

## An investigation into the effect of NTA on scale deposition from CaCO<sub>3</sub> sludge on copper metal surface

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### ABSTRACT

Experiments were carried out to investigate the effect of Nitrilotriacetic acid (NTA) on CaCO<sub>3</sub> scale depositions from its sludge on copper substrate at two different temperatures 60 °C and 100 °C. The substrate was subjected to deposition from a solution containing sludge synthesized by addition of Na<sub>2</sub>CO<sub>3</sub> on CaCl<sub>2</sub>, for a period of 10 days. The studies were carried out to elucidate the effect of direct and indirect contact with the sludge. The CaCO<sub>3</sub> scale deposited on copper substrate were characterized by FTIR, XRD and SEM techniques; the different present polymorphs and their morphology were identified. The data revealed that both the method of heating and presence of NTA significantly influenced the morphology and polymorphic composition of the scale.

**Keywords:** *inorganic compounds; crystal growth; X-ray diffraction; surface properties.*

### 1. INTRODUCTION

(Times New Roman 10) Heat exchangers, boilers and cooling towers are inevitable components of any process industry. Formation of scale is one of the most common problems associated with such equipments. CaCO<sub>3</sub> is also one of the major constituents present in such scale [1-3]. The physical properties of the scale largely depend on the polymorphic composition [4-5]. Though CaCO<sub>3</sub> gained much attention in the recent decades due to its presence in the living system and its wide applications in bio mineralization [6-8], its association with scale inhibition is still an unexplored area of research.

CaCO<sub>3</sub> has three anhydrous crystalline forms (calcite, aragonite and vaterite) and three hydrated forms (amorphous CaCO<sub>3</sub> (ACC), monohydrocalcite (CaCO<sub>3</sub>.H<sub>2</sub>O) and ikaite (CaCO<sub>3</sub>.6H<sub>2</sub>O)) [9, 10]. Calcite is the most stable, while aragonite and vaterite are metastable polymorphs which can be easily transformed into the stable phase calcite. Reports suggest that the scale often contain calcite and aragonite [11] and vaterite is seldom found.

Generally organic phosphonic acids, chelating agents and polymer type scale inhibitors are used to prevent the formation of scale [12,

13]. The main action mechanisms of this scale inhibitor are believed to be chelating effect, lattice deformation and electrostatic repulsion [14-15]. Many additives have been studied for their effect on controlling the polymorphism, structure and morphologies of CaCO<sub>3</sub> under different experimental conditions [16-19] such as pH, temperatures, aging time, concentration of additives, etc. The studies reveal that amorphous calcium carbonate (ACC) is formed first, which will transform to calcite via vaterite and aragonite following the step rule while vaterite and aragonite are stabilized at higher temperatures, in the presence of some chelating agents [20-24].

Although these reports are available, they are limited to powder samples. Nevertheless the formation of scale on a metal surface is often effected by the constant contact of the metal surface with the sludge. To the best of our knowledge, there are no reports on the deposition of scale on metal surfaces from sludge. The objective of this study was to understand the effect of NTA on CaCO<sub>3</sub> scale deposition on copper substrate from its sludge.

### 2. EXPERIMENTAL SECTION

Analytical grade CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> and NTA were obtained from Himedia chemicals, and were used as supplied without further purification. De-mineralized water was used for the preparation of aqueous solutions.

The experimental set up and the procedure followed here is similar to the one detailed by Palanisamy K [25]. 100 ml 0.1M CaCl<sub>2</sub> solution and 20 ml 0.1 M NTA were taken in a round bottom flask. Two copper coins of 0.92 X 10<sup>-2</sup> m in diameter and 0.75 X 10<sup>-3</sup> m thickness were used as substrate for deposition. In order to study the effect of direct and indirect contact with the sludge, one coin was kept at the bottom of the flask and another was kept suspended at 1 cm above the solution (from the bottom).

The system was heated to 60 °C using a mantle with temperature controller (+/- 1°C) and 150 ml 0.05 M Na<sub>2</sub>CO<sub>3</sub> was introduced drop by drop from a burette 20 min after attaining the temperature.

