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Determination of Polyacrylamides in Coal Washery Effluents by Ultrafiltration/Size-Exclusion Chromatography–Ultraviolet Detection Techniques

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■ The use of a combined technique of ultrafiltration and aqueous size-exclusion high-performance liquid chromatography–UV detection for monitoring trace levels of residual polyacrylamide flocculants in coal washery process water is described. Flocculants of both anionic and nonionic types in effluents are analyzed by chromatography on a TSK 5000 PW type hydrophilic and semirigid porous polymer gel with 0.05 M Na_2SO_4 in water as the mobile phase and by UV detection at 208-nm wavelength for detection. Precision studies gave a relative standard deviation of 5.8% and a precision of 2.2% at the 95% confidence level in the concentration range of 20 ppm. The lower limit of detection for the method is 1.0 μg. Prior to chromatography, fractionation and concentration of the polyacrylamide in effluents are achieved by ultrafiltration with a hollow fiber cartridge having a nominal molecular weight cutoff of 100 000, and recoveries are determined by spiking studies. The application of the techniques for the analysis of residual flocculant in a coal washery thickener feed effluent sample is described.

Introduction

During coal cleaning processes, the tailings from the flotation section of coal washery are first fed to a number of classifier cyclones, and the cyclone overflow is then discharged to thickeners. In order to achieve sufficient clarity of the water from the thickeners for either subsequent reuse or discharge to streams, flocculants such as polyacrylamides (PAM) are usually added as settling aids (*1*). Because of the environmental constraints, e.g., water conservation, limited land for disposal, and general stream pollution, the major portion of process water requirements is now reclaimed from the thickeners. Residual flocculants in the reclaim water can affect processing operations, for example, flotation of coal fines. Therefore, a fast reliable analytical method is needed to monitor traces of residual flocculants in these reclaim waters. In addition, monitoring of treated effluent for residual PAM is also necessary prior to discharge into streams.

The measurement of trace levels of PAM in coal process waters has not been a simple analytical problem because these samples normally contain materials that show serious interferences when previously reported classical turbidimetric procedures are used (*2*). These procedures are based on the formation of insoluble complexes by reacting an anionic polyacrylamide with a fatty cation or a cationic polyelectrolyte and measuring the resultant turbidities by a light scattering technique. A major difficulty in the determination and measurement of residual PAM is their isolation from other interfering substances. Since the PAM are high molecular weight compounds and since their amide functionality shows strong UV absorption in the 185–210-nm wavelength range, a method for their determination based on size-exclusion high-performance liquid chromatography (SEHPLC) together with UV detection is possible if the PAM traces could be isolated in a concentrate fraction from a large volume of effluent samples.

This paper describes a new routine method for PAM determination that is simple, rapid, and highly sensitive. We have found that both anionic and nonionic PAM types of flocculants can be separated and analyzed free from any interferences by a combination of ultrafiltration (UF) and SEHPLC–UV chromatographic procedures. This combined technique has been applied for monitoring residual PAM in the supernatants of a coal washery thickener feed sample flocculated with an increasing dosage of an anionic polyacrylamide. The results of the above studies are described in this paper.

Experimental Section

Preparation of PAM Standards. The three anionic carboxylated PAM [Separan MG700 (Dow Chemical Co.), Percol E-10 (Allied Colloids), and Hercofloc 1021 (Hercules Chemical Co.)], one nonionic type [Superfloc 127 (Cyanamid)], and a cationic PAM [Percol 352] used as reference standards were purchased from commercial sources. Stock solutions of the standards were prepared by dissolving them in 0.05 M Na_2SO_4 at 100 ppm concentration. Appropriate dilutions with 0.05 M Na_2SO_4 were made to obtain the workable concentration of the standards prior to spiking, flocculation, and chromatographic analysis.

