Evaluation of Chemical Clarification Polymers and Methods for Removal of Dissolved Metals from CDF Effluent

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PURPOSE: This technical note reports results of a study to evaluate novel chemical clarification polymers and methods for CDF effluent treatment to remove dissolved metals.

BACKGROUND: Clarification processes used to separate solid and liquid phases in the dredging slurry discharged to confined disposal facilities (CDFs) have typically consisted of sedimentation and chemical flocculation. Clarification is intended for removal of solids from CDF effluent, and in doing so, much of the metals contamination is also removed with the solids. Likewise, the ability of the chemical flocculation to remove dissolved phase contaminants should also be considered, since this may be an important, simultaneous benefit. As effluent discharge standards become more stringent, the benefits of new chemical flocculation agents may outweigh their added costs. The ability of polymers to remove dissolved metals as well as solids from dredging applications should be considered.

Polymer flocculants for dredging application were previously investigated in screening tests (Wang and Chen 1977, Jones et al. 1978, Schroeder 1983, Wade 1988). The Engineer Manual on Confined Disposal of Dredged Material (U.S. Army Corps of Engineers (USACE) 1987) provides guidance on CDF effluent clarification and lists several polymers as possible candidates in chemical coagulation applications.

INTRODUCTION: Specific objectives of this study were to evaluate new polymer coagulants introduced in the last five years for use in clarifying CDF effluent and evaluate removal of selected dissolved contaminants during chemical clarification.

POLYMER SCREENING FOR SOLIDS REMOVAL USING LABORATORY JAR TESTS

Method. Jar tests screen a large number of polymers to select the most effective polymers for additional study. Tests were conducted using total suspended solids (TSS) concentrations of 2 g/L. A total of 46 polymers were screened for their ability to remove solids. Table 1 lists the polymers that were evaluated and their reported properties. Polymers were diluted with distilled deionized (DDI) water to a concentration of approximately 2 g/L for test application. Note, however, that Storm-Klear Liquifloc polymer, which consists of 1 percent chitosan-acetate, was not further diluted.

Table 1
Properties of Polymers Evaluated in Screening Tests

Manufacturer/Trade Name	Form	Charge	Charge Intensity	MW
Ciba Specialty Chemicals Corporation				
Magnafloc 10	Powder	Anionic	weak	
Magnafloc 24	Powder	Anionic		
Magnafloc 155	Powder	Anionic		
Magnafloc 338	Powder	Anionic		
Magnafloc 351	Powder	Nonionic		
Magnafloc 368	Powder	Cationic		60,800
Zetag 7692	Granular	Cationic	low	high
Zetag 7888	Dispersion	Cationic	very high	medium
Zetag 7635	Granular	Cationic	high	medium
Zetag 7867	Dispersion	Cationic	medium	high
Zetag 7587	Microbeads	Cationic	high	medium
Zetag 7197	Liquid	Cationic		
Zetag 7125	Liquid	Cationic	high	very low
Zetag 7623	Granular	Cationic	very low	very high
Zetag 7195	Liquid	Cationic	high	very low
Cetco				
C 110	Liquid	Cationic	low	<100,000
C 891	Liquid	Cationic	100	> 175,000
F 870 C	Liquid	Cationic	70	11,000,000
Hychem, Inc.				
Hyperfloc CP 626	Liquid	Cationic	100	100,000
Hyperfloc AE 853	Emulsion	Anionic	30	15,000,000
Hyperfloc AF 307	Powder	Anionic	30	15,000,000
Hyperfloc AF 307-HH	Powder	Anionic	30	20,000,000
GE Betz				
PC1190	Liquid	Cationic	high	low
PC1192	Liquid	Cationic	high	low
PC1195	Liquid	Cationic	high	low
CE1168	Emulsion	Cationic	low	low
CE2651	Emulsion	Cationic	low	medium
CE1169	Emulsion	Cationic	medium	medium
CE2681	Emulsion	Cationic	low	high
CE2680	Emulsion	Cationic	medium	high
CE2688	Emulsion	Cationic	high	high
AE1115	Emulsion	Anionic	low	low
AE1117	Emulsion	Anionic	low	medium
AE1125	Emulsion	Anionic	high	high

(Continued)

Manufacturer/Trade Name	Form	Charge	Charge Intensity	MW
Table 1 (Concluded)				
Ondea-Nalco				
Nalco 8799 Plus	Liquid			
Nalcolyte 8105	Liquid			
Ultrion 8185	Liquid			
Ultrion 8186	Liquid			
Ultrion 8187	Liquid			
Optimer 7194 Plus Flocculant	Emulsion	Cationic		
71301 Flocculant	Emulsion	Cationic		
Nalclear 7767 Flocculant	Emulsion	Anionic		
Nalclear 7768 Flocculant	Emulsion	Anionic		
Nalcolyte 7181 Flocculant	Emulsion	Non-ionic		
Natural Site Solutions (Chitosan Acetate)				
Storm-Klear Liqui-Floc	Liquid	Cationic	*100*	*161 * n*
Storm-Klear Gel-Floc	Gel	Cationic	*100*	*161 * n*

For the purpose of creating a simulated CDF effluent, sediment was obtained from the bank of the Yazoo River, just south of Greenwood, MS. Mixing water was obtained from the Yazoo Canal in the Vicksburg, MS area. A suspension of approximately 2 g/L was prepared by diluting the Yazoo sediment with water from the canal.

The jar tests were conducted according to procedures listed in Appendix E ("Jar Test Procedures for Chemical Clarification") of the Engineer Manual titled "Confined Disposal of Dredged Material" (USACE 1987). Jar tests are generally based on site-specific samples and conditions, which would typically yield estimates of suspension concentration, mixing conditions, settling time, and effluent requirements. In the absence of site-specific information, guidance from USACE (1987) suggests a TSS concentration of approximately 2 g/L (which is a typical effluent concentration from a well-designed containment area with freshwater sediments containing clays) and the percent coarse material (as defined by the percentage of material retained by the No. 200 sieve) less than 10 percent on a dry weight basis. Likewise, in lieu of site-specific conditions, mixing intensities of 100 to 120 rpm for 1 minute, followed by 20 rpm for 5 minutes and settling for 10 minutes are suggested. This is also the mixing intensity specified by the American Society for Testing and Materials (ASTM) for jar tests (ASTM 1999). These TSS and mixing conditions are more representative of conditions encountered as the CDF fluid passes from a primary to a secondary basin as opposed to flocculent injection into the dredging pipeline. Table 2 summarizes the jar test conditions for the polymer screening evaluation. The test apparatus included a Phipps & Bird six-paddle programmable jar tester with B-KER^2 square containers.

To determine a dosage scheme for the jar tests, a beaker was filled with 1 L of suspension and mixed at 100 rpm. Polymer was incrementally added to the suspension until flocs appeared and that dosage was noted. A dosage scheme was then created by multiplying the dosage at which

flocs appeared by reasonably spaced factors (usually 0, 0.5, 1, 2, 3, and 5). The jar tests were then performed according to Table 2. Upon completion of settling, samples were withdrawn from the 700-ml level B-KER[2] ports, wasting the first few milliliters to flush the port of trapped flocs. The turbidity of each sample was measured using a Hach 2100N turbidimeter. The suspended solids concentration was measured using the filtration method described in Technical Report D-83-2 (Schroeder 1983).

Table 2 Jar Test Conditions for Polymer Screening	
Simulated injection location	Primary Settling Basin
TSS concentration	<5 g/L
Rapid mix speed	100 rpm
Rapid mix duration	1 minute
Rapid mix Gt[1]	~12,000
Slow mix speed	20 rpm
Slow mix duration	5 minutes
Slow mix Gt[1]	~6,000
Settling time	10 minutes

[1] Gt is the net mixing, the product of the mean velocity gradient or mixing intensity, (second^{-1}) and duration (seconds) (USACE 1987).

Results. Data from the jar tests were plotted as fraction solids remaining (C/C_o) vs. polymer concentration application (mg/L), where C is the TSS concentration resulting from the polymer addition, and C_o is the resulting TSS concentration with no polymer addition. Furthermore, a criterion was established for evaluating polymer effectiveness. Jar test conditions that produced at least 95-percent solids removal using an application concentration of no more than 10 mg/L polymer received a passing grade. Only nine polymers met this criterion including: Magnafloc 10, Magnafloc 368, Zetag 7635, Zetag 7587, Zetag 7888, Zetag 7125, Polyfloc CE 1169, CETCO F870C, and StormKlear Liquifloc. Note that each of these polymers is cationic with the exception of Magnafloc 10, which is anionic. The results for the most effective polymers (those with "passing" results) are shown in Figure 1.

