ACUMER™ 2000 Phosphate and Zinc Stabilizer

Description

ACUMER™ 2000 high-performance acrylate copolymer is designed to provide exceptional stabilization of phosphate-based water treatment programs. The product is also highly effective as a stabilizer for zinc-containing programs. In addition, ACUMER 2000 polymer disperses commonly encountered inorganic particulates and is resistant to pH upsets.

ACUMER 2000 polymer is stable under highly alkaline storage conditions. This stability enables the formulator to manufacture one-package treatments.

Typical Properties

ACUMER™ 2000 polymer is supplied as a partially neutralized (20%) aqueous solution. Table 1 summarizes typical physical properties of ACUMER 2000 polymer.

Typical Physical Properties

Table 1
These properties are typical but do not constitute specifications

Appearance	Clear Solution
Total Solids (%)	43
Active Solids (%)	39.5
pH	4.2
Molecular Weight[1]	Mw=4500 Mn=3300
Density lbs/gal (g/cc) at 25°C	10.1 (1.2)
Brookfield Viscosity (cps at 25°C)	300

[1] Measured by Aqueous GPC and reported as acid form.

Suggested Applications

Calcium Phosphate Stabilization

The increasing use of inorganic phosphates for corrosion inhibition and the trend toward higher cooling water pH increase the demand placed upon the stabilizers used in today's formulations. ACUMER™ 2000 polymer was developed to respond to these increased performance requirements. The presence of soluble iron in most systems and variability of pH also serve to increase the stress placed upon the stabilizer.

Effect of pH

The ability of ACUMER™ 2000 polymer to provide exceptional performance under conditions of varying pH is demonstrated through testing conducting in Dow laboratories and summarized in Table 2. As indicated by the test results, ACUMER 2000 polymer outperforms a leading competitive polymer at each pH level. Please note that details of the test procedures are provided in the Appendix.

Table 2
Precipitation Inhibition of Calcium Phosphate at Varying pH (9 ppm Active Polymer)

Polymer	Percent Phosphate Inhibition		
	pH 7.5	pH 8.6	pH 9.5
ACUMER™ 2000	90	80	37
Competitive Polymer N	40	36	12
(2.5 ppm Fe^{+3}/6 ppm PO_4/250 ppm Ca^{+2}, as $CaCO_3$/70°C (158°F)/17 hours)			

Effect of Iron

The presence of soluble iron in the system also has a deleterious effect on the performance of most polymeric inhibitors. ACUMER 2000 polymer provides excellent iron tolerance, as demonstrated by Table 3.

Table 3
Precipitation Inhibition of Calcium Phosphate as a Function of Iron Concentration (9 ppm Active Polymer)

Polymer	Percent Phosphate Inhibition	
	No Iron	2.5 ppm Fe^{+3}
ACUMER 2000	100	90
Competitive Polymer N	91	55
No Polymer	6	6
(6 ppm PO_4/250 ppm Ca^{+2}, as $CaCO_3$/70°C (158°F)/7.5/17 hours)		

Test results indicated that, ACUMER 2000 polymer is more iron tolerant. The standard calcium phosphate antiprecipitation test incorporates 2.5 ppm of Fe+3 since nearly all recirculating water contains some level of soluble iron.

Filter Paper Results

The standard Dow laboratory test (see Appendix) for calcium phosphate stabilization employs a filtration step for separation of precipitated calcium phosphates and other species from the unprecipitated ions. Figure 1 is a photograph of the filter papers that were used during a recent series of tests in Dow laboratories. These tests, conducted at 10 ppm active polymer dosage, compared the performance of ACUMER 2000 polymer with that of two competitive phosphate stabilizers and with that of a control.

ACUMER 2000 polymer performed exceptionally well. A dark color on the filter paper visibly indicates heavy deposits of iron phosphate and iron hydroxide found with the competitive polymers.

