Δελτίο της Ελληνικής Γεωλογικής Εταιρίας, τόμος L, σελ. 2009-2017
Πρακτικά 14ου Διεθνούς Συνεδρίου, Θεσσαλονίκη, Μάιος 2016

Bulletin of the Geological Society of Greece, vol. L, p. 2009-2017
Proceedings of the 14th International Congress, Thessaloniki, May 2016

MINERALOGICAL AND SPECTROSCOPIC STUDY OF NESQUEHONITE SYNTHESIZED BY REACTION OF GASEOUS CO_2 WITH MG CHLORIDE SOLUTION

Skliros V.[1], Anagnostopoulou A.[2], Tsakiridis P.[1] and Perraki M.[1]

[1] *National Technical University of Athens, School of Mining* and *Metallurgical Engineering, 15780, Athens, Greece, sklirosbill@metal.ntua.gr, ptsakiri@metal.ntua.gr, maria@metal.ntua.gr*

[2] *Hellenic Open University, School of Science* and *Technology, 26 335, Patra, Greece, kanagnostopoulou@windowslive.com*

Abstract

Nesquehonite, a hydrous carbonate with promising uses such as building raw material and *treatment of wastewaters, was synthesized under low pressure conditions by reaction of gaseous CO_2 with Mg chloride solution* and *it was studied by means of X-Ray Diffraction, optical* and *scanning/transmission electron microscopy,* and *FT-IR* and *Raman spectroscopic methods. Synthesized nesquehonite forms elongated fibers, exhibiting transparent to translucent diaphaneity* and *vitreous luster. It is characterized by high crystallinity. IR* and *Raman spectroscopy indicated the presence of OH^-* and *HCO_3^- in the crystal structure of nesquehonite. The nesquehonite synthesis described herein constitutes a potential permanent storage of CO_2 emissions.*

Keywords: *nesquehonite, hydrous magnesium carbonate, low-pressure mineralization, CO2 storage.*

Περίληψη

Στην παρούσα εργασία πραγματοποιήθηκε η σύνθεση νεσκεχονίτη, ενός ένυδρου ανθρακικού ορυκτού, υπό χαμηλές συνθήκες πίεσης με αντίδραση CO_2 σε διάλυμα χλωριούχου μαγνησίου. Ο νεσκεχονίτης μπορεί να αξιοποιηθεί ως πρώτη ύλη σε δομικά υλικά και επιπλέον στην διαχείριση υγρών αποβλήτων. Ο νεσκεχονίτης μελετήθηκε με περιθλασιομετρία ακτίνων-X, υπέρυθρη φασματοσκοπία (FT-IR) και φασματοσκοπία Raman, διοφθάλμιο στερεοσκόπιο, Ηλεκτρονικό Μικροσκόπιο Σάρωσης και Ηλεκτρονικό Μικροσκόπιο Διερχόμενης Δέσμης Ηλεκτρονίων. Ο παραγόμενος νεσκεχονίτης αναπτύσσει επιμήκεις διαφανείς έως ημιδιαφανείς βελονοειδείς κρυστάλλους με υαλώδη λάμψη. Η υπέρυθρη φασματοσκοπία (FT-IR) και η φασματοσκοπία Raman υπέδειξαν την παρουσία OH^- και HCO_3^- στην κρυσταλλική δομή του νεσκεχονίτη. Η διαδικασία σύνθεσης που περιγράφεται στην παρούσα εργασία μπορεί να χρησιμοποιηθεί στην διαδικασία της ορυκτοποίησης για μόνιμη αποθήκευση των εκπομπών CO_2.

Λέξεις κλειδιά: *νεσκεχονίτης, ένυδρο ανθρακικό ορυκτό του μαγνησίου, ορυκτοποίηση, αποθήκευση του διοξειδίου του άνθρακα.*

1. Introduction

Nesquehonite is a magnesium carbonate mineral with proposed chemical formula either $MgCO_3*3H_2O$ (Kloprogge *et al.*, 2003; Dong *et al.*, 2009; Stephan and McGillavry, 1972) or $Mg(OH)(HCO_3)*2H_2O$ (Hales *et al.*, 2008; Hales *et al.*, 2008; Frost and Palmer, 2011), named after a location in Pennsylvania, USA, where found for first time. It is crystallized in the monoclinic crystal structure in space group P21/n, Z = 4 and it has unit cell parameters of a = 7.70Å, b = 5.37Å, c = 12.12 Å and $\beta = 90^o$, 45΄as described by Stephan and MacGillavry (1972) and by Giester *et al.* (2000). Its structure consists of infinite flat ribbons of corner-sharing MgO_6 octahedra (Fig. 1a) along the b axis of the crystal, which is the fiber axis, linked by hydrogen bonds and contains only one crystallographically inequivalent carbon (Fig.1b). Within the chains, CO_3 groups link three MgO_6 octahedra by one edge and two common corners. The Mg atoms are in a distorted coordination, and each atom is coordinated by two H_2O ligands; one free H_2O molecule is located between the chains as shown in Figure 2 (Wang *et al.*, 2008; Ferrini *et al.*, 2009; Ballirano *et al.*, 2009; Giester *et al.*, 2000; Moore *et al.*, 2015; Stephan and McGillavry, 1972). In Greece, natural nesquehonite has been reported in Lavrion (Giester *et al.*, 2000).