ANIONIC/CATIONIC POLYMER CO-MIX – EFFECT ON SOLIDS REMOVAL

Method. It was hypothesized that co-mixing polymers could improve removal of dissolved metals as well as metals associated with solids. For these purposes, it was presumed that addition of anionic polymer to the slurry first to attach dissolved metal cations followed by another polymer addition to remove solids along with the metal-laden polymers would enhance metals removal. Prior to examining metal removal capabilities, the effect of co-mixing on solids removal was evaluated using additional jar tests.
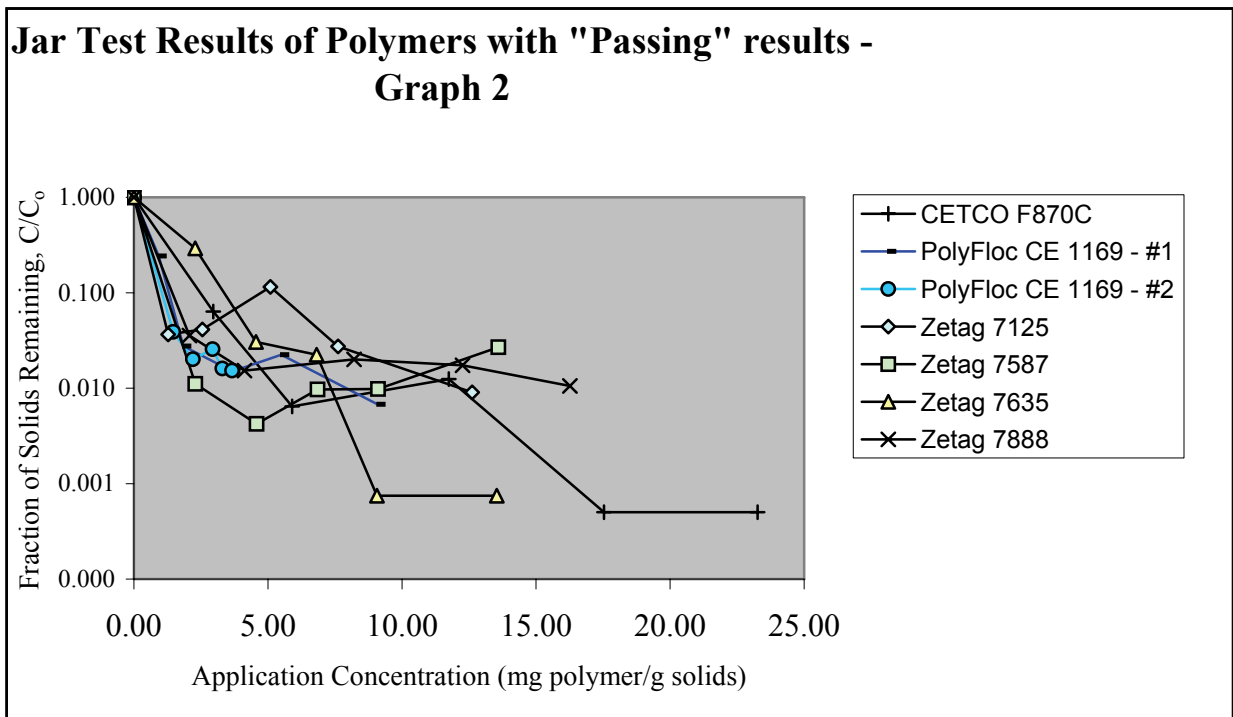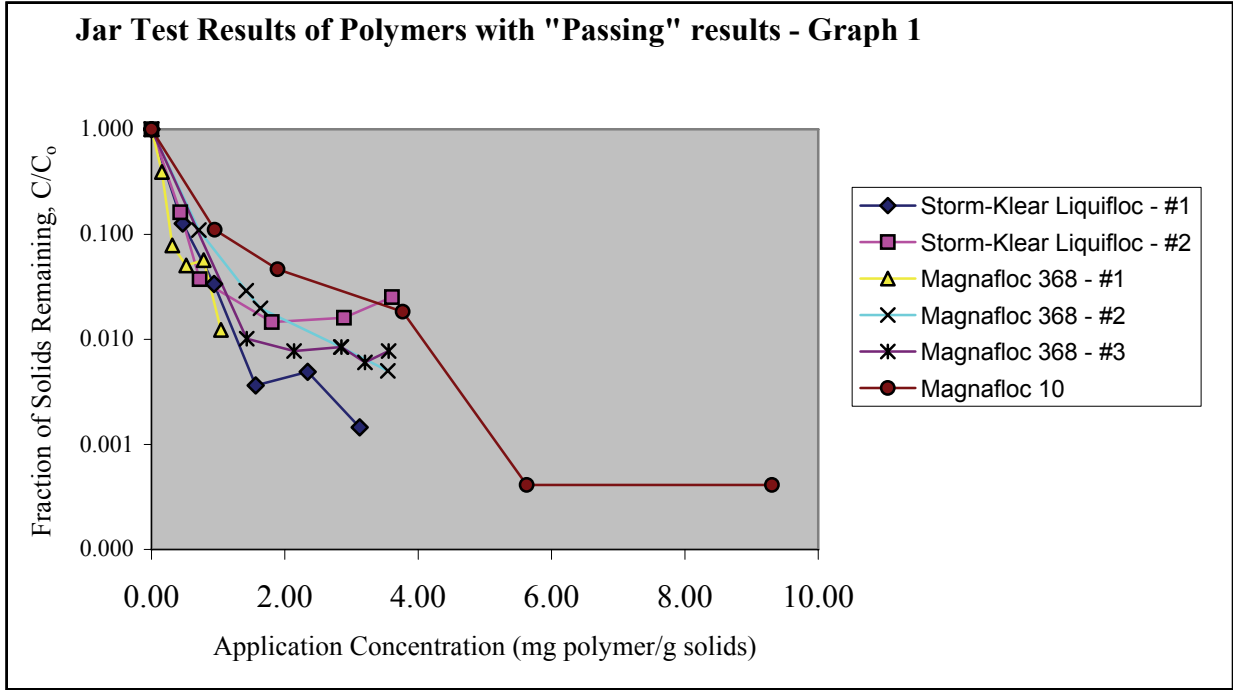
Jar Test Results of Polymers with "Passing" results - Graph 1

Fraction of Solids Remaining, C/C_o

Application Concentration (mg polymer/g solids)

- ◆ Storm-Klear Liquifloc - #1
- ■ Storm-Klear Liquifloc - #2
- △ Magnafloc 368 - #1
- ✕ Magnafloc 368 - #2
- ✳ Magnafloc 368 - #3
- ● Magnafloc 10

Jar Test Results of Polymers with "Passing" results - Graph 2

Fraction of Solids Remaining, C/C_o

Application Concentration (mg polymer/g solids)

- + CETCO F870C
- ■ PolyFloc CE 1169 - #1
- ● PolyFloc CE 1169 - #2
- ◇ Zetag 7125
- ☐ Zetag 7587
- △ Zetag 7635
- ✕ Zetag 7888

Figure 1. Jar test results of most effective polymers

Based on the polymer screening results, several polymers were selected for the co-mix tests. One cationic polymer (Magnafloc 368), one anionic (Magnafloc 10), and StormKlear Liquifloc were selected for testing. These jar tests were similar to the new polymer screening, except that anionic polymer (Magnafloc 10) was initially added and rapid mixed for 30 seconds, then

another polymer was added with another 30 seconds of rapid mixing (100 rpm), followed by 5 minutes of slow mixing (20 rpm) and 10 minutes of settling. The tests were initially conducted (Set 1) by varying the anionic dosage (0, 0.5, 1, 2, 4, and 8 mg/L) with a constant dosage of the cationic polymer and repeating for several doses of the cationic polymer (2, 4, and 6 mg/L). The tests were then conducted in the opposite manner (Set 2), with the anionic dosages constant (1, 8, and 40 mg/L), and varying cationic dosages (0, 0.5, 1, 2, 4, and 8 mg/L).