Suggested Applications (Cont'd)

FIGURE 1

PHOSPHATE PRECIPITATION INHIBITION IN IRON-CONTAMINATED COOLING WATER

ACUMER 2000	COMPETITIVE POLYMER A	COMPETITIVE POLYMER B	NO POLYMER
99% INHIBITION	52% INHIBITION	30% INHIBITION	0% INHIBITION

CONDITIONS:
6 ppm PO_4^{-3}
2.5 ppm Fe^{+3}
250 ppm Ca^{+2}, as $CaCO_3$
pH 9.5
70°C/17 hours
10 ppm active polymer

Zinc Stabilization

Zinc is another corrosion inhibitor of choice in cooling water programs. Zinc forms insoluble zinc hydroxide at high pH and a polymeric stabilizer is required to control deposits of the zinc salt. ACUMER™ 2000 polymer effectively performs this function.

To demonstrate its effectiveness, ACUMER 2000 polymer was tested in highly alkaline water. Since the formation of zinc hydroxide is favored by high pH, the severity of the test increases as pH rises. The higher the amount of zinc remaining in solution, the more effective the stabilizer. Test results are summarized in Table 4.

Table 4
Zinc Stabilization

Polymer	Soluble Zinc, ppm	
	pH 8	pH 9
ACUMER 2000	3.8	1.4
Polyacrylic Acid	2.4	0.8
None	0.6	0.3
(5 ppm Zn^{+2}/20 ppm active polymer/250 ppm Ca^{+2}, as $CaCO_3$/150 ppm Mg^{+2}, as $CaCO_3$/300 ppm M-Alkalinity, as $CaCO_3$/40°C (104°F)/24 hours)		

Often, both zinc and phosphate are present in the water system via the treatment program or the feedwater. ACUMER 2000 and ACUMER 3100 were more effective than ACUMER 1000, competitive polyacrylates (B1 and B2), and sulfonated styrene/maleic acid copolymer (SSMA) for stabilizing these corrosion inhibitors in water with a Ryznar Index (RI) of 5.7. These results are listed in Table 5.

Table 5
Zinc/Phosphate Stabilization

Polymer	% Zinc Stabilization			% Phosphate Stabilization		
Polymer (ppm)	7.5	10	20	7.5	10	20
ACUMER™ 1000	14	14	36	59	59	62
ACUMER 2000	19	55	96	77	100	100
ACUMER 3100	48	93	98	77	100	100
Competitive Polymers						
B1	7	7	13	55	55	54
B2	3	3	3	49	49	53
SSMA 1	6	17	87	53	65	59
SSMA 2	13	13	15	54	60	59
None	3	3	3	48	48	48
(pH 8/ 5 ppm zinc/ 10 ppm phosphate/ 200 ppm M-Alkalinity/ 210 ppm Ca^{+2}, as $CaCO_3$/ 90 ppm Mg^{+2}, as $CaCO_3$/ 150 ppm SiO_3/ 0.5 ppm Fe^{+3}/ 49°C (120°F)/ 18 hours)						

Calcium Carbonate Inhibition

In addition to providing calcium phosphate and zinc stabilization, ACUMER 2000 polymer can inhibit other commonly encountered scale formers, such as calcium carbonate. Table 6 compares the performance of ACUMER 2000 polymer with that of a leading competitive polymer as well as with that of ACUMER 1000 polyacrylic acid.

Table 6
Precipitation Inhibition of Calcium Carbonate at Varying Polymer Dosage

Polymer	Percent $CaCO_3$ Inhibition		
	1.0 ppm	2.5 ppm	5.0 ppm
ACUMER 2000	55	73	87
Competitive Polymer N	39	55	83
ACUMER1000	58	70	100
No Polymer	0	0	0
(pH 8.5/1100 ppm $CaCO_3$/70°C (158°F)/5 hours)			

Dispersancy

A polymer must also keep the silt and inorganic particulates suspended and prevent their settling out onto heat transfer surfaces. The dispersancy offered by ACUMER 2000 polymer compares favorably with that of, Tamol™ 731 dispersant, and with that of a leading competitive polymer.

