PARTICULATE AND THM PRECURSOR REMOVAL WITH FERRIC CHLORIDE

By Amy E. Childress, Eric M. Vrijenhoek, Menachem Elimelech, Theodore S. Tanaka, and Mark D. Beuhler

ABSTRACT: Pilot-scale experiments were performed to investigate the effectiveness of enhanced coagulation in removing particles and trihalomethane (THM) precursors from two surface source waters: California State Project water and Colorado River water. The removal of suspended particles and natural organic matter at various ferric chloride doses and coagulation pHs was assessed through source water and filter effluent measurements of turbidity, particle count, UV254, TOC, and THM formation potential. Overall, it was found that optimal removal of particles and THM precursors by enhanced coagulation with ferric chloride is obtained at high coagulant doses (>16 mg/L) and low pH conditions. Generally, turbidity removal is more efficient and head loss is more moderate at ambient pH compared with pH 5.5. Additionally, filter effluent particle counts were found to be consistent with residual turbidity data. The removal of THM precursors by enhanced coagulation is significantly enhanced at pH 5.5 compared with ambient pH. The reduction in THM formation potential is consistent with the trends observed for the THM precursor removal data (i.e., UV254 and TOC data). Furthermore, specific UV absorbance was used to estimate the proportion of humic substances in the raw waters. Enhanced coagulation was found to be less effective for the source water with the lower specific UV absorbance.

INTRODUCTION

Particles are removed during coagulation by either (1) adsorption/charge neutralization or (2) sweep-floc coagulation (O’Melia 1972; Dempsey 1984). Charge neutralization usually occurs at low coagulant doses through the adsorption of dissolved metal species or metal hydroxide precipitates; sweep-floc coagulation typically occurs at high coagulant doses (Amirtharajah and O’Melia 1990; Ching et al. 1994). Because most coagulant doses used in this investigation significantly exceed the solubility limit, sweep-floc coagulation is more likely to predominate. In sweep-floc coagulation, metal hydroxide precipitates promote coagulation by increasing the interparticle collision rate and enmeshing suspended particles (Edwards and Amirtharajah 1985; Montgomery 1985).

The removal of natural organic matter (NOM) from solution occurs by either (1) precipitation of metal-humic complexes or (2) adsorption of humic substances onto metal hydroxide precipitates (Dempsey et al. 1984; Edwards and Amirtharajah 1985; Randtke 1988; Amy et al. 1989; Cheng et al. 1995; Dennett et al. 1995; Krasner and Amy 1995). The mechanism that occurs is dependent on the pH of the system and the coagulant dose (Dempsey et al. 1984; Edwards and Amirtharajah 1985; Dennett et al. 1995; Krasner and Amy 1995). Generally, precipitation of metal-humic complexes is the dominant mechanism at lower coagulant doses and lower pH conditions; adsorption of humics onto metal hydroxide precipitates is dominant at higher coagulant doses and higher pH conditions (Edwards and Amirtharajah 1985; Cheng et al. 1995; Krasner and Amy 1995; Dennett et al. 1996).

Optimal turbidity (e.g., clay) removal with metal coagulants typically occurs at pH 6.5–7.5 (Hall and Packham 1965) and optimal NOM removal typically occurs around pH 5 (Hall and Packham 1965; Kavaugh 1978; Randtke et al. 1988). More specifically, the optimum pH for coagulation of NOM with ferric chloride (FeCl3) is approximately 4–5 (Hall and Packham 1965; Kavaugh 1978; Randtke 1988; Amirtharajah et al. 1993). This is lower than the optimum pH for coagulation of NOM with aluminum salts (pH 5–6) (Hall and Packham 1965; Kavaugh 1978; Randtke 1988) due to the higher acidity of Fe(III). The zero point of charge for ferric hydroxide precipitates occurs between pH 6.5 and 8.5, whereas for alum precipitates it occurs around pH 7 (Bottero and Bersillon 1989).

