Calcium Carbonate Precipitation in the Presence of Inhibitors

Zahid Amjad and Robert W. Zuhl,
Lubrizol Advanced Materials, Inc., Cleveland, Ohio

This article presents a study on the precipitation of calcium carbonate ($CaCO_3$) in aqueous solutions with varying degrees of calcite supersaturation in the presence of inhibitors. Results are discussed in terms of retardation rate of $CaCO_3$ precipitation by phosphonates, polymers, and phosphonate/polymer blends, and the influence of inhibitors on crystal morphology.

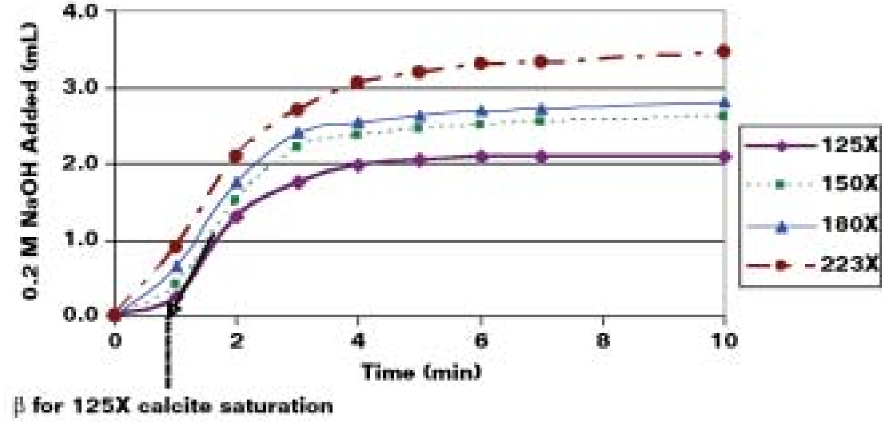
Calcium carbonate ($CaCO_3$) is one of the most commonly encountered scale deposits. It occurs in different crystalline forms: calcite, aragonite, vaterite, $CaCO_3$ monohydrate, and $CaCO_3$ hexahydrate. The precipitation and stabilization of these polymorphs depends upon the precipitation conditions—degree of supersaturation, pH, ionic medium, and concentration and type of impurities. The precipitation and deposition of $CaCO_3$ continues to pose serious operational problems in industrial water systems. The formation of these deposits reduces heat transfer and internal diameter of pipes, increases the operating pressure of pumps, and enhances the probability of corrosion. Major progress has been made toward the understanding of phosphonate solution and precipitation chemistry as well as how this relates to fouling problems in industrial water systems.

Ashcraft,[1] in his study on the interaction of calcium ions with various phosphonates, showed 2-phosphonobutane 1,2,4–tricarboxylic acid (PBTC) to be superior to aminotrismethylene phosphonic acid (AMP) and 1-hydroxyethylidine 1,1-diphosphonic acid (HEDP) in the presence of high calcium ion presumably due to the greater solubility of Ca-PBTC salt.

Amjad[2] recognized that the relatively poor calcium tolerance of phosphonates can be improved by the addition of acrylic acid-based co- and terpolymers. The precipitation of Ca-phosphonate salts can directly cause heat exchanger fouling and indirectly cause severe $CaCO_3$ scaling because of the decrease in phosphonate concentrations.