Suggested Applications (Cont'd)

Table 7
Dispersancy, NTU's at Varying Polymer Dosage

Polymer	Kaolin		Iron Oxide
	5 ppm	20 ppm	3 ppm
ACUMER™ 2000	43	730	316
Competitive Polymer N	750	820	243
OROTAN™ 731A	893	852	912
No Polymer	41	41	108

Kaolin Dispersancy: 1000 ppm Kaolin/200 ppm Ca^{+2}, as $CaCO_3$/pH 7.5/settle 2 hours.
Iron Oxide Dispersancy: 700 ppm Fe_2O_3/200 ppm Ca^{+2}, as $CaCO_3$/pH 7.5/settle 4 hours.

Pilot Cooling Tower Trials

Stabilized Phosphate

In stabilized phosphate trials, treatment programs based on ACUMER™ 2000 maintained heat transfer much better than a control program with SSMA and one without polymer (Figure 2, page 7). In the control without polymer, the relative heat transfer rate dropped precipitously for the first four hours of the test and continued to decline at a slower rate until the test was terminated after 110 hours. The exchange surfaces were heavily scaled, and the corrosion rate at the end of the test was high – 5 mpy* (Table 8).

The SSMA program maintained a better level of heat transfer and a lower corrosion rate. As Figure 2 (page 7) shows, the heat transfer rate remained nearly 100 percent for the first 40 hours of the trial. Thereafter, it declined steadily to the 38 percent heat transfer level it showed at the end of the test. The iron introduced into the system when the pH was temporarily lowered at the 70-hour point accelerated the deterioration in heat transfer. At the end of the test (150 hours), the heat transfer surfaces showed heavy scaling.

At equal polymer dosage of 5 ppm, ACUMER 2000 was shown to be more effective than SSMA. Unlike the SSMA program, heat transfer did not drop as drastically after the programmed pH "excursion." As a result, the heat transfer rate in the ACUMER 2000 trial was still above 60 percent at 150 hours, and the exchange surface showed only moderate scaling. The corrosion rate was 1.6 mpy. At a higher polymer level of 10 ppm, ACUMER 2000 showed a further increase in performance. Heat transfer rate remained at 100 percent for over 50 hours, and corrosion rate dropped to 1.0 mpy. The heat transfer rate remained above 80 percent for the duration of the test.

Alkaline Zinc

The pilot cooling tower evaluations of alkaline zinc programs clearly establish the merits of using ACUMER 2000 in this type of water treatment. Zinc regimens demand a polymer that will permit a corrosion-inhibiting film to deposit on cathodic sites, but that film must remain thin for good heat transfer.

Pilot Cooling Tower Trials (Cont'd)

ACUMER™ 2000 acrylate copolymer effectively stabilizes zinc at a pH of 8.0, but it drops off sharply above that point. An alkaline zinc program without a polymer showed an early loss of heat transfer and a high corrosion rate throughout its duration. However when ACUMER 2000 was employed, heat transfer remained near 100 percent for the test (Figure 3, page 7), and the corrosion rate dropped to 4 mpy (Figure 4, page 8).

*mpy = mils per year. It refers to how far below the surface corrosion will extend in a metal substrate over the course of a year.

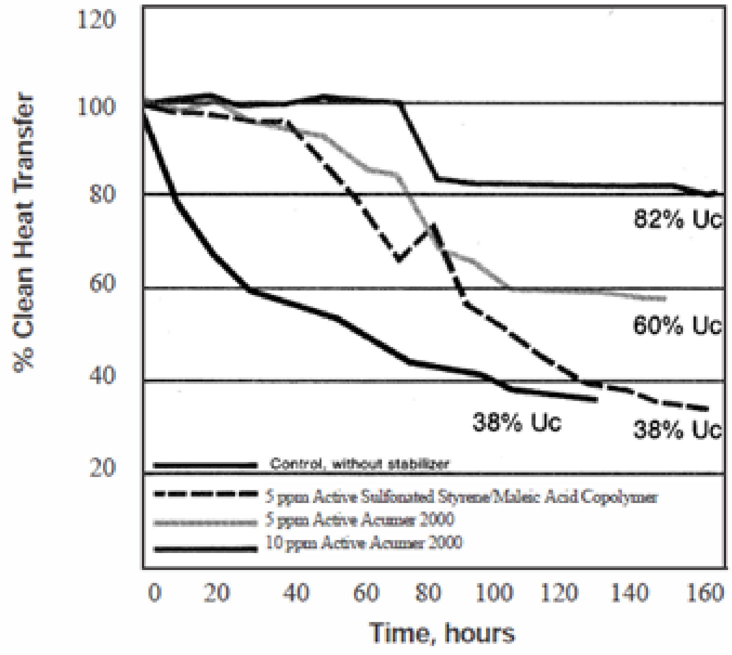
Table 8
Stabilized Phosphate Program Corrosion Rates[1]
(After 150 hours unless otherwise indicated)