Results. As mentioned above, it was speculated that adding anionic polymer to attach metals prior to adding another polymer for flocculation would increase removal of dissolved metals. However, the effect on dissolved metals would be irrelevant if solids removal was negatively impacted. Therefore, testing was performed to determine the effect of co-mixing polymers on solids removal.

As previously described, tests were first performed with an anionic dosage scheme, and constant cationic dosages, which increased over three subsequent jar test sets. Alternatively, the second set of tests was performed with a constant anionic dosage, which increased over three subsequent sets, and a cationic dosage scheme, which remained the same throughout the sets. Results are shown in Figures 2-5. Results showed no apparent negative effect on solids removal by addition of anionic polymer prior to cationic polymer addition.
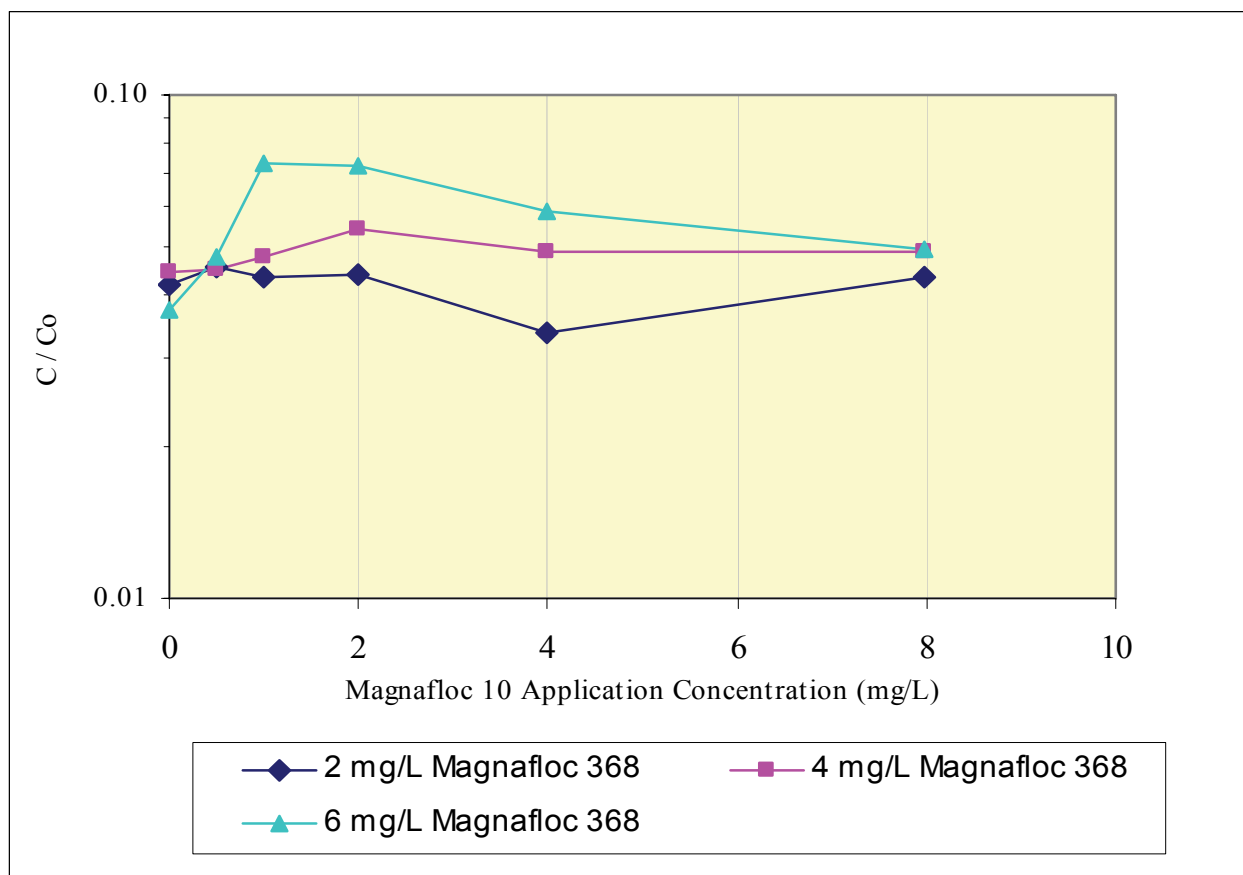
Figure 2. Co-mix jar tests for Magnafloc 10 / Magnafloc 368 – Set 1
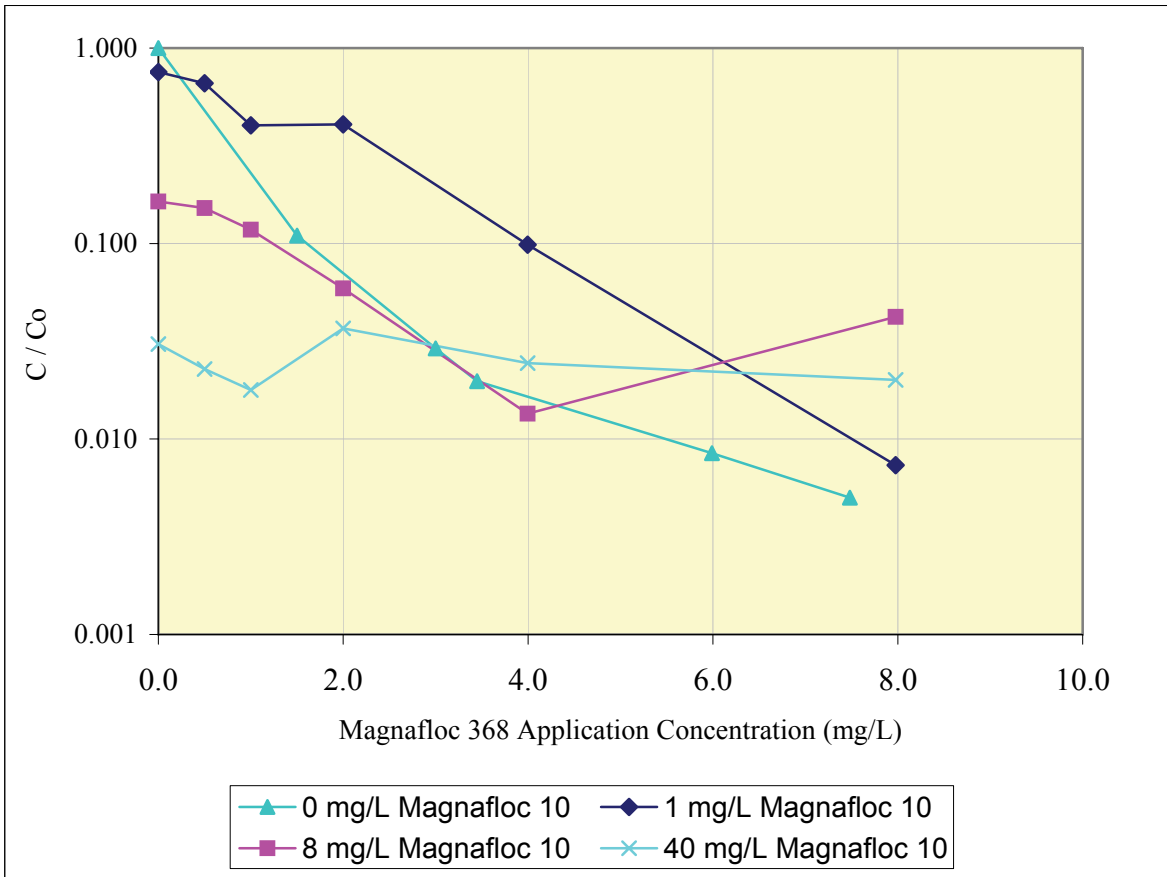
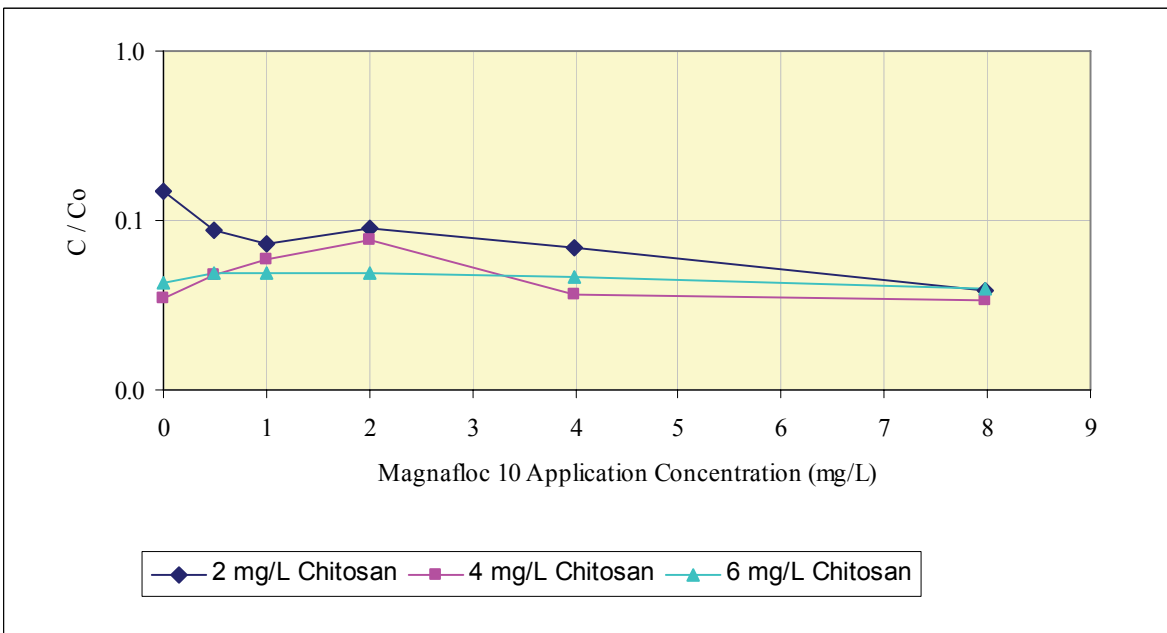Figure 3. Co-mix jar tests for Magnafloc 10 / Magnafloc 368 – Set 2