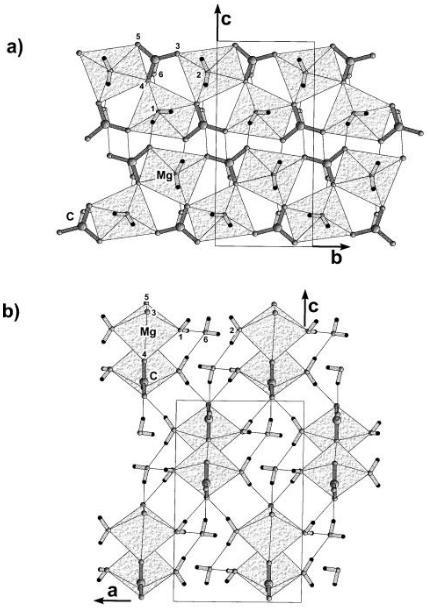

Figure 1 – Crystal structure of nesquehonite in projections parallel to a [100] and b [010] (Giester *et al.*, 2000).

Nesquehonite exhibits promising uses as a raw material of magnesium cement (Ferrini *et al.*, 2009) as well as in wastewater treatment (Shan *et al.*, 2013). Besides, recent studies showed that nesquehonite can be the product of CO_2 mineralization under low pressure conditions (Ferrini *et al.*, 2009; De Vito *et al.*, 2012). Given that nowadays, the reduction of CO_2 emissions has become a first priority for all industrial activities, CO_2 mineralization, i.e. CO_2 carbonation, constitutes one of the main carbon capture and sequestration (CSS) methods (Verduyn, 2011). Whereas, first studies dealt with the laboratorial reaction of CO_2 with the Mg-rich minerals of ultramafic rocks under high pressure conditions to form pure magnesite (Lackner *et al.*, 1995) followed by studies on the in-situ storage of high pressure CO_2 gas in ophiolite complexes (Kelemen and Matter, 2008; Kelemen *et al.*, 2011), an increasing interest on CO_2 mineralization under low pressure conditions is coming up (Ferrini *et al.*, 2009; De Vito *et al.*, 2012). Apart from the synthesis procedure, of great interest is the detailed characterization of the synthesized nesquehonite.

In this work, nesquehonite was synthesized under low pressure conditions by reaction of gaseous CO_2 with Mg chloride solution and its characterization was carried out by means of X-Ray Diffraction, optical and scanning/transmission electron microscopy, and FT-IR and Raman spectroscopic methods.

2. Materials and Methods

1.1 Analytical methods

X-Ray Diffraction patterns were obtained with a Bruker D8 Focus diffractometer in a θ-θ configuration employing CuKα radiation ($\lambda = 1.5406$ Å) with a fixed divergence slit size of 0.5° and a rotating sample stage. The samples were scanned between 4 and 70° 2θ. The step size and time per step were set to 0.017° 2θ and 80 s, respectively. Stereoscopic study was carried out under a Leica MZ8 binocular stereoscope. Scanning Electron Microscopy (SEM) was performed using a JEOL 6380LV-SEM equipped with an Oxford EDS-WDS. Transmission Electron Microscopy was performed with a JEOL 2100 HR–TEM at 200kV. A Fourier-transform infrared FT-IR spectrophotometer, Perkin Elmer Spectrum GX, and a Renishaw's inVia-micro-RAMAN (532 nm excitation laser wavelength) were employed to obtain additional information on nesquehonite composition and structure.

1.2 Synthesis of Nesquehonite

Nesquehonite was synthesized at laboratory conditions by using a gas cylinder of CO_2 and chemical reagents $MgCl_2*6H_2O$ and $NaHCO_3$. 80g $MgCl_2*6H_2O$ were dissolved into 500 ml of dionized water. CO2 gas was then introduced into the solution at pressure of 0.1kbar under continuous magnetic stirring at 1100rpm. A solution of 60g $NaHCO_3$ was added by using peristaltic pump. CO_2 gas was continually added into the solution for an hour under stirring. After that, the solution was left to precipitate for 24 hours. During the experiment solution temperature was kept stable at 25 ^oC. The chemical reaction that took place was