Size-Exclusion High-Performance Liquid Chromatography. A TSK gel 5000 PW column (7.5 mm × 30 cm; 17-μm particle size; molecular weight exclusion limits, 3×10^4–8×10^6; semirigid porous particles of a hydrophilic polymer gel containing the group CH_2–CHOH–CH_2O as the main constituent component) and a TSK gel 2000 PW precolumn (7.5 mm × 10 cm)—both columns purchased from Beckman Instruments—were used in a Beckman Model 112 HPLC with a 0.05 M Na_2SO_4 mobile phase. The flow rate used was 0.75 mL/min, and a 250-μL loop was used as the injection volume. A Beckman Model 165 variable-wavelength UV detector was used at a 208-nm wavelength, and a Spectra-Physics SP 4100 computing integrator was used for data handling. The peak observed in the sample chromatographic profile was identified on the basis of retention time and comparison with the PAM standard. The peak area method was used for calibration and quantitation.

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Ultrafiltration. An ultrafiltration apparatus (Amicon Model DC2 hollow fiber dialysis/concentrator, 100–2000-mL capacity) was used for the concentration/fractionation studies of trace levels of PAM in process water samples with a Diaflo hollow fiber cartridge, Type H1P 100-20 (nominal molecular weight cutoff 100 000), at a 110 mL/min flow rate, at 20 psig pressure, and at ambient temperature. A concentration factor of 10 was achieved by the procedure.

Spiking and Recovery Studies. The PAM spiking and recovery studies were performed with both distilled water and a filtered coal washery thickener feed sample. The procedure for spiking studies with distilled water was as follows: To either 1 or 10 L of water was added a known volume of 100 ppm PAM stock solution, the mixture was shaken vigorously, and the solution was then subjected to a concentration/fractionation step by ultrafiltration. Two different procedures were used in UF studies. In one procedure, the fractionation/concentration was performed by single-pass UF, and about 100 mL of retentate fraction containing the high molecular weight PAM was collected from either 1- or 10-L samples. The retentate was then evaporated to dryness in a rotary evaporator at 30 °C under reduced pressure, the dried residue dissolved in a known volume of 0.05 M Na_2SO_4 and filtered with Millex-SR (0.5 μm, Millipore Corp.), and the clear filtrate analyzed. In another variation, a double-pass and triple-water wash cycle UF procedure was used. In this procedure, a 200-mL (2 × 100 mL) retentate fraction was initially isolated by a double-pass UF (100 mL of retentate fraction was collected from the 1-L sample by the first pass; to the 900-mL permeate fraction was added 100 mL of distilled water, and from the total 1000 mL was collected another 100 mL of retentate fraction by a second pass). To the above 200 mL of retentate was added 800 mL of distillated water, the total 1 L was subjected to UF (first wash), and 100 mL of retentate was collected. Another double wash of the 100-mL retentate with distilled water (2 × 900 mL) was given. The final 100-mL retentate isolated by the above double-pass and triple-wash cycle procedure was then evaporated to dryness at 30 °C under reduced pressure in a rotary evaporator. The dried residue was dissolved in a known volume of 0.05 M Na_2SO_4 and filtered with Millex-SR (0.5 μm), and the clear filtrate was analyzed.

For studies with the coal washery filtrate, the sample of a thickener feed suspension (pH 6.0; percent suspended solid, 1.10; percent total solids, 1.34) was first allowed to stand for 6 h, and the turbid supernatant was decanted and filtered with Whatman 541 filter paper. The filtrate (1 L) was then spiked with PAM and shaken vigorously and the suspension was filtered with a Whatman glass fiber filter (934-AH). The clear filtrate was then subjected to UF following the procedures described above and the retentate fraction analyzed for PAM.

Flocculation and Analysis of Residual PAM in Thickener Feed Effluent. Flocculation experiments of a thickener feed sample with Separan MG 700 (anionic PAM) at 1.0, 2.4, 4.9, 6.7, 9.2, and 11.3 ppm dosage were carried out, and the residual flocculant was analyzed by UF and SEHPLC–UV procedures. The following procedure for flocculation was used. To a 1-L thickener feed suspension taken in a graduated cylinder was added a known volume of flocculant dropwise within 1–2 min from a 100 ppm stock solution, the suspension was shaken by end to end inversion 20 times and allowed to stand for 1 h, and the supernatants were decanted. The supernatants and the sludges were then separately filtered with a Whatman glass fiber filter (934-AH) and the filtrates combined. The filtrate was then subjected to a double-pass/triple-wash cycle UF following the procedures described above, and the retentate fractions were analyzed for residual PAM.