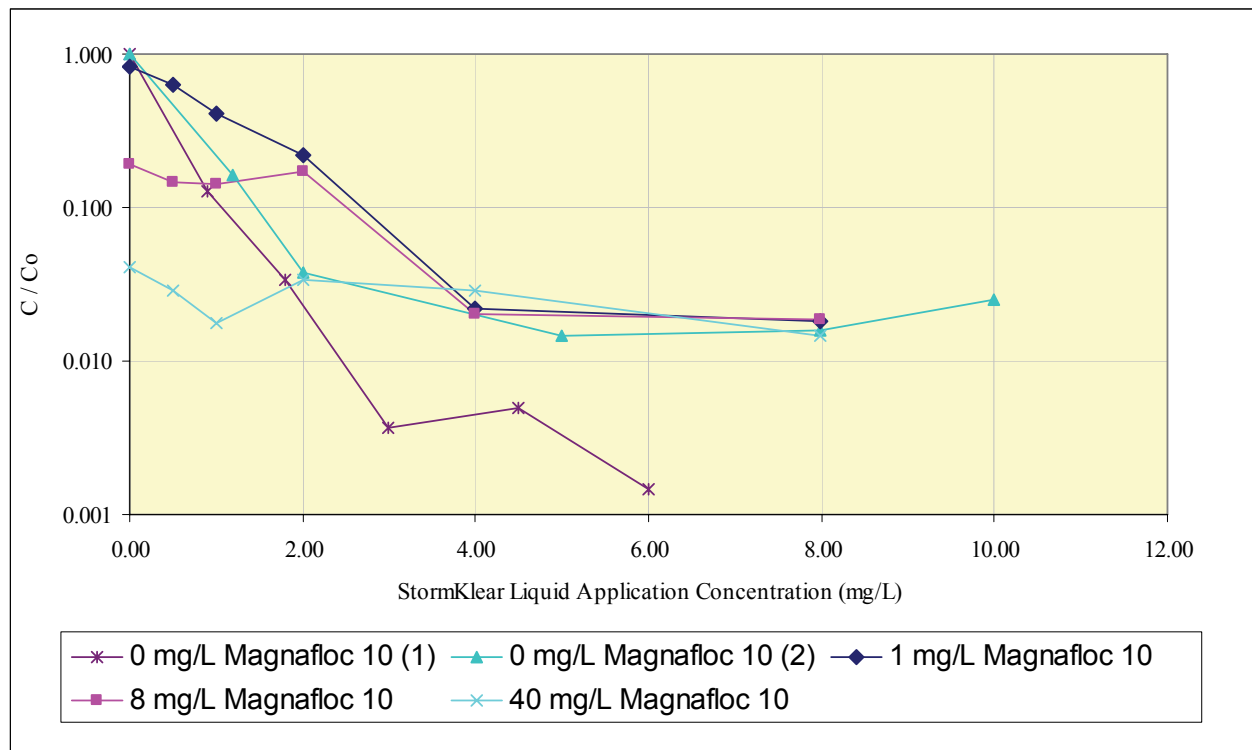Figure 4. Co-mix jar tests for Magnafloc 10 / Storm-Klear Liquifloc – Set 1

Figure 5. Co-mix jar tests for Magnafloc 10 / Storm-Klear Liquifloc – Set 2

REMOVAL OF DISSOLVED METALS BY POLYMERS IN THE ABSENCE OF SOLIDS

Method. To determine the ability of polymers to remove dissolved metals, batch tests were performed, mixing polymers with metal solutions. The batch tests were performed by placing a 100-ml metal solution in a 250-ml beaker with a stir bar on a stir plate. Polymer was added to the solution and was rapidly stirred for 1 minute, then slowly stirred for 5 minutes. The solution was then poured into a beaker containing powdered activated carbon (PAC), then immediately filtered through a 0.45-µm filter. The purpose of the PAC was to give the flocculate something solid to attach to, allowing the polymer and carbon to be filtered out. The resulting filtrates were then analyzed using Perkin Elmer 5100 flame atomic absorption spectrophotometer, SW846 methods 7130, 7210, 7420, and 7950 for cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn), respectively (USEPA 1992a).

A metal solution was made using salts of cadmium, copper, lead, and zinc. A separate solution of arsenic (As) was also made using $Na_2HAsO_4 \cdot 7H_2O$ because arsenic addition caused the other metals to precipitate out of solution. Initially, salts were weighed out to produce a 10-mg/L solution, although analysis showed the concentrations to be significantly lower. The initial tests showed only slight metal reductions; therefore, the polymer:metal ratio was increased for a second batch of tests. For the second batch, the metal solutions were diluted 1:4.

Polymer amounts include 0, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 ml of 1 g/L polymers for the first batch, and 1.0, 2.0, and 6.25 ml of 2 g/L polymers for the second batch. Polymers analyzed

include Magnafloc 368 (cationic), Magnafloc 10 (anionic), Magnafloc 351 (nonionic), and Storm-Klear Liquid (cationic).

Results. Four polymers were batch tested with metal solutions to determine the effect on removal of dissolved metals. Note that the solutions with the anionic polymer, Magnafloc 10, were viscous and extremely slow to filter and appeared to coagulate the powdered activated carbon. Note also that metal concentrations, especially arsenic, were very close to the instrument detection limits, which restricts conclusions based on the results. As PAC could be responsible for some metals uptake, results were reported relative to the concentrations of metals contacted with PAC without polymer. Thus the reported C/Co values are the concentrations of metals remaining after polymer addition divided by the concentration resulting from contact with PAC alone.