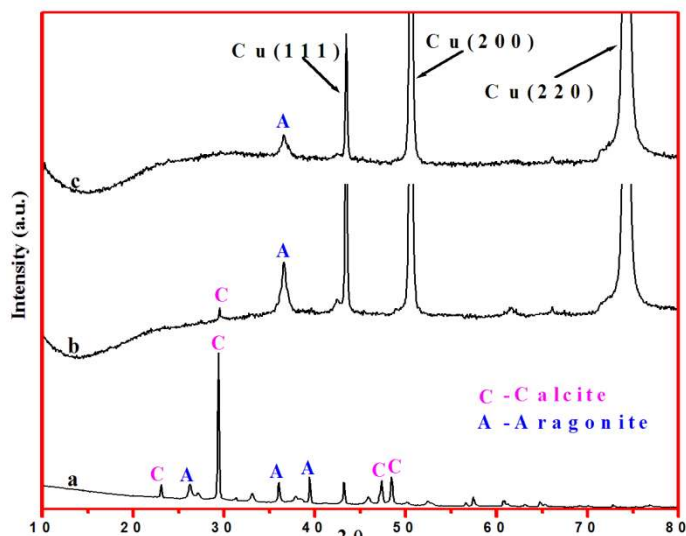
The system was incubated for 10 days under this condition to have sludge deposited on the metal surfaces. A water condenser was used to avoid the loss of water. After 10 days, the copper coins were collected and rinsed with cold distilled water.

The precipitate from the bottom of the flask was also collected using a Whatman 40 filter paper. All the samples were washed thrice with distilled water and dried at 45°C in a hot air oven. The experiments were repeated at 100 °C.

The copper coins and the powder samples were characterized by XRD for identification of the polymorphs deposited. The XRD spectra were recorded on the X'PERT PRO model X-ray diffractometer from PAN Analytical instruments operated at a voltage of 45 kV and a current of 30 mA with Cu K $\alpha$  radiation at  $\lambda = 1.5406 \text{ \AA}$ . The morphological studies were done

### 3. RESULTS SECTION

The XRD pattern of the samples prepared at 60 and 100 °C in the presence of NTA are presented in Figure 1 and Figure 2 respectively. At 60 °C, the sludge (Figure 1a) contained a binary mixture of calcite and aragonite. This was confirmed by the appearance of peaks at  $2\theta \sim 29.4^\circ$  (104),  $39.4^\circ$  (113),  $47.3^\circ$  (018) and  $48.4^\circ$  (116) (JCPDS: 86-2334) and  $26.2^\circ$  (111),  $33.1^\circ$  (012),  $36.1^\circ$  (200) respectively.



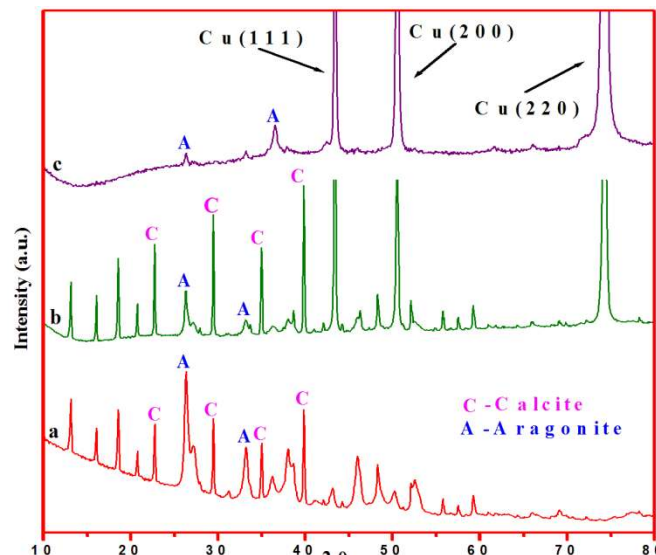
**Figure 1.** XRD pattern of samples prepared at 60°C in the presence of NTA; (a) sludge CaCO<sub>3</sub>, (b) copper coin-direct contact with sludge, (c) copper coin-suspended.

