Research and Development

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# **Project Summary**

# Trihalomethane Removal by Coagulation Techniques in a Softening Process

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This research program investigated various potable water treatment processes in combination with lime softening to effect maximum removal of trihalomethane precursor compounds.

A study of the literature was used to guide the initial test work. Bench-scale jar tests investigated various combinations of coagulants that earlier studies indicated would be promising. The test work evaluated the relative effectiveness of lime softening, alum coagulation, ferric coagulation, and clay coagulation with respect to their ability to remove THM precursors by themselves and in various combinations with lime softening.

The bench-scale test work was followed by a series of eight pilot-plant test runs using the U.S. Environmental Protection Agency's trailer-mounted pilot facility at the 45.4-MLD (12-MGD) Ralph F. Brennan Water Treatment Plant in Daytona Beach, Florida. The raw water studied is a moderately colored, high-hardness groundwater emanating from the Floridan aquifer.

Various treatment processes studied included single-stage coagulation/lime softening, two-stage coagulation/lime softening, lime softening/coagulation, bentonite clay with lime softening, and polymeric coagulant/clay coagulation/lime softening.

Extensive analytical data were collected and summarized on raw water for test samples, pilot-plant process waters, Brennan Treatment Plant samples, and Daytona Beach distribution system samples. These data were used to evaluate the effectiveness of each process studied, as well as to compare pilot-plant performance with full-scale plant results.

This Project Summary was developed by EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

#### Introduction

In 1979, the U.S. Environmental Protection Agency (EPA) promulgated an amendment to the National Interim Primary Drinking Water Regulations establishing a maximum contaminant level (MCL) of 0.10 mg/L for total trihalomethanes (TTHM's). Two previous investigations at the Ralph F. Brennan Municipal Water Treatment Plant in Daytona Beach, Florida, indicated that the level of trihalomethanes (THM's) in the finished water exceeded the MCL by several fold.

These reports further concluded that the level of THM production could be reduced by improving coagulation and by altering the point of chlorination in the treatment process. These studies did not, however, determine a treatment process that would reduce the effluent THM concentration below the legislated maximum.

Before radical alternatives such as air stripping, activated carbon, or alternative disinfectants were investigated, this project was undertaken to study further THM reductions by means of improved coagulation/lime softening techniques to remove precursor organics.

# **Procedures**

# Literature Search

To guide and optimize jar test work and

pilot-plant efforts, reports on previous work by others (including those at the Brennan Plant) were reviewed. Results of various investigations generally agreed that THM precursors were definitely removed through coagulation with alum and ferric salts, but the removal efficiency varied significantly with the raw water source. These studies generally indicate that coagulation of THM precursors is a function of pH and chemical dose. Widespread disagreement exists, however, as to the dosage levels required for maximum THM reduction.

# Jar Test Program

The purpose of the jar test was to refine and confirm the results of the two earlier studies done at the Brennan Plant and to investigate those parameters that the literature indicated might be effective. The raw water studied was a moderately colored, high-hardness groundwater emanating from the Floridan aquifer (see Table 1).

Eight areas of study for THM precursor removal efficiency were identified:

- Aluminum sulfate (alum) versus ferric sulfate (ferric) as a coagulant;
- 2. Coagulant dose (alum and ferric);
- 3. Coagulant pH (alum and ferric);
- Coagulation followed by lime softening;
- Lime softening followed by coagulation:
- Softening at a high pH (approximately 11) with magnesium carbonate;
- Several other coagulant aids including sodium aluminate, a bentonite clay, and CatFloc-T\* and;
- 8. Bentonite clay with lime softening.

To pursue these eight areas effectively, an initial series of jar tests investigated the following parameters:

- Optimization of lime dose for softening and THM precursor removal.
- Effect of pH on color and THM precursor removal.
- Effect of pH and alum dosage on color and THM precursor removal when treating lime-softened water.
- Effect on THM precursor removal when softening with lime after coagulating with alum.
- Effect on THM precursor removal when using clay and CatFloc-T in combination with lime.
- Effect of sodium aluminate on THM precursor removal when treating lime-softened water.

Table 1. Daytona Beach Raw Water Analysis, 1976-81

Parameter	5/76	11/77	.8/78	5/79	10/80	11/81
pH	7.31	6.8	7.0	7.1	6.9	6.8
Color, PCU	34	20	20	15	15	15
TDS, mg/L	392	323	424	362	383	452
Turbidity, NTU	1.8	0.26	0.25	0.4	0.3	0.1
Total Hardness, mg/L as CaCO3	294	316	284	298	294	296
Calcium, mg/L as Ca <sup>+2</sup>	104	114	101	95	111	102
Magnesium, mg/L as Mg <sup>+2</sup>	8.5	7.2	7.4	14.3	3.8	9.5
Alkalinity, mg/L as CaCO3	276	254	274	260	276	274
Chloride, mg/L	50	<i>37</i>	33	42	36	54
Sulfate, mg/L as SO <sub>4</sub> -2	2.0	4.3	4.3	2.0	9.8	6.2

Once the results of this first series were analyzed, additional jar tests studied the following:

- Effectiveness of ferric sulfate for THM precursor and color removal at various dosages and pH levels.
- Effect on THM precursor removal by adding magnesium sulfate and sodium carbonate at high pH.
- Effect on THM precursor removal by using CA-35 clay in combination with Rohm and Haas XE-392 polymeric coagulant.