Results from analysis of the dissolved metals remaining after polymer addition and subsequent filtration with activated carbon (Figures 6-9) suggest Magnafloc 10, as expected, to be the most effective polymer for metals removal. Magnafloc 351 was nearly as effective, also removing significant levels of each metal. The cationic polymers Magnafloc 368 and Storm-Klear Liquid showed possible reduction of lead and arsenic at low concentrations and perhaps slight removal of cadmium, copper, and zinc. Overall, the results warrant further testing with metals-contaminated sediment to determine if polymer could be effective for removal of dissolved metals in addition to solids.
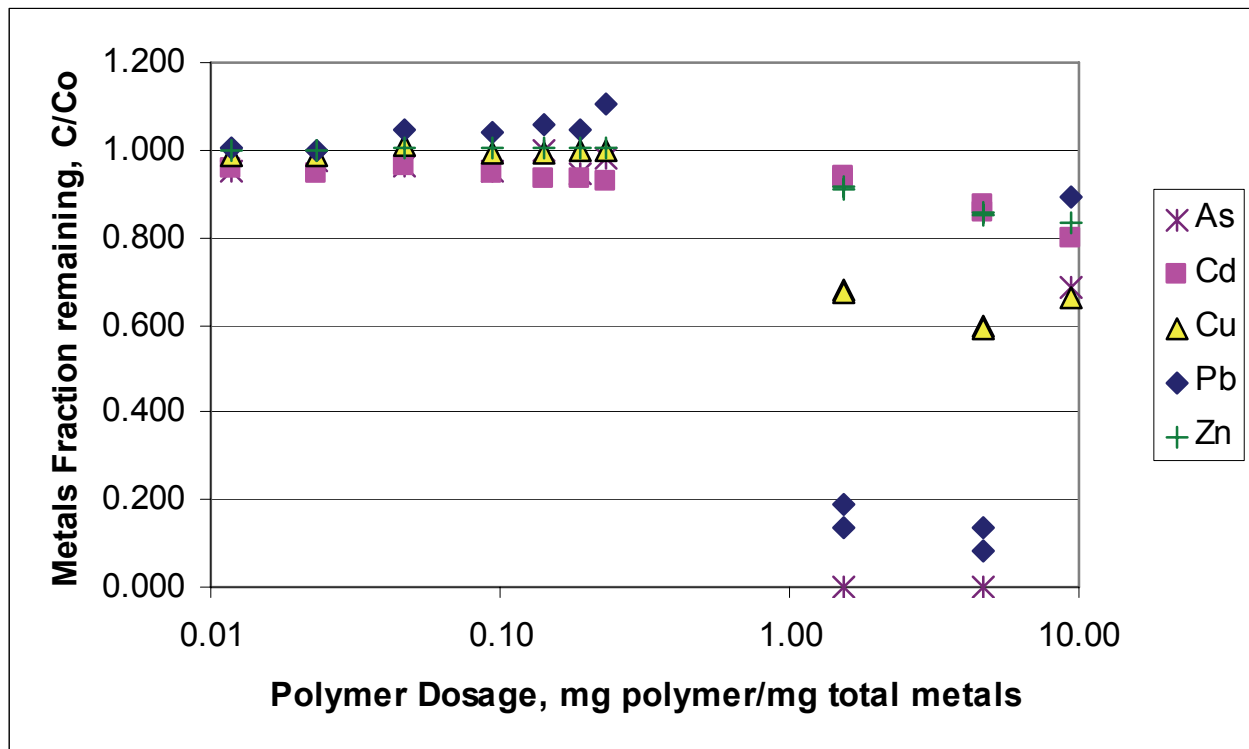

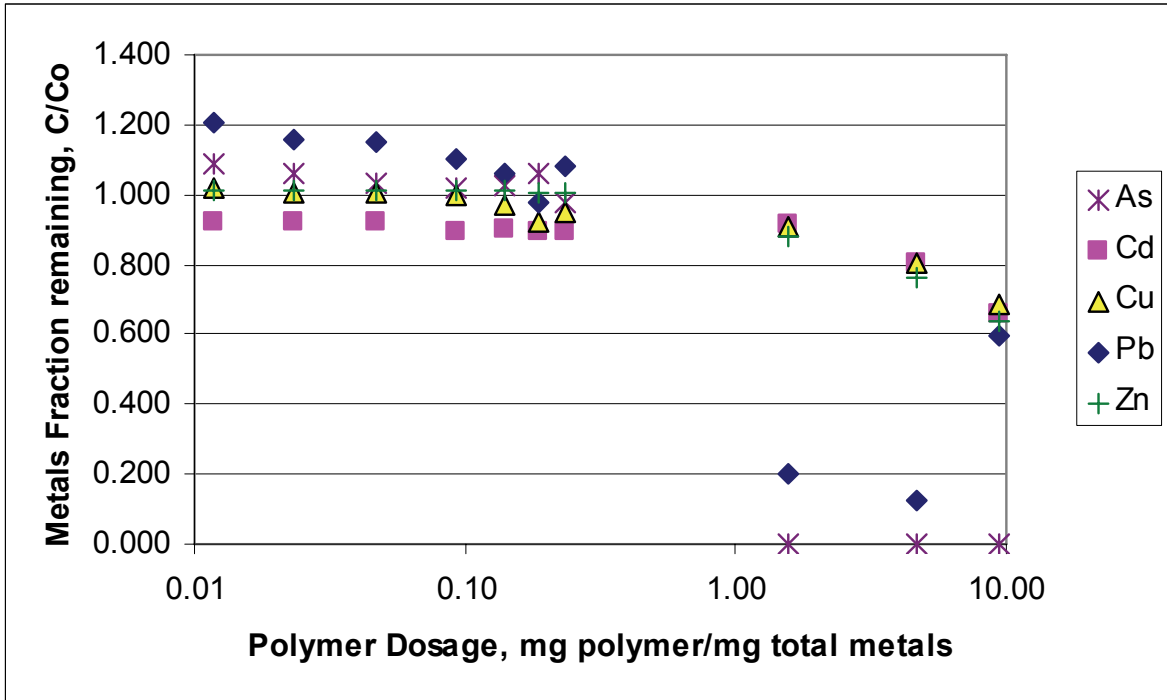Figure 6. Removal of dissolved metals by Magnafloc 368 cationic polymer

Figure 7. Removal of dissolved metals by Magnafloc 351 nonionic polymer
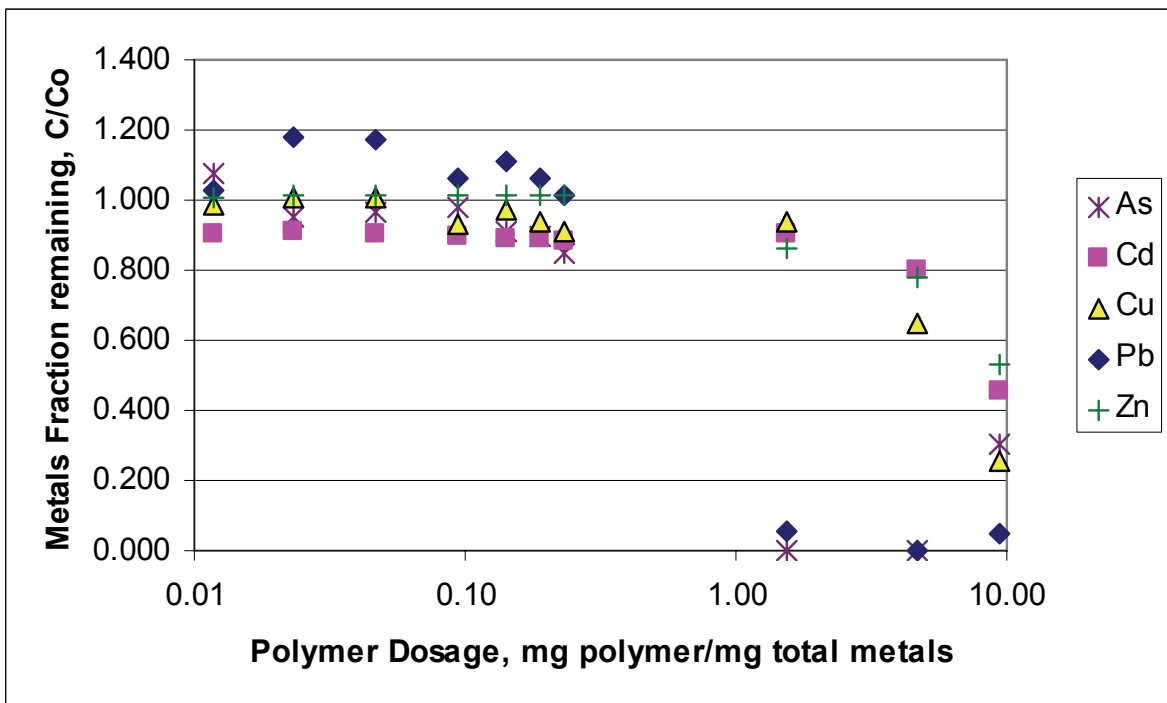