Polymer	Rate
None	5.0 mpy (after 110 hours)
SSMA (5 ppm)	1.7 mpy
ACUMER 2000 (5 ppm)	1.6 mpy
ACUMER 2000 (10 ppm)	1.0 mpy

[1] Rate is expressed as depth of corrosion from surface in mils per year (mpy).

FIGURE 2

STABILIZED PHOSPHATE PROGRAM



Pilot Cooling Tower Trials (Cont'd)

FIGURE 3

ALKALINE ZINC PROGRAM
CLEAN HEAT TRANSFER (% Uc)

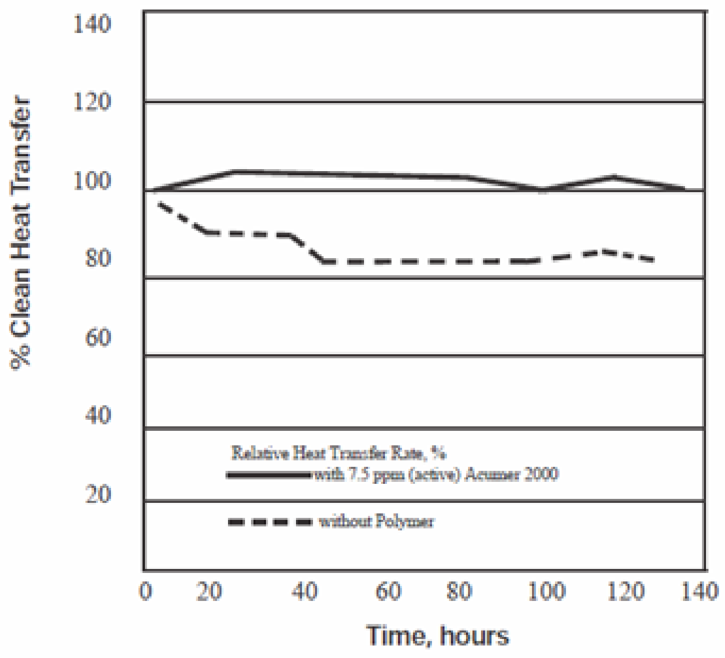
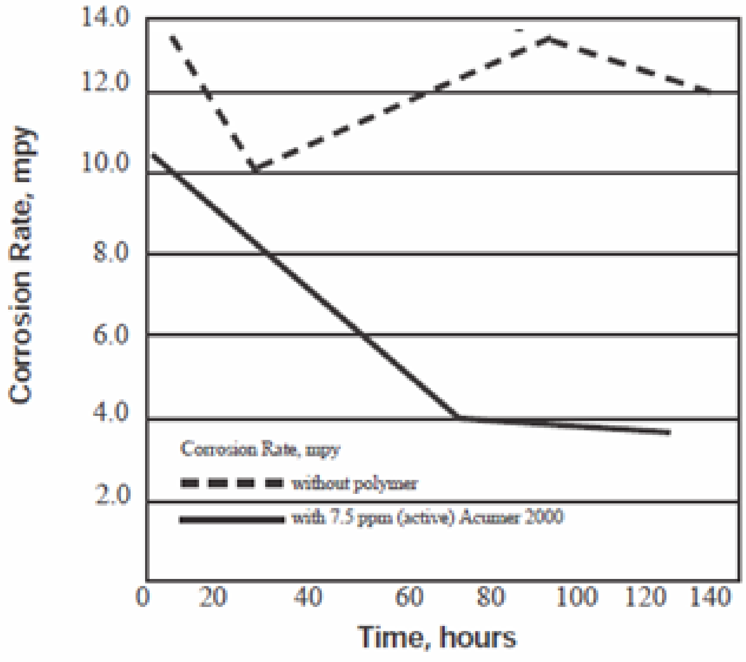