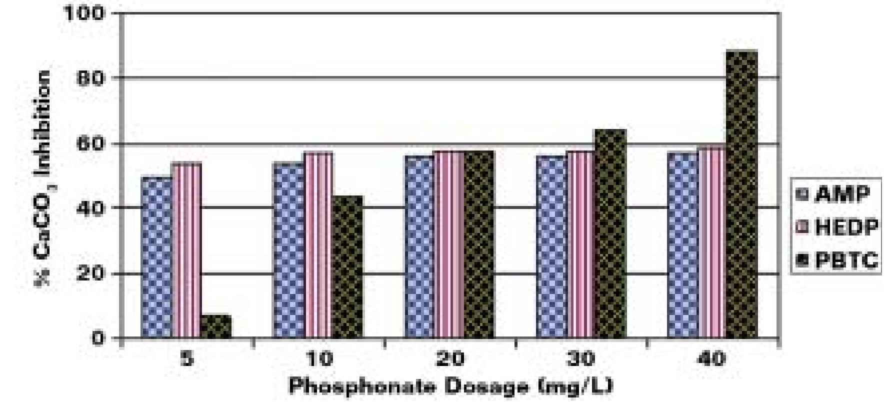
During the last two decades, investigations of polymeric inhibitors to prevent or retard $CaCO_3$ scaling have attracted the attention of academic and industrial researchers. Common inhibitors evaluated include poly(acrylic acid), poly(maleic acid), and co-polymers containing acrylic acid or maleic acid and other monomers with different functionality. Investigations of these and several other mineral scale inhibitors suggest that inhibitor effectiveness depends on the functional groups in the inhibitor molecule, molecular weight (MW), and polymer composition.[3-4] In the present study, the performance of phosphonates, polymers containing different functional groups, and phosphonate/polymer blends as precipitation inhibitors for $CaCO_3$ in aqueous solution has been investigated by the pH-stat technique. This study also presents results on the crystal morphology of $CaCO_3$ by various inhibitors.

FIGURE 1



Precipitation of $CaCO_3$ at several calcite supersaturations.

FIGURE 2



Effect of phosphonate concentration on $CaCO_3$ inhibition at 180X calcite saturation.

Experimental Procedures

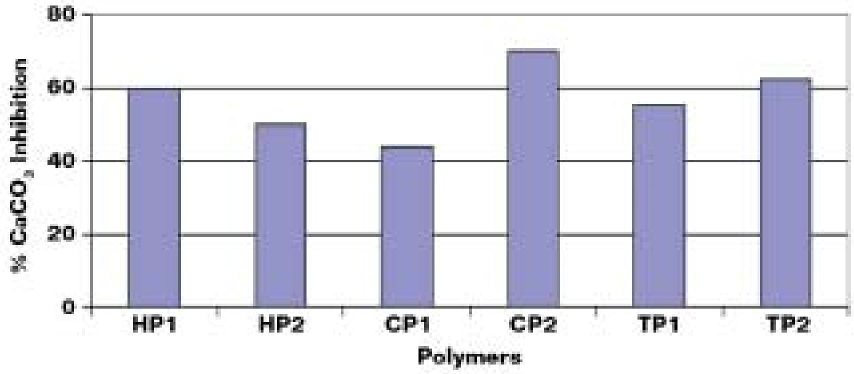
The stock solutions of calcium chloride and magnesium chloride were prepared from reagent grade chemicals and were standardized by atomic absorption spectroscopy. The sodium carbonate and sodium bicarbonate solutions were prepared on the day of each experiment. Phosphonates and polymers used in this study were commercial materials and stock solutions of these inhibitors were prepared on an active solids basis. The polymers tested include: (a) poly(acrylic acid), HP1, MW <5k; poly(maleic acid), HP2, MW <2k; (b) co-polymers of acrylic acid:maleic acid, CP1, MW <3k, and acrylic acid:2-acrylamido-2-methylpropane sulfonic acid, CP2, MW <15k; and (c) multifunctional polymer, TP1, MW <15k, and acrylic acid: 2-acrylamido-2-methylpropane sulfonic acid: sulfonated styrene, TP2, MW <15k. The phosphonates evaluated were AMP, HEDP, and PBTC. Table 1 summarizes the water chemistries used in the $CaCO_3$ precipitation experiments. Note: CP2 and TP2 are Carbosperse™ K-775 and K-798 polymers, respectively, supplied by Lubrizol Advanced Materials, Inc. (Cleveland, Ohio).