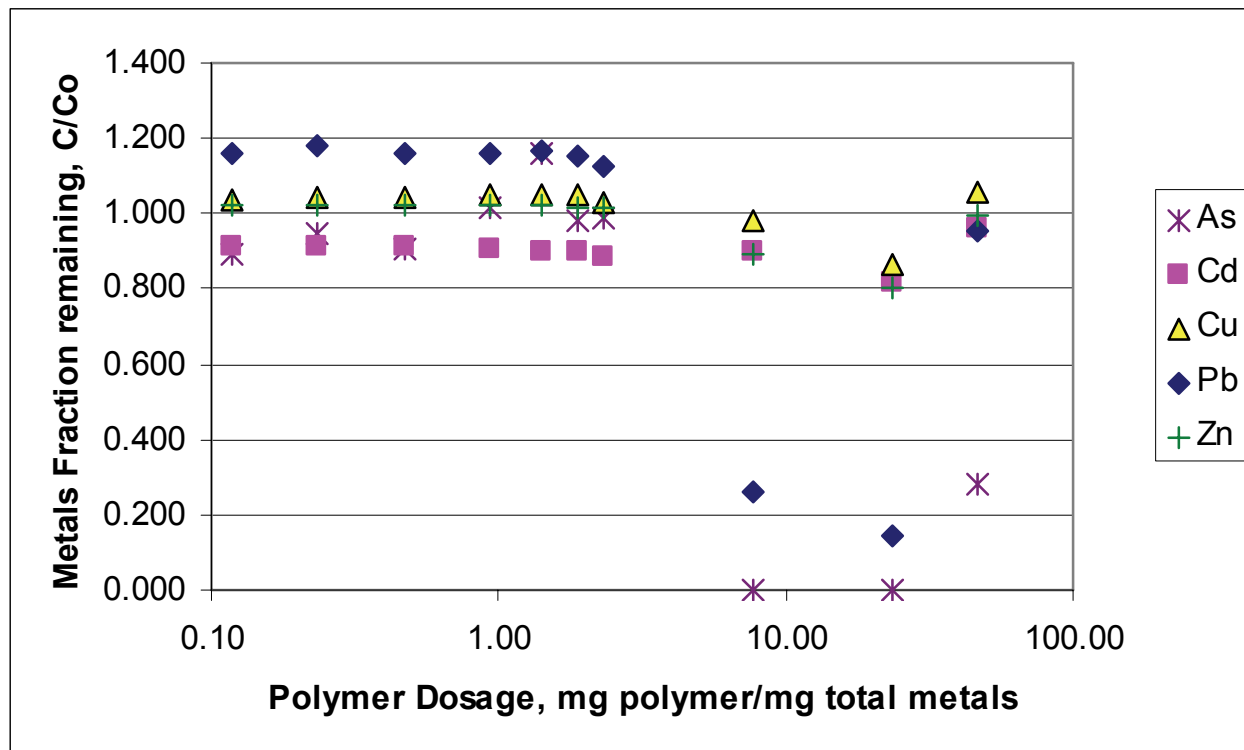Figure 8. Removal of dissolved metals by Magnafloc 10 anionic polymer

Figure 9. Removal of dissolved metals by Storm-Klear Liquifloc cationic polymer

EVALUATION OF POLYMERS FOR REMOVAL OF METALS FROM MILLTOWN CONTAMINATED SEDIMENT

Method. The most promising methods of metal removal from the tests above were evaluated using sediment from Milltown Reservoir. Milltown (about 7 miles above Missoula, Montana) is a Superfund site contaminated by metals from mining and smelting activities on the Upper Clark River. Milltown sediment was collected in March of 2003 by Seattle District personnel.

Tap water was mixed with the Milltown sediment to create a slurry of about 55 g/L solids. The slurry was then allowed to settle approximately 1 hour, and the supernatant was pumped off to simulate CDF effluent. This effluent had a measured TSS around 1.0 g/L solids and was used for the Milltown jar tests. A filtered sample of the effluent was analyzed for metals using flame atomic absorption spectrometry. Although the results are inconclusive due to lack of instrument sensitivity, the instrument gave readings of the dissolved concentrations in the effluent of 11.6 µg/L Cd, 51.8 µg/L Cu, 336.9 µg/L Zn, and Pb and As levels below detection. The results did, however, seem to correspond to metal concentrations that were predicted using partitioning coefficients determined from the results of dredging elutriate testing (DRET) and modified elutriate testing (MET) (Memorandum for Record prepared for Mr. Russ Forba, Montana Superfund Office, EPA Region 8 by P. Schroeder, 25 September 2003). The predicted metal concentrations are as follows: 0.29 µg/L Cd, 79.19 µg/L Cu, 61.11 µg/L Zn, 12.63 µg/L Pb, and 49.85 µg/L As.

Jar tests were performed in duplicate on the Milltown sediment using cationic polymer (Magnafloc 368), anionic polymer (Magnafloc 10), StormKlear Liquifloc, and co-mixing of the anionic and cationic polymers. The jar test procedures were the same as those described above for the screening tests and co-mix tests. Turbidity and TSS were measured for each sample, and filtrate (through 0.45-µm filter) was collected for dissolved metals analysis by ICP-AES (SW 846 Method 6010B (USEPA 1992b)). Several unfiltered samples were also collected for analysis of total metals using method 3015 (USEPA 1992c) for digestion followed by ICP-AES analysis.

Results. Initial solids content of the Milltown slurry was approximately 1.05 g/L. Total suspended solids at the end of the jar tests averaged 1.00 g/L for the samples without polymer addition. Suspended solids removal by the polymers is shown in Figure 10. Each polymer demonstrated effective solids removal with "passing" results.
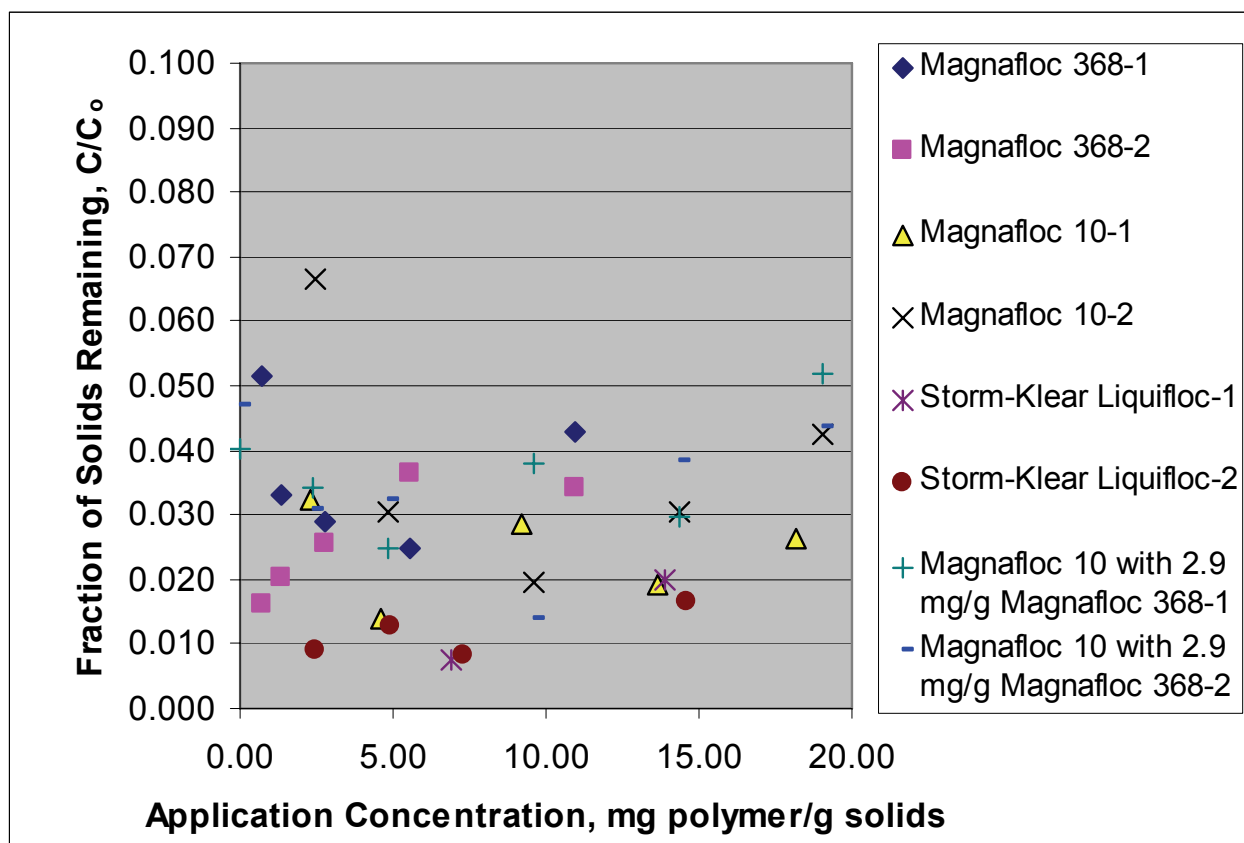