Figure 1 (b) and (c) represent the XRD patterns of copper coins kept at the bottom and that kept hanging respectively. The copper coin kept at the bottom exhibited characteristic peaks for aragonite and calcite at  $2\theta \sim 36.5^\circ$  (JCPDS: 03-0893) and  $29.4^\circ$  (104) respectively whereas the copper coin under suspension showed peak only at  $36.5^\circ$  (JCPDS: 03-0893) confirming the presence of only aragonite. The characteristic peak for calcite at  $2\theta \sim 29.4^\circ$  (104) was absent in this sample. Peaks corresponding to vaterite were also absent in all the samples. It could also be concluded from the intensities of calcite and aragonite peaks in Figure 1(b) that the major constituent present is aragonite and only very little calcite is present in the bottom sample.

The XRD pattern of sludge sample at 100 °C (Figure 2 a) exhibited peaks at  $2\theta \sim 26.3^\circ$  (111)  $32.9^\circ$  (121)  $38.1^\circ$  (112)  $45.5^\circ$  (040) (JCPDS: 03-0405) and  $29.5^\circ$  (104)  $39.5^\circ$  (113)  $48.6^\circ$  (116) confirming the presence of both aragonite and calcite respectively. Unlike the sample at 60 °C, the sludge contained mostly aragonite and the peaks corresponding to calcite were found to be less in intensity. The copper coin kept at the bottom of the flask (Figure 2 b) had characteristic peaks of aragonite at  $2\theta \sim 26.3^\circ$  (111)  $33.1^\circ$  (121)  $35.0^\circ$  (102) (JCPDS: 03-0405) and calcite at  $2\theta \sim 29.4^\circ$  (104)  $39.4^\circ$  (113)  $47.6^\circ$  (018)  $48.5^\circ$  (116) (72-1652). As in the case of 60

using JEOL JSM-6610LV scanning electron microscope at a beam voltage of 20 kV. The samples were coated with gold prior to imaging. The powder samples collected from the bottom of the flask was characterized by FTIR in the range 500 to 4000 cm<sup>-1</sup> using FT-IR (SHIMADZU), after KBr pelletization.

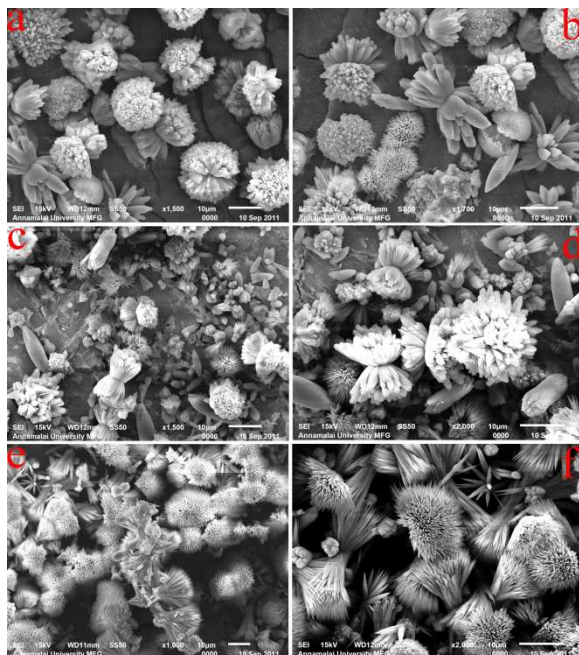
°C, here also the copper coin kept in the hanged position (Figure 2 c) exhibited the presence of peaks corresponding to aragonite alone at  $2\theta \sim 26.3^\circ$  (111)  $33.1^\circ$  (121) and  $36.1^\circ$  (102) (JCPDS: 03-0405).



**Figure 2.** XRD pattern of samples prepared at 100°C in the presence of NTA; (a) sludge CaCO<sub>3</sub>, (b) copper button-direct contact with sludge, (c) copper button-suspended.

The data also revealed that the intensity of calcite peaks in the bottom sample increased with rise in temperature from 60 to 100 °C. The XRD patterns of the blank samples showed that at 60 °C the CaCO<sub>3</sub> sludge and the copper coin which had direct contact with the CaCO<sub>3</sub> sludge contained only calcite while the copper coin under suspension contained aragonite also while the copper coin under suspension contained less amount of calcite compared to the one subjected to direct heating. Nevertheless, at 100°C both calcite and aragonite were confirmed in the CaCO<sub>3</sub> sludge. No Characteristic peaks of any polymorph of CaCO<sub>3</sub> were present in the XRD patterns of both copper coins.

