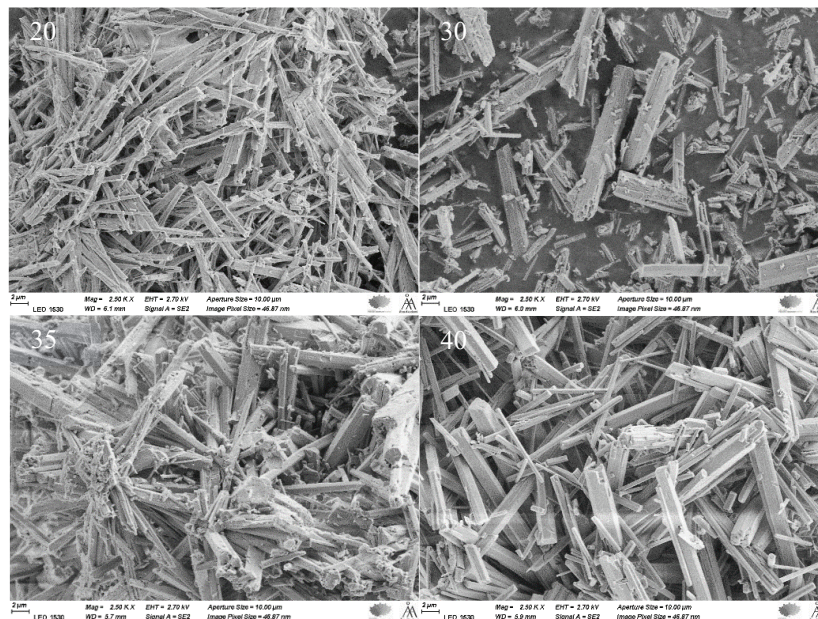


Figure 7: SEM images of NQ formed using KOH at 20, 30, 35 and 40 °C

In the NH_4OH experiments one can observe that the crystals seem to grow both longer and wider as temperature increases. This did not, however, translate into a higher yield in the 40 °C experiment compared with the 35 °C experiment. The SEM images from the NaOH experiments suggests that the temperature does not play a critical role in crystal length or width. Furthermore, the yields were close to each other for the 30, 35 and 40 °C experiments compared with the NH_4OH and KOH experiments.

4.2 XRD analysis

XRD analysis on the samples is shown for NH_4OH , NaOH and KOH as the pH raise agent, respectively, given in Figures 8, 9 and 10, respectively.