# Pilot-Plant Program

The results of the jar tests and continuous re-evaluations during the pilot-plant phase of the study ultimately led to eight pilot-plant test runs:

- Simulation of full-scale Brennan Plant conditions for development of baseline data.
- Clay and Calgon CatFloc-T in combination with lime softening.
- Alum at 20 mg/L with American Cyanamid Magnifloc 985N in combination with lime softening.
- Alum at 40 mg/L with Magnifloc 985N in combination with lime softening.
- Two-stage coagulation/softening involving 40 mg/L alum with sulfuric acid pH adjustment followed by lime softening.
- Two-stage coagulation/softening involving sulfuric acid pH adjustment with 80 mg/L alum followed by lime softening.
- Two-stage softening/coagulation involving Nalco 8184 with lime followed by 50 mg/L alum with final NaOH pH adjustment.
- Use of Calgon CA-35 clay in conjunction with Rohm and Haas XE 391 and XE 392 coagulants.

## **Results and Conclusions**

#### Jar Test Results

The initial jar tests showed that maximum hardness reduction could be effected at a lime dose rate of 250 mg/L. For subsequent jar tests, 220 mg/L lime feed was used to duplicate actual Brennan Treatment Plant practice. This work confirmed earlier results, which showed that lime coagulated with a polyelectrolyte was inefficient as a precursor removal process on the well water at the Daytona Beach plant.

Subsequent jar tests compared ferric sulfate in combination with lime softening as opposed to alum with lime. Dosage of the coagulants was varied, as was order of treatment. Alum at higher doses removed color more effectively than ferric sulfate, though both performed similarly with respect to precursor removal. Anionic and cationic polymers were tested in combination with alum to improve floc settling characteristics of the light alum floc. Results were poor, but further jar tests indicated that little benefit would be realized in removing this floc even through an intermediate filtration step.

Low pH coagulation of previously softened high pH water was also attempted and resulted in effluent THM values in the 200 to 300  $\mu$ g/L range.

Additional jar tests were conducted using clay with CatFloc-T and with sodium aluminate, both in combination with lime softening. Neither process showed results that were substantially better than the conventional alum/lime combination.

Brief initial jar tests involving magnesium sulfate and sodium carbonate in combination with lime softening showed very promising results, with THM values in the 200  $\mu g/L$  range. Subsequent retesting failed to duplicate this removal efficiency, however, so further testing was discontinued.

<sup>\*</sup>Mention of trade names or commercial products does not constitute endorsement or recommendation for use

Extensive jar testing was accomplished using the experimental Rohm and Haas polymeric coagulant. This material was tested at various doses as well as various ratios of cationic to anionic polymer. Further tests evaluated the use of clay in conjunction with the polymers, as well as the effect of chlorinating before filtration as opposed to chlorinating after filtration.

The summary results of the jar tests were used to establish the pilot-plant operating program.

### Pilot-Plant Test Results

The average THM concentration for the eight pilot-plant runs are listed in Table 2.

The first pilot-plant run was intended to simulate the full-scale operation of the Brennan Treatment Plant to establish baseline parameters. Pilot-plant performance generally paralleled treatment plant performance, though higher 3-day THM's were realized in the pilot-plant effluent samples. This result is thought to be caused by the lack of sludge recirculation capability in the pilot plant, which results in decreased efficiency.

The second pilot test showed a slight improvement over the baseline condition, but the results were not promising enough to warrant further investigation of the clay-polymer combination.

The use of alum as studied in the third and fourth runs showed additional improvement in THM precursor removal, but the 300+  $\mu$ g/L levels obtained in stored samples still fell far short of the desired 100 µg/L MCL.

The two-stage coaquiation/softening process attempted in the fifth and sixth pilot runs showed continued improvement, but at the expense of a significant increase in process complexity and operational costs. Of the conventional softening/coagulation schemes studied, this one shows the most promise; but it still did not approach the 100 µg/L goal.

The seventh pilot run, in which softening was followed by coagulation, resulted in 3-day THM readings comparable to those in the single-stage process evaluated in the third pilot run.

