

Flocculation of Metal-Bearing Waste Waters Using Cellulose and Its Graft Copolymers

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Synopsis

Several types of cellulose (wood pulp) and their graft copolymers with water-soluble monomers were tested for their activity as flocculation aids. They were employed as additives to lime in flocculation experiments involving a simulated mine water containing iron, zinc, and copper salts. The results show that all the cellulosic products had a beneficial effect on the removal of iron, and to a lesser extent on the removal of zinc. The final concentration of ferric ions after 30 min was comparable with that produced by commercial flocculants (Magnifloc, Aquafloc). No improvement of flocculation activity was obtained upon grafting various polar monomers and their mixtures onto dissolving pulp.

INTRODUCTION

Large volumes of effluent having high dissolved metal concentrations are produced in base metal mining. Such effluents, which are usually highly acidic, are normally treated by the addition of calcium hydroxide (lime). Lime raises the pH of the effluent thus causing the dissolved metals to precipitate in the form of sparsely soluble hydroxides. However, the rate of settling of these hydroxides is generally slow. Various additives have been developed and used commercially to help speed up the settling process. These are mostly polymeric substances, usually based on polyacrylamide.

Certain graft copolymers have also been investigated in connection with their possible use in flocculation. Fanta and co-workers¹⁻⁴ grafted several hydrophilic

TABLE I
Characterization of Mine Waters

Characteristic	Brunswick no. 12 mine water (average)	Simulated mine water
pH	2.8	2
Sulfate (mg/L)	7090	~7000
Lead (mg/L)	4.3	0
Zinc (mg/L)	1160	1160
Copper (mg/L)	10	100
Iron (mg/L)	1580	1580
Suspended solids (mg/L)	167	0

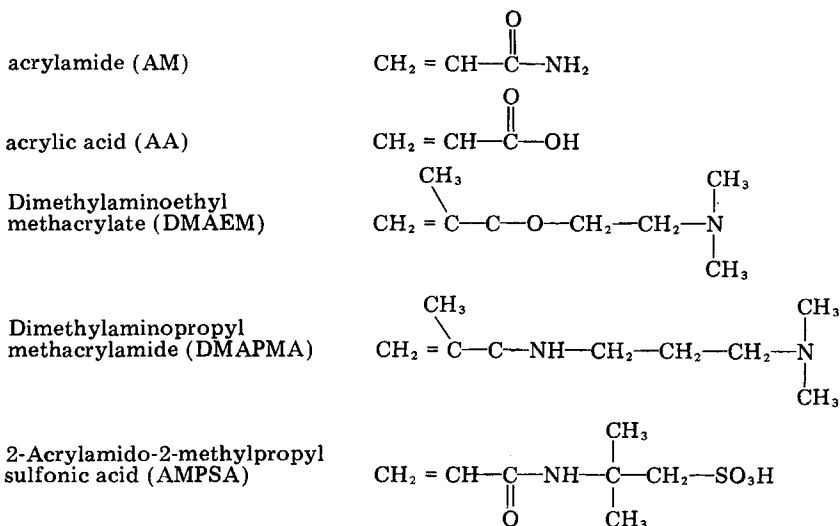
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monomers onto starch and tested the grafted products for their activity in the flocculation of fine suspensions.

It appeared interesting to find out if cellulose and its graft copolymers would also possess some activity in flocculation. Cellulose is a polar macromolecule, and all commercial celluloses (pulp) have a significant carboxyl content. Additional active groups can be introduced by grafting with suitable polar or ionizable monomers.

In a recent study,⁵ cellulose has been grafted with the following water-soluble monomers:



In the present work, these copolymers as well as ungrafted cellulose products are tested as additives to lime in the flocculation of simulated mine water.

EXPERIMENTAL

Materials. The cellulosic products used included dissolving pulp (Canadian International Paper), softwood and hardwood bleached kraft pulps (Consolidated Bathurst), cellulose powder (J. T. Baker), and carboxymethylcellulose (Fisher Scientific). The monomers were furnished by the following suppliers: acrylic acid, J. T. Baker; acrylamide, Matheson, Coleman, and Bell; dimethylaminoethyl methacrylate, Eastman Kodak; dimethylaminopropyl methacrylamide, Jefferson Chemical; 2-acrylamido-2-methylpropyl sulfonic acid, Lubrizol. The method employed to prepare the graft copolymers has been described previously.⁵ Homopolymers were carefully removed before the products were used for flocculation studies.