FIGURE 4

ALKALINE ZINC PROGRAM
CORROSION RATE (mpy)



Starting-Point Formulation

The following starting-point formulation is intended to assist customers in formulating an effective phosphate stabilizer. Ingredients are listed in their recommended order of addition. These formulations are not intended for commercial use “as is,” but should be considered starting-point formulations requiring additional development, modification, and adaptation to specific operating conditions. For technical assistance, customers may contact their local Dow representative.

Stabilized Phosphate Formulation CW-86-2

Ingredients	Percent by Weight	Percent Activity
Water	39.5 to 33.5	-
Phosphoric Acid (75%)	5.5	4.1, as PO_4
HEDP (60% active)	4.0	2.2, as PO_4
ACUMER™ 2000* (39.5% active)	12.0 to 18.0	4.7 to 7.1
Potassium Hydroxide (45%)	29.0	-
Tolytriazole (50%)	3.0	1.5
TKPP	7.0	4.0, as PO_4
*ACUMER 2000 polymer is typically supplied at 43% total solids and 39.5% active solids.		

Suggested Operating Conditions

Maintenance Feed Rate: Sufficient to maintain 6 to 16 ppm PO_4 in the recirculating water.
Maintenance Recirculating Water pH: 7.0 to 8.0

Formulation Stability

Formulated products containing inorganic polyphosphates must be packaged at a high pH to minimize reversion to orthophosphate. Unlike some competitive polymers, ACUMER™ 2000 polymer exhibited no loss of performance after six months of storage at a pH of 13.5. Table 9 compares the storage stability of ACUMER 2000 with that of a leading competitive polymer.

Table 9
Polymer Performance in Phosphate Antiprecipitant Test before and After High pH Storage (15 ppm active polymer)

	Percent Phosphate Inhibition		
	Initial Performance	Storage at pH = 13.5	
Polymer	(no exposure to high pH)	3 Days	6 Months
ACUMER 2000	87	87	87
Competitive Polymer N	60	28	28
(2.5 ppm Fe^{+3}/pH 8.5/6 ppm PO_4/250 ppm Ca^{+2}/70°C (158°F)/17 hours)			

Figures 5 and 6 describe ACUMER 2000 dosage levels for stabilizing 10 and 25 ppm orthophosphate in the recirculating water at 50°C (122°F). Phosphate can enter the system via the treatment formulation or the raw feedwater.

Formulation Stability (Cont’d)

FIGURE 5

100% PHOSPHATE STABILIZATION
(ACUMER 2000 DOSAGE AT 0-1000 PPM CALCIUM CARBONATE)
TEST CONDITIONS: 10 PPM PHOSPHATE / 50°C (122°F) / 21 HOURS

