THE INTERNATIONAL JOURNAL OF
SCIENCE & TECHNOLEDGE

# In presence of EDTA and HEDP Blended, the Crystal Growth, Polymorphism, and Morphology of $CaCO_3$ under $Co_2$ Atmosphere

**S. Bhuvaneswari**
Lecturer, Govt. Arts College, Tindivanam, Tamil Nadu, India
**K. Subramani**
Reader, Issalamiya College, Vaniyampady, Tamil Nadu, India
**V. K. Subramanian**
Assistant Professor, Annamalai University, Tamil Nadu, India
**K. Palanisamy**
Ph. D. Scholar, Annamalai University, Tamil Nadu, India

***Abstract:***
*Polymorphic compositions of CaCO3 synthesized under the influence of a blended system of EDTA and HEDP between 60, 80 ,100 °C using a controlled precipitation technique from CaCl2 solution using co2 gas from Inox cylinder, has been investigated. The phases and structures of the samples were characterized by FTIR, and powder XRD techniques. The morphological studies were carried out using SEM, scanning electron microscope, . Usually, at higher temperatures vaterite and aragonite are transformed into stable calcite. Here, we report the stabilization of metastable aragonite and least stable vaterite in the presence of a blended system of EDTA and HEDP. .At 10ml and 20ml at 100c, We also report a novel morphology, rose like structure for vaterite ,(button rose) which is not reported earlier.*

## 1. Introduction

In recent years, design and synthesis of calcium carbonate (CaCO 3) one of the most abundant natural inorganic mineral has gained much importance due to its wide range of applications in cosmetics, medicines, controlling biomineralization, and so forth.[i–iii] It is also one of the most predominant components of scale found in boiler tubes and in heat exchangers.[iv–vii] .Generally, $CaCO_3$ exists in three crystalline polymorphic forms, in the order of increasing stability: vaterite, aragonite, and calcite. The crystalline structures of these phases are rhombohedral orthorhombic, and hexagonal for calcite, aragonite, and vaterite, respectively.[viii,ix] Traditional strategies for the control of polymorphs often involve changing solvents, temperature, pH and other growth conditions, usage of polymer additives, and so forth.[x,xi] Because different polymorphic forms of same substance have different properties, polymorphism plays an important role in controlling the scale formation using chelating agents or other chemicals used in internal treatment. For example, it is obvious from literature that the predominant polymorphic form of calcium carbonate in scale is calcite and vaterite is seldom present.[xii–xiv] Polymorphism of CaCO3 precipitated in a constant composition environment has been reported by Tai et al. They have reported that the solution pH and temperature are the most important factors that determines which polymorphs are obtained.[xv] However, one of the longstanding challenges of crystallization is the ability to predict and control polymorphism. Reports suggests that, in the presence of scale inhibitors, a substantial amount of vaterite and aragonite occur in scale,whereas in the absence of scale inhibitors, calcite is almost the only crystal form. Moreover, for the scale inhibitor with higher inhibition efficiency, more vaterite and aragonite are present in scale.[xiii,xiv] Appearance of a phase is based on the super saturation of that phase under that particular environment and how the dissolution and recrystallization/transf-ormation takes place. The super saturation "σ" proposed by Nielsen and Toft16 is given by σ = (IP/Ksp)1/2 − 1 (where IP is the ionic product, defined as IP = aCa2+ × aCO3 2− for this system, and Ksp is the solubility product of CaCO3). Similarly, the mechanisms of crystallization and transformation of calcium carbonates has been reported by Swada. The study revealed that the transformation from vaterite to calcite proceed by a recrystallization process.[xvii] Many studies have investigated the influence of additives on the crystallization of CaCO3.[xviii–xx] Most of the methods reported in the literature employed precipitation of CaCO3 under the influence of a single chelating agent/additive.[xxi–xii] To the best of our knowledge, study on the synergistic effect using a blended system of two or more additives to control the CaCO3 scale at higher temperatures has not been reported yet. As a prelude to this exercise, we have chosen a combination (blended system) of two additives ethylenediaminetetraacetic acid disodium salt (EDTA) and commercial grade1-hydroxyethylidene-1,1-diphosphonic acid (HEDP). Ethylenediaminetetraaceticacid (EDTA) and 1-hydroxyethylidene- 1,1-diphosphonic acid (HEDP) are well-known complexing agents and are widely used as a chelating agent in internal water treatment ormulations.[xiii,xxv–xxvii] EDTA is reported to retard the crystal growth of calcite and aragonite.[xxvii] Aquasoft 330, a commercial grade HEDP is widely used in industries in India and reports are available on its ability to control the morphology of CaCO3 and calcium oxalate. $^{xxvii-xxix}$ The purpose of this study is to understand the effect of a blended system of EDTA and HEDP (Aquasoft 330) on the crystal growth, polymorphism and morphology of CaCO3 between $60^0$ and 100 °C.

## 2. Experimental Section

Analytical grade CaCl2 obtained from Himedia chemicals,disodium salt of EDTA (C10H14N2Na2O8.2H2O) from Qualigens Chemicals and commercial grade 1-hydroxyethylidene-1,1-diphosphonic acid ((HEDP (C2H8O7P2),Aquasoft 330) was obtained from Satyajith Chemicals Pvt Ltd., Mumbai.

| Sample No | Temperature | Additives ml EDTA+HEDP | Time | Initial PH | Final PH |
|---|---|---|---|---|---|
| 1 | 60 | 10 | 10hr | 8.10 | 8.31 |
| 2 | 80 | 10 | 10hr | 8.7 | 8.25 |
| 3 | 100 | 10 | 10hr | 8.9 | 8.45 |
| 4 | 60 | 20 | 10hr | 8.8 | 8.30 |
| 5 | 80 | 20 | 10hr | 8.7 | 8.31 |
| 6 | 100 | 20 | 10hr | 8.6 | 8.29 |
| 7 | 60 | 30 | 10hr | 8.9 | 8.45 |
| 8 | 80 | 30 | 10hr | 8.7 | 8.25 |
| 9 | 100 | 30 | 10hr | 8.9 | 8.45 |

*Table 1: Reaction Conditions, Initial and Final pH of Solutions at Various Temperatures*

The above chemicals were used as supplied without further purification. Double distilled water was used to make all aqueous solutions. A rotamantle with temperature controller, manufactured by Remi was used for experiments below 100 °C.

