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Synergetic Effect of EDTA Concentration, Temperature, PH on the Crystal Growth, Polymorphism and Morphology of $CaCo_3$ under Co_2.

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ABSTRACT

Calcium carbonate scale samples were synthesized from calcium chloride solution in the presence of ethylene diammine tetra acetic acid (EDTA) by bubbling CO_2 gas. Samples were prepared with different concentrations of EDTA at 60, 80 and 100^oC and characterized using XRD, FTIR and SEM techniques. The details revealed that EDTA stabilizes aragonite more efficiently at 80^oC. It was also observed that increasing the concentration of EDTA has no significant impact on the polymorphic specificity where as influence the morphology and the size of the particles. With raise in temperature, formation of calcite was predominant.
Keywords: Scale, Crystal growth, Calcite, Morphology

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INTRODUCTION

Research on the control of the crystal shape/polymorphism and morphology of calcium carbonate ($CaCO_3$) has gained much importance in the past few decades due to its industrial uses fillers and dentifrices, and of its biological role as structural supports in skeletons [1-8]. Calcium carbonate appears in six solid modifications: three hydrated forms (amorphous calcium carbonate, calcium carbonate hexahydrate, calcium carbonate monohydrate) and three anhydrous polymorphs (calcite, aragonite and vaterite) [9–14].

Hard water generates adherent deposits of scale on the internal walls of industrial or domestic equipments which cause severe technical problems with a great economical impact. The clogging of pipes is the consequence of the scale formation which reduces heat transfer efficiency, leading sometimes to the shutdown of an industrial plant in the many cases [15]. $CaCO_3$ is one of the major constituents in scale. Scale mainly constitutes crystalline forms of calcite (rhombohedric structure) and aragonite (orthorhombic) [17]. Vaterite (hexagonal) is very rarely found in scale. Of all these crystalline forms Calcite is thermodynamically the most stable, followed by aragonite and vaterite is the least stable polymorphs. The forms and the habits of the crystals depend on several parameters such as supersaturation, solvents, additives, etc [18].

Scaling can be prevented by physical and chemical techniques [19]. Chemical methods consist of adding chemical reagents like chelating agents [20], to complex Ca^{2+} and usage of antiscalants or chemical inhibitors by means of dispersion [21] and other inhibitiors [22-24]. In desalination processes, the use of antiscalants is the most commonly used technique [25,26]. Many studies have shown that a wide range of additives can influence the shape of crystalline $CaCO_3$ [27–32].

Chemicals for water treatment have been in use for more many decades. Subsequent studies on the use of chemical additives for scale inhibition have proven the efficiency of various effects on retardation of crystal growth. Generally, the mechanism suggested for the scale inhibition is adsorption of antiscalant on the crystal surface, which blocks the active crystal growth sites. After the adsorption phase, several modes of actions are considered: delaying germination, slow down crystal growth rate, favoring homogeneous germination on the detriment of heterogeneous germination or deforming the crystals, giving them a friable structure that weakens its adherence to a flow surface [33] There is large information available in the literature about the precipitation and the effects of inhibitors on scale kinetics [34-37].

Even though there are quite a large number of literatures available on the synthesis of $CaCO_3$, most of them are by direct addition of a carbonate solution into a calcium solution. Here in this work, we report the synthesis of $CaCO_3$ from $CaCl_2$ by bubbling CO_2 gas. The experiments were carried out in the presence of EDTA at three different temperatures 60, 80 and 100^oC. The details of the findings reveal that EDTA has a marked influence on controlling the polymorphic composition in the sample.

EXPERIMENTAL PROCEDURES

Materials

Analytical grade $CaCl_2$ and EDTA were obtained from Hi-media. De-mineralized water was used for the preparation of aqueous solutions. The reagents were used as such. Double distilled water was used to make all aqueous solutions. Analytical grade hydrochloric acid and sodium hydroxide were used to adjust the pH whenever necessary. Experiments were conducted at pH 7. CO_2 gas (80-85) bubbles per minute was obtained in a cylinder from Inox Ltd.