Removal of particles and NOM is central to several of the new drinking water regulations. As part of the microbial/disinfection by-products cluster of the 1996 Safe Drinking Water Act amendments, the U.S. Environmental Protection Agency (USEPA) has established the Interim Enhanced Surface Water Treatment Rule (IESWTR) and the Stage 1 Disinfectants/Disinfection By-Products (D/DBP) Rule (Pontius 1999). The IESWTR applies to surface water systems and ground-water systems under the direct influence of surface water. It requires a 2-log reduction in Cryptosporidium for systems that filter (“Disinfectants” 1998). Additionally, it lowers the existing monthly turbidity limits from 0.5 to 0.3 NTU. The Stage 1 D/DBP Rule regulates the chemicals used for disinfection and the by-products that are formed when a disinfectant is added to water that contains NOM. It lowers the existing trihalomethane (THM) standard from 0.1 to 0.08 mg/L (“Interim” 1998). It also requires most systems using surface water or ground water directly influenced by surface water to implement enhanced coagulation or softening to remove DBP precursors.

Enhanced coagulation is the extension of traditional coagulation from turbidity removal to both turbidity and NOM removal. Enhanced coagulation involves selection of the most appropriate coagulant(s), higher dosages of the coagulants, and pH adjustment (Kavaugh 1978; Edwards and Amirtharajah 1985; Randtke 1988; Amy et al. 1989; Cheng et al. 1995; Crozes et al. 1995; Dennett et al. 1995; Krasner and Amy 1995; Vrijenhoek et al. 1998). The current investigation explores the use of enhanced coagulation with ferric chloride to remove both particles and THM precursors.
The current investigation was performed at a permanent, two-train, pilot-scale facility located adjacent to the F. E. Weymouth Filtration Plant in La Verne, Calif. Each train of the pilot plant includes a rapid-mixing tank, a flocculation basin, a sedimentation tank, and three filter columns. A general description of the pilot plant is given below; details can be found elsewhere (Ching 1994).

Source water was diverted from the F. E. Weymouth Filtration Plant and pumped to a holding tank at the pilot plant. From the holding tank, the raw water was pumped to a rapid-mixing tank where FeCl3 and cationic polymer were added. Detention time in the rapid mixing tank was approximately 2 min. After rapid mixing, the flow entered a three-stage flocculation basin. Each stage of the flocculation basin had a separate, paddle-type, low-speed mixer with variable speed control. Total detention time in the flocculation basin was about 20 min. In experiments with high FeCl3 doses (≥8 mg/L), flow leaving the flocculation tank entered a sedimentation basin with a detention time of approximately 60 min. In experiments with low FeCl3 doses (<4 mg/L), direct filtration was simulated, and flow leaving the flocculation tank entered a sump. Then, the water was pumped to dual-media and triple-media filters. The dual-media filters contained 508 mm (20 in.) of anthracite coal with an effective size of 1.0 mm, 203 mm (8 in.) of silica sand with an effective grain size of 0.6 mm, and 76 mm (3 in.) of gravel. The triple-media filter contained 508 mm (20 in.) of anthracite coal with an effective size of 1.0 mm, 203 mm (8 in.) of silica sand with an effective size of 0.6 mm, 76 mm (3 in.) of ilmenite sand with an effective size of 0.22 mm, and 51 mm (2 in.) of gravel. Head loss through the filters was monitored continuously using differential pressure indicators.

Source Waters

The source waters used in this investigation were California State Project water (SPW) and Colorado River water (CRW). SPW originates at the Sacramento–San Joaquin Delta and is supplied by the California Aqueduct; CRW is diverted from the Colorado River at Lake Havasu and is supplied by the Colorado River Aqueduct. The two source waters are of relatively good quality and are free of industrial pollutants. As shown in Table 1, turbidity, UV absorbance at 254 nm (UV254), and total organic carbon (TOC) are higher in SPW, whereas alkalinity and hardness are higher in CRW. The pH of SPW ranges from 7.85 to 8.2 and total organic carbon (TOC) ranges from 106 to 112 mg/L. This relatively small pH change at high FeCl3 dose is due to the buffering capacity of the SPW and CRW.

