Probing the Inhibitory Mechanism of Calcite Precipitation by Organic Phosphonates in Industrial Water Cooling System

Mingzhu Xia and Chunyu Chen

Abstract—The effect of three phosphonic acids (ethylene diamine tetra (methylene phosphonic acid), EDTMP; hexamethylene diamine tetra (methylene phosphonic acid), HDTMP; and diethylene triamine penta (methylene phosphonic acid), DTPMP on the growth of $CaCO_3$ has been investigated by pH curve method (pHCM). The result shows the inhibitor effectiveness: DTPMP > EDTMP > HDTMP. Meanwhile, the interaction of three phosphonic acids with the calcite (104) surface has been also studied by means of molecular dynamic simulation under the periodic boundary condition in industrial water environment. The results indicate that strong electrostatic interactions between the oxygen atom in phosphonate functional groups and the Ca^{2+} of the calcite (104) face play a dominant role in their adsorption. For the calcite (104) surface, the binding energy has a sequence in agreement with the pHCM experiment. The weakest inhibition of $CaCO_3$ is HDTMP because of the only one phosphonate group in contact well with the surface.

Index Terms—Phosphonate, pH curve method, inhibition, molecular dynamic simulation.

I. INTRODUCTION

The precipitation of calcium carbonate is of fundamental importance in great many researches for instance medicine, industry, and households [1]-[3]. Calcium carbonate particles are found as different polymorphs, consisting of calcite, aragonite, vaterite, calcium carbonate monohydrate and calcium carbonate hexahydrate [4]. Among them, calcite is by far the most stable phase under normal atmospheric conditions, and is extensively investigated as a scale product in many industrial processes [5]. The (104) surface is the most stable plane of calcite and dominates the observed morphology [6], [7].

Phosphonate additives are often used to inhibit the formation of this scale in industrial water cooling system [8], [9]. Phosphonates have a strong tendency to adsorb onto a variety of surfaces, e.g., calcite [10], barite [11] and iron oxides [12].

To date, more relevant studies have concentrated on understanding the dominant mechanisms of calcite crystal growth in the presence of inhibitors. It appears, for instance, that the ionization of the phosphonate group is significant;

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that is, a deprotonated phosphonate molecule inhibits precipitation more strongly [11]. Gill *et al.* have proposed the theory of lattice matching that there is a link between the mineral lattice and the functional group spacing which dominates inhibitory power [13].

Moreover, Franca *et al.* have studied the adsorption of two phosphonate groups from different amine groups on barite crystal. It has been found that both stereochemical hindrance and complexation strength differences results in different inhibitory power [14]. Bromley *et al.* investigated the effect of chain length between the two phosphonates. They found that the greastest inhibition of barite growth occurred when the link was greater than 6 Å. C. M. Pina presented the effect of five phosphonic acid on the growth of barite (001) using atomic force microscopy (AFM), and indicated that only kink sites along monomolecular steps can be considered as possible inhibition sites [15]. Molecular modeling could also been used to identify organo metallic interaction [16]. Ibrahim has studied the effect of industrial waste disposal south of Cairo on the molecular structure of Nile River sediment by both Fourier transform infrared spectroscopy (FT-IR) and density functional theory (DFT) [17].
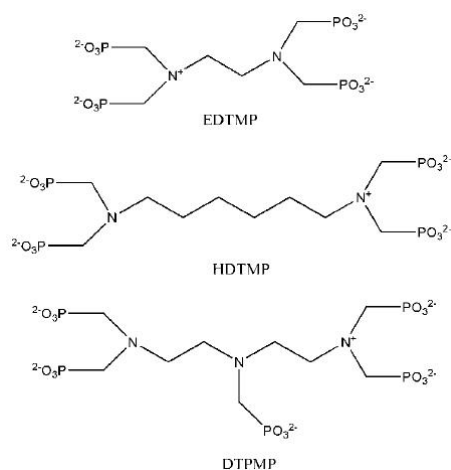

Fig. 1. Structures of depronated phosphonic acids at pH around 8.

In previous work, the interaction of three phosphonates (EDTMP, HDTMP and DTPMP) with calcite surfaces was examined by both the pH curve method and molecular dynamic simulation in the absence of water molecules [18]. The results show that phosphonates have a high affinity for calcite. But the stimulant conditions don't conform to the actual circulating water system. The aim of this work described here is to investigate the effect of molecular adsorption of the three phosphonates on calcite (104) surface using the same method in an alkalescent industrial water

environment. EDTMP and HDTMP have four phosphonate functional groups attached to amine nitrogen atoms through methylene chain. The only diffference is the length of the backbone methylene chain. But DTPMP has five phosphonate groups attached to three N atoms. The structures (see in Fig. 1) are deprotonated referring to the pH values in the range of 7-8 in an alkalescent industrial water environment.