### *2.1. Synthesis of Samples*

CaCO3 samples were synthesized by using co2 gas from inox air cylinder. ( 80-85) bubbles per minute . In a typical synthesis,200 mL of 0.1 M CaCl2 and 10 mL of 0.1 M EDTA, 10 mL of 0.1 M HEDP were taken in a round-bottom flask and heated to 60 °C using rotamantle with constant stirring. For a system at 60 °C, the sample was aged for 10 h. In practice, it was necessary to provide more time at elevated temperatures. Hence, for experiments at all other temperatures the samples were follow given the above table. After digestion, the samples were filtered through (Whatman 40) filter paper and washed 6−7 times with hot distilled water to remove any residual chelants and dried at 45 °C in a hot air oven. The details of reaction conditions are provided in Table 1. The initial and the final pH of the solution were measured.

;

### *2.2. Characterization*

The composition of the samples was confirmed by Fourier transform infrared spectroscopy (FTIR), and Powder XRD methods and the morphological studies were done using scanning electron microscope (SEM) . FTIR spectra were taken in the range 500 to 4000 cm−1 using Avatar-330 and JASCO-5300, after KBr pelletization. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced XRD diffractometer with Cu Kα radiation at λ = 1.5406 Å with step size of 0.091063. Microscopic morphological images were taken using Philips XL30-ESEM using a beam voltage of 20 kV .

## 3. Results and Discussions

### *3.1. Characterization and Quantitative Estimation Using Powder Diffraction Technique*

The powder XRD pattern and Table 2 represents the polymorphic compositions of the samples determined by Kontoyannis equation.30 It could be observed that a binary mixture of calcite. vaterite and aragonite formed. At 100.C ternary mixture of calcite, vaterite, and aragonite formed . The samples corresponding to 10 ml,20ml at 1oo.c showed peaks corresponding to vaterite with very little aragonite. A significant amount of aragonite was found only at 60 °C. The data indicated that, the trend from aragonite to vaterite is obvious at 60, 80.c (JCPDS-741867). Appearance of aragonite at 80 °C and gradual decrease in its mole fraction with increase in temperature and the steady increase in mole fraction of vaterite between 80 and 100 °C demonstrated that the blended system favours the formation of vaterite at 100, 80, and 60 °C. Calcite was formed only at 60 °C and the mole fraction indicated that its presence is insignificant. The diffraction peaks well matched with JCPDS cards 862339, 760606, and 741867 for calcite, aragonite, and vaterite, respectively. For the phase identification of respective polymorphs, individual XRD spectra are provided with peak values as Supporting Information .

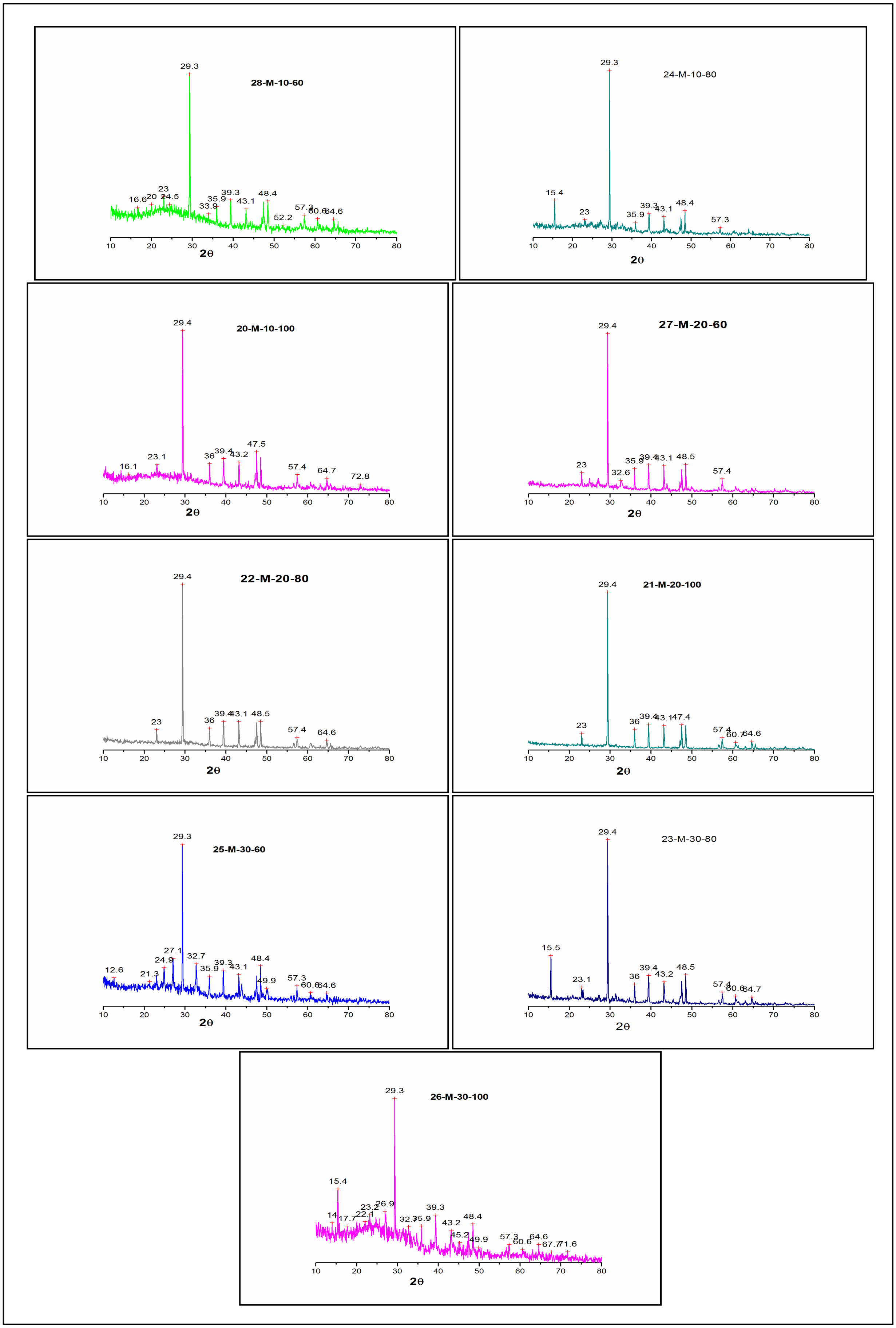


*Figure 1: Samples*

| | With out any additive | | | In the presence of EDTA +HEDP | | |
|---|---|---|---|---|---|---|
| **Temperature** | **Calcite** | **Aragonite** | **Vaterite** | **Calcite** | **Aragonite** | **Vaterite** |
| 60 | 81 | 19 | 00 | 04 | 46 | 50 |
| 80 | 12 | 88 | 00 | 13 | 22 | 65 |
| 100 | 35 | 65 | 00 | 02 | 04 | 94 |