Preparation of $CaCO_3$

$CaCO_3$ was crystallized by a modified method from a described one [22]. A typical procedure is as follows: 200 ml 0.1 M $CaCl_2$,10ml. 20ml,30ml of 0.1 M EDTA were consecutively added in a round bottom flask, connected to a water condenser and heated using a rotamantle having a thermostat control with accuracy +/- 1^oC. The rotamantle was then heated to 60 °C. After attaining the temperature for 15 minutes, CO_2 gas was passed through the solution at a pressure of 1 atm for 2 h. and digested at the same temperature for 24 h. Experiments were carried out in the similar way at 80 and 100^oC. After digestion the sample was filtered,

washed with distilled water and then dried at 45 °C in an oven. A schematic representation of the experimental set up is provided in Fig. 1.
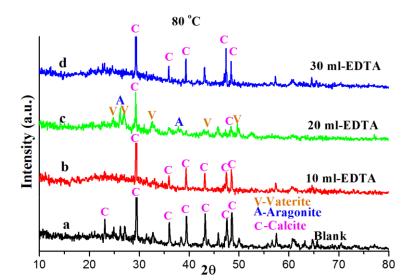
Figure 1: Schematic representation of the experimental set up
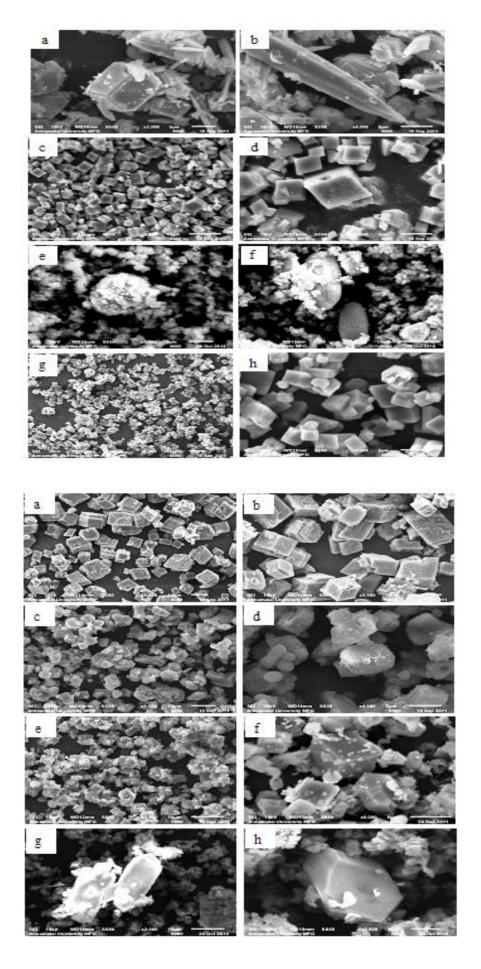

Characterization

The structure of the samples was confirmed by FTIR, Raman spectroscopy and XRD methods and the morphological studies were done using SEM and FESEM. FT-IR spectra were taken in the range 500 to 4000 cm^{-1} using Avatar-330 FTIR and JASCO-5300 FTIR instruments after pelletizing with KBr. Raman spectra of the samples were obtained with the WI Tec Confocal Raman Microscope alpha 300 R Raman spectrometer, excited by laser line having a wavelength of 488nm, provided by an argon laser. The X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced XRD diffractometer with Cu Ka radiation at λ = 1.5406 Å. Microscopic morphological images were taken using Philips XL30 -ESEM Scanning Electron Microscope(SEM) using a beam voltage of 20 kV and FESEM CARL ZESIS with In lens detectors. The samples were coated with gold prior to imaging
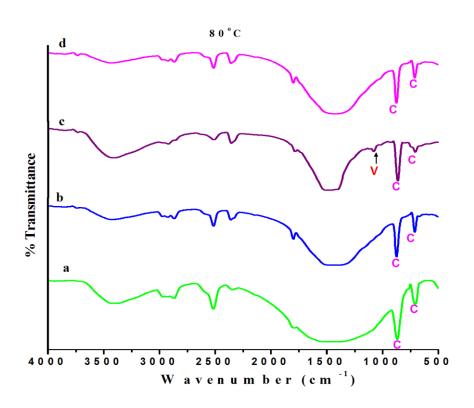
RESULTS AND DISCUSSIONS