II. EXPERIMENT

A. Materials

CaCl$_2$ (AR grade, Nanjing Chemical Regent CO., LTD); NaHCO$_3$ (AR grade, Shanghai LingFeng Chemical Regent CO., LTD); EDTMP, HDTMP and DTPMP are commercial samples from Shangdong Zaozhuang Xudong Chemical Regent CO., LTD.

A PHS- 3C pH meter from Shanghai Precision Scientific Instrument CO., LTD and a 78-1 magnetic heating stirrer from Jintan Jiangnan Instrument CO., LTD were seperately used for pH measurement and stirring.

B. The pH Curve Method (pHCM)

The concentration of OH$^-$ increases owing to escape of CO$_2$ by stirring. The precipitation of CaCO$_3$ occurs, when OH$^-$ reacts with HCO$_3^-$. Consequently, the pH value drops due to the formation of CaCO$_3$ scale (seen in (1)).

$$OH^- + HCO_3^- \rightleftharpoons CO_3^{2-} + H_2O$$
$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_3 \downarrow \tag{1}$$
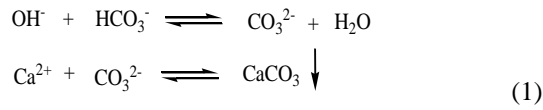
250 mL of stable supersaturated solution of calcium carbonate (8mmol/L) was prepared by the addition of a known volume of calcium chloride solution (0.1mol/L) and sodium bicarbonate (0.2mol/L). The mixed solutions were measured of pH values after the addition of a range of different concentrations of the phosphonate acids at the temperature of 25℃.

C. Molecular Dynamics (MD) Simulation Method

The space group of calcite, is R-3C and its lattice parameters are $a = b = 4.99$ Å, $c = 17.06$ Å, $\alpha = \beta = 90.0°$, $\gamma = 120.0°$. Calcite crystallographic surface was built by cleaving along the (104) face, followed by minimized using Newton under the periodic boundary conditions with a non-bond cutoff distance of 9.5 Å.

We have simulated the three deprotonated nitrogen-containing phosphonates (EDTMP[7-], HDTMP[7-] and DTPMP[9-]) onto the calcite (104) face in industrial water environment using Materials Studio v3.0 (MS) under compass force field used in the previous studies [19]. Simulation details of MD are shown in Table I.

The strength of interaction of the surface with the inhibitor is shown by binding energy, calculated according to (2):

$$E_{bind} = -(E_{system} - E_{inhibitor+water} - E_{surface+water} + E_{water}) \tag{2}$$

where E$_{system}$ is the total energy of the simulation system, E$_{surface+water}$ is the energy of the surface with water,

E$_{inhibitor+water}$ is the energy of the free inhibitor moelcule with water, and E$_{water}$ is the energy of the free water molecule after calculation.

TABLE I: SIMULATION DETAILS OF MD

Simulation parameter	value
Force field	Compass
Non-bond	Vdw, Coulomb
Ensemble	NVT
Thermostat	Berendsen
Time step	1fs
Frame output	100
Dynamic time	500ps
Cut-off distance	0.95nm
Dielectric constant	78.0
Summation method	Atom Based
Simulation temperature	350K
Minimization	Smart Minimizer
Convergence level	Medium
Maximum iterations	5000
Energy deviation	5000kal/mol
Number of Steps	500000
Production Steps	15ps
Decay constant	0.1ps

III. RESULTS AND DISCUSSIONS
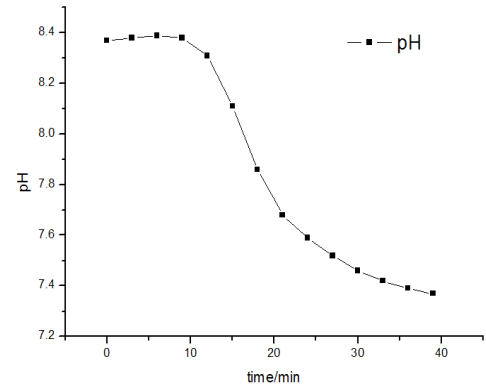
A. The pHCM Exprements

Fig. 2. The pH value in the absence of the phosphonates.
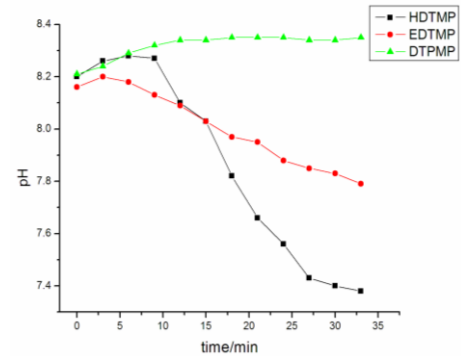

Fig. 3. the pH values in presence of the phosphonates at the concentration of 0.0002 mmol/L.