Results and Discussion

Size-Exclusion High-Performance Liquid Chromatography (SEHPLC). The polyacrylamides commonly used for flocculation of coal washery thickener feed (CWTF) effluents are water-soluble high molecular weight polymers. Aqueous SEHPLC is therefore an attractive technique for their analysis in coal washery effluent. This technique has been used in the past for the analysis of polyacrylamides in acrylamide monomer with surface-modified controlled pore glass packings (e.g., Gly-CPG) and recently in oil field production water from enhanced oil recovery (EOR) processes with diol-bonded silicas (*3*, *4*). Although these rigid glass or silica packings are reported to have both low adsorptivity and hydrophobicity, they generally suffer from drawbacks of pore size, adsorption, and adequate resolution.

Use of newer types of semirigid hydrophilic microparticulate polymer gel packings having surfaces modified with hydroxylated polyether groupings such as $-CH_2-CHOH-CH_2O-$ has been reported in the molecular weight (M_r) and molecular weight distribution (MWD) analysis of polyacrylamide polymer with no evidence of adsorption (*5*). These packings marketed by Toy Soda Manufacturing Co. Ltd. as TSK gel PW types are available in different pore sizes. For our study, we selected the TSK gel 5000 PW type having molecular weight exclusion limits between 3×10^4 and 8×10^6 so that all the polyacrylamide molecules ($M_r > 10^5–10^6$) are excluded from the pores and a single sharp peak suitable for quantitative analysis is obtained.

Both refractive index (RI) and UV detection at 190 nm have been used in the past in the SEHPLC analysis of polyacrylamide (*4*, *5*). RI detection lacks adequate sensitivity in trace PAM analysis. We have found that operation of a UV detector at short wavelength, e.g., 190 nm, results in high background noise and poor base-line stability. Since the amide functionality in the polyacrylamide polymer shows reasonably strong UV absorption at 208 nm, we have selected this wavelength in this study. Use of a similar UV detection has been reported by Skelly and Hussar (*6*) in the determination of acrylamide monomer in polyacrylamide and in environmental samples by C_{18} HPLC.

Adjustment of proper ionic strength in the mobile phase was found necessary in the aqueous SEHPLC work with the TSK gel packings. This is to prevent or minimize adsorption effects due to solute–gel interactions. We used 0.05 M Na_2SO_4 as the mobile phase, which is transparent in the UV at 208 nm. This ionic strength is found most suitable for the resolution of polyacrylamide. Mobile phases such as 0.08 M Tris–HCl and 0.1 N ammonium nitrate used previously (*3*, *5*) in the analysis of polyacrylamide are found unsuitable because they absorb UV light at 208-nm wavelength.

Figure 1 shows a typical TSK gel SEHPLC chromatogram of 40 ppm of an anionic polyacrylamide (Separan MG 700) obtained with UV detection at 208 nm with 0.05 M Na_2SO_4 as the mobile phase. The polymer elutes in approximately 9 min as a sharp single peak without any evidence of adsorption. Similar profiles were also obtained for the two anionic PAM, namely, Percol E-10 and Hercofloc 1021, and one nonionic type (Superfloc 127) studied. The cationic PAM type, e.g., Percol 352, is not resolved