*Table 2: Molar Fraction of CaCo3, Polymorphs in the presence of EDTA +HEDPand absence of additive at various Temperatures.*

### *3.2. FTIR Spectrosco py.*

It is well known that different crystal forms of CaCO3 show different bands in FTIR spectrum.[xxxi−xxxiii] Hence, the polymorphic compositions of CaCO3 crystals were primarily identified by FTIR and represented in . The reference bands observed around 700−745, 856−874, 1435−1480 cm−1 were assigned to the ν4 in-plane bending,ν2 out-of-plane bending, and ν3 asymmetric stretching modes of CO3 2−, respectively. The principal bands corresponding to aragonite (A), vaterite (V), and calcite (C) are highlighted, and wherever necessary, the FTIR were deconvoluted (660−800 cm−1) to distinguish calcite from aragonite (713 and 700 cm−1) as shown in Figure. The individual FTIR spectra with band values are provided in Figure as Supporting Information. The results demonstrated that, in the presence of EDTA and HEDP formation of vaterite and aragonite is facilitated with a decrease in calcite on increasing the temperature from 80 to 100 °C. This phenomenon is abnormal and against the Ostwald rule of stages. Although most reports about CaCO3 agree with this rule, our earlier studies also reported similar observations.

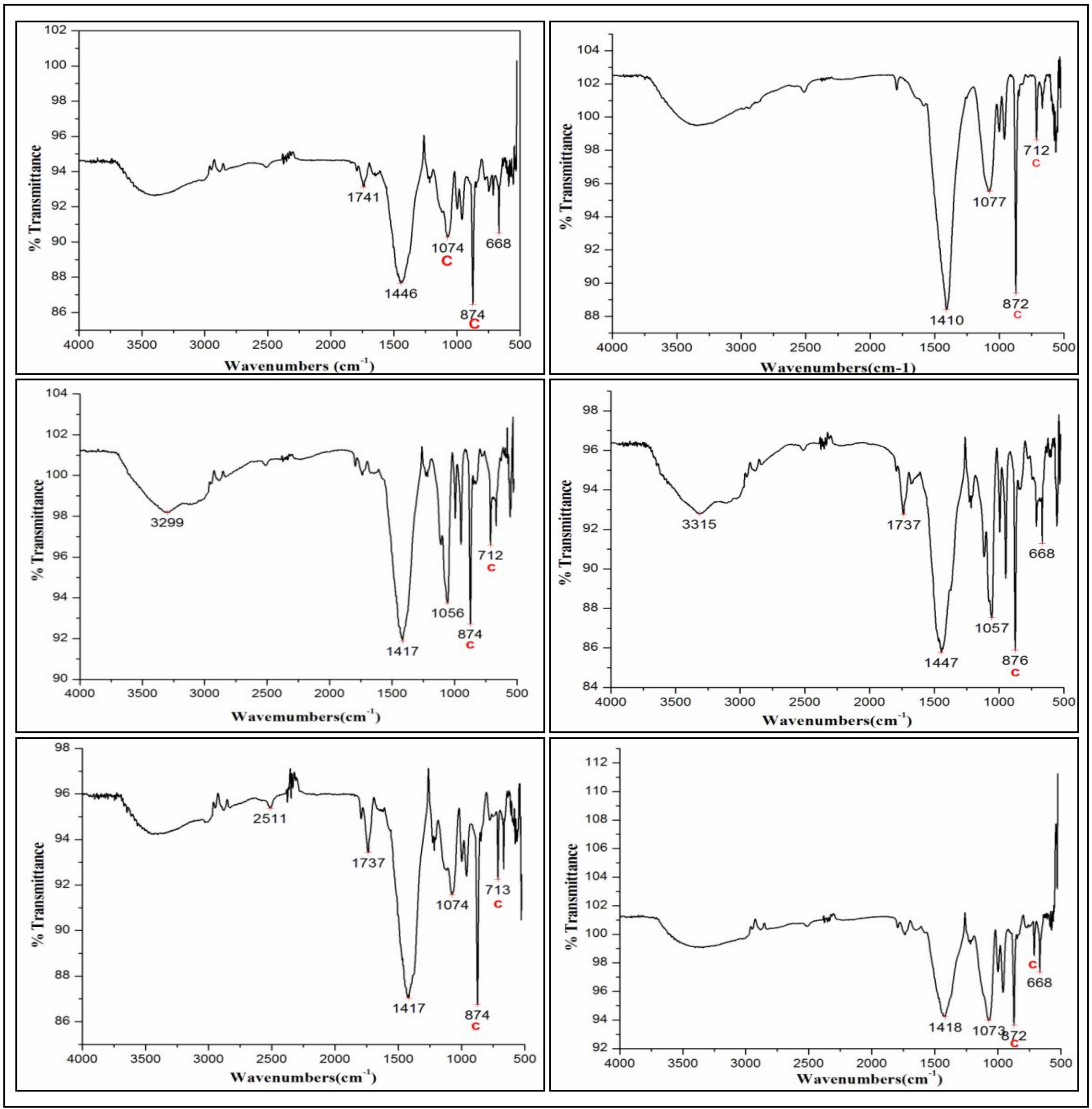


*Figure 2: Samples*

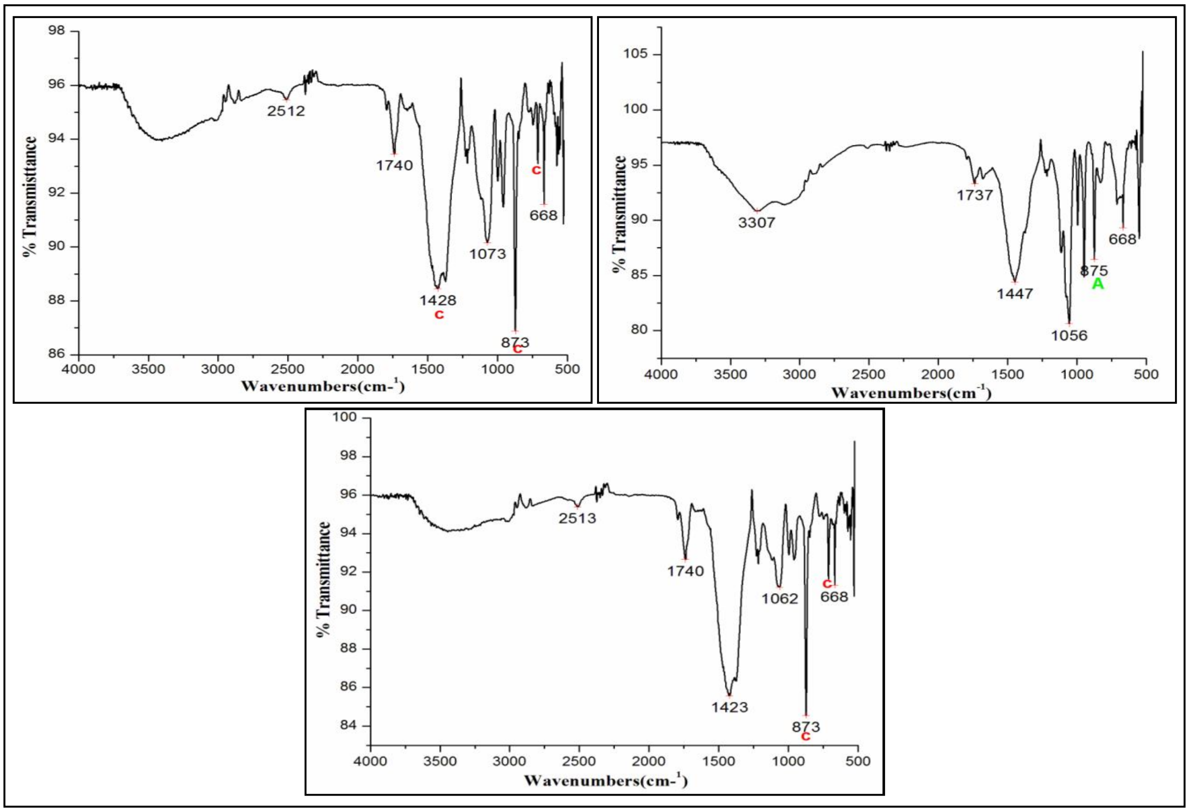
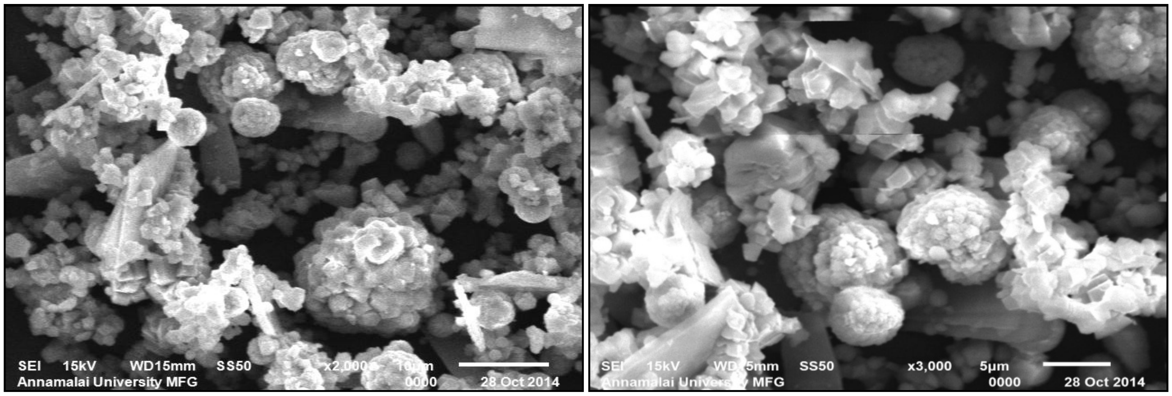


*Figure 3: Samples*