The two commercial flocculants used included Aquafloc (Dearborn Chemicals) and Magnifloc (Dow Chemicals). A sample of acrylamide polymer was purchased from Dayac Laboratories Inc. (MW \approx 200,000). Calcium hydroxide was a reagent quality product supplied by Fisher Scientific Co.

Simulated Mine Water. The metal-bearing water used in this work was formulated after the Brunswick no. 12 mine water, the composition of which is

shown in Table I. However, only three metals were included in the simulated mine water: iron, zinc, and copper. The concentration of copper in the simulated mine water was increased to 100 mg/L with the hope of increasing the accuracy of copper analysis. However, the concentrations of copper after flocculation still remained too low in comparison to experimental error. As a consequence of this, only the residual concentrations of iron and zinc will be discussed.

Flocculation Studies. Flocculation studies were conducted by means of the standard jar test described by Huck et al.⁶ Beakers of 1500-mL capacity were employed, each equipped with a variable speed (0–100 rpm) agitator. In a typical experiment, 1000 mL of mine water were first added to the beaker. The agitator speed was then adjusted to 100 rpm, and lime was added to the solution until its pH changed from the original value of 2 to 9.5 ± 0.1 . The agitation was continued for a total of 10 min, whereupon 1 mL of polymer solution (or dispersion) was injected into the slurry by means of a syringe. On the 11th minute, the agitator speed was reduced to 25 rpm, and the slurry was agitated at this speed for 5 min. The agitator was subsequently stopped, and the slurry was allowed to settle. Samples of the supernatant liquid were withdrawn after 5, 10, 15, and 30 min from just beneath the surface where the water was the clearest. The samples were placed into 50-mL flasks containing 1 mL of 35% hydrochloric acid in order to acidify the mixture and to prevent further coagulation. The metal content of the samples was determined by using atomic absorption spectroscopy.

The two commercial flocculants and polyacrylamide were used in the form of 1% aqueous solutions. As the celluloses and graft copolymers are insoluble in water, they were used in the form of fine suspensions. These were obtained by treating 1% suspension of the fibrous material in a Waring blender (at 10,000 rpm) prior to an experiment. This treatment was found to considerably improve the reproducibility of the results. All metal concentration results shown in this paper represent the average of two independent measurements, unless indicated otherwise. The flocculation regime described above (residence time, pH, type and size of impeller, agitation speed, mode of lime, and polymer addition) was strictly adhered to in all experiments in order to obtain good reproducibility.

RESULTS AND DISCUSSION

Commercial Polymers and Polyacrylamide as Additives to Lime. Table II shows the results obtained with Aquafloc, Magnifloc, and polyacrylamide as additives to lime. The two commercial flocculants performed much better than the unmodified, lower-molecular-weight, acrylamide polymer. The most important characteristics of a flocculation aid is to what extent it can speed up the settling process. Both Aquafloc and Magnifloc are very good in this respect, giving residual metal concentration levels after 5 min which require 30 min settling time with lime alone. The final (30 min) concentrations are almost identical for the three products. They are about three times lower than those obtained with lime alone. It should be noted that the concentration of the polymer additives is very small (1 ppm in respect to the solution to be precipitated).

TABLE II
Effect of Commercial Flocculants and Polyacrylamide on Metal Removal

Metal	Time	Residual concentration (ppm)			
		Polyacryl amide	Aquafloc	Magnifloc	Lime only
Fe ³⁺	5	3.33	1.26	0.95	5.11
	10	1.53	0.90	0.75	2.70
	15	0.79	0.67	0.62	1.73
	30	0.56	0.67	0.62	1.50
Zn ²⁺	5	1.60	1.09	0.80	3.35
	10	0.68	0.54	0.52	2.15
	15	0.46	0.34	0.37	1.26
	30	0.26	0.25	0.29	0.86

Nongrafted Cellulose Products as Additives to Lime. The effectiveness of a graft copolymer in promoting flocculation will depend on the character of the cellulosic grafting substrate as well as on the type of polymer grafted. Prior to preparing graft copolymers, therefore, several types of cellulose (pulp) were screened as to their flocculation activity.