The $CaCO_3$ precipitation experiments were done in a 250-mL double-walled Pyrex[†] glass cell thermostatted by water circulated from a constant temperature bath. The working solution was stirred with a Teflon[†]-coated stirring bar. The pH was measured by a combination electrode. The $CaCO_3$ supersaturation conditions used in this study were determined by using common ion computer modeling. The appropriate volume of HCO_3/CO_3 solutions were combined to create supersaturated conditions. The supersaturated solutions (223 mL total volume) were prepared in the reaction cell by adding a known volume of stock solutions containing Na_2CO_3, $NaHCO_3$, and inhibitor. After equilibrating the solutions at 50°C for 30 min, a known volume of stock solution of $CaCl_2$ and $MgCl_2$ was added. The pH of the $CaCO_3$ supersaturated solutions was quickly (typically <20 s) adjusted to 9.00 and kept constant by the automatic addition of 0.2 M sodium hydroxide (NaOH) solution. The uptake of NaOH was also recorded on a strip chart recorder. At the end of precipitation experiments, the solutions were filtered and filtrate-analyzed for Ca by the atomic absorption method. The $CaCO_3$ solids collected on the membrane filters were analyzed by

---

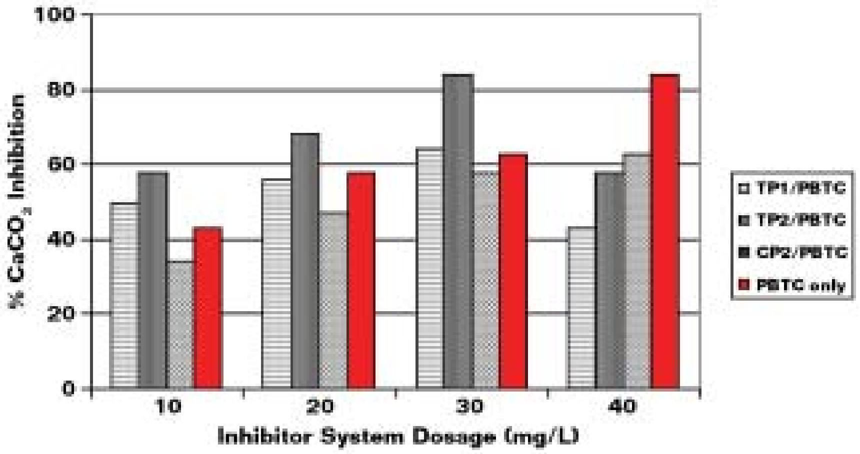
[†] Trade name.

FIGURE 3



$CaCO_3$ inhibition in the presence of 30 mg/L of polymer dosages at 180X calcite saturation.

FIGURE 4



$CaCO_3$ inhibition by polymer/PBTC blends (3:1) at 180X calcite saturation.

x-ray diffraction (XRD) and scanning electron microscopy (SEM). Inhibitor efficacy as $CaCO_3$ inhibitor was calculated using the following equation:

$$\text{Inhibition } (\%) = [([\text{Ca}]_{\text{sample}} - [\text{Ca}]_{\text{control}}) / ([\text{Ca}]_{\text{initial}} - [\text{Ca}]_{\text{control}})] \times 100 \quad (1)$$

where $[\text{Ca}]_{\text{sample}}$ = concentration of Ca in the filtrate in the presence of inhibitor at 1 h, $[\text{Ca}]_{\text{control}}$ = concentration of Ca in the filtrate in the absence of inhibitor at 1 h, and $[\text{Ca}]_{\text{initial}}$ = concentration of Ca in the solution at 0 h. Because $CaCO_3$ precipitation reaction in the absence of inhibitor is essentially completed in <10 min, we chose a 1-h precipitation period as the basis for comparing results.

Results and Discussion

Using the pH-stat method, a large number of experiments were conducted to study $CaCO_3$ precipitation from supersaturated solution as a function of time. The experiments reported here had good reproducibility (±7%). Figure 1 shows the amount of NaOH required (added) as a function of time to maintain a constant pH in calcite-saturated (ranging from 125X to 223X) solutions (without inhibitors) as $CaCO_3$ forms.

As illustrated in Figure 1, a measurable lag (delay) or induction time occurs (hereafter called β) in the development of precipitate. The determination of β is illustrated in Figure 1. It is evident from Figure 1 that the β value decreases as the calcite saturation is increased. For example, the β value that was obtained for the 125X calcite saturation is 48 s compared to 20 s obtained for 223X calcite saturation.