Figure 10. Milltown jar tests – solids removal by polymer addition

Total (unfiltered) metals concentrations were measured for the samples without polymer addition. Results showed total metals concentrations of 0.608 mg/L As, 0.232 mg/L Cd, 3.80 mg/L Cu, 0.546 mg/L Pb and 3.61 mg/L Zn. Dissolved metals were analyzed on the filtered samples and are shown in Figures 11-15.
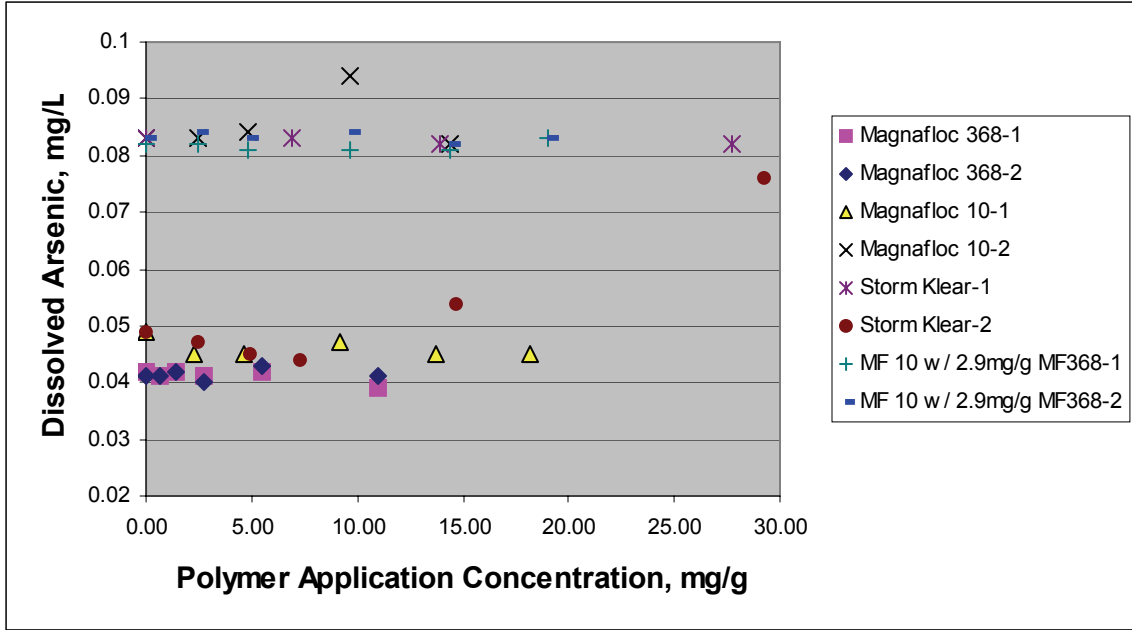
Figure 11. Milltown jar tests - dissolved arsenic concentration vs. polymer application rate
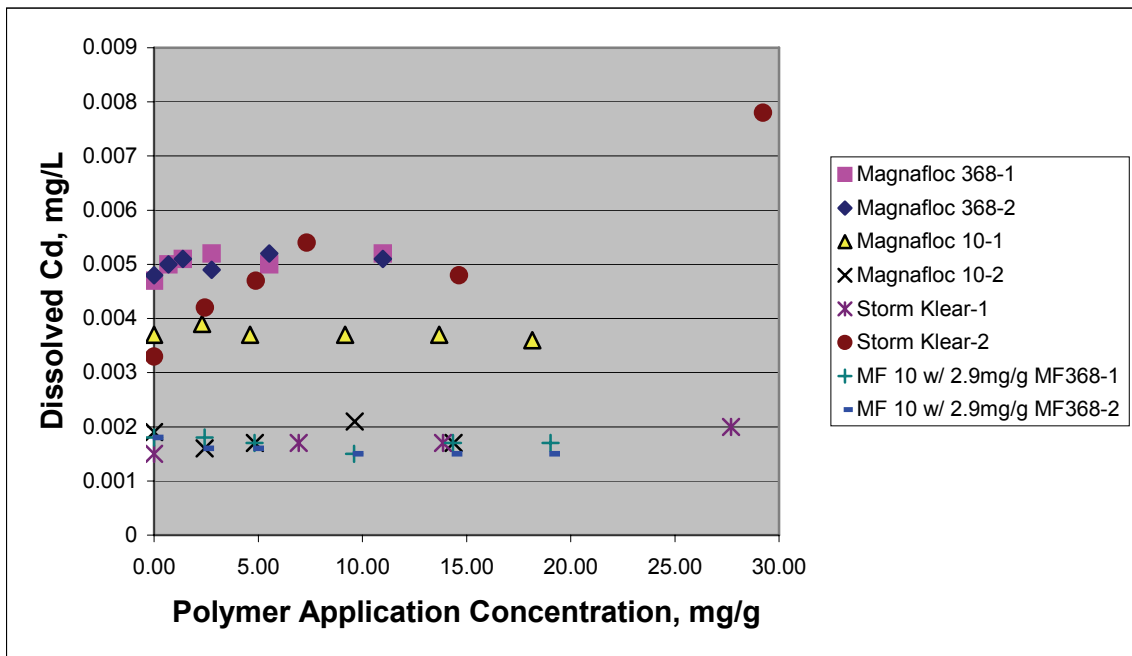