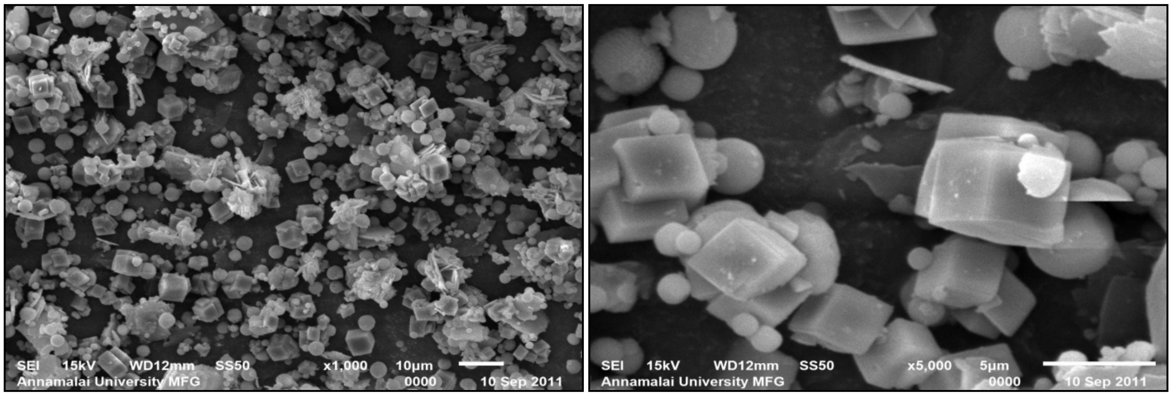
### *3.3. Morphological Studies Using SEM.*

To analyze the detailed morphology, SEM performed and are presented in 4 It is evident from , that the sample prepared at 60 °C consisted of three different morphologies: spherical, flower with elongated prolate spheroid- like petals, and elongated prolate spheroids. Our earlier studies have resulted similar morphological combinations 10ml,20ml , in the presence of EDTA at 100 °C, where we had confirmed the flower and spherical morphologies to vater ite and the elongated prolate spheroids as aragonite.27 Here, in the presence of EDTA and HEDP generally at 60,80,100 °C, the SEM images have spherical vaterite and they formed roselike structure (button rose) were resulted when Both spherical and rhomboidal morphologies are present in the SEM image confirming a binary mixture of vaterite and calcite in the sample. The XRD, FTIR, revealed presence of aragonite in this sample. There can be two reasons for the absence of morphologies corresponding to aragonite. First, the molar fraction of calcite and aragonite in this sample were too low and might not have been covered in the scan area. The second reason could be a possibility of an almost similar morphology as that of vaterite. The chance for the second possibility is more because the spherical morphology of vaterite in this sample is not uniform and contains some elongated prolate spheroids .