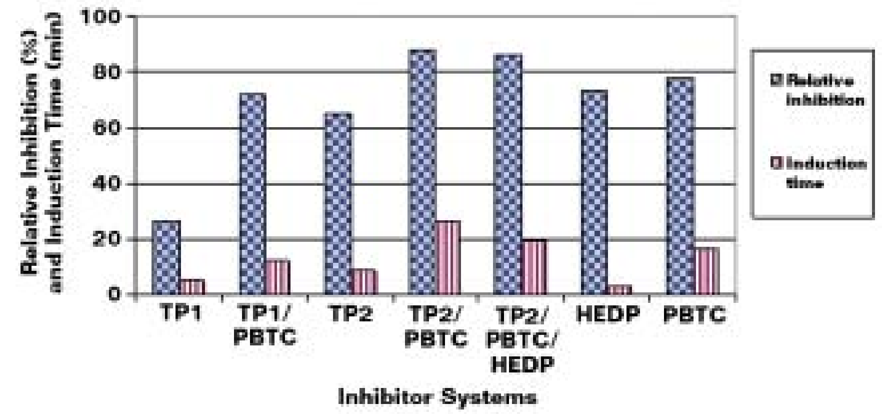
Effect of Phosphonates

To study the effect of phosphonates on $CaCO_3$ precipitation at low-to-medium calcite saturation (150X and 180X), a series of experiments was performed in the presence of AMP, HEDP, and PBTC. Figure 2 shows the plots of $CaCO_3$ inhibition as a function of phosphonate dosages for AMP, HEDP, and PBTC. It can be seen that at 180X calcite saturation, none of the phosphonates completely inhibited $CaCO_3$ precipitation. It is worth noting that the $CaCO_3$ inhibition data for low phosphonate dosages (<10 mg/L) indicate much poorer performance for PBTC compared to AMP and HEDP. However, as illustrated in Figure 2, all three phosphonates at 20 mg/L dosages provide similar performance. Furthermore, when the phosphonate dosage is increased to 40 mg/L, PBTC exhibits better performance than both HEDP and AMP.

Effect of Polymers

The efficacy of various homo-, co-, and terpolymers as $CaCO_3$ inhibitors was evaluated at various polymer dosages. Figure 3 presents results on percent $CaCO_3$ inhibition in the presence of 30 mg/L polymer dosages. It can be seen that HP1 (P-AA) performs better than HP2 (P-MA). Among co-polymers, CP2 (AA:SA) exhibits better $CaCO_3$ inhibition than CP1 (AA:MA). In addition, as illustrated in Figure 3, TP2 is a better inhibitor than TP1. This difference in performance may be attributed to different molecular weight and polymer composition.

FIGURE 5



$CaCO_3$ relative inhibition and induction time at 223X calcite saturation in the presence of 40 mg/L of various inhibitor systems.

Effect of Polymer/Phosphonate Blends

Figure 4 presents $CaCO_3$ inhibition data for three polymer/PBTC (3:1) blends (incorporating high-performance polymers [i.e., TP1, TP2, and CP2] as components) at various dosages (10 to 40 mg/L) and 180X calcite saturation. The data clearly show that polymers impact $CaCO_3$ scale inhibition performance in different ways and that the TP2/PBTC blend is the most effective. Although the data are not presented herein, it is noteworthy that a similar synergistic effect was observed with polymer/HEDP (3:1) blends. Under the experimental conditions employed (i.e., 180X calcite saturation, 30 mg/L inhibitor concentration), the following order in terms of decreasing effectiveness was observed:

TP2/HEDP > TP1/HEDP >
HP1/HEDP > CP1/HEDP

Kinetic Aspects of $CaCO_3$ Precipitation and Inhibition

As discussed in this study, we have investigated the influence of a variety of polymers, phosphonates, and polymer/phosphonate blends by a pH-stat method for their performance as $CaCO_3$ inhibitors. Several concentrations of each inhibitor were tested, giving results ranging from no inhibition to induction times of 3 to >300 min. To determine the impact of inhibitors on the kinetics of precipitation, we have used the initial rate of precipitation as calculated from the uptake of NaOH vs time profiles for various inhibitors. The precipitation rates relative to the absence of inhibitor were calculated using the following equation:

$$\text{Relative Inhibition (\%)} = (1 - R_i/R_o) \times 100\% \qquad (2)$$

In Equation (2), R_o is the precipitation rate in the absence of inhibitor and R_i is the precipitation rate in the presence of inhibitor. Figure 5 presents induction time (β) and relative inhibition (%) data for 40 mg/L dosages of several inhibitor systems. There are two points worth mentioning. First, the β value obtained for PBTC is 16 min, which is more than 500% larger than the β value for HEDP (3 min). Similarly, TP2 gives a higher induction time than TP1, suggesting that sulfonate groups in TP2 improve the performance of PBTC. Second, both terpolymers work synergistically with PBTC and HEDP, but the TP2/PBTC (3:1) blend at 40 mg/L performs better than TP1/PBTC under similar experimental conditions. For example, relative inhibition values obtained for TP2/PBTC and TP1/PBTC blends are 88% and 72%, respectively. The higher performance exhibited by TP2 over TP1 is consistent with earlier investigations on the performance of these polymers as precipitation control agents for calcium phosphate and calcium phosphonates.[5-6]

Effect of Phosphonates, Polymers, and Phosphonate/Polymer Blends on $CaCO_3$ Crystal Morphology

As discussed above, we investigated a number of polymers, phosphonates, and phosphonate/polymer blends by a pH-stat method for their efficacy as $CaCO_3$ inhibitors. Several concentrations of each inhibitor were tested, giving results ranging from induction time of <1 min (in the absence of inhibitor) to >120 min. The $CaCO_3$ crystals formed in the absence and presence of inhibitors were examined by XRD and SEM for crystal morphology.

Table 1 summarizes the composition of $CaCO_3$ polymorphs formed in the presence and absence of inhibitors as determined by XRD data. It is evident from Table 1 that at the four (4) $CaCO_3$ supersaturations investigated, in the absence of inhibitors the crystals formed are a mixture of calcite, vaterite, and aragonite, with calcite, the thermodynamically most stable polymorph, as a major component (~60%).

It is interesting to note that at low supersaturation (i.e., 125X calcite saturation), the percent calcite formed increases to 81% compared with ~60% obtained at higher calcite supersaturations. However, the situation in the presence of phosphonate, polymer, and phosphonate/polymer blends is different because the predominant polymorph is calcite (>90%) and vaterite is a minor (<10%) component. This suggests that both aragonite and vaterite polymorphs are stabilized by inhibitors evaluated in the present study. The XRD data obtained for $CaCO_3$ crystals formed in the absence of

TABLE 1

A. Water Chemistries Corresponding to Calcite Saturation Used in CaCO$_3$ Inhibition Experiments

Calcite Saturation	223X	180X	150X	125X
LSI	2.89	2.76	2.66	2.55
Calcium (mg/L as Ca)	250	210	180	154
Magnesium (mg/L as Mg)	75	63	54	46
Sodium (mg/L as Na)	240	228	196	166
Bicarbonate (mg/L as HCO$_3$)	450	380	326	280
Carbonate (mg/L as CO$_3$)	100	100	100	100
Chloride (mg/L as Cl)	626	558	480	41
pH	9.00	9.00	9.00	9.00
Temperature (°C)	50	50	50	50

B. Data for CaCO$_3$ Polymorphs Formed Under Different Water Chemistries and in the Presence of Various Inhibitors

Ca (mg/L)	Inhibitor	% Calcite	% Aragonite	% Vaterite
250	None	65	22	13
210	None	59	29	12
180	None	58	36	6
154	None	85	8	7
210	TP2 @ 30 mg/L	81	19	0
210	HP1	96	4	0
210	AMP @ 5 mg/L	95	5	0
210	HEDP @ 5 mg/L	96	4	0
210	PBTC @ 5 mg/L	96	4	0
210	TP2/PBTC (3:1) blend @ 30 mg/L	92	8	0
220[A]	Control	5	0	95
220[A]	Fulvic Acid @ 5 mg/L	100	0	0
220[A]	Poly(acrylic acid) @ 0.5 mg/L	0	0	100