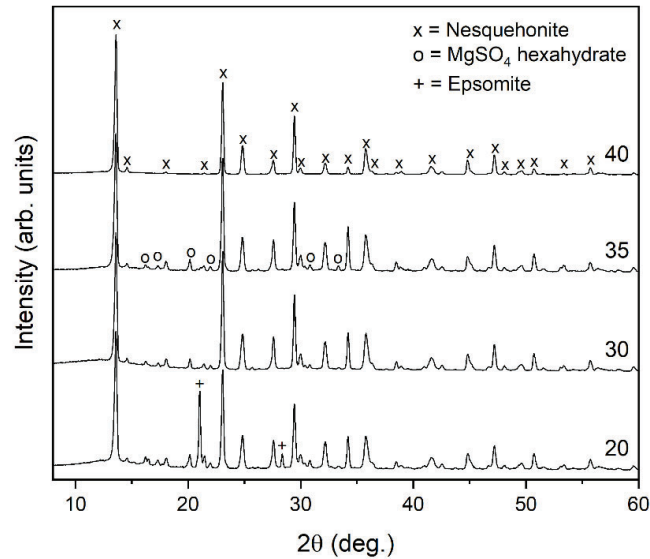


Figure 8: XRD spectra of NQ formed using NH_4OH at 20, 30, 35 and 40 °C

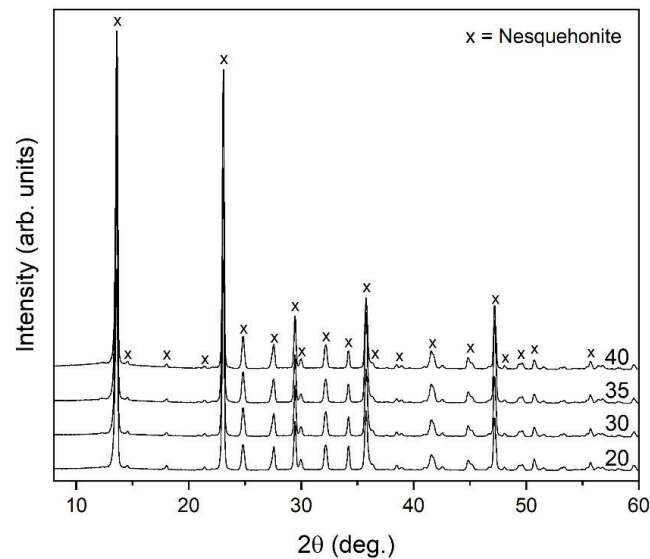


Figure 9: XRD spectra of NQ formed using NaOH at 20, 30, 35 and 40 °C

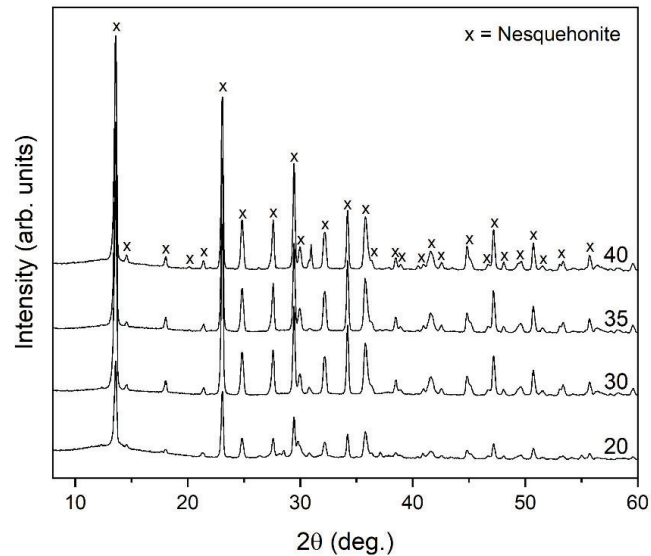


Figure 10: XRD spectra of NQ formed using KOH at 20, 30, 35 and 40 °C

While the XRD spectra do not indicate significant levels of impurities for most of the products, with the exception being the 20, 30 and 35 °C NH_4OH experiments, SEM-EDS does give information on concentrations of sulfur and other elements present in the carbonation reactor. Table 4 lists this for the NQ products from the three test series.

Table 4: Results from SEM-EDS elemental analysis on the NQ samples

No.	Sulfur S (%-wt)	Alkali, Na or K (%-wt)	Mg (%-wt)	Mg to S ratio (kg/kg)
1-1	0.41		7.30	17.80
1-2	0.12		2.11	17.58
1-3	0.30		4.49	14.97
1-4	-		6.58	-
2-1	0.27		22.43	83.07
2-2	-		23.71	-
2-3	-		24.75	-
2-4	-		23.85	-
2-5	-		24.36	-
3-1	0.38	3.83	23.65	62.23
3-2	0.32	0.38	25.54	79.81
3-3	0.37	0.62	24.86	67.19
3-4	0.36	0.31	23.19	64.41
3-5	N/A	N/A	N/A	N/A

The 3-5 sample was not taken to SEM-EDS analysis. The elemental analysis gives an indication about the purity of the products. However, the instrument also gathers information about the background tape that the sample is glued to, to stay in place in the microscope which introduced carbon to the analysis system. Therefore, carbon is overrepresented in the SEM-EDS analysis and not given in the table, Table 4. Hydrogen, H – which is present in the NQ crystal in the crystal water – is not detected by the SEM-EDS and are thus excluded from the analysis.

The sulfur in experiments 1-1, 1-2 and 1-3 are bound in MgSO_4 , in its hexa- and heptahydrate (epsomite) forms, as can be concluded from the XRD analysis.