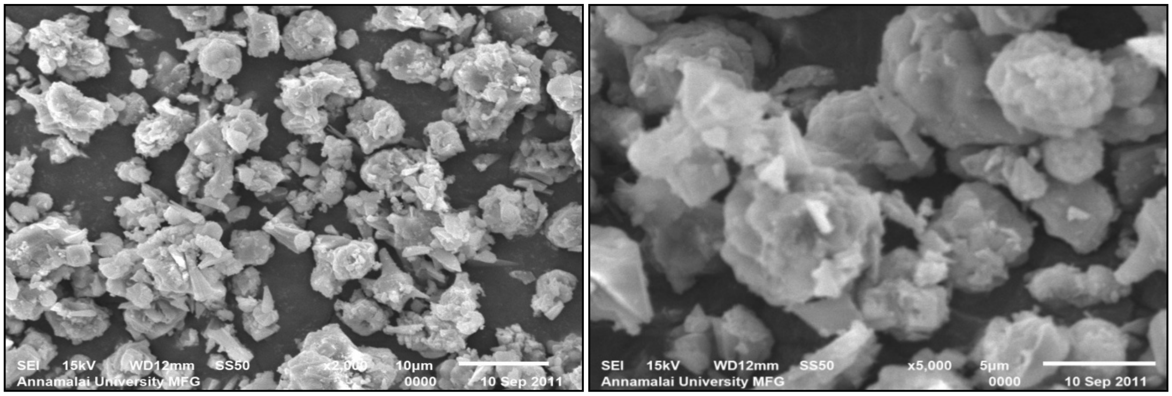
SEM, 10ml at .60.c



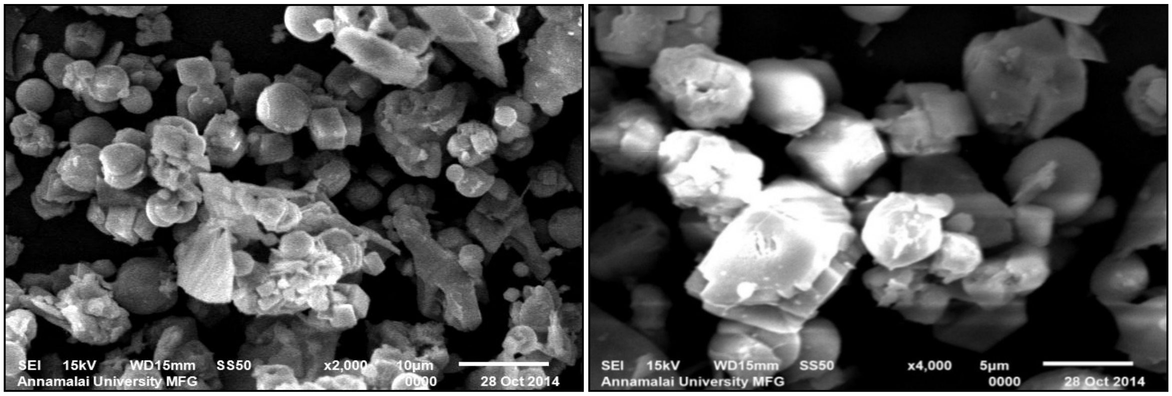
10ml at 80.c



10ml at 100.c



20ml at 60.c



20ml at 80.c

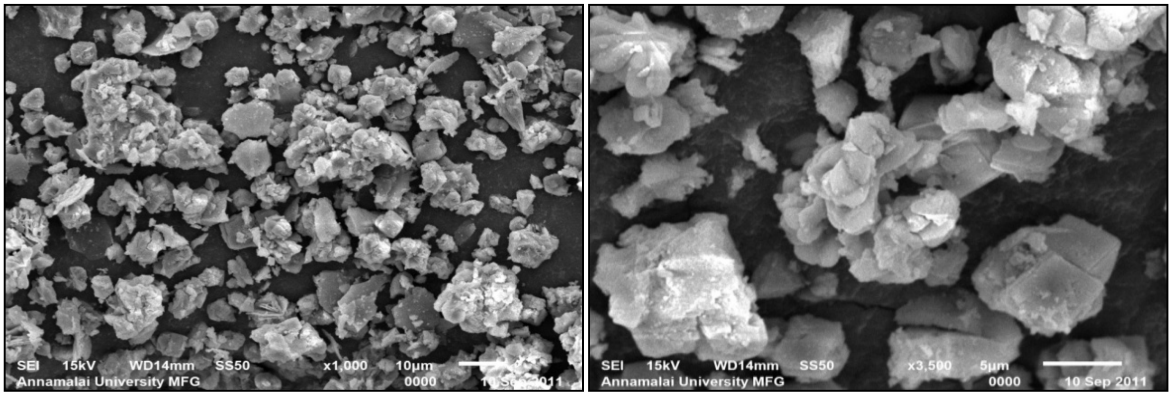
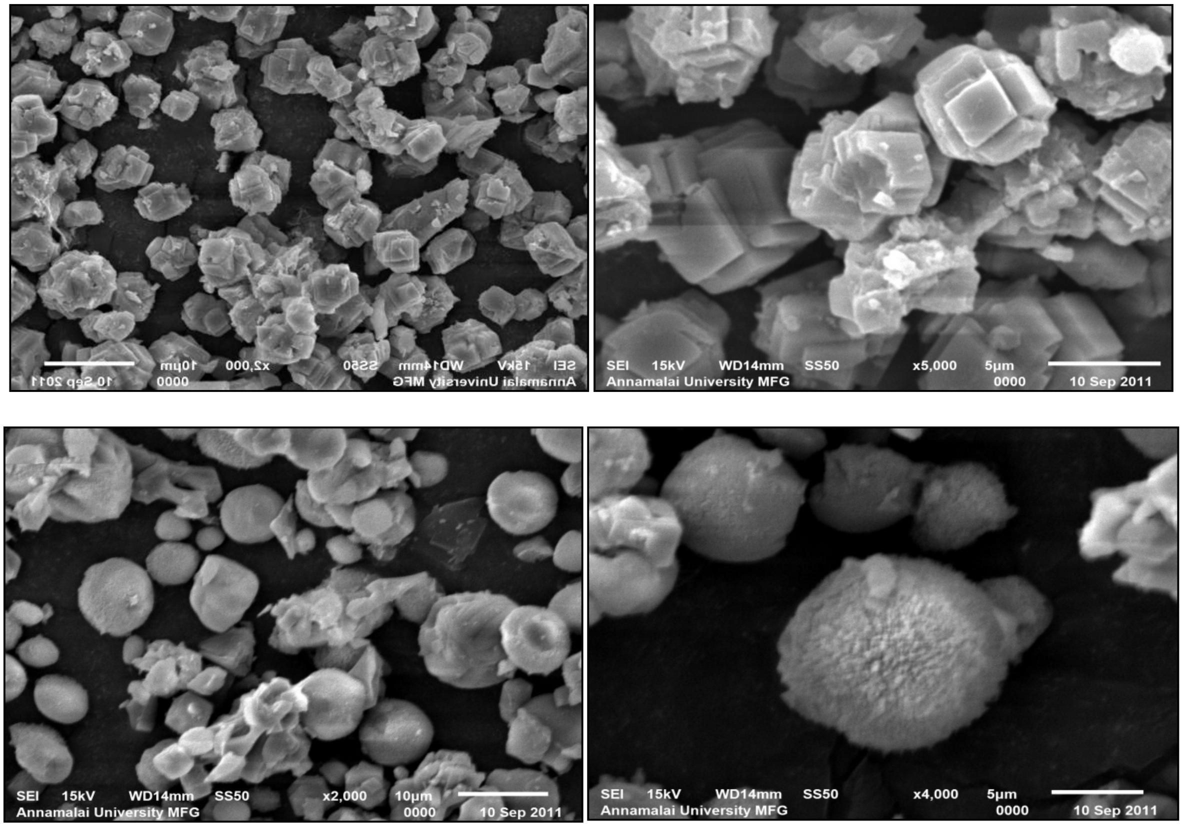
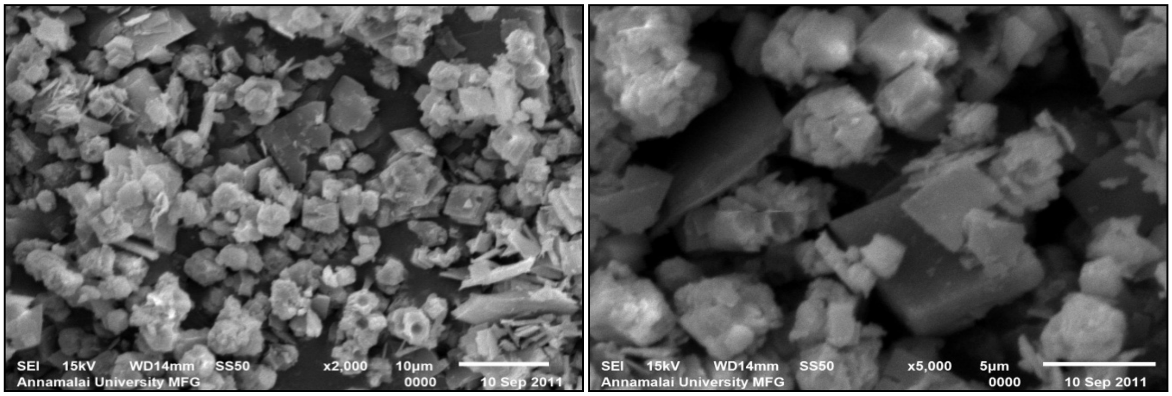


*Figure 4: Samples*

20ml at 100.c



30ml at80.c



30ml at 100.c

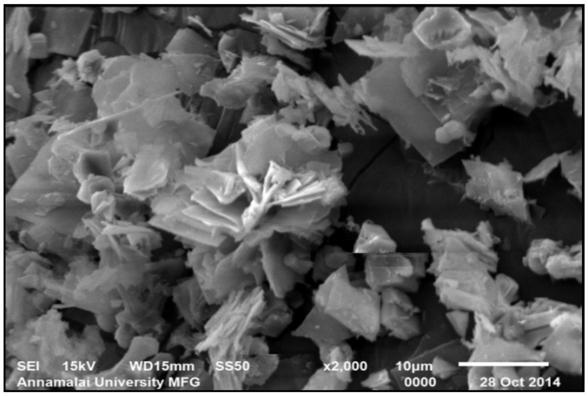


*Figure 5: Samples*

The morphology resembled like a closely packed bed of roses. However, it is obvious that the individual roses are not clearly distinguishable. Interesting morphological changes were observed on raising the reaction temperature from 80 to at100 °C . The highly thickly packed bed of roses secede to give individual roselike structures having size 400 to 500 nm and petals ranging from 200 to 250 nm. It is evident from this image that the sample at 100 °C is like a closely packed bed of roses. The FTIR, and XRD results confirmed the presence of vaterite with very little aragonite in this sample. However, the molar fraction of aragonite in this sample is found to be negligible. and hence this morphology is assigned to vaterite.

### *3.4. Mechanism*

Our previous experiments without any additive resulted into a binary mixture of calcite and aragonite below 100 °C. At 60 °C, calcite was the only polymorph which was stable. Vaterite was observed in any of the sample rarely. When EDTA was used, we found a considerable amount of vaterite at various temperatures particularly at 60 and 100 °C.[xxvii] Similarly, our experiments with HEDP at various concentrations have shown presence of vaterite at different temperatures. [xxviii] Both EDTA and HEDP have shown different morphologies for vaterite. Although EDTA favored three dimensional sprouts-like morphology, HEDP favored two dimensional growth leading to a sunflower like morphology.