Figure 12. Milltown jar tests - dissolved cadmium concentration vs. polymer application rate
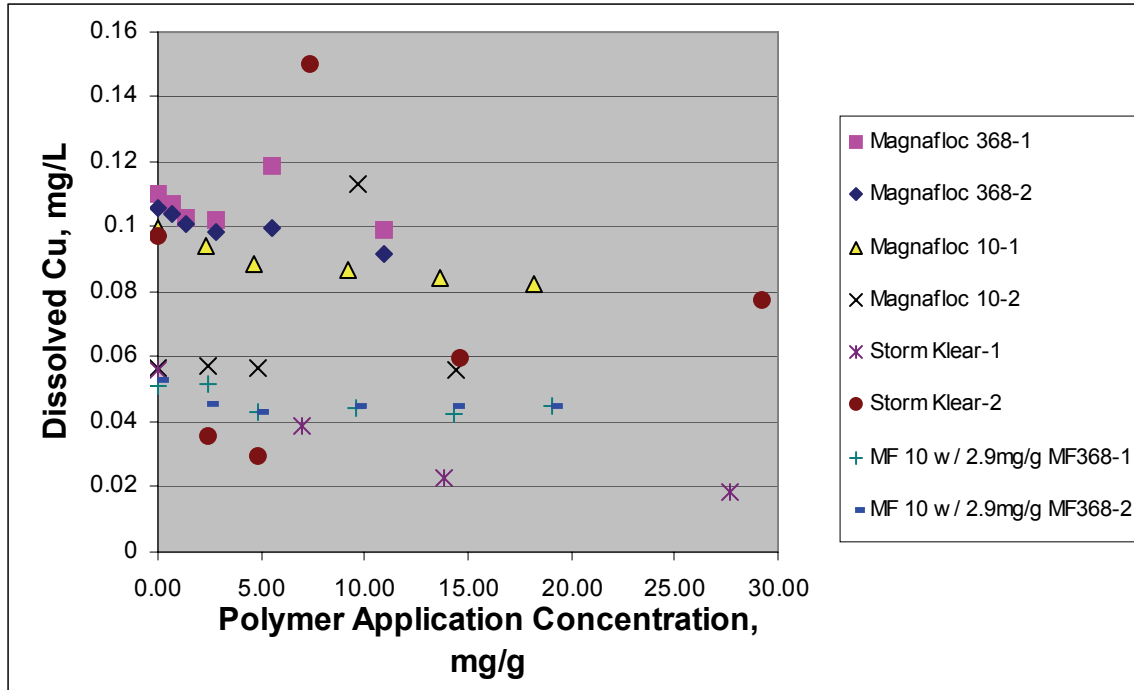
Figure 13. Milltown jar tests - dissolved copper concentration vs. polymer application rate
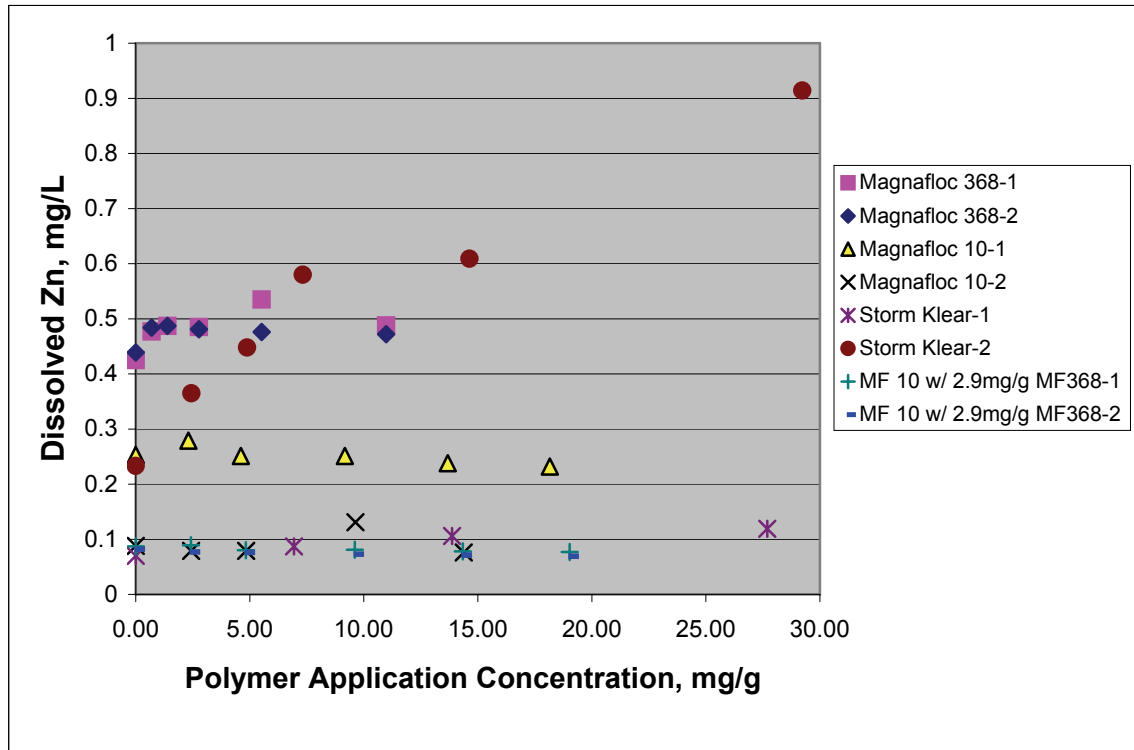

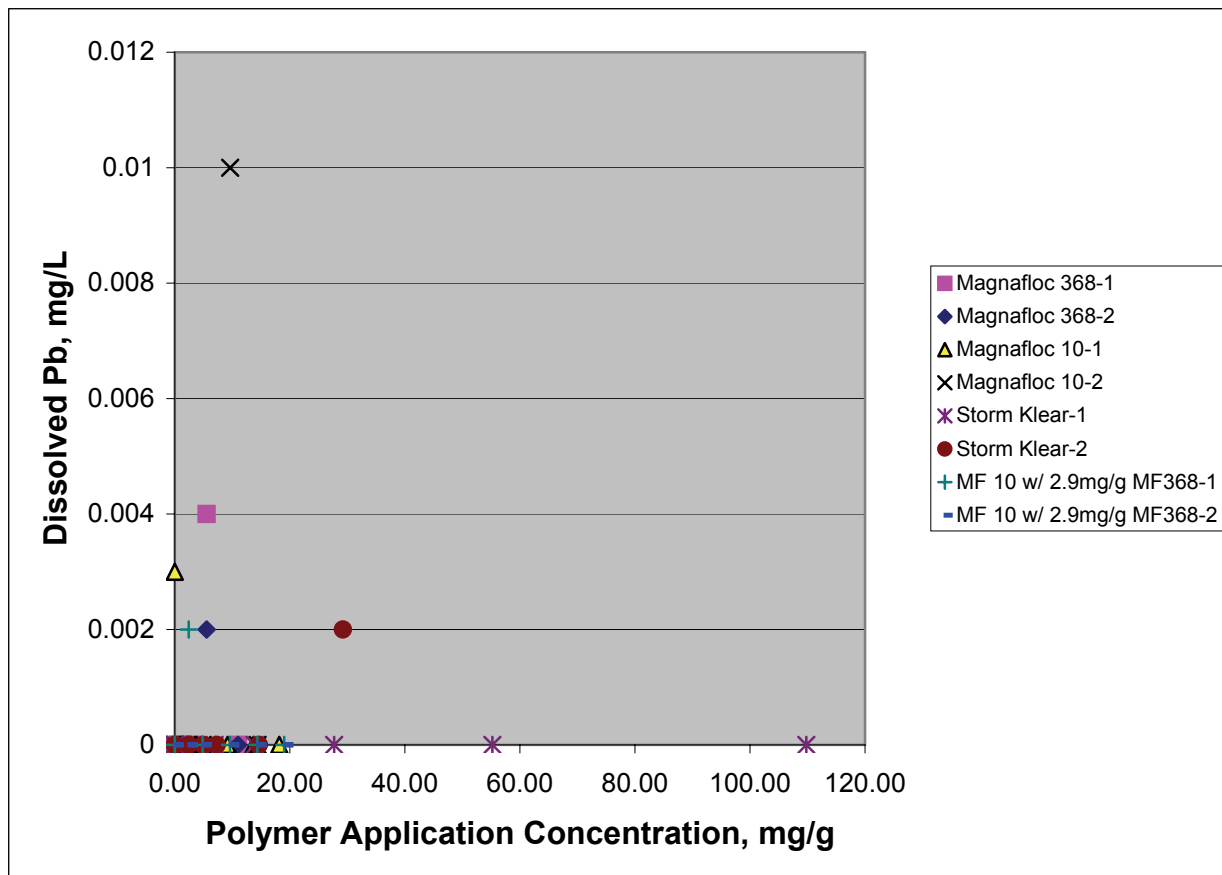Figure 14. Milltown jar tests - dissolved zinc concentration vs. polymer application rate

Figure 15. Milltown jar tests - dissolved lead concentration vs. polymer application rate

Results from the dissolved metals analysis are, for the most part, inconclusive due to discrepancies between replicates. The data do appear to predict slight removal of Cd, Cu, and Zn by co-mixing the anionic and cationic polymers. In some instances, there appeared to be some metals increase due to polymer addition; for example, Cd and Zn with StormKlear Liquifloc. This could be due to the presence of polymers changing the metal solubilities in solution. Results for dissolved Pb were inconclusive since most samples were below detection limits. Based on these data, it cannot be concluded that polymer application contributes to significant dissolved metals removal.

CONCLUSIONS: An initial polymer screening using clean sediment found 9 polymers out of 45 tested to be effective for removal of 95-percent solids using a dosage of 10 mg polymer/L slurry or less. All but one of these polymers are cationic. Analysis of co-mixing of anionic polymer with cationic polymer showed that the addition of anionic polymer prior to cationic addition did not appreciably affect solids removal. Furthermore, both nonionic and anionic polymers appeared to remove dissolved metals more effectively than cationic polymers.

Testing showed that the dissolved metals content of the Milltown simulated effluent was in violation of water quality standards. Jar tests on the Milltown effluent using cationic, anionic, and multiple polymers did not show appreciable metals removal.

Based on the dissolved metals results, it appears possible that polymers may have some effect on dissolved metals removal. However, for the Milltown sediment, metal removal was slight at best, and was not capable of removing metals below water quality standards. Therefore it is not likely that polymers would be effective for removing appreciable dissolved metals.

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