**Table 1. Influent Water Quality Parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CRW (1)</th>
<th>SPW (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (NTU)</td>
<td>1.1 to 3.5</td>
<td>0.64 to 1.7</td>
</tr>
<tr>
<td>pH</td>
<td>7.2</td>
<td>6.8 to 8.0</td>
</tr>
<tr>
<td>TOC (mg/L)</td>
<td>2.41 to 2.68</td>
<td>2.47 to 2.78</td>
</tr>
<tr>
<td>THMFP (µg/L)</td>
<td>378 to 403</td>
<td>100 to 127</td>
</tr>
<tr>
<td>Alkalinity (mg/L as CaCO3)</td>
<td>74 to 75</td>
<td>132 to 150</td>
</tr>
<tr>
<td>Hardness (mg/L as CaCO3)</td>
<td>370 to 430</td>
<td>287 to 303</td>
</tr>
<tr>
<td>UV254 (cm-1)</td>
<td>0.033 to 0.038</td>
<td>0.115 to 0.119</td>
</tr>
</tbody>
</table>

*Data obtained during period of January 6 to March 10, 1993.
Data obtained from Liang (1992).
Data obtained during period of July 9 to September 2, 1992.

Water samples were taken from three locations in the pilot plant. Raw water characteristics were established by daily sampling of pH, turbidity, electrophoretic mobility (EM), and particle count; and weekly sampling of UV254, nonpurgeable TOC (NPTOC), trihalomethane formation potential (THMFP), and simulated distribution system trihalomethane (SDS THM) formation potential. The rapid-mix effluent was analyzed for pH, turbidity, EM, and particle count. The filter effluent was analyzed for pH, turbidity, particle count, UV254, NPTOC, THMFP, and SDS THM. Filter effluent samples were collected after 2 h of filtration. Filter ripening was complete after <60 min in all experiments.

**Analytical Methods for Organics**

Analyses of UV254, NPTOC, THMFP, and SDS THM were conducted at the Metropolitan Water District’s Water Quality Laboratory in La Verne, Calif. Water samples were preserved with a reagent-grade phosphoric acid at pH <2. UV absorbance was measured using a UV/visible spectrophotometer (Perkin Elmer Lambda 5, Norwalk, Conn.) at a wavelength of 254 nm. All samples for UV254 analyses were filtered through a 0.45-µm syringe filter prior to the measurement. NPTOC analyses were performed with a TOC analyzer (Dohrmann Model DC-180, Cincinnati) using the persulfate-ultraviolet oxidation method for nonpurgeable organic carbon as described in Standard Methods 5310C.

THMs were analyzed using the method described by Koch et al. (1988). Pentane was used as the extraction solvent, and sodium sulfate was added to improve the partitioning from the aqueous phase to the solvent. A capillary gas chromatograph (Varian Instrument Group, Sunnyvale, Calif.) equipped with an electron capture detector was utilized for adequate resolution and detection of the THMs (i.e., CHCl3, CHBrCl3, CHClBr2, and CHBr3).

THMFP analyses were conducted according to USEPA method 510.1 (Koch et al. 1991). The USEPA THMFP procedure estimates the maximum formation of THMs in a water
sample. Sufficient chlorine (9–12 mg hypochlorite-buffer solution as Cl₂ per liter) was added to the water samples to maintain a free chlorine residual for the entire 7-day THM formation period. All samples were stored at 25°C.

The SDS THM formation potential method was performed as described by Koch et al. (1991). The SDS THM method estimates the amount of THMs that would form in a distribution system when free chlorine is used as a disinfectant. The filter effluent was dosed with a hypochlorite buffer solution to a concentration of 3.3 mg/L (as Cl₂) and incubated for 3 h to represent the average duration of treated water traveling to specific locations in the distribution system. The applied chlorine dose was comparable to the total chlorine dose used at the adjacent F. E. Weymouth Filtration Plant.