The SEM images of the samples synthesized in the presence of NTA at 60 °C are presented in Figure 3. It could be seen that the sludge sample (Figure 3 a, b) contained two morphologies; one resembling to chrysanthemum and another one similar to a cluster of leafy structures originated from a common base and grown towards opposite directions. The XRD data indicated that this sludge sample contained a binary mixture of calcite and aragonite (Figure 1 a). In an earlier study made by us, we observed that at 60 °C and in the presence of NTA, the resulted powder sample contained only aragonite over a digestion period of 10h [26].



**Figure 3.** SEM images of samples in presence of NTA at 60°C; (a, b) Sludge, (c, d) copper coin-direct contact with sludge, (e, f) copper coin-suspended.

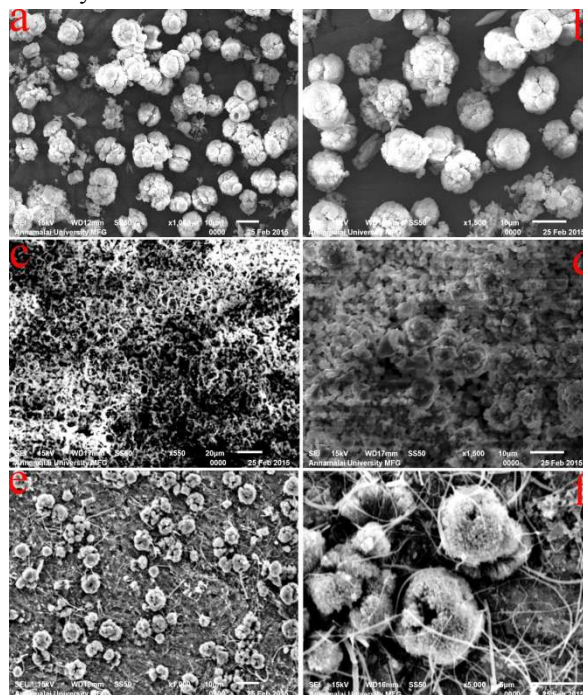
Here, the presence of calcite in addition to aragonite reason could be due to the extended digestion period (10 days) that could have facilitated some of the aragonite to get transformed to calcite. The morphology for aragonite observed there was similar to the dandelion morphology observed here. Moreover, from the SEM images it could be noticed that the chrysanthemum structure observed here is formed by the agglomeration of fine needle like structures.

The needle like structure is the most commonly observed morphology for aragonite. Hence this structure could be attributed to aragonite. Apart from the above two structures, some lone leaf structures having tapered ends are also observed (Figure 3b). These lone petals could have been resulted from the dissolution of the edges and corners of rhomboidal calcite.

It could be also noticed that, the leafy structure failed to keep or maintain their tapered/pointed ends and exhibited tendency for agglomeration and form the leafy cluster structure. Thus this agglomerated leafy structure could be attributed to calcite. The morphology of the copper coin which had direct contact with the sludge contained all the three morphologies observed in the sludge (Figure 3c, d). Nevertheless deposited scale exhibited smaller sized crystallites (below 10  $\mu$ ) formed the initial layer and the larger crystallites comparable to the size of the sludge sample were found to be only overlaid and had contact with smaller particles in the initial layer at least at some points. This is a clear evidence for the greater adhesion ability of the smaller particle on to the metal surfaces than the larger particles and the latter need a primary layer to have a firm adhesion. The smaller particles were completely absent in the sludge indicating the adhesion on the metal surfaces have prevented them from dissolution and recrystallization as bigger particles.

The copper coin under suspension (Figure 3 e, f) exhibited rampant growth of needle like aragonite formed in clusters like a stack of hay covering the entire area without sparing any bare metal surface. As observed in the bottom copper coin,

here also smaller particles were involved in the formation of the base layer and larger particles could only contribute in building up the further layers.



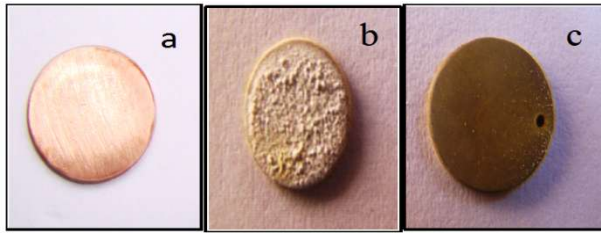
**Figure 4.** SEM images of samples in presence of NTA at 100°C; (a, b) Sludge, (c, d) copper coin-direct contact with sludge, (e, f) copper coin-suspended.