Keeping the experimental data of individual chelating agents and the blended system side by side, the probable mechanism of synergistic effect could be drawn as follows. When both of the additives are added together, the Ca2+ ion present in the system will form complex with both EDTA and HEDP. At room temperature (30 °C) the TDS of the solutions showed 3260 ppm after addition of EDTA and HEDP. The amount of Ca2+ present in the solution addition of EDTA and HEDP could be about 4000 ppm. This requires 100 mL of 0.1 M EDTA or HEDP or both put together to form 100% complex with all Ca2+ ions. On addition of 20 mL each of EDTA and HEDP, which is only 40% of the stoichiometric the concentration of Ca2+ ions are supposed to be 2400 ppm.

Filtration of sample after cooling can redissolve a small portion of CaCO3, but could be significant only, if additives/chelating agents are absent. Because a sufficient quantity of EDTA and HEDP is present in the system, they can easily complex the redissolved Ca2+ ion. HEDP, being a pentadentate ligand and having less affinity toward Ca2+ than EDTA, could release the Ca ions first in to the solutions with increase in temperature. As EDTA is sufficiently coordinated with Ca ions, it cannot accommodate the released Ca2+ ions under increasing temperature and pressure. This could increase the number of species in the system and thereby increase the entropy of the system. As the supersaturation is reached, Ca2+ ions are forced to form CaCO3. As the temperature is very high,before this reaction attains equilibrium, the Ca ions coordinated to EDTA are also released in to the system. Now, the presence of HEDP and EDTA in the environment provides two different activation sites that could act individually and favor both the two and three-dimensional morphological growth of CaCO3 .Although the HEDP which favors sunflower morphology stretches the structure horizontally,

The EDTAwhich favors the spiked flowers acts vertically. As a result, the sunflower morphology is crammed resulting into cone shapes. This effect further enhances with the release of chelating agents (EDTA and HEDP) with time, forcing them to get wrapped in concentric circles, one over the other, finally resulting into a rose structure .From the above discussions, it is obvious that the self-assembly of these petals are induced by the synergistic effect of EDTA and HEDP.

## 4. Conclusion

In summary, exclusive formation of vaterite was attained through controlled precipitation of CaCO3in the presence of a blended system of EDTA and HEDP at 60 and100 °C. A binary mixture of aragonite and vaterite was obtained at 60 and 100 °C and a ternary mixture of calcite, aragonite and vaterite at 60 °C. 10ml at 60.c , 10ml, 20ml at at100 °C, roselike morphology was observed for vaterite, which was a result of the synergetic effect of EDTA and HEDP.

## 5. References

i. Morse, J. W.; Arvidson, R. S.; Luttge, A. Calcium Carbonate Formation and Dissolution. Chem. Rev. 2007, 107, 342.
ii. Gehrke, N.; Cölfen, H.; Pinna, N.; Antonietti, M.; Nassif, N. Superstructures of Calcium Carbonate Crystals by Oriented Attachment. Cryst. Growth Des. 2005, 5, 1317
iii. Payne, S. R.; Butler, M. H.; Butler, M. F. Formation of Thin Calcium Carbonate Films on Chitosan Biopolymer Substrates. Cryst. Growth Des. 2007, 7, 1262.
iv. Yu, J.; Guo, H.; Davis, S. A.; Mann, S. Fabrication of Hollow Inorganic Microspheres by Chemically Induced Self-Transformation. Adv. Funct. Mater. 2006, 16, 2035.
v. Cölfen, H. Precipitation of Carbonates: Recent Progress in Controlled Production of Complex Shapes. Curr. Opin. Colloid Interface Sci. 2003, 8, 23.
vi. Braga, D. From Amorphous to Crystalline by Design: Bio-Inspired Fabrication of Large Micropatterned Single Crystals. Angew. Chem., Int. Ed. 2003, 42, 5544.
vii. Yang, Q. F.; Liu, Y. Q.; Gu, A. Z.; Ding, J.; Shen, Z. Q. Investigation of Calcium Carbonate Scaling Inhibition and Scale Morphology by AFM. J. Colloid Interface Sci. 2001, 240, 608.
viii. Macipe, A. L.; Morales, J. G.; Clemente, R. R. Calcium Carbonate Precipitation from Aqueous Solutions Containing Aerosol OT. J. Cryst. Growth 1996, 166, 1015.
ix. Ahmed, J.; Menaka; Ganguli, A. K. Controlled Growth of Nanocrystalline Rods, Hexagonal Plates and Spherical Particles of the Vaterite form of Calcium Carbonate. CrystEngComm 2009, 11, 927.
x. Xiao, J.; Wang, Z.; Tang, Y.; Yang, S. Biomimetic Mineralization of CaCO3 on a Phospholipid Monolayer: From an Amorphous Calcium Carbonate Precursor to Calcite via Vaterite. Langmuir 2010, 26, 4977.

xi. Chen, S. F.; Yu, S. H.; Jiang, J.; Li, F. Q.; Liu, Y. K. Polymorph Discrimination of CaCO3 Mineral in an Ethanol/Water Solution:Formation of Complex Vaterite Superstructures and Aragonite Rods. Chem. Mater. 2006, 18, 115.

xii. Hart, J. R. Ethylenediaminetetraacetic Acid and Related Chelating Agents. In Ullmann's Encyclopedia of Industrial Chemistry; Wiley-VCH: Weinheim, Germany, 2000.

xiii. Zhang, G. C.; Ge, J. J.; Sun, M. Q.; Pan, B. L.; Mao, T.; Song, Z. Z. Investigation of Scale Inhibition Mechanisms Based on the Effect of Scale Inhibitor on Calcium Carbonate Crystal Forms. Sci. China B Chem. 2007, 50, 114.

xiv. Tang, Y.; Yang, W.; Yin, X.; Liu, Y.; Yin, P.; Wang, J. Investigation of CaCO3 Scale Inhibition by PAA, ATMP and PAPEMP. Desalination 2008, 228, 55.

xv. Tai, C. Y.; Chen, F. B. Polymorphism of CaCO3 Precipitated in a Constant-Composition Environment. AIChE J. 1988, 44, 1790.

xvi. Nielsen, A. K.; Toft, J. M. Electrolyte Crystal Growth kinetics. J. Cryst. Growth 1984, 67, 278.

