Condensed Version of Laboratory Notes on Original Development of TRC-233 Copolymer

Discovery of TRC-233

TRC-233 is a result of an extensive Calgon research effort begun in 1982 to develop a proprietary phosphate-based non-heavy metal treatment to prevent corrosion and scale in cooling water. In the course of investigating a series of candidate materials, copolymers of acrylic acid and AMPS (2-acrylamido-2-methylpropylsulfonic acid) were found which demonstrated impressive capabilities for threshold inhibition of calcium phosphate precipitation. Since control of calcium phosphate precipitation was a major prerequisite for the development of a phosphate-based treatment which would have applicability over a broad range of cooling water compositions, this finding provided the key to further development efforts.

Other candidate materials that were screened included polysalts (i.e. salts representing combinations of anionic and cationic homopolymers), homopolymers, copolymers, and terpolymers involving monomer entities such as DMDAAC, acrylic acid, maleic anhydride, acrylamide, METAMS, acrylic ester, 2-hydroxpropylacrylate, and AMPS. Screening tests were also performed on combinations of polymers with materials such as sodium hexametaphosphate and non-polymeric building blocks, AMP-O and HEDP.

It was recognized initially that performance exceeding that of competitive materials in the marketplace was an essential goal. Betz 2020, a calcium phosphate scale inhibitor which was touted as the best cooling water treatment program at the time, was selected as the reference product against which to compare the performance of the AA/AMPS copolymers. Thus, the basis of comparison for all subsequent testing was the raw material used in Betz 2020, which is Natrol® 42, a copolymer of acrylic acid and 2-hydroxypropylacrylate.

Selection of TRC-233 AA/AMPS Ratio

Based on consideration of all the performance and process characteristics evaluated for the candidate inhibitor materials screened, 60/40 AA/AMPS copolymer was selected as the material best satisfying the goals of the development program. The principal factors that entered into the decision were:

1. AA/AMPS copolymers clearly demonstrated better performance than AA/DMDAAC/AM terpolymers for inhibition of calcium phosphate precipitation.

2. Certain AA/AMPS copolymers consistently produced better calcium phosphate inhibition results than Natrol® 42.

3. Intermediate AA:AMPS ratio copolymers provided the best results for calcium phosphate inhibition. (See Figure 5).

The choice of the 60/40 AA/AMPS copolymer for development into a commercial product provided a building block with impressive calcium phosphate inhibition capabilities while also possessing significant inhibition capabilities for calcium carbonate and calcium sulfate as well as other very beneficial characteristics.

TRC-233 Testing

All of the testing performed demonstrated that TRC-233 was a highly effective calcium phosphate inhibitor which also had significant capabilities for inhibition of other scale/deposit forming salts such as calcium carbonate, calcium sulfate, calcium phosphonate, zinc hydroxide and zinc phosphate. Comparative testing with Natrol® 42 indicated TRC-233 was the superior threshold inhibitor for calcium phosphate.

Corrosion tests and dynamic bench-scale and pilot-scale tests indicated that the use of TRC-233 with the metaphosphate/orthophosphate corrosion inhibitor pair provided very satisfactory inhibition of steel corrosion under elevated pH levels and calcium concentrations that would be intolerable without calcium phosphate inhibition.

In addition to the laboratory screening tests and a series of dynamic tests in bench-scale and pilot-scale recirculating cooling water systems, completion of two successful field trials with TRC-233 provided further understanding of this product's capabilities. The completed field trials demonstrated steel corrosion rates below 2 mpy in phosphonate and phosphonate/ polyphosphate treated systems while operating at pH 8.5 without calcium phosphate deposition problems despite calcium and orthophosphate levels well beyond calcium phosphate saturation.

Patent Information

The use of AA/AMPS copolymers for threshold inhibition of various scale forming salts, including calcium phosphate, was covered by the Persinski, Ralston and Gordon U.S. Patent No. 3,928,196 which issued on December 23, 1975.

In the interest of expanding the patent coverage of the application technology associated with AA/AMPS copolymers, a series of tests were undertaken to evaluate the synergistic effects between TRC-233 and a substantial number of other materials with regard to several treatment functions. These treatment functions included threshold inhibition of calcium carbonate, calcium sulfate and calcium phosphate, dispersion of iron oxide, and inhibition of steel corrosion. Materials tested in combination with TRC-233 included building blocks currently used in our cooling water products, as well as other candidate materials considered to have promise as building blocks for new cooling water products. As a result of this work and other related observations, a patent application covering "Synergistic Scale and Corrosion Inhibiting Admixtures Containing Carboxylic Acid/Sulfonic Acid Polymers" was filed on March 4, 1983.

Process Optimization

After 60/40 AA/AMPS copolymer was identified as the inhibitor of choice for development efforts, work was undertaken to optimize the process chemistry for preparing the copolymer. Different polymerization process conditions on the Ca/PO_4 inhibition capabilities of three 60/40 AA/AMPS copolymers illustrated that optimization of process chemistry was an essential part of maximizing the performance of the inhibitor of choice. This optimization enhanced the performance of the 60/40 copolymer beyond that observed in the screening tests.

When the process chemistry optimization was completed and the commercial production feasibility of the finalized product composition had been demonstrated, the resultant development product was named TRC-233.

TRC-233 Applications

For recirculating cooling water systems, future trends are expected to continue toward increasing cycles of concentration and decreasing makeup water quality (e.g. treated sewage). Beyond the needs that currently exist, these expectations represent compelling needs for treatment systems that can accommodate higher levels of calcium and orthophosphate while enabling higher pH operation to enhance corrosion control and eliminate or minimize the need for acid feed.

A need of comparable importance is an environmentally acceptable non-heavy metal treatment that provides control of corrosion, scale and deposition over a broad range of cooling water compositions. The proven technology of the metaphosphate/orthophosphate inhibitor pair is a prime candidate to satisfy this need provided that the phosphate-based treatment program incorporates a viable and palatable means of controlling calcium phosphate.

TRC-233 represents a key element in an integrated treatment approach which provides cost effective control of corrosion, scale and deposition in a manner fully compatible with these expected future trends.

TRC-233 and the formulations incorporating it are potent tools that are applicable to a broad range of present and future boiler and cooling water treatment needs. The development of this product was intended to provide the best possible technical basis for pursuing these markets.

FIGURE 5

CALCIUM PHOSPHATE THRESHOLD INHIBITION

Conditions:

Stagnant Flask Test	pH 8.5 Buffered
60°C	200 mg/l Ca
5 mg/l Inhibitor (Active)	6 mg/l PO_4
2.5μ Filtered PO_4 Test