The SEM images of samples prepared at 100 °C are presented in Figure 4 (a-f). The SEM images of the sludge sample (Figure 4 a, b) exhibited presence of aragonite in the form of twin cauliflowers joined back to back. It is apparent that this morphology was resulted from the manifestation of the chrysanthemum morphology observed at 60 °C through the smoothing of the sharp tips of the needle like petals. A few ellipsoidal shaped particles similar to the calcite crystallites observed at 60 °C are also present. The XRD of the powder samples showed the presence of calcite and aragonite and the intensities of the peaks indicated the major polymorph in the sample as aragonite.

The SEM image of the copper coin at the bottom (Figure 4 c, d) contained a dense deposition of scale. The morphology of the scale deposit elucidate that a large number of distorted rhomboidal and trigonal structures in the range of 2-4  $\mu$  been fused together to form layers of scale. Though less in quantity, the cauliflower morphology observed in the sludge sample was also found to be present over this thick layer of scale. Our earlier studies have revealed that presence of NTA facilitates calcite with trigonal morphology [26]. The SEM observation is also in good agreement with the XRD data (Figure 2 b) which confirmed calcite as the major polymorph along with aragonite. The SEM images of the suspended sample depicted the morphology (cauliflower like) similar to the sludge along with filamentous structures crisscrossing over the entire area of the coin.

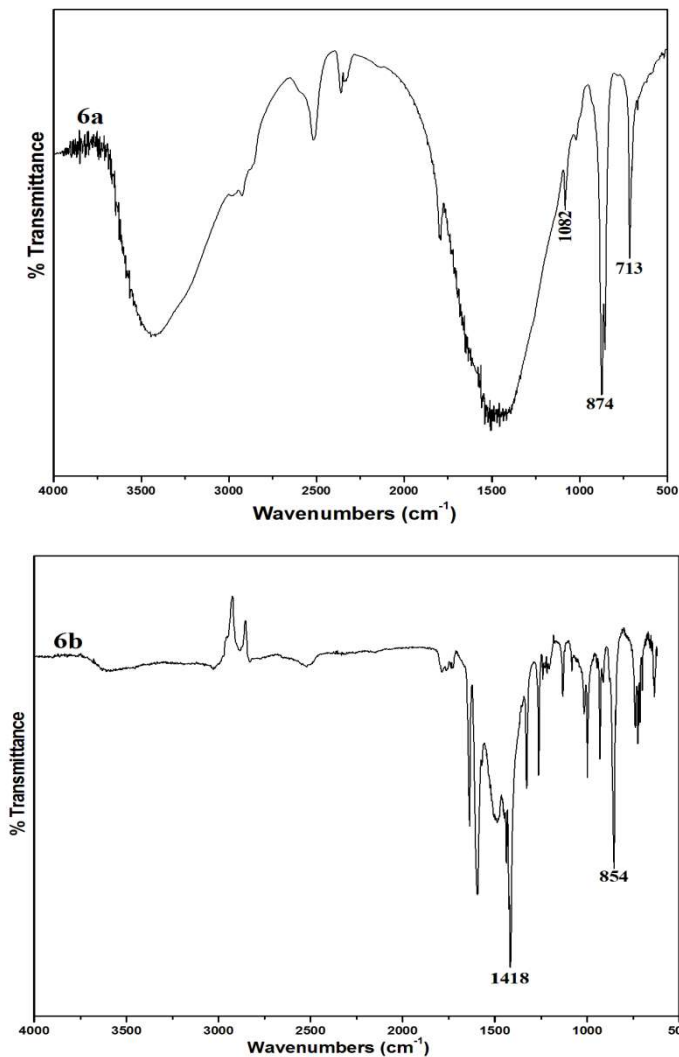
The XRD data indicated only aragonite in this sample. Hence this morphology could be assigned to aragonite. The photos of the coins are provided in Figure 5. The blank substrate (Figure 5 a) which doesn't have any deposition has shining surface and the

copper coin with direct contact with the sludge (Figure 5 b) depicts the intensity and physical appearance of the scale which ascertains the deposition is very thick. The hanged copper coin (Figure 5 c) contained only moderate scale deposition in the metal surface.