It is well known that different crystal forms of CaCO3 shows different bands in FTIR spectrum [38-40]. The polymorphic composition of calcium carbonate crystals were identified by FTIR. The reference bands observed around 700-745, 874, 1435-1418 cm^{-1} were assigned to the in-plane bending (v_4), out-of-plane bending (v_2), and asymmetric stretching (v_3) modes of CO_3^{2-}, respectively. The FTIR patterns of samples prepared at 60, 80 and 100°C with different concentrations of EDTA are presented in Fig. 2, 3 and 4 respectively. It is obvious from the images that invariably all the samples contained calcite. Charecteristic peaks of calcite were prominent in all samples at 713, 875 and 1476 cm^{-1}. Only samples prepared at 60 °C with 20 ml (Fig. 2 c) and 30 ml (Fig. 2 d) EDTA and at 80°C with 20 ml EDTA (Fig. 3c) contained a shallow peak at 700 indicating presence of aragonite. Sample prepared at 80°C with 20 ml EDTA also exhibited the characteristic peak corresponding to vaterite at 745 cm^{-1}. For confirming this, spectra is deconvoluted and is presented in Fig. 5.
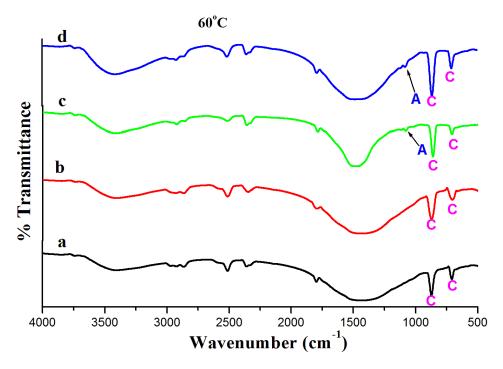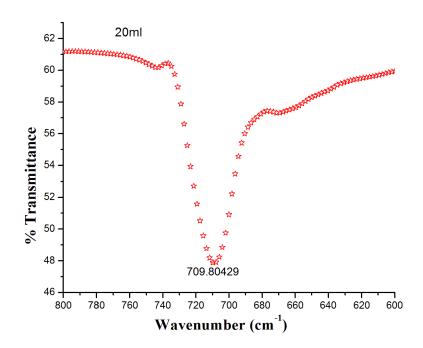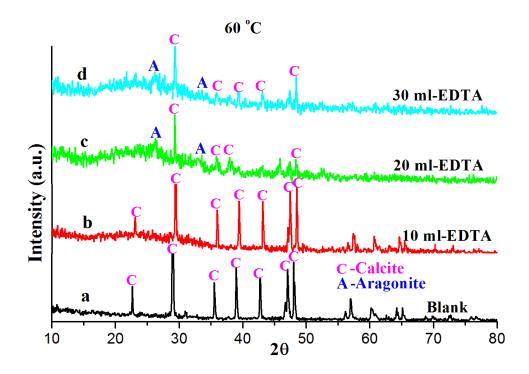
These observations are further confirmed by XRD. The XRD patterns of the samples prepared with different concentrations of EDTA and blank at 60, 80 and 100 ^{o}C are presented in Fig. 6, 7 and 8 respectively. It is evident from the presence of characteristic peaks of calcite at 2θ ~ 29.4 (104) that invariably all the samples contained calcite. As observed in the case of FTIR, only sample prepared at 80 ^{o}C with 20 ml (Fig. 7 c) contained characteristic peak of vaterite at 2θ ~ 32.7 (112) (022). Aragonite was found to be present in very little mole fraction in samples prepared at 60 ^{o}C with 20 ml and 30 ml EDTA (Fig. 6 b,c). The presence of aragonite was confirmed by the appearance of low intensity peaks at 2θ ~ 26.2 (1
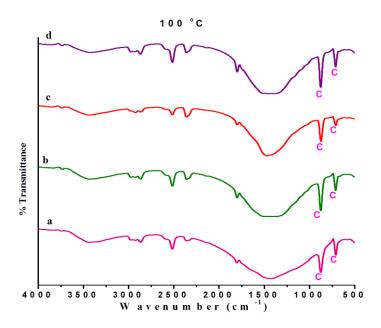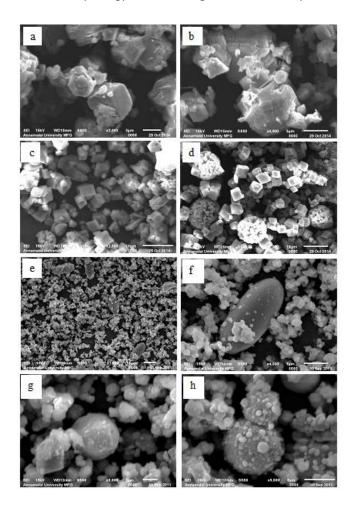
Fig. 9 depicts the SEM images of the sample prepared at 60 ^{o}C. The morphology of the sample prepared without EDTA (Fig. 9 a, b) is found to be rhomboidal and confirmed to be that of calcite as calcite alone was present in this sample. The morphology of samples prepared with 10 ml of EDTA is presented in Fig. 9 c and d. It is obvious that the rhomboidal blocks of calcite are the major constituent in the image. There are few spherical morphology also observed in the sample. The XRD pattern confirmed the presence of calcite alone in these samples too. Hence the morphology could be assigned to calcite only.
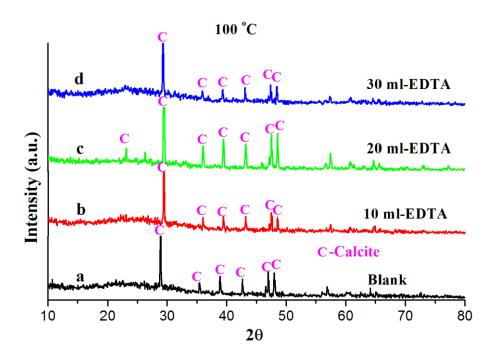
As the temperature is further increased at 80 ^{o}C the morphology exhibited marked difference and presence of spherical particles became more prominent. The XRD and FTIR confirmed the presence of aragonite in this sample. There could be larger sized particles with cucumber shape. This could be assigned to calcite. This indicated that the vaterite formed just before has been converted into a binary mixture of aragonite and calcite.