xvii. Sawada, K. The Mechanisms of Crystallization and Transformation of Calcium Carbonates. Pure Appl. Chem. 1997, 69, 921.

xviii. Ketrane, R.; Saidani, B.; Gil, O.; Leleyter, L.; Baraud, F. Efficiency of Five Scale Inhibitors on Calcium Carbonate Precipitation from Hard Water: Effect of Temperature and Concentration. Desalination 2009, 249, 1397.

xix. Euvrard, M.; Martinod, A.; Neville, A. Effects of Carboxylic Polyelectrolytes on the Growth of Calcium Carbonate. J. Cryst. Growth 2011, 317, 70.

xx. Lee, K. B.; Park, S. B.; Jang, Y. N.; Lee, S. W. Morphological Control of CaCO3 Films with Large Area: Effect of Additives and Self- Organization under Atmospheric conditions. J. Colloid Interface Sci. 2011, 355, 54.

xxi. Wang, T.; Che, R.; Li, W.; Mi, R.; Shao, Z. Control Over Different Crystallization Stages of CaCO3-Mediated by Silk Fibroin. Cryst. Growth Des. 2011, 11, 2164.

xxii. Chakrabarty, D.; Mahapatra, S. Aragonite Crystals with Unconventional Morphologies. J. Mater. Chem. 1999, 9, 2953.

xxiii. Liu, Y.; Cui, Y.; Mao, H. Y.; Guo, R. Calcium Carbonate Crystallization in the Presence of Casein. Cryst. Growth Des. 2012, 12,4720.

xxiv. Yan, G.; Wang, L.; Huang, J. The Crystallization Behavior of Calcium Carbonate in Ethanol/Water Solution Containing Mixed Nonionic/Anionic Surfactants. Powder Technol. 2009, 192, 58.

xxv. Altay, E.; Shahwan, T.; Tanoglu, M. Morphosynthesis of CaCO3 at Different Reaction Temperatures and the Effects of PDDA, CTAB, and EDTA on the Particle Morphology and Polymorph Stability. Powder Technol. 2007, 178, 194.

xxvi. Westin, K. J.; Rasmuson, A. C. Crystal Growth of Aragonite and Calcite in Presence of Citric Acid, DTPA, EDTA and Pyromellitic Acid. J. Colloid Interface Sci. 2005, 282, 359.

xxvii. Gopi, S. P.; Subramanian, V. K. Polymorphism in CaCO3 – Effect of Temperature under the Influence of EDTA (di sodium salt). Desalination 2012, 297, 38.

xxviii. Gopi, S. P.; Vijaya, P.; Subramanian, V. K. Morphological and Crystallization Process of CaCO3 in the Presence of Aqua Soft 330 (AS 330). Powder Technol. 2012, 225, 58.

xxix. Vijaya, P.; Gopi, S. P.; Aushiq, H. W.; Rajasekharan, M. V.; Subramanian, V. K. Effect of Ethylenediaminetetraacetic Acid (di sodium salt) and Aquasoft 330 on Crystal Growth and Morphology of Calcium Oxalate. Adv. Powder Technol. 2012, 23, 771.

xxx. Kontoyannis, C. G.; Vagenas, N. V. Calcium Carbonate Phase Analysis using XRD and FT-Raman Spectroscopy. Analyst 2000, 125,251.

xxxi. White, W. B., The Carbonate Materials. In The Infrared Spectra of Minerals; Farmer, V. C., Ed.; The Mineralogical Society of Great Britain and Ireland: London, 1974; Monograph 4, pp 227−284.

xxxii. Vagenas, N. V.; Gatsouli, A.; Kontoyannis, C. G. Quantitative Analysis of Synthetic Calcium Carbonate Polymorphs using FT-IR Spectroscopy. Talanta 2003, 59, 831.

xxxiii. Andersen, F. A.; Brecevic, L. J. Infrared Spectra of Amorphous and Crystalline Calcium Carbonate. Acta Chem. Scand. 1991, 45, 1018. (34) Gopi, S. P.; Subramanian, V. K.; Palanisamy, K. Aragonite-calcitevaterite: A Temperature Influenced Sequential Polymorphic Transformation of CaCO3 in the Presence of DTPA. Mater. Res. Bull. 2013, 48, 1906.

xxxiv. Gopi, S. P.; Subramanian, V. K. Anomalous Transformation of Calcite to Vaterite: Significance of HEDTA on Crystallization Behavior and Polymorphism at Elevated Temperatures. Indian J. Chem., Sect. A:

xxxv. Inorg., Bio-inorg., Phys., Theor. Anal. Chem. 2013, 52A, 342.

xxxvi. Wehrmeister, U.; Soldati, A. L.; Jacob, D. E.; Hagera, T.; Hofmeister, W. Raman Spectroscopy of Synthetic, Geological and Biological Vaterite: a Raman Spectroscopic Study. J. Raman Spectrosc. 2010, 41, 193.

xxxvii. Tlili, M. M.; Amor, M. B.; Gabrielli, C.; Joiret, S.; Maurin, G.; Rousseau, P. Characterization of CaCO3 Hydrates by Micro-Raman Spectroscopy. J. Raman Spectrosc. 2002, 33, 10.

xxxviii. Dandeu, A.; Humbert, B.; Carteret, C.; Muhr, H.; Plasari, E.; Bossoutrot, J. M. Raman Spectroscopy - A Powerful Tool for the Quantitative Determination of the Composition of Polymorph Mixtures: Application to CaCO3 Polymorph Mixtures. Chem. Eng. Technol. 2006, 29, 221.

xxxix. Lanigan, K. C.; Pidsosny, K. Reflectance FTIR Spectroscopic Analysis of Metal Complexation to EDTA and EDDS. Vib. Spectrosc. 2007, 45, 2.

xl. Zenobi, M. C.; Luengo, C. V.; Avena, M. J.; Rueda, E. H. An ATRFTIR Study of Different Phosphonic Acids in Aqueous Solution. Spectrochim. Acta, Part A 2008, 70, 270.

xli. Bilton, M.; Brown, A. P.; Milne, S. J. Investigating the Optimum Conditions for the Formation of Calcium Oxide, used for CO2 Sequestration, by Thermal DDecomposition of Calcium Acetate. J.Phys.: Conf. Ser. 2012, 371, 1.