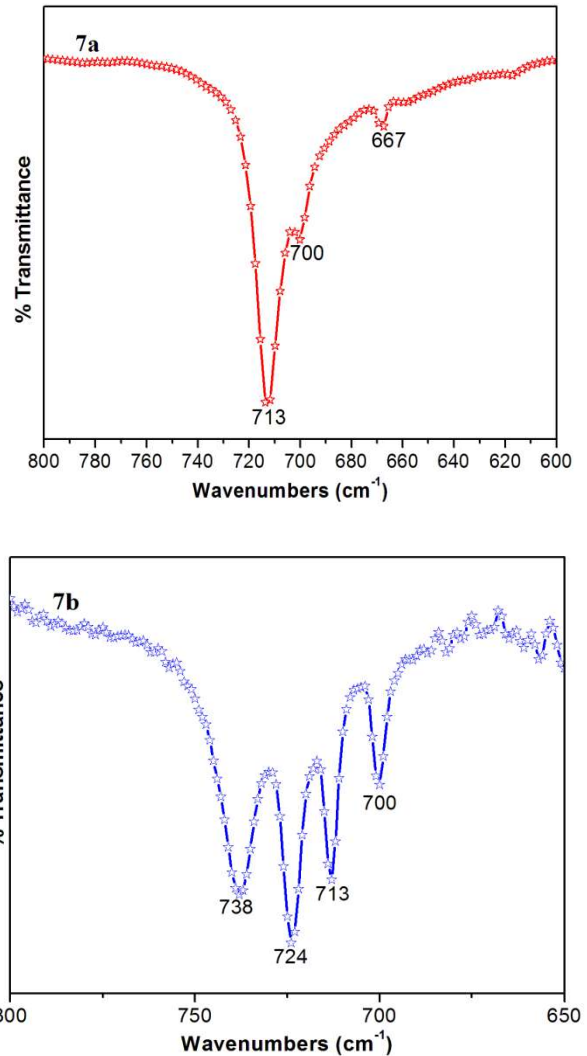
**Figure 5.** Photo of copper coins. (a) Blank, (b) at 100°C in the presence of NTA and direct contact with sludge, (c) suspended sample at 100°C, in the presence of NTA.

The FTIR of the sludge samples obtained at 60 and 100 °C are presented in Figure 6a and 6b respectively. Since the characteristic peaks of aragonite and calcite in the in plane bending mode are very close to each other and overlap the spectra were deconvoluted in the range 600 to 800 cm<sup>-1</sup> and are presented in Figure 7. Presence of characteristic band around 700 cm<sup>-1</sup> confirmed that both the samples contained aragonite [27].



**Figure 6.** FTIR of the sludge in the presence of NTA at 60 (a) and 100 °C (b).

It is apparent from the above discussions that presence of NTA has enhanced the deposition of CaCO<sub>3</sub> scale when in contact with the sludge. This is in contrast to the general expectation and has proved the usage of NTA or NTA based internal treatment programmes could adversely affect the system, particularly at 100 °C.



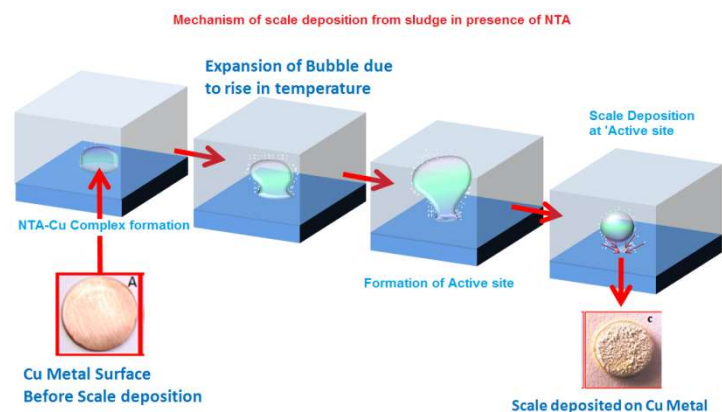
**Figure 7.** Deconvoluted FTIR of the sludge in the presence of NTA at 60 (a) and 100°C (b).