Another reason could be that the corners and edges of the rhomboidal structures are rounded off due to the presence of EDTA. This phenomenon of rounding of the edges and corners are characteristics of redissolution of crystallites [41]. This became more severe as the concentration is further increased to 30 ml (Fig. 9 g, h). It could be seen only spherical particles in this case which the usual morphology of vaterite is. But the XRD and FYTIR data indicated that calcite is the major constituent with very little aragonite. This indicates that as the concentration of EDTA increases it could significantly influence the crystallization behavior of CaCO$_3$.

The SEM images of the samples prepared at 80 ^{o}C are presented in Fig. 10. The morphology of the sample prepared without EDTA (Fig. 10 a, b) and with 10 ml EDTA (Fig. 10 c, d) contained only rhomboidal structures and confirmed that they belongs to calcite

The samples prepared with 20 ml EDTA exhibited morphology very similar to those obtained at 60 ^{o}C. The XRD data confirmed that the sample constituted a tertiary mixture of calcite, aragonite and vaterite. This accentuated that the possibility of the vaterite formed getting converted into a ternary mixture of vaterite, aragonite and calcite is more appropriate than the possibility of the corners and edges of the rhomboidal structures becoming rounded due to the presence of EDTA. At 30 ml concentration of EDTA, the SEM images contained only rhomboidal calcite structures.