The final pilot series deviated significantly from the rest of the study in that an experimental polymeric coagulant was used in combination with clay and lime. This series was the most promising by far (Figure 1), resulting in a 3-day THM average of 158 µg/L. Because the pilotplant baseline tests indicated that fullscale operation of the Brennan Plant exceeded the performance of the pilot unit, it is expected that this process might

Table 2. Average THM Concentration in Pilot Plant (µg/L) Type of Water and THM Run #3 Run #4 Run #1 Run #2 Run #5 Run #6 Run #7 Run #8 RW: 0.00 CHCI<sub>3</sub> 1.14 .743 1.15 1.61 0.00 0.00 0.00 CHBrCl<sub>2</sub> 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 CHBr<sub>2</sub>CI 0.000.00 0.00 0.00 0.00 n n0.00 0.00 CHBr<sub>3</sub> 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 TTHM 0.00 0.00 1 14 743 1 15 1 61 0.00 0.00 RWSC: CHCI<sub>3</sub> 268 377 376 364 356 273 314 272 81.4 75.3 61.7 73.5 58.6 57.5 CHBrCl<sub>2</sub> 76.8 56.3 CHBr<sub>2</sub>CI 11.0 7.77 8.37 8.76 6.78 7.43 8.38 6.66 CHBr<sub>3</sub> 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 TTHM 360 460 461 432 438 336 380 338 FWID: 51.0 41 8 44 0 544 31.4 416 21.1 CHCIa 36.7 CHBrCl<sub>2</sub> 15.7 9.90 11.1 11.2 7.35 9.6 10.6 8.60 4.28 3.10 2.49 2.62 3.13 CHBr<sub>2</sub>CI 3.63 3.12 2.23 CHBr<sub>3</sub> 0.00 0.00 0.00 0.00 0.00 0.00 0.00 0.00 **TTHM** 70.3 56.0 58.2 68.7 46.3 43.5 54.8 32.8 FWSC: CHC<sub>13</sub> 249 262 248 238 219 155 203 98.3 72.6 CHBrCI<sub>2</sub> 79.3 66.6 59.6 57.1 54.1 **57.0** 44.0 CHBr<sub>2</sub>CI 22.8 15.8 14.4 14.7 17.2 10.4 12.6 14.9 CHBr<sub>3</sub> 0.00 0.28 0.000.00 0.831 43 1.23 .234 TTHM 351 351 329 312 295 220 273 158 ACSC: ACSC LCSC ACSC CHCI<sub>2</sub> 205 195 339 CHBrCl<sub>2</sub> 43.0 71.2 39.3 CHBr<sub>2</sub>CI 4.66 5.80 13.4 CHBr<sub>3</sub> 0.00 0.00 0.00 **TTHM** 

\*Abbreviations:

0.00 Below detection limits.

Lime clarifier, super chlorinated, stored 72 hours. LCSC

RW Raw water.

Raw water, super chlorinated, stored 72 hours. RWSC Finished water, immediately dechlorinated. **FWID** 

**FWSC** Finished water, super chlorinated.

Alum clarifier, super chlorinated, stored 72 hours. ACSC

approach the required 100  $\mu$ g/L in a fullscale sludge recirculation operation.

#### Recommendations

Full-scale testing of the Rohm and Haas polymeric coagulant with clay and lime should be accomplished at the Brennan Water Treatment Plant. To improve the mechanism of THM removal. precursor materials should be identified through additional analytical work.

The full report was submitted in fulfillment of Cooperative Agreement CR80742601 by Russell & Axon, Engineers-Planners-Architects, Inc., under the sponsorship of the U.S. Environmental Protection Agency.

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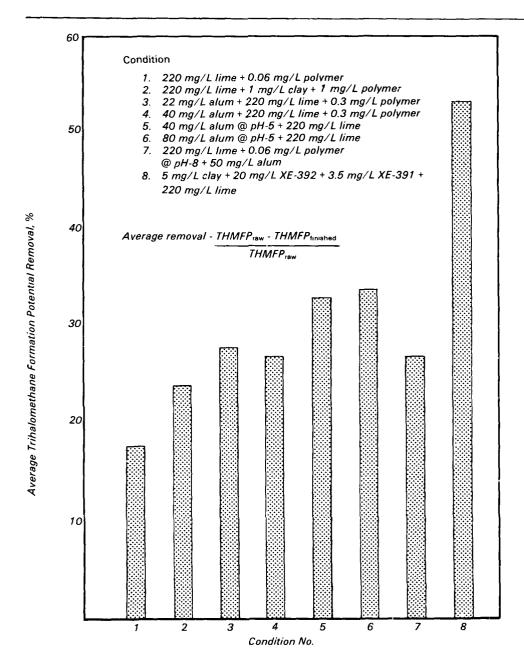


Figure 1. THM formation potential removal in the pilot plant

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O. Thomas Love, Jr. is the EPA Project Officer (see below).

The complete report, entitled "Trihalomethane Removal by Coagulation Techniques in a Softening Process," (Order No. PB 83-151 845; Cost: \$11.50, subject to change) will be available only from:

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