It was feared that the high pH from the first pH raise in experiment 3-1 would induce the precipitation of magnesium hydroxide ($\text{Mg}(\text{OH})_2$) rather than NQ, but this was not observed in the SEM or in the XRD. When it comes to purity, the NaOH seems to give the purest product with no sulfur or sodium residue.

4.3 Heat-up test

An earlier produced NQ was heated up in an oven at 80 and 120 °C. The samples were kept at 80 °C for 1 h and then at 120 °C for 14 h. The mass losses are given in Table 5.

Table 5: results from oven experiment

Temperature (°C)	Retention time (h)	Mass loss (%)
80	1	11.4
120	12	30.2

Three samples were taken for SEM and XRD analysis, the NQ before the oven experiment, a sample that had undergone the oven treatment at 80 °C for 1 h and a sample that had undergone the oven treatment at 120 °C for 14 h. The SEM pictures can be seen in Figure 11 and the XRD results in Figure 12.

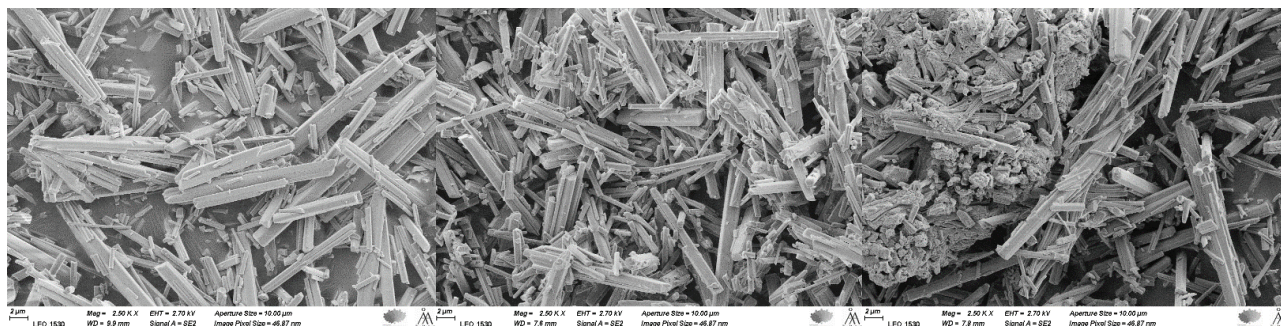


Figure 11: SEM pictures of the NQ before the oven experiment and after the 80 °C and 120 °C experiment respectively

The NQ crystal does not seem to lose its structure or form, even after 120 °C for 14 h. In the last picture one can see some impurities on the left side of the picture.

Interestingly, while studying how stable the NQ structure is during a heat-up, the XRD suggests a loss of structure, towards an amorphous material while SEM pictures on the heated samples do not show any significant changes compared to the 35 °C produced material.

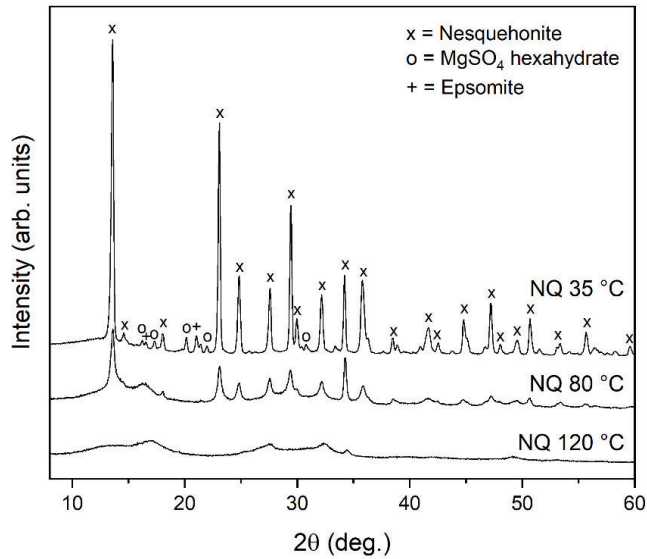


Figure 12: XRD analysis of the NQ before the oven experiment and after the 80 °C and 120 °C experiment respectively

The mass of the crystal water in NQ is 39.1 %. There are three crystal water molecules per NQ molecule. As only 30.4 % of the mass has disappeared after the oven experiment one can conclude that not all crystal water has disappeared. A TGA analysis was made on the NQ with a heat-up rate of 10°C/min. The max temperature of the TGA test was 555 °C with a runtime of 80 minutes. The results are presented in Figure 13.