Table I. Precision Measurement for Anionic Separan MG 700 by TSK Gel SEHPLC-UV

	20 ppm			40 ppm		
	RT, min	area, units	concn found, ppm	RT, min	area, units	concn found, ppm
day 1						
injection 1	8.93	25205	21.2	9.04	40743	35.2
injection 2	8.96	26012	21.9	9.02	47334	40.9
injection 3	9.1	25332	21.3	8.93	48519	42.0
day 2						
injection 1	8.91	22415	18.9	8.89	49368	42.7
injection 2	8.98	23542	19.8	9.05	48458	41.9
injection 3	9.14	24961	21.0	8.96	43410	37.5
day 3						
injection 1	8.96	24951	21.0	8.90	49175	42.5
injection 2	9.00	25472	21.4	8.97	41835	36.2
injection 3	9.10	22000	18.5	8.75	42244	36.5
day 4						
injection 1				8.89	41444	35.8
injection 2				8.97	43606	37.7
injection 3				8.91	44310	38.3
day 5						
injection 1				8.93	46149	39.9
injection 2				9.07	50701	43.8
injection 3				8.97	50739	43.9
average			20.5			39.76
standard deviation			1.19			3.07
relative standard deviation, %			5.81			7.73
precision, 95% confidence level			±2.2			±6.14

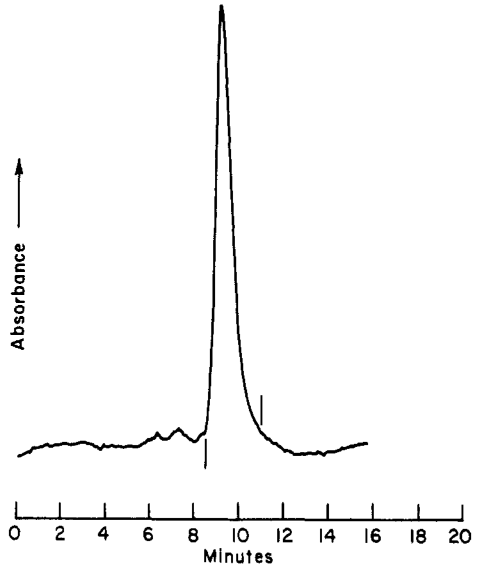

Figure 1. Size-exclusion chromatogram of 40 ppm anionic polyacrylamide (Separan MG 700). Chromatographic conditions: 7.5 mm i.d. × 30 cm TSK gel 5000 PW column in series with 7.5 mm i.d. × 10 cm TSK gel 2000 PW precolumn, 0.05 M Na_2SO_4 mobile phase, 0.75 mL/min flow rate, 250-μL injection volume, and UV detection at 208 nm.

under the conditions used. A separate study had shown that good resolution of this PAM type can be achieved by SEHPLC on Gly-CPG packings (from Electro Nucleonics Inc.) with similar UV wavelength at 208 nm but with water as the mobile phase. Proper adjustment of ionic strength and pH by using buffered mobile phases may be necessary to analyze the cationic PAM type on TSK gel packings.

Table I demonstrates the precision data achievable with the TSK gel SEHPLC-UV system. The precision of the technique was studied by injecting 250-μL samples of the anionic Separan MG 700 at 20 and 40 ppm concentrations and running over three or more days to show day to day variations. As shown in the table, the retention times are found highly reproducible, and the peak areas also displayed fairly good precisions. At 20 and 40 ppm concentration, the relative precision is respectively 2.2 and 6.14% at the 95% confidence level. This implies that at the 2.2% level of precision an average value, for example, 0.4 ppm residual PAM in coal washery effluent, will lie between 0.39 and 0.41 ppm when determined by the TSK gel SEHPLC-UV technique.

Analysis of samples prepared from serial dilutions of 100 ppm concentration of anionic Separan MG 700 gave a nearly linear response from 5 to 100 ppm. The limit of detection of the PAM analyzed by the method is about 1.0 μg. This represents the amount of standard PAM material giving a response height of 1 cm, which is roughly twice the background noise. The actual method sensitivity in the analysis of PAM in process water would, however, depend on the amount of sample material injected, the background noise (interference), and the recovery throughout the method. Thus, for example, assuming 75% recovery during sample preparation steps, a 250-μL injection of the PAM extract from a 1-L process water sample concentrated to a 5-mL retentate fraction will give a method sensitivity of about 0.02 ppm for the Separan MG 700. Other anionic (having similar charge density) and nonionic PAM studied are likely to show similar low limits of detection because of their observed similar chromatographic response.