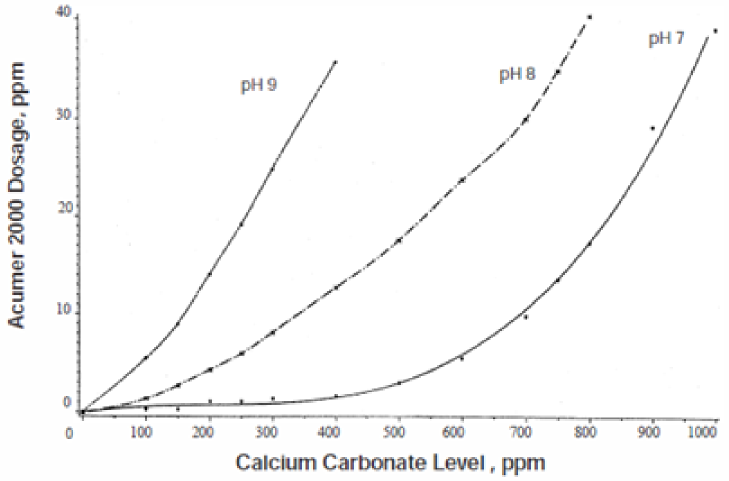
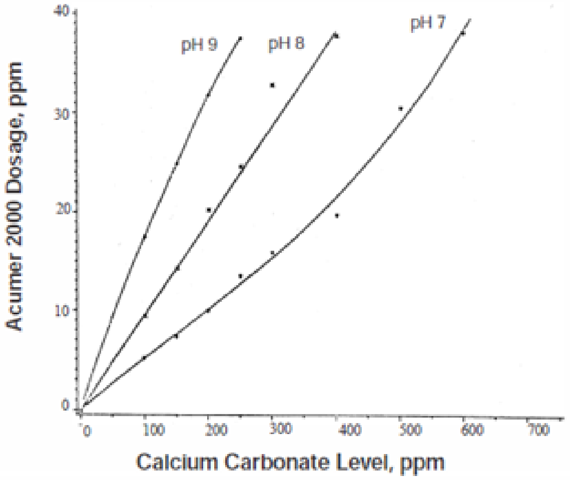


FIGURE 6
100% PHOSPHATE STABILIZATION
(ACUMER 2000 DOSAGE AT 0–1000 PPM CALCIUM CARBONATE)
TEST CONDITIONS: 25 PPM PHOSPHATE / 50°C / 21 HOURS

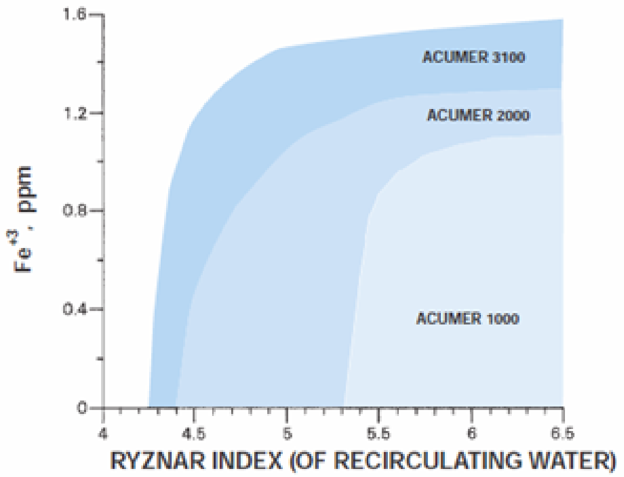


Formulation Stability (Cont’d)

These results are based on beaker tests similar to those described in the Appendix. Note that under more stressed conditions (higher phosphate and hardness levels), more ACUMER™2000 is required to solubilize the phosphate in the recirculating water.

To determine the effect of iron on polymer performance for phosphate stabilization, separate tests were run on ACUMER 1000, ACUMER 2000, and ACUMER 3100 in the presence of iron. Figure 7 describes those conditions (iron levels and Ryznar Index) in which these polymers will prevent the precipitation of phosphate. For example, ACUMER 2000 (at 10 ppm active polymer) provides excellent stabilization at RI above 5 in the presence of 1 ppm iron. Higher iron levels in the recirculating water would require ACUMER 3100.

FIGURE 7
STABILIZED PHOSPHATE PROGRAM



Conditions:

10 ppm Active Polymer
Temperature: 49°C (120°F)
Time: 20 hours
pH: 7-9

200 ppm M-Alkalinity
400 ppm Calcium as $CaCO_3$
200 ppm Magnesium as $CaCO_3$
10 ppm Orthophosphate

Acrylate Test Method

ACUMER™ 2000 polymer may be analyzed at use concentration with the Hach polyacrylic test kit. This kit employs a patented method developed by The Dow Chemical Company. The kit was jointly developed by The Dow Chemical Company and the Hach Company.

Safe Handling Information

CAUTION! Contact may cause eye irritation and slight skin irritation.