The results of these tests are compiled in Table III. Each type of cellulose was tested at two concentrations: 1 ppm and 10 ppm. It appears that removal of the two ions is affected differently by the addition of cellulose. All five types of cellulose improve the removal of the ferric ion. All of the cellulosic products had a favorable effect on zinc removal when the settling times were longer than 5 min. It is also noted that both kraft pulps work better at the lower concentration (1 ppm).

The enhancement of metal removal by an addition of cellulose is somewhat puzzling. It is normally assumed that to provide a bridging effect necessary for the formation of large flocs, a polymer must be soluble in water. The present work indicates that a fine suspension of hydrophilic fibers such as cellulose may be also effective.

It appeared from Table III that dissolving pulp has shown the best results in removing both ferric and zinc ions. This material was consequently selected as the substrate for graft copolymerization.

Grafted Dissolving Pulp as Additive to Lime. The results obtained with DMAPMA- and DMAEM-grafted cellulose are shown in Tables IV and V, respectively. It is obvious that neither polymer improves the performance of the cellulosic substrate. In the case of the Fe³⁺ ion, it would appear that products containing more polymer (higher copolymer loading) are less effective, although their performance is still better than that of lime alone. As far as Zn²⁺ ions are concerned, however, the addition of graft copolymer brings about no improvement. In fact, some of the results obtained after 5 min show higher zinc concentrations than that obtained with lime alone.

As shown in Table VI, acrylamide-grafted cellulose is less effective for metal removal than acrylamide homopolymer. None of the two-monomer combinations listed in Tables VI and VII show any improvement. In particular, the graft copolymers containing AMPSA alone or in combination with another monomer show very poor metal removal efficiency.

TABLE III
Effect of Cellulosic Products on Metal Removal

Metal	Time (min)	Residual metal concentration (ppm)											
		Dissolving pulp		Cellulose powder		Carboxymethyl-cellulose		Hardwood		Bleached kraft pulp		No additive	
		1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm		
Fe ³⁺	5	2.73	2.76	3.14	3.02	4.00	3.14	2.90	3.18	2.80	3.61	5.11	
	10	1.19	1.21	1.78	1.59	1.91	1.30	1.25	1.30	1.46	1.59	2.70	
	15	0.88	1.05	1.40	1.06	1.60	1.28	1.10	1.03	1.09	0.96	1.73	
Zn ²⁺	30	0.53	0.58	0.69	0.46	0.90	0.71	0.55	0.86	0.54	0.60	1.50	
	5	2.75	2.48	4.04	3.47	3.96	3.12	2.85	3.39	2.61	3.42	3.35	
	10	1.10	1.05	1.65	1.63	1.48	1.31	1.21	1.71	1.27	1.36	2.15	
15	0.78	0.98	1.41	1.13	1.23	0.86	1.40	1.30	0.92	0.83	1.26		
30	0.48	0.47	0.60	0.70	0.70	0.46	0.42	0.89	0.50	0.49	0.86		

TABLE IV
Effect of DMAPMA-Grafted Cellulose on Metal Removal

Metal (ppm)	Time (min)	Copolymer loading (%)											
		40		33		19		9		0			
		1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm		
Fe ³⁺	5	4.07	3.53	3.76	3.84	2.92	3.27	2.84	3.60	2.73	2.76		
	10	2.37	1.77	1.94	2.39	1.49	1.57	1.37	1.98	1.19	1.21		
	15	1.80	1.56	1.52	1.70	1.19	1.21	1.04	1.20	0.88	1.05		
Zn ²⁺	30	0.98	0.72	0.76	0.90	0.58	0.64	0.69	0.72	0.53	0.58		
	5	3.18	3.72	3.62	3.32	3.34	3.37	3.22	3.38	2.75	2.48		
	10	1.85	1.93	1.68	1.72	1.22	1.84	1.46	1.56	1.10	1.05		
15	1.08	1.67	1.25	1.07	0.93	0.97	1.01	0.84	0.84	0.78			
30	0.57	0.56	0.56	0.57	0.48	0.42	0.49	0.44	0.48	0.47			