[A] 220 mg/L Ca; 2,426 mg/L Na; 336 mg/L HCO$_3$; 3,940 mg/L Cl; pH 8.5; and 35°C

magnesium are presented in Table 1. It is interesting to note that at low calcite saturation and in the absence of magnesium ion, the predominant (>90%) polymorph is vaterite with calcite as a minor component. This agrees with other studies which reported that when spontaneous precipitation occurs, vaterite is the initially forming polymorph.[7] As shown in Table 1, both fulvic acid (or FA, a natural polymer containing phenolic and carboxyl groups) and a synthetic polymer [i.e., poly(acrylic acid) or P-AA] used at low concentrations exhibit different effects on the crystal morphology. It is evident from the data in Table 1 that calcite is the predominant polymorph formed in the presence of FA whereas vaterite is the predominant polymorph in the presence of P-AA. The change in crystal morphology observed in the presence of FA and P-AA suggest that functional groups present in the inhibitors not only influence the kinetics of precipitation but also affect the stabilization of different CaCO$_3$ polymorphs.

Summary

The data presented in this article suggest that both nonpolymeric (i.e., phosphonates) and polymeric (homo-, co-, and terpolymers) inhibitors exhibit different influences on the precipitation of CaCO$_3$ from supersaturated solutions. It has been found that under high-stressed water chemistries used in the present investigations, neither phosphonates nor any type of polymeric inhibitors completely prevent the precipitation of CaCO$_3$. It has also been observed that blends of terpolymer (i.e., TP2) with PBTC exhibit synergistic influence on the precipitation inhibition of CaCO$_3$.

The XRD data on crystals formed during precipitation in the presence of inhibitors reveal that crystal morphology strongly depends upon solution supersaturation and the type and concentrations of inhibitors. It has been found that phosphonates, polymers, and phosphonate/polymer blends favor the formation of calcite, thermodynamically the most stable polymorph, whereas in the absence of inhibitors a mixture of calcite, vaterite, and aragonite is formed. The $CaCO_3$ crystals formed in the absence (control) and presence (TP2/PBTC blend) of inhibitors were also investigated by SEM. Although scanning electron micrographs are presented herein, it was observed that $CaCO_3$ crystals (calcite and aragonite) formed in the absence of inhibitor are <10 µm and have regular shapes (mostly cubical). Whereas the $CaCO_3$ crystal structures formed in the presence of inhibitors (inhibited system) are fewer in number, most are >10 µm and significantly distorted with spherical shapes. The inhibited (TP2/PTBC) system $CaCO_3$ crystals are more readily dispersed and less likely to adhere to heat exchanger surfaces.

References

1 R.H. Ashcraft, CORROSION/85, paper no. 132 (Houston, TX: NACE International, 1985).

2 Z. Amjad, "Performance of Polymers as Precipitation Inhibitors for Calcium Phosphonates," Tenside Surfactants Detergents 34, 2 (1997).

3 M.P.C. Weijnen, G.M. Rosmalen, Desalination 54, 55 (1985).

4 J.E. Hoots, G.A. Crucil, CORROSION/86, paper no. 13 (Houston, TX: NACE, 1986).

5 Z. Amjad, J. Pugh, J. Zibrida, B. Zuhl, MP 36, 32 (1997).

6 Z. Amjad, R. Zuhl, J. Zibrida, "The Use of Polymers to Improve Control of Calcium Phosphonate and Calcium Carbonate in High Stressed Cooling Water Systems" (Nashville, TN: Association of Water Technologies Annual Conference, 2004).

7 G. Xyla, P.G. Koutsoukos, Poster No. 3, Pg. 743 in 31st International Congress on Pure and Applied Chemistry, Sofia, Bulgaria 7 (1987).

ZAHID AMJAD is a senior fellow at Lubrizol Advanced Materials, Inc., 9911 Brecksville Rd., Cleveland, OH 44141. He has more than 27 years of experience with the application of water-soluble polymers, crystal growth and inhibition, solid/liquid separation, and other related areas. He has an M.S. degree from Punjab University, Pakistan; a Ph.D. from Glasgow University, U.K.; and was a post-doctoral fellow at the State University of New York at Buffalo. A 20-year member of NACE, Amjad has received several awards, holds 29 patents, authored more than 100 publications, and edited five books.