The pHCM exprements have been performed in the presence of the three phosphonates. Fig. 2 shows the pH value speedily raised in the absence of the phosphonates in ten minutes, afterwards decreased rapidly that indicates the growth of CaCO$_3$ sediment. In order to qualitatively analyze the inhibiting effect of the EDTMP, HDTMP, and DTPMP, the pH values of the mixed solutions are measured after the

addition of the inhibitors in different concentrations (0.0001mM ~ 0.0004mM). For direct elucidation, it only shows the pH values at the inhibitor concentration of 0.0002mM in Fig. 3.

When 0.0002mmol/L concentrations are employed, pH slowly raised. Hence, the inhibition of $CaCO_3$ growth by DTPMP is fully successful. At the same concentration, the pH decrease of HDTMP is faster than EDTMP; that is, the inhibition effect of HDTMP is weaker than EDTMP.

B. Interaction of Deprotonated Phosphonates with the Calcite (104) Face in Water

In order to conform to the aqueous medium of industrial water treatment, the movement and effect of water in the total system has been considered by means of setting the permittivity (dielectric constant, ε) and adding water molecules. In this paper, ε is set of 78.0 and a mass of water molecules are added to each surface of calcite according with water environment.
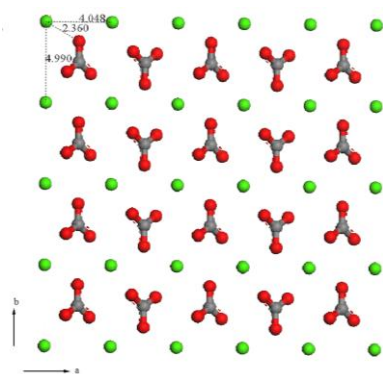

Fig. 4. Top view of the calcite(104) face. Color codes: calcuim atom= green; carbon atom= grey; oxygen atom= red.
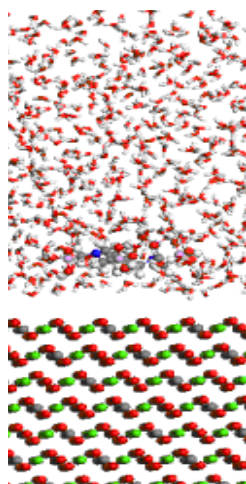

Fig. 5. Side view of original state on calcite (104) face.

The Ca-Ca distances of the calcite (104) surface are separately 4.048 Å and 4.990 Å; the Ca-O length is 2.360 Å (Fig. 4). All the three phosphonate acids were also first minimized by the same minimization method before doing MD simulations. The vacuum chamber is divided into three parts. More specifically, the vacuum is at the top; water molecules and scale inhibitor are in the middle of the box, while the calcite (104) surface is at the bottom. The simulative dimensions of vacuum brake are 24.28 Å×19.96 Å×86.27 Å, and $α=β=γ=90$ °. There are approximately 2400

atoms in the box, for instance, shown in Fig. 5. We have separately considered the interaction of three phosphonate acids with the calcite (104) face. In Fig. 6, it clearly shows all of the phosphate molecules point towards the calcite (104) surface instead of water molecules. The results suggest that the phosphonates interact well with the calcite (104) surface on account of its oxygen atoms of phosphate group contacting well with calcium ions on the surface.
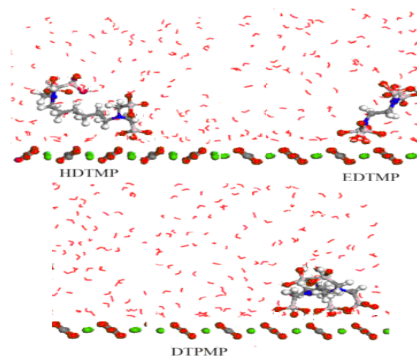

Fig. 6. Side view of 3 compounds adsorption on the calcite (104) surface.

Both EDTMP and HDTMP have four phosphonate functional groups attached to amine N atoms. The only difference is the length of the backbone methylene chain connecting the two N atoms. Bromley *et al*. recognize that one of the amine groups "approaches" the barite crystal surface [20]. It has been seen from the above images that one of the amine groups of two phosphonates interacts with the calcite surface.