$$MgCl_2*6H_2O + 2NaHCO_3 + 3CO_2 \rightarrow MgCO_3*3H_2O + 2NaCl + 4H_2CO_3$$

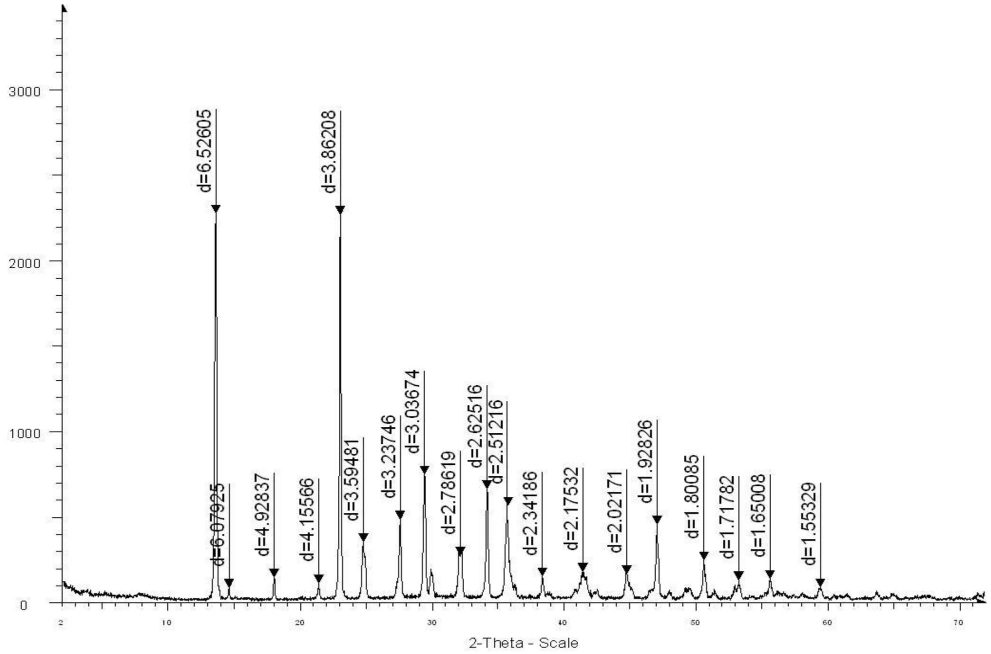

Figure 2 - XRD pattern of the nesquehonite synthesized herein.

The precipitated nesquehonite was then separated from the solution by using a vacuum pump and suitable paper filters and washed out with dionized water to dissolve any salts that might have been remained. Moisture was removed from the sample by putting it into an oven at 50°C for 24 hours.

3. Results and Discussion

As can been seen in the representative XRD diagram (Fig. 2) the produced precipitate is pure nesquehonite, with characteristic peaks at d= 6.52, 3.86, 3.04, 2.62, 2.51 and 1.92 Å, which corresponds to [-101], [200], [-211], [021], [-301] and [400] Miller indices (Stephan and McGillavry, 1972).

Nesquehonite formed as a white precipitate. Study under the binocular stereoscope, showed that it exhibits transparent to translucent diaphaneity and vitreous luster and it forms elongated fibers (Fig. 3).

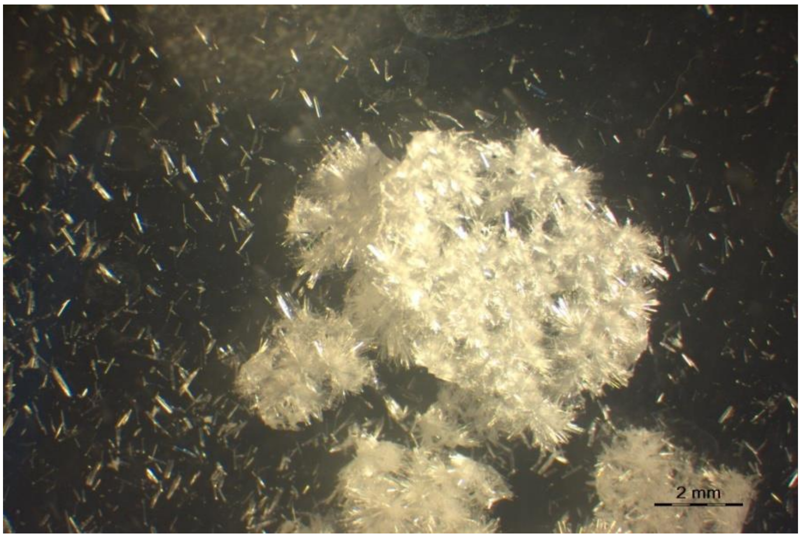

Figure 3 – Stereoscopic view of the nesquehonite synthesized herein.