RESULTS AND DISCUSSION
Electrophoretic Mobility of Particles

Fig. 1 shows the effect of FeCl₃ addition on the EM of particles in the rapid mix effluent. Prior to coagulant addition, the EM of the particles in both source waters was negative. Generally, as the FeCl₃ dose increases, the EM becomes slightly less negative due to adsorption/deposition of the positively charged ferric hydroxide precipitates onto the particle surface. Charge reversal is not observed at any of the FeCl₃ doses investigated. Also, for all FeCl₃ doses, the EM of the particles in SPW is more negative than it is in CRW. This is attributed to the higher levels of humics and lower hardness in SPW (O’Melia 1985; Liang and Morgan 1990). A higher level of negatively charged humic macromolecules and a lower concentration of divalent hardness cations result in more negatively charged particles in SPW.

For both waters, the FeCl₃ doses are more effective at reducing the negative EM of the particles at ambient pH than at the adjusted pH of 5.5. The formation of ferric hydroxide precipitates is more favorable at ambient pH than at pH 5.5 (O’Melia 1972; Edwards and Amirtharajah 1985; Randtke 1988; Ching et al. 1994); therefore, the EM is more substantially reduced at ambient pH than at pH 5.5. Additionally, greater adsorption of NOM at pH 5.5 than at ambient pH may be responsible for the more negative EM at pH 5.5 (Hall and Packham 1965; Kavanaugh 1978; Hubel and Edzwald 1987; Randtke et al. 1988).

Residual Turbidity of Filter Effluent and Filter Head Loss

The effects of FeCl₃ doses on the residual turbidity in the filter effluent for CRW and SPW are shown in Figs. 2 and 3,
respectively. Residual turbidity is higher in SPW than in CRW for all FeCl₃ doses investigated. This is again attributed to the higher humic concentration and lower hardness in SPW, which results in greater negative EMs and reduced coagulation efficiency. For CRW at both pH conditions, residual turbidity generally decreases with increasing FeCl₃ dose. For SPW, greater turbidity removal occurs at ambient pH than at pH 5.5. At ambient pH, residual turbidity levels are below 0.1 NTU at FeCl₃ doses >8 mg/L. At these doses, the dominant mechanism of aggregation is sweep-floc coagulation (Johnson and Amirtharajah 1983). At pH 5.5, effective coagulation is achieved only at high FeCl₃ doses (>16 mg/L). For both CRW and SPW at pH 5.5, the residual turbidity spikes briefly with increasing FeCl₃ dose. In CRW as the FeCl₃ dose is increased from 0.5 to 2 mg/L, the residual turbidity increases from 0.1 to 0.18 NTU; in SPW as the FeCl₃ dose is increased from 0.5 to 8 mg/L, residual turbidity increases from 0.1 to 0.32 NTU. The formation of insoluble colloidal ferric hydroxide and ferric-humate precipitates in the submicrometer size range is the most likely explanation for the observed spike. The precipitate solids either deposit onto the surface of retained particles in the filter or remain suspended in solution. Adsorption of NOM to the colloidal precipitates enhances their colloidal stability and therefore reduces their capture by the granular filter. The presence of these precipitates in the filter effluent increases the residual turbidity.

The relative head loss (i.e., head loss divided by clean bed head loss) through the filters at the end of the 2-h run is shown in Figs. 2 and 3 as a function of FeCl₃ concentration. Head loss increases with increasing FeCl₃ dose due to the increasing concentration of ferric hydroxide precipitates depositing on the filter media. Particulary for CRW, the head loss is lower at ambient pH than at pH 5.5. Therefore, for particle removal, operation of the filters at ambient pH not only reduces chemical costs but also provides increased filter run times.

### Particle Count of Filter Effluent

Particle counts were performed because they provide more detailed information on particle removal than traditional turbidity measurements. Table 2 shows residual particle number concentration and percent removal of particles in CRW and SPW for the adjusted pH condition (pH 5.5). For both source waters, the majority of influent and residual particles are in the size range of 2–6 μm. At low FeCl₃ concentrations (<2 mg/L), the percent removals of particles in CRW are lower than those in SPW. This difference is most likely attributed to the much lower influent particle concentration in CRW that results in fewer collisions between particles during coagulation.