ROBERT W. ZUHL is global business manager—Dispersants & Water Treatment Chemicals at Lubrizol Advanced Materials, Inc. He has seven years of environmental engineering experience and more than 25 years in marketing and sales of specialty chemicals. He has an M.S. degree in environmental engineering from Michigan State University and an M.B.A. from Baldwin Wallace College. A member of several professional societies including more than 20 years in NACE, Zuhl is a registered professional engineer and has authored more than 20 publications.

Statement of Ownership, Management, and Circulation

1. Publication Title: Materials Performance. 2. Publication Number: 0094-1492. Filing Date: September 21, 2007. 4. Issue Frequency: Monthly. 5. Number of Issues Published Annually: 12. 6. Annual Subscription Price: $12 Members, $115 Nonmembers. 7., 8. Complete Mailing Address of Known Office of Publication and Headquarters: NACE International, 1440 South Creek Drive, Houston, Harris County, Texas 77084-4906. 9. Publisher: Gretchen Jacobson; Managing Editor: Gretchen Jacobson; Technical Editor: John Fitzgerald III; NACE International, 1440 South Creek Drive, Houston, Harris County, Texas 77084-4906. 10. Owner: NACE International; Complete Mailing Address: 1440 South Creek Drive, Houston, Harris County, Texas 77084-4906. 11. Known Bondholders, Mortgagees, and Other Security Holders Owning or Holding 1 Percent or More of Total Amount of Bonds, Mortgages, or Other Securities: None. 12. Tax Status: Has Not Changed During Preceding 12 Months. 13. Publication Title: Materials Performance. 14. Issue Date for Circulation Data Below: September 2007. 15. Extent and Nature of Circulation: Average Number of Copies Each Issue During Preceding 12 Months: (a) Total Number of Copies (net press run) = 18,970; (b) Paid and/or Requested Circulation: (1) Paid/Requested Outside-County Mail Subscriptions Stated on Form 3541 = 11,921; (2) Paid In-County Subscriptions Stated on Form 3541 = 0; (3) Sales Through Dealers and Carriers, Street Vendors, Counter Sales, and Other Non-USPS Paid Distribution = 5,762; (4) Other Classes Mailed Through the USPS = 0; (c) Total Paid and/or Requested Circulation = 17,683; (d) Free Distribution by Mail: (1) Outside-County as Stated on Form 3541 = 560; (2) In-County as Stated on Form 3541 = 0; (3) Other Classes Mailed Through the USPS = 178; (e) Free Distribution Outside the Mail = 374; (f) Total Free Distribution = 1,112; (g) Total Distribution = 18,795; (h) Copies Not Distributed = 175; (i) Total = 18,970; (j) Percent Paid and/or Requested Circulation = 94%. No. of Copies of Single Issue Published Nearest Filing Date: (a) Total Number of Copies Printed (net press run) = 19,176; (b) Paid and/or Requested Circulation: (1) Paid/Requested Outside-County Mail Subscriptions as Stated on Form 3541 = 11,660; (2) Paid In-County Subscriptions Stated on Form 3541 = 0; (3) Sales Through Dealers and Carriers, Street Vendors, Counter Sales, and Other Non-USPS Paid Distribution = 6,200; (4) Other Classes Mailed Through the USPS = 0; (c) Total Paid and/or Requested Circulation = 17,860; (d) Free Distribution by Mail: (1) Outside-County as Stated on Form 3541 = 490; (2) In-County as Stated on Form 3541 = 0; (3) Other Classes Mailed Through the USPS = 210; (e) Free Distribution Outside the Mail = 410; (f) Total Free Distribution = 1,110; (g) Total Distribution = 18,970; (h) Copies Not Distributed = 206; (i) Total = 19,176; (j) Percent Paid and/or Requested Circulation = 94%. 16. This Statement of Ownership will be printed in the October 2007 issue of this publication. 17. I certify that all information furnished on this form is true and complete: (signed) Gretchen Jacobson, Publications Director.