Spiking and Recovery Studies. Sample preparation prior to chromatographic analysis included a membrane ultrafiltration step for the isolation of trace PAM residual flocculant from a large volume of coal washery effluent. A UF technique for concentrating high molecular weight polyelectrolyte flocculant from dilute aqueous solution has been reported in the past (7). The main advantage of this method is that PAM are not likely to be decomposed or otherwise unchanged during the isolation procedure. For our study, we selected a membrane with a nominal molecular weight cutoff of 100000 in the molecular filtration step to achieve the separation and concentration of the high molecular weight PAM (M_r >10^5–10^6) in the retentate fraction free from other interfering impurities, e.g., humic acids (M_r <100000) and salts present in coal process water.

Table II. Spiking and Recovery Studies[a]

expt no.	vol of sample spiked	vol of 100 ppm PAM added, mL	PAM spiking level, ppm	UF retentate vol, mL	concn factor	final retentate vol, mL	% recovery
		Single-Pass Ultrafiltration					
I	10 L of dist. H_2O[b]	10 mL of Separan MG 700	0.1	100	100:1	100	100
II	1 L of dist. H_2O	5 mL of Separan MG 700	0.5	100	10:1	10	100
III	1 L of dist. H_2O	10 mL of Separan MG 700	1.0	100	10:1	5	88
IV	1 L of dist. H_2O	50 mL of Separan MG 700	5.0	100	10:1	100	100
V	1 L of dist. H_2O	5 mL of Separan MG 700	0.5	100	10:1	10	100
VI	1 L of dist. H_2O	50 mL of Percol E-10	5.0	100	10:1	100	100
VII	10 L of dist. H_2O	10 mL of Superfloc 127	0.1	100	100:1	100	100
VIII	1 L of CWTF filtrate[c]	25 mL of Separan MG 700	2.5	100	10:1	30 (salt)	30
		Double-Pass/Triple-Wash Cycle Ultrafiltration					
IX	1 L of dist. H_2O	10 mL of Separan MG 700	1.0	100	10:1	5	74
X	1 L of dist. H_2O	50 mL of Separan MG 700	5.0	100	10:1	5	78
XI	1 L of CWTF filtrate	25 mL of Separan MG 700	2.5	100	10:1	5	50[d]

[a] Analysis by TSK gel SEHPLC–UV; see chromatographic conditions in Figure 1. [b] dist. H_2O = distilled water. [c] CWTF = coal washery thickener feed. [d] Of the PAM loss of 50%, loss from double-pass triple-wash cycle UF is 24.0% (average of experiments IX and X) and the remaining 26% loss is attributed to the interaction of the PAM with the soluble impurities in the CWTF filtrate.

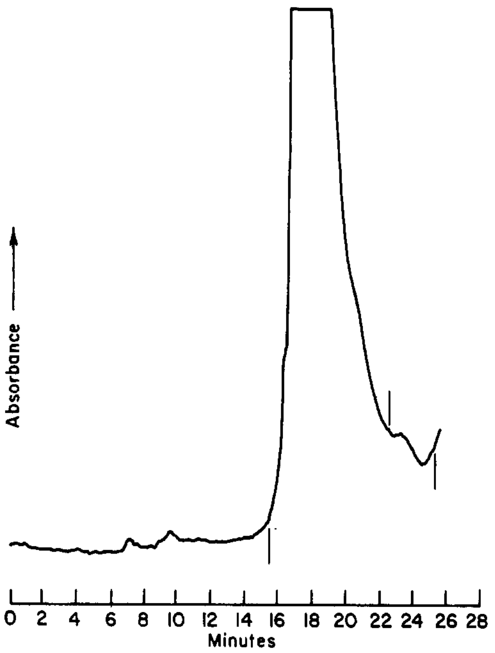

Figure 2. Size-exclusion chromatogram of ultrafiltration retentate of a coal washery effluent sample showing background level. Chromatographic conditions same as in Figure 1.