In particular, only one phosphonate group of HDTMP has been adsorbed on the face owing to the methylene chain bending itself, while two phosphoante groups are absorbed in EDTMP. Both EDTMP and HDTMP have four phosphonate functional groups attached to amine N atoms. More importantly, the potency varies with the length of alkyl chain connecting the two N atoms, which induces the effect: EDTMP > HDTMP. It might be that the length of the backbone chain is too longer to increase the steric hindrance. The length of the backbone chain in HDTMP is 9.077 Å, whereas the length in EDTMP is 3.114 Å. DTPMP has five phosphonate groups, and three of them "approach" the surface. Thus, the greater the number of phosphonate groups, the greater the inhibition of scale formation.
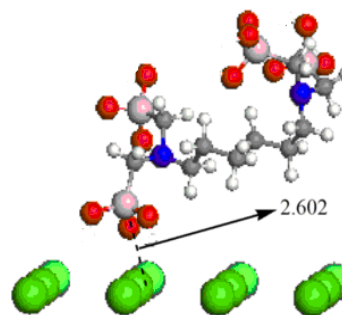

Fig. 7. Adsorption of HDTMP[7-] on calcite (104) face, and the combination of Ca^{2+} with oxygen atom.

It has been found that, in general, the dominant mechanism of interaction for the additives on calcite is via the deprotonated groups with calcium ions on the surface. For

example, Fig. 7 displays the adsorbed mode of HDTMP on the calcite (104) surface and the combination of Ca^{2+} with oxygen atom. The Ca-O (P) distances are about 2.6 Å in accordance with the Ca-O bond length in experience, while the distances are separately 2.52 Å and 2.67 Å in EDTMP, and 2.47 Å, 2.55 Å, 2.63 Å in DTPMP. Apparently, DTPMP has the most significant inhibition effect compared with the remaining two phosphonate additives.

For further analysis of the effectiveness of inhibition, we consider the binding energy of interaction between the three phosphonate molecules and the calcite (104) surface in the aqueous phase listed in Table II. It clearly indicates the energy of interaction is dominated by electrostatic interaction, whereas the van der Waals interaction plays a very small role in the non- bonded interaction. Based on the data in Table II, the interaction energy is exothermic and the effectiveness of inhibiton is DTPMP> EDTMP> HDTMP in agreement with the pH curve experimental result. Hence, it has been proved that molecular modeling can predict the phosphonate's ability to inhibit precipitation under the simulation details. In short, inhibition could be tested easily and more cheaply on computers than by experiment.

TABLE II: ENERGIES BETWEEN 3 COMPOUNDS AND CALCITE (104) SURFACE (UNIT: EV)

Molecule	E_{vdw}	$E_{coulomb}$	$E_{nonbond}$	E_{bind}
HDTMP	-2.04	-39.12	-41.18	42.57
EDTMP	-2.50	-63.63	-66.15	67.64
DTPMP	-2.45	-95.37	-97.86	99.95

It is noted that there is a strongest adsorption peak at the range from 2 Å to 3 Å (Fig. 8) which indicates the interaction between the calcium atoms and the oxyen atoms in inhibitors. Our these findings are consistent with the above analysis.
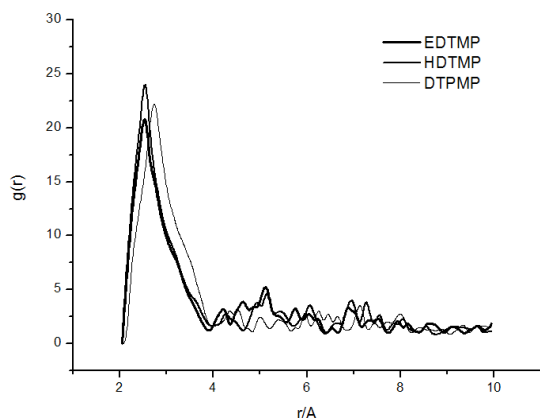

Fig. 8. Pair correlatiom function of oxygen atoms in inhibitors with calcium atoms in calcite (104) surface.

IV. CONCLUSION

This work is a study of molecular interaction between phosphonate acids with calcite in presence of water. In summary, organic phosphonates have a significant effect on precipitation. Both the pHCM experiments and molecular dynamics simulation method have proved the conclusion that the inhibition of three organic phosphonates is DTPMP > EDTMP > HDTMP according to their group number and the length of the backbone methylene chain. It also indicates the

energy of interaction is dominated in electrostatic interaction, whereas the van der Waals interaction plays a very small role in the non- bonded interaction. This paper provides an easy and cheap means to determine the inhibition potency of additives. Future work will focus on studies of the interaction of phosphonates with the aragonite and vaterite surfaces in presence of water and the interaction of the calcite stepped surfaces with phosphonates in presence of Na^+ or Zn^{2+} ions.

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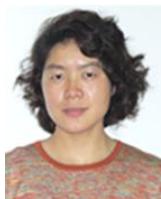
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