TABLE V
Effect of DMAEM-Grafted Cellulose on Metal Removal

Metal	Time (min)	Copolymer loading (%)											
		54		44		31		21		6		0	
		1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm	1 ppm	10 ppm
Fe ³⁺ (ppm)	5	3.88	6.49	3.71	4.26	3.69	4.20	3.72	4.18	3.54	3.76	2.73	2.76
	10	2.30	3.20	1.87	2.10	1.53	1.87	1.78	1.81	2.27	1.95	1.19	1.21
	15	1.60	2.16	1.41	1.42	1.25	1.35	1.42	1.34	1.15	1.21	0.88	1.05
Zn ²⁺ (ppm)	30	0.86	1.00	0.70	0.80	0.79	0.90	0.80	0.66	0.65	0.75	0.53	0.58
	5	4.27	6.33	3.38	3.94	3.28	4.01	3.94	3.82	3.60	3.94	2.75	2.48
	10	2.42	2.18	1.68	2.04	1.34	1.53	1.70	1.74	1.58	1.68	1.10	1.05
	15	1.56	1.65	1.16	1.34	1.01	1.00	1.11	1.12	1.04	1.10	0.78	0.98
	30	1.00	0.63	0.65	0.67	0.65	0.72	0.56	0.52	0.51	0.57	0.48	0.47

TABLE VI
Effect of Cellulose Grafted with a Binary Mixture of Acrylamide and Another Monomer^a

Metal	Time (min)	Polyacrylamide	Comonomer			
			none CL ^b = 31%	DMAEM CL = 51%	DMAPMA CL = 35%	AMPSA CL = 8%
Fe ³⁺ (ppm)	5	3.33	4.28	3.56	5.19	4.90
	10	1.53	3.27	1.74	3.34	2.27
	15	0.79	2.37	1.55	2.13	1.83
	30	0.56	0.90	1.23	1.31	1.10
Zn ²⁺ (ppm)	5	1.60	3.55	3.77	4.04	4.07
	10	0.68	2.58	1.88	3.02	1.63
	15	0.48	1.33	1.86	2.41	1.27
	30	0.26	0.47	1.61	1.21	0.47

^a Concentration of additive: 1 ppm.

^b Copolymer loading.

TABLE VII
Effect of Cellulose Grafted with a Binary Mixture of a Cationic and an Anionic Monomer^a

Metal	Time (min)	Monomers			
		AMPSA only CL ^b = 19%	DMAEM +AMPSA CL = 124%	DMAPMA +AMPSA CL = 102%	AMPSA +AA CL = 35%
Fe ³⁺ (ppm)	5	4.48	4.58	3.94	4.26
	10	2.10	2.14	2.02	1.99
	15	1.69	1.46	1.39	1.47
	30	0.65	0.73	0.75	0.80
Zn ²⁺ (ppm)	5	3.94	4.37	3.61	3.48
	10	1.48	1.60	1.67	1.17
	15	0.78	1.27	1.03	0.90
	30	0.53	0.58	0.44	0.33

^a Concentration of additive: 1 ppm.

^b Copolymer loading.

CONCLUSIONS

The following conclusions can be drawn concerning the flocculation activity of the products investigated in this work:

(1) While all five cellulosic products improved the removal of iron, only one (dissolving pulp) had a beneficial effect on the removal of zinc.

(2) The commercial flocculants Aquafloc and Magnifloc showed the best overall performance. However, the concentrations of iron after 30 min obtained with the cellulosic products were comparable to those obtained with the commercial flocculants.

(3) Dissolving pulp grafted with polyacrylamide was less effective than either of the two components alone.

(4) No improvement in flocculation activity was obtained by grafting DMAEM, DMAPMA, AMPSA, AM, AA, and their mixtures onto dissolving pulp.

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