The key factors involved for this unexpected result could be attributed to five parameters: temperature, effect of heating method, proximity of the substrate to the sludge, size of the particles in the sludge and the presence of NTA. It will not be illogical to say that increase in temperature, direct heating and direct contact with the sludge could enhance the deposition. It is obvious from the SEM images that smaller the particles greater the tendency for direct adherence on metal surfaces. This indicates that metal (copper)-nonmetal (CaCO<sub>3</sub>) bond leading to the formation of scale is a phenomena related to the size of the particles and area of contact.

The optimum range of size falls below 10 μ above which the particle exhibit less tendency for adhesion. Once smaller particles form a layer they enhance the adherence ability of larger particles and form further layers. The blank bottom sample hardly contained any scale whereas with NTA the enormous scale was noticed.

A possible mechanism for the anomalous behaviour of NTA could be explained as follows and the schematic

representation of the same is given in Figure 8. The presence of a substantial amount of aragonite in the sludge samples in the presence of NTA indicates that the polymorphic transformation is halted by the latter's presence. This is due to the slow and steady release of calcium ions from the NTA-calcium complex.



**Figure 8.** Mechanism of scale deposition on a metal surface.

#### 4. CONCLUSIONS

The studies demonstrated that the  $\text{CaCO}_3$  scale deposition on copper metal surface was rampant in the presence of NTA at 100 °C. NTA significantly retarded the polymorphic transformation of aragonite to calcite. The nature of heating, contact with the sludge and size of the particles play a major role in the scale deposition. It was observed that particles below 10  $\mu$  form the first layer of scale and larger particles form subsequent

#### 5. REFERENCES

- [1] Tang Y, Yang W, Yin X; Liu Y, Yin P, Wang J, Investigation of  $\text{CaCO}_3$  scale inhibition by PAA, ATMP and PAPEMP, *Desalination*, 228, 55, **2008**.
- [2] Keysar S, Semiat R, Hasson D, Yahalon J, Effect of surface-roughness on the morphology of Calcite crystallizing on Mild-Steel., *J. Coll. Interface Sci.*, 162, 311, **1994**.
- [3] Hasson D, Bramson D, Limoni-Relis B, Semiat R, Influence of the flow system on the inhibitory action of  $\text{CaCO}_3$  scale prevention additives. *Desalination*, 108, 67, **1996**.
- [4] Thachepan S, Li M, Davis S A, Mann S, Additive-mediated crystallization of calcium carbonate in reverse microemulsions, *Chem Mater*, 18, 3557, **2006**.
- [5] Kelland M A, The effect of various cations on the dynamic performance testing of different classes of commercial scale inhibitors. *Ind. Eng Chem Res.*, 50, 5852, **2011**.
- [6] Ahmadi T S, Wang Z L, Green T C, Henglein A, El-Sayed M A, Shape-controlled synthesis of colloidal platinum nanoparticles, *Science*, 272, 1924, **1996**.
- [7] Matijevic E, Controlled colloide formation. *Curr. Opin. Colloid Interface Sci*, 1, 176, **1996**.
- [8] Cölfen H, Qi L, A systematic examination of the morphogenesis of calcium carbonate in the presence of a double-hydrophilic block copolymer, *Chem. Eur. J*, 7, 106, **2001**.
- [9] Yang X, Xu G; Chen Y, Liu T, Mao H, Sui W, Ao M, He F, The influence of O-carboxymethylchitosan on the crystallization of calcium carbonate, *Powder Technol*, 204, 228, **2010**.
- [10] Tang H, Yu J, Zhao X, Controlled synthesis of crystalline calcium carbonate aggregates with unusual morphologies involving the phase transformation from amorphous calcium carbonate. *Mater. Res. Bull.*, 44, 831, **2009**.
- [11] 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

This process releases free NTA into the system which forms complex with copper metal. As the metal surface get heated the water just above the metal surface becomes steam, form bubble and they get inflated with time and temperature and reaches a situation where it cannot hold on to the surface. When they leave the surface, a very small area of highly clean (due to erosion by NTA) and dry surface which may be referred as 'Active site' is created.

This was evident from the colour of the solution which turned bluish after a day and the intensity increased with time. The 'Active site' on the metal surface is instantly splashed with the water just above it which contains a very large number of very fine crystals/colloidal  $\text{CaCO}_3$  particles. As they hit the 'Active site' which is clean, overheated and dry, the smaller particles get adsorbed and larger particles skid off. This action continues in the nearby vicinity and expedites the action of scale deposition. However due to the lack of direct heating, in the hanged sample the possibility of dry surface does not arise and hence deposition is obviously slow.

layers. In the presence of NTA the scale deposition increases with temperature and contact with the sludge.