Scanning Electron Microscopy (SEM) showed that nesquehonite fibers were developed around a centerpiece creating a structure called rosettes (Fig. 4). EDS point analyses (Fig. 5) showed the presence of only one chemical phase; any salts might have been removed during the sample preparation.

Transmission Electron Microscopy (TEM) study showed that nesquehonite is highly crystalline (Fig. 6). The Selected Area Diffraction (SAED) pattern (Fig.7) confirms the high crystallinity of the nesquehonite crystals and the absence of any amorphous phase (Egerton, 2005).

Fourier-Transform Infrared (FTIR) and Raman analyses were performed in the samples, to obtain additional information on their chemistry and structure. IR spectra (Fig. 8) showed the symmetric stretching (*v1*) and the bending (*v2*) modes of CO_3^{2-} at 1097.94 cm^{-1} and at 853.61 cm^{-1}, respectively. The three bands at 1520, 1466.06, 1420.06 cm^{-1} are ascribed to the split *v3* antisymmetric stretching mode (Kloprogge *et al.*, 2003; Coleyshaw *et al.*, 2003; Morgan *et al.*, 2015).The stretching of the O-H and the H_2O molecule gives rise to broad bands in the region between 2500-4000 cm^{-1} (Ferrini *et al.*, 2008; Kloprogge *et al.*, 2003). The bands at 3326.33, 3455.14, 3564.25 cm^{-1} can be ascribed to OH-stretching modes of water in the crystal structure of the nesquehonite (Hopkinson *et al.*, 2012; Hopkinson *et al.*, 2008). At 1653.43 cm^{-1} a H-O-H bending band is observed, which is associated with structural H_2O (Lanas and Alvarez, 2004; Hopkinson *et al.*, 2008; Hopkinson *et al.*, 2012) and absorbed H_2O (Kloproggre *et al.*, 2003).

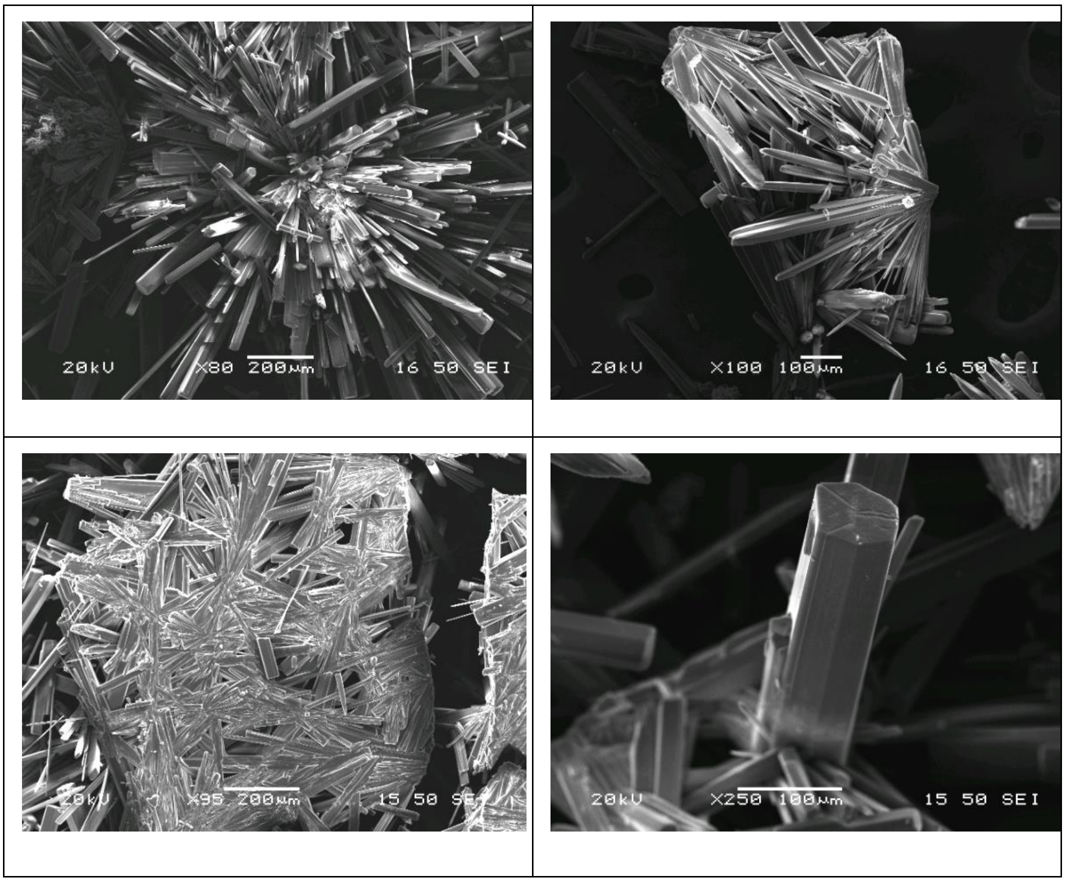

Figure 4 – Secondary electron (SE) images of nesquehonite showing prismatic crystals in the form of rosettes.