The samples prepared at 100 ^{o}C invariably contained rhomboidal structures (Fig. 10 a-h). The XRD and FTIR data indicated the presence of only calcite in these samples. It could be noticed that as the concentration of EDTA was increased, smooth edges and corners were observed for rhomboidal structures. This is in contradictory to the observation made at 80 ^{o}C with 20 ml EDTA. In any case, the significance of EDTA is maximum at 20 ^{o}C and has a major role in inhibiting the calcite formation at this concentration. Another inference drawn from the morphological studies is that as the concentration of EDTA is increased, the uniformity of the rhomboidal structure is affected. It could be seen that very small and very large rhomboidal structures (Fig. 10 c-h) resulted as the concentration is increased. By adding high concentration of EDTA , the Calcite structure is affected, and give small rhomboidal calcite. The concentrations increases ,at the same

time PH decreases .The temperature increases ,on the other hand PH decreases. By adding EDTA 20 ml at 60 ^{o}C initial PH is 8.2 by adding EDTA it reduces at 3.4 then final PH is 8.1

EDTA 10ml

Temperature	Initial PH	Adding additives	Final
60	9.8	3.8	7.0
80	9.9	3.6	7.9
100	9.9	3.5	7.4

EDTA 20ml

Temperature	Initial PH	Adding additives	Final
60	8.2	3.3	7.0
80	8.3	3.2	8.1
100	8.4	3.1	7.6

EDTA 30ml

Temperature	Initial PH	Adding additives	Final
60	9.9	3.8	7.3
80	9.9	3.5	7.9
100	9.8	3.2	7.6

CONCLUSION

The studies carried out to understand the effect of EDTA on the crystal growth, polymorphism and morphology of the $CaCO_3$ synthesis from $CaCl_2$ by CO_2 bubbling has resulted in to the following conclusions. Firstly, the optimum concentration of EDTA is 20 ml at all temperatures. Secondly, at 100 ^{o}C the effect is minimum irrespective of the concentration. Thirdly at higher concentrations, the morphology is less uniform. The results could be of importance in water treatment associated with return line treatment from boilers, where EDTA is used to control scale formation.

REFERENCES

[1]   H. Lowenstam and S. Weiner, On Biomineralization, Oxford University Press, New York, 1989.
[2]   L. Addadi and S. Weiner, Angew. Chem., Int. Ed. Engl., 1992, 31, 153.
[3]   A. Berman, J. Hason, L. Leiserowitz, T. F. Koetzle, S. Weiner and L. Addadi, Science, 1993, 259, 776.
[4]   S. Weiner and L. Addadi, J. Mater. Chem., 1997, 7, 689.
[5]   B. R. Heywood and S. Mann, Adv. Mater., 1994, 6, 9.
[6]   S. Mann and G. A. Ozin, Nature, 1996, 382, 313.
[7]   S. Mann, J. Mater. Chem., 1995, 5, 935.
[8]   J. A. H. Oates, Lime and Limestone: Chemistry and Technology, Production and Uses, Wiley-VCH, Weinheim, 1998.
[9]   Y. Tang, W. Yang, X. Yin, Y. Liu, Y.P. Yin, J. Wang, Desalination 228 (2008) 55–60.
[10]   K.D. Demadis, E. Mavredaki, A. Stathoulopoulou, E. Neofotistou, C. Mantzaridis,Desalination 213 2007) 38–46.
[11]   Chen, A. Neville, M. Yuan, J. Pet. Sci. Eng. 46 (2005) 185.
[12]   H.A. El Dahan, H.S. Hegazy, Desalination 127 (2000) 111–118.
[13]   J.Y. Gal, Y. Fovet, N. Gatche, Water Res. 36 (2002) 755.
[14]   S.J. Dyer, G.M. Graham, J. Pet. Sci. Eng. 37 (2003) 171–181.
[15]   P. Shakkthivel, R. Sathiyamoorthi, T. Vasudevan, Development of acrylonitrile copolymers for scale control in cooling water systems, Desalination 164 (2004) 111–123.
[16]   Vesna Noethig-Laslo* and Ljerka Brec.evic , Mode and sites of incorporation of divalent cations in vaterite. J. Chem. Soc., Faraday T rans., 1998, 94(14), 2005È2009
[17]   L.N. Plummer, E. Busenberg, The solubilities of calcite, aragonite and vaterite in CO2–H2O solutions between 0 to 90 °C, and an evaluation of the aqueous model for the system CaCO3–CO2–H2O, Geochim. Cosmochim. Acta 46 (1982) 1011–1040.