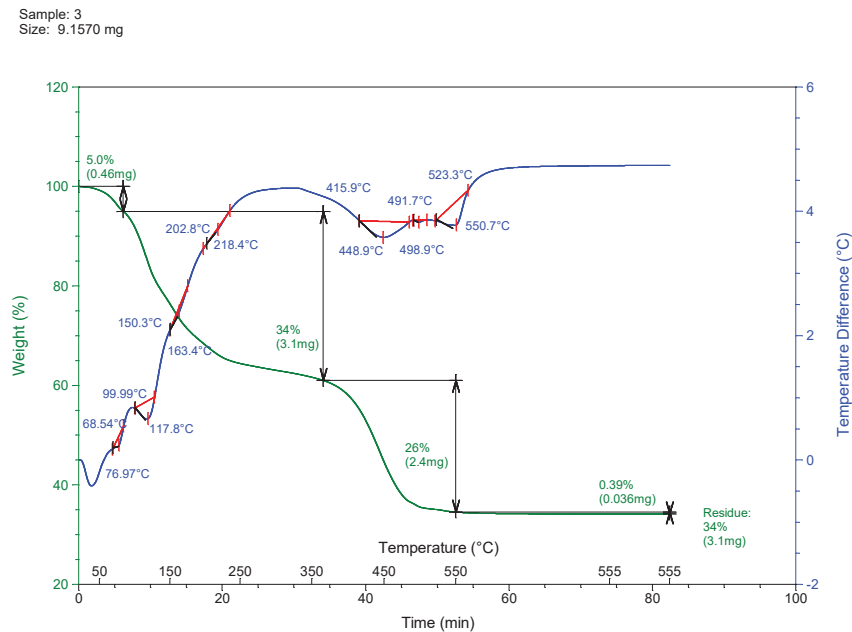


Figure 13: TGA analysis of the NQ product

It seems that all the water has been released from the NQ after 350 °C, totalling to 39 % of the original mass. After that CO₂ starts exiting the NQ. The mass of the bound CO₂ should be 31.8 %, however the TGA only shows a mass loss of 26 % between 350 °C and 555 °C. This suggests that not all CO₂ exited the crystals or there are some impurities in the sample.

5 CONCLUSIONS

The main conclusions from the experiment series can be concluded as the following bullet items:

- KOH seems to be a good agent for the pH rise since it buffers the solution, and it is thus easier to keep the pH at desired level
- KOH as pH agent gives the highest yields compared to NH₄OH and NaOH
- NaOH as pH agent gives the cleanest (most pure) NQ products while the NH₄OH as a pH raiser does not seem to manage to transform all Mg to NQ, but some Mg is still present as MgSO₄, in its hexa- and heptahydrate forms.

Thus, it appears attractive and feasible to use NaOH or KOH as the pH raise agent instead of NH₄OH but it needs to be confirmed (ongoing work) that the BPMED system can produce the needed NaOH and KOH from the Na₂SO₄ or K₂SO₄ solution that remains after filtration of the NQ product.

For future work, tests with mixtures of NH₄OH with KOH or NH₄OH with NaOH are planned since NH₄OH and the two other salts both have beneficial effects on NQ formation and the downstream processing of the solution using BPMED. Soon the focus of the work will return to the use of the NQ for TES application, proceeding with the work started at our lab by R. Erlund.

NOMENCLATURE

BPMED	Bipolar membrane electrodialysis
CCU	Carbon capture and utilization
CSM	Carbon capture and storage by mineralization
NQ	Nesquehonite
SEM-EDS	Scanning electron microscope - Energy dispersive X-ray spectroscopy
TES	Thermal energy storage
XRD	X-ray diffraction

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