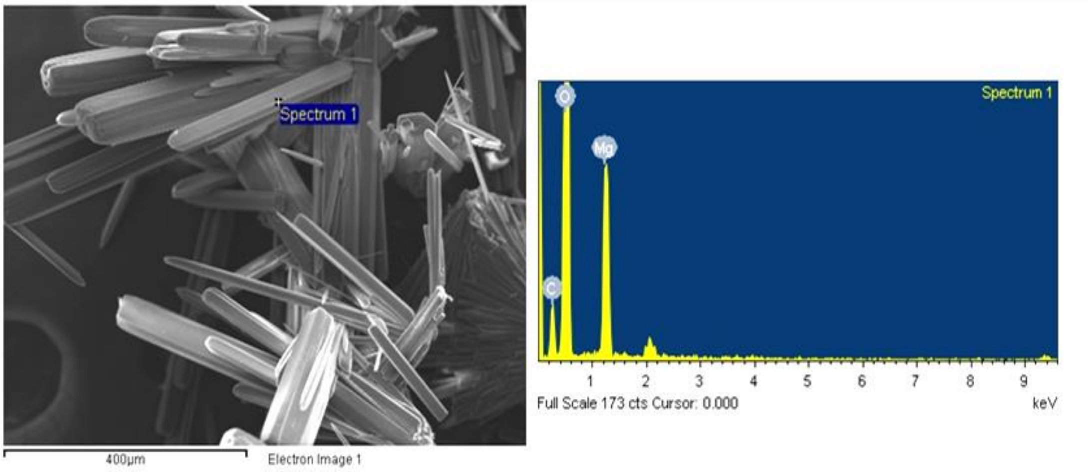

Figure 5 – Nesquehonite SE image (left) and the respective EDS spectrum (right), showing the presence of a magnesium carbonate mineral phase.

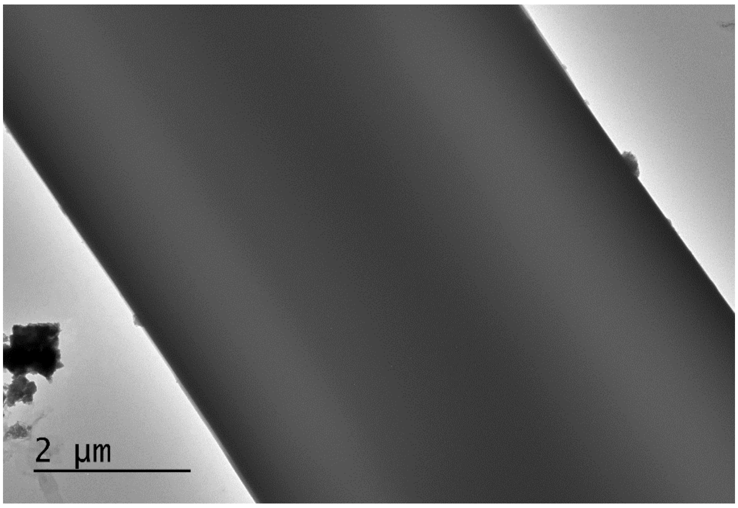

Figure 6 – TEM image showing the highly crystalline structure of the nesquehonite sample.

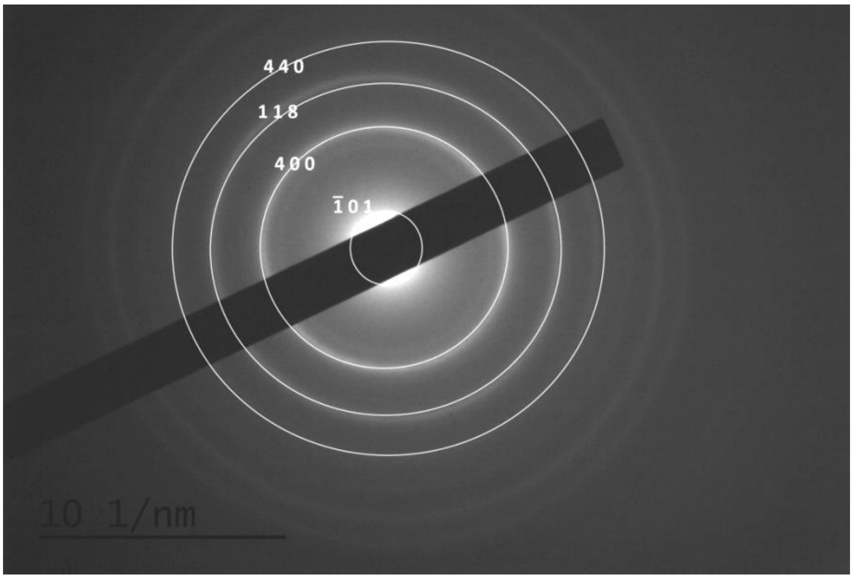

Figure 7 – SAED pattern of nesquehonite crystal indicating a highly crystalline structure. Each ring is created by Hall Effect and is assigned to d-spacing values which correspond to a certain set of hkl, compared with the diffraction data from literature (Egerton, 2005; American Mineralogy Crystal Structure Database; Stephan and McGillavry, 1972).