[18]   Dong-Ki Keum, Kensuke Naka, Yoshiki Chujo Unique crystal morphology of hydrophobic CaCO3 composite by sodium trisilanolate in a mixture of a water-miscible organic solvent and water Journal of Crystal Growth 259 (2003) 411–418

[19]   F. Alimi, M. Tlili, C. Gabrielli, M. Georges, M. Ben Amor, Effect of a magnetic water treatment on homogeneous and heterogeneous precipitation of calcium carbonate, Water Res. 40 (2006) 941–1950

[20]   T.Y. Chen, S.H. Chan, Novel biological inhibitors of fouling and scale formation onheat transfer surfaces through genetic engineering, Microscale Thermophys. Eng.4 (2000) 103–108.

[21]   X. Wang, B.I. Lee, L. Mann, Dispersion of barium titanate with polyaspartic acid inaqueous media, Colloid Surf. A 202 (2002) 71–80.

[22]   D. Lisitsin, Q. Yang, D. Hasson, R. Semiat, Inhibition of CaCO3 scaling on ROmembranes by trace amounts of zinc ions, Desalination 183 (2005) 289–300.

[23]   R. Ketrane, B. Saidani, O. Gil, L. Leleyter, F. Baraud, Efficiency of five scale inhibitorson calcium carbonate precipitation from hard water: effect of temperature andconcentration, Desalination 249 (2009) 1397–1404.

[24]   N.N. Al-Mutairi, F.A. Aleem, M.I. Al-Ahmad, Effect of antiscalants for inhibition ofcalcium sulfate deposition in thermal desalination systems, Desalin. Water Treat.10 (2009) 39–46

[25]   J. Macadam, S.A. Parsons, Calcium carbonate scale control, effect of material andinhibitors, Water Sci. Technol. 49 (2) (2004) 153–159.

[26]   S.S. Al-Jaroudi, A. Ul-Hamid, J.A. Al-Matar, Prevention of failure in a distillationunit exhibiting extensive scale formation, Desalination 260 (2010) 119–128.

[27]   L.B. Gower, D.J. Odom, J. Crystal Growth 210 (2000)719.

[28]   W. Wang, G. Wang, Y. Liu, C. Zheng, Y. Zhan, J. Mater. Chem. 11 (2001) 1752.

[29]   K. Naka, Y. Tanaka, Y. Chujo, Y. Ito, Chem. Commun. (1999) 1931.

[30]   K. Naka, D.K. Keum, Y. Tanaka, Y. Chujo, Chem. Commun. (2000) 1537.

[31]   F. Manoli, E. Dalas, J. Crystal Growth 204 (1999) 369.

[32]   A. Kai, T. Miki, Jpn. J. Appl. Phys. 39 (2000) 1071.

[33]   R. Ketrane B. Saidani , Gil , L. Leleyter , F. Baraud . Efficiency of five scale inhibitors on calcium carbonate precipitation from hard water: Effect of temperature and concentration. Desalination 249 (2009) 1397–1404.

[34]   I. Drela, P. Falewicz, S. Kuczkowska, New rapid test for evaluation of scale inhibitors,Water Res. 32 (10) (1998) 3188–3191.

[35]   M.M. Reddy, A.R. Hoch, Calcite crystal growth rate inhibition by polycarboxylic acids, J. Colloid Interface Sci. 235 (2001) 365–370

[36]   P.V. Brady, W.A. House (Eds.), Physics and Chemistry of Mineral Surfaces, CRC Press, New York, 1996, p. 225.

[37]   C. Gabrielli, G. Maurin, G. Poindessous, R. Rosset, Nucleation and growth of calciumcarbonate by an electrochemical scaling process, J. Cryst. Growth 200 (1999) 236–250

[38]   W. B. White, In Infrared Spectra of Minerals ; Mineralogical Society: London, 1974; pp 227-284.

[39]   N. V. Vagenas, A. Gatsouli and C. G. Kontoyannis, Talanta, 2003,59, 831–836

[40]   F. A. Andersen and L. J. Brecevic, Acta Chem. Scand., 1991,45, 1018–1024.

[41]   M. Dinamani, P. Vishnu Kamath, R. Seshadri, Electrochemical synthesis of calcium carbonate coatings on stainless steel substrates, Mater. Res. Bull 37 (2002) 661–669.