Fig. 4 shows the total residual number concentration of particles (2–60 μm) in the filter effluent as a function of FeCl₃ dose for both pH conditions. For all FeCl₃ doses, the residual number concentration of particles in SPW is greater than that...
in CRW. This is due to the much higher initial number concentration of particles in SPW compared to CRW.

For both source waters, greater overall removal of particles in the size range of 2–60 μm was observed at pH 5.5 than at ambient pH. At ambient pH, particle number decreases with increasing FeCl₃. At pH 5.5 for SPW, particle number increases as the FeCl₃ dose increases from 0.5 to 2 mg/L. This is attributed to an increase in the number of particles in the size range of 2–6 μm (Table 2). As described earlier, the increase in smaller particles is most likely due to the formation of insoluble colloidal ferric hydroxide and ferric-humate precipitates during coagulation at lower FeCl₃ doses and lower pHs.

Greater total removal of particles at pH 5.5 than at ambient pH may appear to be in contrast with residual turbidity results presented in Fig. 3. However, at pH 5.5, small precipitates (<2 μm) contribute significantly to the turbidity readings but not to particle counts because they are below the detection limit of the particle counter. The filter removal efficiency of the small particles (<2 μm) appears to be much lower than for larger particles (>2 μm).

The above data have implications for the ability of ferric chloride enhanced coagulation to meet IESWTR requirements. The particle counts in Table 2 give a good indication of particle removal in the size range of protozoa (e.g., 3–7 μm for Cryptosporidium and 8–10 μm for Giardia) but cannot replace microbiological detection methods. Additionally, there is considerable uncertainty in measuring high log removals of particles whose concentrations in the raw water are very low (Vrijenhoek et al. 1998).

TOC, UV Absorbance, and SUVA

The effect of FeCl₃ dose on the removal of TOC and UV₂₅₄ absorbance in CRW and SPW is shown in Figs. 5 and 6. With some exceptions, the percent removals of TOC and UV₂₅₄ absorbance in SPW (Fig. 6) increase as the FeCl₃ dose increases. An exception to this occurs between 1 and 4 mg/L FeCl₃ for SPW at pH 5.5 where the percent removal of UV₂₅₄ absorbance decreases with increasing FeCl₃ dose. This provides further support to the earlier supposition that small colloidal precipitates are formed during coagulation. These small precipitates scatter light in the filtered water and thus increase the UV₂₅₄ absorbance reading. This same phenomenon was considered to be responsible for the increased turbidity levels and particle counts at low FeCl₃ doses. With no exceptions, the percent removals of TOC and UV₂₅₄ absorbance in CRW (Fig. 5) increase with increasing FeCl₃ dose.

Because the optimal pH for NOM removal is around 5 (Hall and Packham 1965; Kavanaugh 1978; Randtke et al. 1988), lowering the pH to 5.5 enhances the removal of TOC and UV₂₅₄ absorbance. From Fig. 5, the maximum removals attained for TOC and UV₂₅₄ absorbance at ambient pH for CRW are 23 and 31%, respectively, whereas the maximum removals of TOC and UV₂₅₄ absorbance at pH 5.5 for CRW are 48 and 53%, respectively. At low FeCl₃ dose (≤8 mg/L), the enhanced removal at pH 5.5 is attributed to the formation of insoluble ferric-humate complexes (Edwards and Amirtharajah 1985; Cheng et al. 1995; Krasner and Amy 1995). At FeCl₃ doses >16 mg/L, enhanced removal is due to increased NOM adsorption onto amorphous ferric hydroxide precipitates (Edwards and Amirtharajah 1985; Cheng et al. 1995; Krasner and Amy 1995).

From Figs. 5 and 6, the percent reductions of UV₂₅₄ absorbance were higher than those of TOC in both source waters. The humic fraction, which absorbs UV light at 254 nm, is more effectively removed by coagulation than the nonhumic fraction (Edzwald et al. 1985; Najm et al. 1994; Krasner and Amy 1995). This explanation also accounts for the greater per-
cent removal of UV$_{254}$ absorbance and TOC in SPW than in CRW. The higher humic fraction in SPW results in greater humic fraction removal and greater overall NOM removal. The SUVA of the water sources supports this conclusion. The SUVA represents the amount of NOM considered to be humic substances; for SPW the SUVA is 297 L/mg-m and for CRW the SUVA is 149 L/mg-m.