The two peaks observed at 699.97 cm^{-1} and 607.12 cm^{-1} are assigned to the *v4* in-plane bending mode of the HCO_3^- (Hales *et al.*, 2008; Frost and Palmer, 2011).

Raman spectra showed a very strong vibration at 1100 cm^{-1} (Fig. 9) that is ascribed to the *v1* symmetric stretching vibration of the CO_3^{2-} (Hales *et al.*, 2008). The peak at 1515 cm^{-1} (Fig. 9) corresponds to *v1* antisymmetric stretching vibration of CO_3^{2-} and appears less intense. The two bands at 3123 cm^{-1}(Fig. 9) and 3444 cm^{-1}(Fig. 10) are assigned to the stretching vibration of H_2O molecules. The peak at 3556 cm $^{-1}$ (Fig. 10) corresponds to the vibration tendency of O-H hydroxyl. The vibration at 1423 cm^{-1} (Fig. 9) is ascribed to the antisymmetric stretching of the HCO_3^- (Hales *et al.*, 2008; Frost and Palmer, 2011).

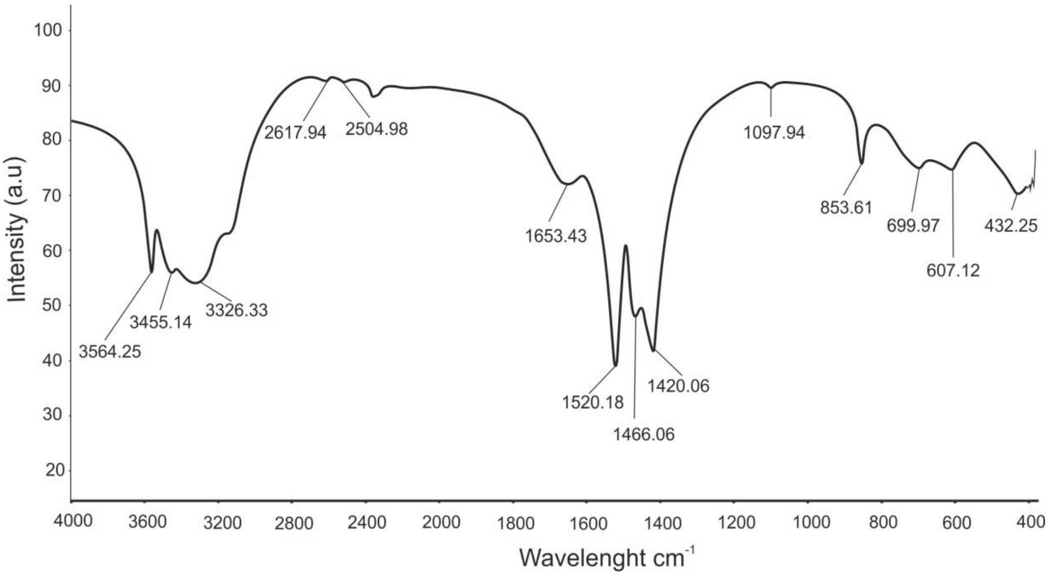

Figure 8 – FTIR spectrum of the nesquehonite synthesized herein.