First Aid Information

Contact With Skin:	Wash skin immediately with soap and water. Remove contaminated clothing and launder before rewearing.
Contact With Eyes:	Flush eyes with plenty of water for at least 15 minutes and call a physician.
If Swallowed:	If victim is conscious, dilute the liquid by giving the victim two glasses of water to drink and then call a physician immediately. Never give an unconscious person anything to drink.

First Aid Information (Cont'd)

Table 10
Toxicity and Irritation of ACUMER™ 2000

Acute oral (LD_{50}), rats	>5 g/kg
Acute dermal (LD_{50}), rabbits	>5 g/kg
Eye irritation, rabbits	Slight
Skin irritation, rabbits	Practically none
Aquatic Toxicity (LC_{50}) ppm	
Daphnia (48 hours)	>1000
Bluegill (96 hours)	>1000
Trout (96 hours)	>1000

Standard Calcium Phosphate Precipitation Inhibition

1. For each test sample, add the following to a 4 oz. (125 ml) jar:
   a) 50 ml of 12 ppm Na_2HPO_4 as PO_4^{-3}
   b) 1 ml of 0.1% polymer treatment
   c) 50 ml of 500 ppm $CaCl_2$ as $CaCO_3$ (with 5 ppm Fe^{+3} added)

2. Adjust each sample to the appropriate pH with dilute NaOH (<1%).

3. Place lid on sample jars and store in a 70°C (158°F) oven for 17 hours.

4. Remove samples from oven one at a time and filter each sample through a 0.22 µm millipore filter immediately after it is removed from the oven.

5. Allow samples to cool to room temperature.

6. Dilute samples by placing 30 ml of test sample into a 100 ml volumetric and QS with DI H_2O.

7. Spectrophotometrically analyze the dilute samples for PO_4^{-3} concentration by the ascorbic acid method (APHA Standard Methods, 13th Ed. 532 (1971); Hach spectrophotometer at 700 NM; Phosver III phosphate reagent).

8. $$\% \text{ Inhibition} = \frac{[PO_4], \text{ Sample}}{[PO_4], \text{ 100\% Inhibition}} \times 100$$

<u>Final Concentrations:</u>
250 ppm Ca^{+2}, as $CaCO_3$
6 ppm PO_4^{-3}
2.5 ppm Fe^{+3}
10 ppm Active Polymer

Zinc Precipitation Inhibition

1. For each test sample, add the following to a 4 oz. (125 ml) jar:

   a) 10 ml of 50 ppm $ZnCl_2$, as Zn^{+2}, stock solution at pH 1
   b) 2 ml of 0.1% polymer treatment
   c) 90 ml of stock solution containing:

      278 ppm Ca^{+2}, as $CaCO_3$
      167 ppm Mg^{+2}, as $CaCO_3$
      333 ppm M-Alkalinity, as $CaCO_3$

2. Adjust each sample to pH 8 or 9 with dilute NaOH (<1%).

3. Place lid on sample jars and store in a 40°C (104°F) oven for 24 hours.

4. Remove samples from oven one at a time and filter each sample through a 0.22 µm millipore filter immediately after it is removed from the oven.

5. Allow samples to cool to room temperature.

6. Analyze the dilute samples for Zn^{+2} concentration by atomic absorption.

Final Concentrations:
250 ppm Ca^{+2}, as $CaCO_3$
150 ppm Mg^{+2}, $CaCO_3$
300 ppm M-Alkalinity, as $CaCO_3$
20 ppm Active Polymer

Kaolin Dispersancy Test

1. Place the following into a multimix cup:

   430 ml of 200 ppm $CaCO_3$ ($CaCl_2$ as $CaCO_3$)
   0.43 g Hydrite UF Kaolin (1000 ppm Kaolin)