SUVA of the filter effluent as a function of FeCl$_3$ dose is shown in Fig. 7. Except for the previously discussed spike at 4-mg/L FeCl$_3$, the SUVA in SPW generally decreases with increasing coagulant dose, indicating preferential removal of the humic fraction. Conversely, virtually no change in SUVA was observed in CRW. This result supports the conclusion that CRW’s NOM was not as amenable to chemical coagulation because of its larger nonhumic fraction. Therefore, enhanced coagulation was less effective at reducing DBP precursors in CRW.

**SDS THM and THMFP**

The SDS THM and THMFP tests were used to evaluate THM formation. The tests differ in incubation time (3 h for SDS THM and 7 days for THMFP) and the chlorine dose applied (higher dose in THMFP test). Much higher levels of total THMs (TTHMs) would be expected to form in the THMFP test.

TTHM (determined by the SDS method) and total THMFP (TTHMFP) (determined by the THMFP method) as a function of FeCl$_3$ dose are shown in Figs. 8 and 9. Reduction in TTHMs is attributed to removal of THM precursors. Thus, the trends in TTHM and TTHMFP reduction as a function of FeCl$_3$ dose are similar to the TOC and UV$_{254}$ reduction trends. In both cases TTHMs were reduced as FeCl$_3$ dose increased. Generally, TTHMs and TTHMFPs were much higher in SPW than in CRW due to the higher humic content of SPW. It is generally accepted that the humic fraction of NOM is more re-

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**FIG. 7.** Specific UV Absorbance of Filter Effluent as Function of Ferric Chloride Dose for: (a) CRW; (b) SPW. For Ferric Doses of 2 and 4 mg/L, 1 mg/L Cationic Polymer Was Used; For Ferric Chloride Doses $\geq$8 mg/L, 2 mg/L Cationic Polymer Was Used

**FIG. 8.** TTHMs (Determined by SDS Method) in Filter Effluent as Function of Ferric Chloride Dose for: (a) CRW; (b) SPW

**FIG. 9.** TTHMs (Determined by THMFP Method) in Filter Effluent as Function of Ferric Chloride Dose for: (a) CRW; (b) SPW
active than the nonhumic fraction in forming THMs (Krasner and Amy 1995; Vrijenhoek et al. 1998).

For all FeCl₃ doses and for both source waters, greater removals were observed at pH 5.5 than at ambient pH. At pH 5.5 and low FeCl₃ dose, removal of THM precursors is induced by the formation of insoluble ferric-humate complexes. Although these complexes are very small, they are still filterable. As the FeCl₃ dose increases, both ferric hydrolysis species and ferric hydroxide precipitates exist, and both removal mechanisms (i.e., formation of metal-humate complexes and NOM adsorption onto ferric hydroxide precipitates) may occur simultaneously. At higher FeCl₃ doses (>16 mg/L), the predominant removal mechanism of THM precursors is thought to be adsorption onto the ferric hydroxide precipitates. At ambient pH, formation of ferric-humate complexes is not as significant because of the low concentration of positively charged ferric hydrolysis species; therefore, THM precursor removal is almost solely due to adsorption onto the ferric hydroxide precipitates (Edwards and Amirtharajah 1985).

The results of the SDS THM tests may provide realistic estimates of how efficiently enhanced coagulation is able to comply with the pending D/DBP Rule. CRW had an initial SDS THM concentration <40 µg/L—the proposed maximum concentration level (MCL) for Stage 2 of the D/DBP Rule. The low THM formation of CRW is attributed to its low humic fraction in raw waters. As SUV A reaches a constant value with increasing ferric chloride dose, the removal of THM precursors only improves marginally.

- Enhanced coagulation is not as beneficial for source waters with lower humic fractions and, hence, lower SUVAs. Such water, however, may not form elevated concentration of DBPs because of the lower reactivity of nonhumic NOM.

ACKNOWLEDGMENTS

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APPENDIX. REFERENCES