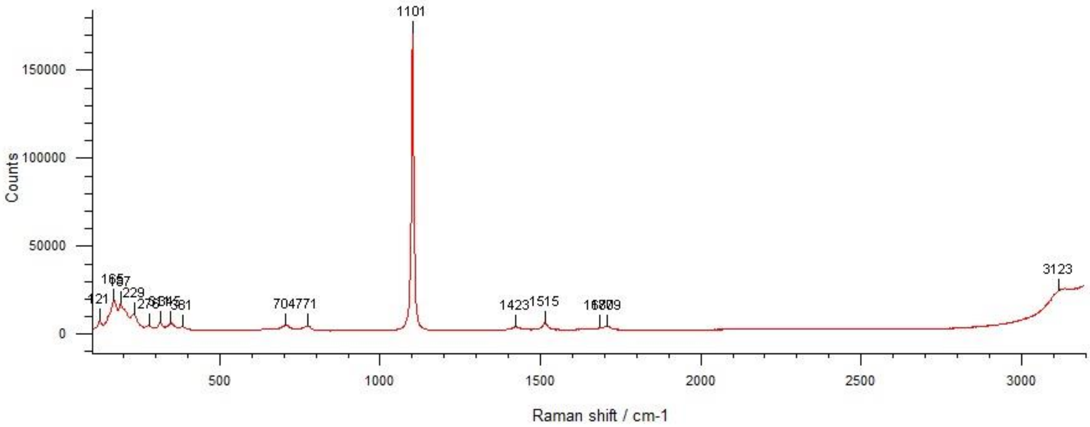

Figure 9 – Raman spectrum of the nesquehonite synthesized herein, from 50-3200 cm^{-1} wavelengths.

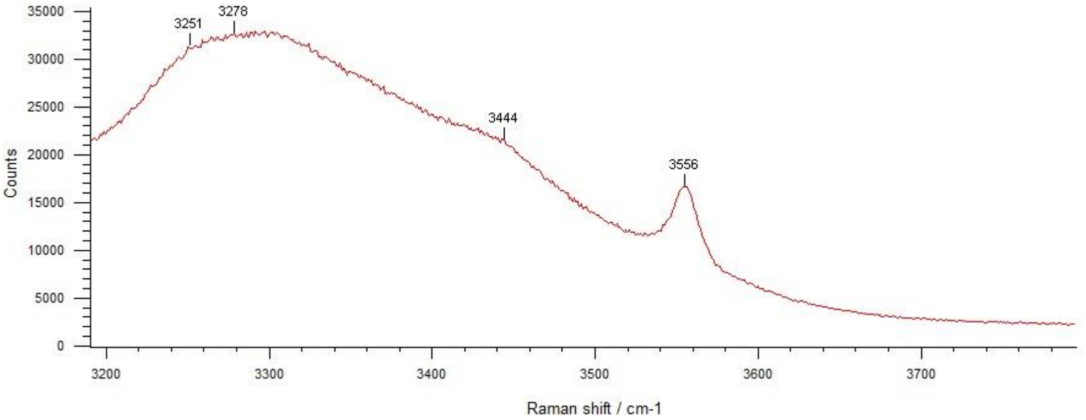

Figure 10 – Raman spectrum of the nesquehonite synthesized herein, from 3200-4000 cm^{-1} wavelengths.

Nesquehonite has a chemical composition of $MgCO_3$*$3H_2O$ (Kloprogge *et al.*, 2003; Dong *et al.*, 2009; Stephan and McGillavry, 1972), but has been described also as $Mg(OH)(HCO_3)$*$2H_2O$ (Hales *et al.*, 2008; Hales *et al.*, 2008; Frost and Palmer, 2011). Our IR and Raman results showed the presence of OH^- and HCO_3^- in the crystal structure of nesquehonite.

4. Conclusion

Nesquehonite, a hydrous carbonate, was synthesized under low pressure conditions by reaction of gaseous CO_2 with Mg chloride solution. Detailed study by means of X-Ray Diffraction, optical and scanning/transmission electron microscopy, and FT-IR and Raman spectroscopic methods showed that the synthesized nesquehonite

- forms elongated fibers developed as rosettes around of centerpieces with transparent to translucent diaphaneity and vitreous luster
- exhibits high crystallinity
- is characterized by the presence of OH^- and HCO_3^- in its crystal structure.

Nesquehonite is a thermodynamically and chemically stable solid product. The nesquehonite synthesis described herein is simple, fast and environmentally friendly and it constitutes a potential long-term CO_2 storage method. It might be applied in larger/industrial scale with the aim to capture and permanent store CO_2 emissions.

5. References

Ballirano, P., De Vito, C., Ferrini, V. and Mignardi, S., 2010. The thermal behaviour and structural stability of nesquehonite, MgCO3·3H2O, evaluated by in situ laboratory parallel-beam X-ray powder diffraction: New constraints on CO2 sequestration within minerals, *Journal of hazardous materials*, 178(1-3), 522-528.

Coleyshaw, E., Crump, G. and Griffith, W., 2003. Vibrational spectra of the hydrated carbonate minerals ikaite, monohydrocalcite, lansfordite and nesquehonite, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 59(10), 2231-2239.

De Vito, C., Ferrini, V., Mignardi, S., Cagnetti, M. and Leccese, F., 2012. Progress in carbon dioxide sequestration via carbonation of aqueous saline wastes, *Periodico di Mineralogia*, 81(3), 333-344.

Dong, M., Li, Z., Mi, J. and Demopoulos, G.P., 2009. Solubility and stability of nesquehonite ($MgCO_3 \cdot 3H_2O$) in mixed NaCl + $MgCl_2$, NH_4Cl + $MgCl_2$, LiCl, and LiCl + $MgCl_2$ solutions, *Journal of Chemical* and *Engineering Data*, 54(11), 3002-3007.