2. Mix 10 minutes.

3. Adjust to pH 7.5 with NaOH.

4. Place 100 ml aliquots into 4 oz. (125 ml) jars (shake solution after pouring all aliquots).

5. Add 5, 10, 20 ppm active polymer (0.5, 1, 2 ml of 0.1% active solution adjusted to pH 8.0).

6. Cap jars and place on shaker for 15 minutes at low speed.

7. Allow jars to stand 2 hours undisturbed.

8. Place top 20 mls into 1-oz. vials.

9. Read turbidity of solution in vial (0-1000 NTU).

$CaCO_3$ Precipitation Inhibition

Stock Solution 1: 3.25 g/l $CaCl_2 \cdot 2 H_2O$, adjusted to pH 8.5
Stock Solution 2: 2.48 g/l Na_2CO_3, adjusted to pH 8.5

Procedure:

1. Place the following in a 4 oz. (125 ml) jar:

   50 ml Stock Solution 1
   0, 2.5, 5 or 10 ppm active polymer (0, 0.25, 0.5 or 1.0 ml of 0.1% active solution adjusted to pH 8.0)
   50 ml Stock Solution 2

2. Preheat samples in warm (~70°C (158°F)) water for 5 minutes.
3. Heat in oven 5 hours at 70°C (158°F); remove and cool to room temperature.
4. Filter through 0.45 µm filter.
5. Add 4 ml concentrated HCl to 25 ml filtrate and allow to stand 15+ minutes.
6. Dilute to 50 ml with DI H_2O.
7. Add 3 ml 50% NaOH.
8. Add Ca^{+2} indicator.
9. Titrate with EDTA to purple-violet endpoint:

$$\% \text{ Inhibition} = \frac{\text{ml titrant (treated) - ml titrant (no polymer)}}{\text{ml titrant (50 ml of Ca}^{+2}\text{ S.S.I) - ml titrant (no polymer)}} \times 100$$

Iron Oxide Disperancy Test (Fe_2O_3)

1. Place the following into a multimix cup:

   430 ml of 200 ppm $CaCl_2$ $CaCO_3$
   0.30 g Fe_2O_3 (Fosjer Reagent) (700 mg/l Fe_2O_3)

2. Mix 15 minutes.
3. Adjust to pH 7.5 with NaOH.
4. Place 100 ml aliquots into 4 oz. (125 ml) jars (shake solution after pouring all aliquots).
5. Add polymer -3 ppm active (0.3 ml of 0.1% active polymer adjusted to pH 8.0).
6. Cap jars and place on shaker for 15 minutes at low speed.
7. Allow jars to stand 4 hours undisturbed.
8. Pipette top 20 mls into small vials and measure turbidity of vials (0-1000 NTU).

Handling Precautions

Before using this product, consult the Material Safety Data Sheet (MSDS)/Safety Data Sheet (SDS) for details on product hazards, recommended handling precautions and product storage.

Storage

Store products in tightly closed original containers at temperatures recommended on the product label.

Disposal Considerations

Dispose in accordance with all local, state (provincial) and federal regulations. Empty containers may contain hazardous residues. This material and its container must be disposed in a safe and legal manner.

It is the user's responsibility to verify that treatment and disposal procedures comply with local, state (provincial) and federal regulations. Contact your Dow Technical Representative for more information.

Product Stewardship

Dow has a fundamental concern for all who make, distribute, and use its products, and for the environment in which we live. This concern is the basis for our product stewardship philosophy by which we assess the safety, health, and environmental information on our products and then take appropriate steps to protect employee and public health and our environment. The success of our product stewardship program rests with each and every individual involved with Dow products - from the initial concept and research, to manufacture, use, sale, disposal, and recycle of each product.

Customer Notice

Dow strongly encourages its customers to review both their manufacturing processes and their applications of Dow products from the standpoint of human health and environmental quality to ensure that Dow products are not used in ways for which they are not intended or tested. Dow personnel are available to answer your questions and to provide reasonable technical support. Dow product literature, including safety data sheets, should be consulted prior to use of Dow products. Current safety data sheets are available from Dow.

Contact:

North America:	1-800-447-4369
Latin America:	(+55)-11-5188-9000
Europe:	(+800)-3-694-6367
	(Toll) +31-11567-2626
Asia-Pacific:	(+800)-7776-7776
	(Toll) +60-3-7965-5392

http://www.dow.com