This study could form the basis for further studies on the mechanisms of controlling the formation and growth of the different scale substances under various chelating agents and will provide the basic frame work necessary for developing new and more efficient methods for overcoming the scaling problem.

- inhibitor on calcium carbonate crystal forms, *Sci. China B Chem.*, 50, 114, **2007**.
- [12] Amjad Z J, Calcium sulfate dihydrate (gypsum) scale formation on heat exchanger surfaces: The influence of scale inhibitors, *Coll. Interface Sci.*, 123, 523, **1988**.
- [13] Amjad Z, Hooley J, Influence of polyelectrolytes on the crystal growth of calcium sulfate dehydrate, *J. Coll. Interface Sci.*, 111, 496, **1986**.
- [14] Xiao J, Wang Z, Tang Y, Yang S, Biomimetic mineralization of  $\text{CaCO}_3$  on a phospholipid monolayer: from an amorphous calcium carbonate precursor to calcite via vaterite, *Langmuir*, 26, 4977, **2010**.
- [15] Pontoni D, Bolze J, Dingenouts N, Narayanan T, Ballauff M J, Crystallization of calcium carbonate observed in-situ by combined small- and wide-angle x-ray scattering, *J Phys Chem B.*, 107, 5123, **2003**.
- [16] Kim, W, Robertson R E, Zand R, Effects of some nonionic polymeric additives on the crystallization of calcium carbonate, *Cryst. Growth Des.*, 5, 513, **2005**.
- [17] Zieba A G, Sethuraman F P, Nancollas G H, Cameron D, Influence of organic phosphonates on hydroxyapatite crystal-growth kinetics, *Langmuir*, 12, 2853, **1996**.
- [18] Demadis K D, Baran P J, Chemistry of organophosphonate scale growth inhibitors: two-dimensional, layered polymeric networks in the structure of tetrasodium 2-hydroxyethyl-amino-bis(methylenephosphonate), *Solid State Chem*, 17, 4768, **2004**.
- [19] Amjad Z, Constant composition study of dicalcium phosphate dihydrate crystal growth in presence of poly(acrylic acid), *Langmuir*, 5, 1222, **1989**.
- [20] Gopi S P, Subramanian V K, Palanisamy K, Synergistic effect of EDTA and HEDP on the crystal growth, polymorphism, and morphology of  $\text{CaCO}_3$ , *Ind. Eng. Chem. Res.*, 54, 3618, **2015**.
- [21] Wu Q S, Sun D M, Liu H J, Ding Y P, Abnormal polymorph conversion of calcium carbonate and nano-self-assembly of vaterite by a supported liquid membrane system, *Cryst. Growth Des.*, 4, 717, **2004**.

[22] Gopi S P, Subramanian, V. K. Polymorphism in CaCO<sub>3</sub>-Effect of temperature under the influence of EDTA (di sodium salt). *Desalination*, 297, 38, **2012**.

[23] Yang B, Nan Mater Z, Effects of 1,3,5-trimethylbenzene on morphology and polymorph of CaCO<sub>3</sub> crystals in the presence of SDS. *Res. Bull.*, 48, 4319, **2013**.

[24] Gopi S P, Vijaya P, Subramanian, V. K. Morphological and crystallization process of CaCO<sub>3</sub> in the presence of aqua soft 330 (AS 330), *Powder Technol.*, 225, 58, **2012**.

[25] Palanisamy, K. Subramanian, V K, CaCO<sub>3</sub> scale deposition on copper metal surface; effect of morphology, size and area of contact under the influence of EDTA, *Powder Technol.*, 294 221, **2016**.

[26] Gopi S P, Palanisamy K, Subramanian V K, Effect of NTA and temperature on crystal growth and phase transformations of CaCO<sub>3</sub>, *Desalination and water treatment*, 1, **2014**.

[27] Andersen F A, Brecevic L, Infrared spectra of amorphous and crystalline calcium carbonate. *Acta Cshem. Scand.*, 45, 1018, **1991**.

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