Egerton, R., 2005. Physical Principles of Electron Microscopy. Boston, MA, Springer Science and Business Media, Inc.

Ferrini, V., De Vito, C. and Mignardi, S., 2009. Synthesis of nesquehonite by reaction of gaseous CO_2 with Mg chloride solution: Its potential role in the sequestration of carbon dioxide, *Journal of hazardous materials*, 168(2-3), 832-837.

Frost, R.L. and Palmer, S.J., 2011. Infrared and infrared emission spectroscopy of nesquehonite $Mg(OH)(HCO_3)\cdot 2H_2O$-implications for the formula of nesquehonite, *Spectrochimica Acta - Part A: Molecular* and *Biomolecular Spectroscopy*, 78(4), 1255-1260.

Giester, G., Lengauer, C.L. and Rieck, B., 2000. The crystal structure of nesquehonite, $MgCO_3$ $3H_2O$, from Lavrion, Greece, *Mineralogy* and *Petrology*, 70(3-4), 153-163.

Hales, M.C., Frost, R.L. and Martens, W.N., 2008. Thermo-Raman spectroscopy of synthetic nesquehonite - Implication for the geosequestration of greenhouse gases, *Journal of Raman Spectroscopy*, 39(9), 1141-1149.

Hopkinson, L., Kristova, P., Rutt, K. and Cressey, G., 2012. Phase transitions in the system MgO-CO_2-H_2O during CO_2 degassing of Mg-bearing solutions, *Geochimica et Cosmochimica Acta*, 76, 1-13.

Hopkinson, L., Rutt, K. and Cressey, G., 2008. The transformation of nesquehonite to hydromagnesite in the system CaO-MgO-H_2O-CO_2: An experimental spectroscopic study, *Journal of Geology*, 116(4), 387-400.

Kelemen, P.B. and Matter, J., 2008. In situ carbonation of peridotite for CO_2 storage, *Proceedings of the National Academy of Sciences of the United States of America*, 105(45), 17295-17300.

Kelemen, P.B., Matter, J., Streit, E.E., Rudge, J.F., Curry, W.B. and Blusztajn, J., 2011. Rates and mechanisms of mineral carbonation in peridotite: Natural processes and recipes for enhanced, in situ CO2 capture and storage.

Kloprogge, J.T., Martens, W.N., Nothdurft, L., Duong, L.V. and Webb, G.E., 2003. Low temperature synthesis and characterization of nesquehonite, *Journal of Materials Science Letters*, 22(11), 825-829.

Lackner, K.S., Wendt, C.H., Butt, D.P., Joyce Jr., E.L. and Sharp, D.H., 1995. Carbon dioxide disposal in carbonate minerals, *Energy*, 20(11), 1153-1170.

Lanas, J. and Alvarez, J.I., 2004. Dolomitic lime: Thermal decomposition of nesquehonite, *Thermochimica Acta*, 421(1-2), 123-132.

Moore, J., Surface, J., Brenner, A., Skemer, P., Conradi, M. and Hayes, S., 2015. Quantitative Identification of Metastable Magnesium Carbonate Minerals by Solid-State 13 C NMR Spectroscopy, *Environmental Science and Technology*, 49(1), 657-664.

Morgan, B., Wilson, S.A., Madsen, I.C., Gozukara, Y.M. and Habsuda, J., 2015. Increased thermal stability of nesquehonite ($MgCO_3 \cdot 3H_2O$) in the presence of humidity and CO_2: Implications for low-temperature CO2 storage, *International Journal of Greenhouse Gas Control*, 39, 366-376.

American Mineralogist Crystal Structure Database, 2015. Available online at: http://rruff.geo.arizona.edu/AMS/amcsd.php [Accessed 6 Oct. 2015].

Shan, Q., Zhang, Y. and Xue, X., 2012. Removal of copper from wastewater by using the synthetic nesquehonite, *Environental Progress and Sustainable Energy*, 32(3), 543-546.

Stephan, G. and MacGillavry, C., 1972. The crystal structure of nesquehonite, $MgCO_3.3H_2O$, *Acta Crystallographica Section B*, 28(4), 1031-1033.

Verduyn, M., Geerlings, H., Van-Mossel, G. and Vijayakumari, S., 2011. Review of the various CO_2 mineralization product forms, *Energy Procedia*, 2885.

Wang, Y., Li, Z. and Demopoulos, G.P., 2008. Controlled precipitation of nesquehonite ($MgCO_3 \cdot 3H_2O$) by the reaction of MgCl2 with $(NH4)_2CO_3$, *Journal of Crystal Growth*, 310(6), 1220-1227.