UF studies were conducted in two modes, maintaining a concentration factor of 10 with a 1-L sample in both procedures. Initial studies made with single-pass UF have shown that the procedure produces, as expected, a PAM-rich retentate fraction, but the fraction also contains a high concentration of salts originating from coal process water. The salts become partially insoluble and consequently precipitate in the retentate when the retentate is further concentrated to a small volume in a rotary evaporator prior to SEHPLC analysis. Removal of these salts from the retentate is necessary because of the following two reasons: (1) the salts can cause problems in chromatographic analysis by disturbing the ionic strength of the mobile phase; (2) high PAM losses can occur as a result of their insolubilization in high salt concentration. In order to minimize or prevent the permeation of the salt in the retentate fraction, a desalting procedure incorporating a double-pass and triple-wash cycle UF was therefore studied.

The efficiencies of the above UF concentration procedures were tested by PAM spiking and recovery studies. Samples of distilled water (no sample matrix) as well as a coal washery thickener feed (CWTF) filtrate free from suspended fines and with minimum background (see chromatogram in Figure 2) were spiked with PAM at different levels and recoveries determined. Results shown in Table II indicate high PAM recoveries (~100%) from spiked distilled water. In contrast, the spiked CWTF filtrate sample gave a low recovery (~30%) when both samples are fractionated and concentrated in a single-pass UF. Compare the results of experiment VIII with those from experiments I, II, and IV in Table II. This low recovery observed with the filtrate sample is probably caused by the loss of PAM due to (1) the interaction of the polyacrylamide with the soluble impurities present in coal process water and (2) the high salt content in the retentate observed in single-pass UF operation.

When concentration is performed with a double-pass/triple-wash cycle ultrafiltration step, an almost complete desalting of the CWTF filtrate retentate fraction is achieved. However, this variation in UF gave about 76% recovery from spiked distilled water samples (average of recoveries in experiments IX and X in Table II) indicating 24% loss of PAM during the wash cycle. In contrast, the recovery obtained with the spiked CWTF filtrate sample under similar UF conditions is approximately 50%, which is about 20% higher than that observed in single-pass UF. Compare the results of experiments VIII and XI in Table II. It is likely that, of the 50% unrecovered polyacrylamide in the above experiment, about 24% is lost during the UF wash cycle, similar to that observed in distilled water spiking studies, and the remaining 26% is lost due to interaction of the polyacrylamide with the soluble impurities present in coal process water.

Flocculation and Analysis of Residual PAM in Coal Washery Effluent. A case study to demonstrate the applicability of the described UF and SEHPLC–UV techniques was carried out by the analysis of residual PAM in a coal washery thickener feed sample. After initial determination of the background level and PAM recoveries by spiking, the sample was first subjected to a series of flocculation experiments with incremental addition of Separan MG 700, and each supernatant was analyzed for residual PAM by a double-pass/triple-wash cycle UF and SEHPLC. A chromatogram in Figure 3 of the retentate from the 6.7 ppm dosage flocculation run of the feed sample shows a PAM retention time identical with that observed with the reference PAM (see chromatogram in Figure 1). This indicates that the PAM is not altered

Table III. Analysis of Residual Flocculant in Coal Washery Effluent[a]

expt no.	vol of effluent flocculated, mL	amount of 102.8 ppm Separan MG 700 added		flocculant added, ppm	retentate vol, mL	residual flocculant found			loss of flocculant in UF wash cycle, ppm[c]	corrected residual flocculant, ppm
						calibration				
		mL	mg			method A, ppm[b]	method B, ppm[b]	average residuals, ppm		
I	1000	10	1.03	1.02	5	ND[d]	ND	0.00	0.25	0.00
II	1000	24	2.47	2.41	5	0.13	0.12	0.13	0.57	0.70
III	1000	50	5.14	4.90	5	0.65	0.60	0.63	1.17	1.80
IV	1000	70	7.20	6.73	5	1.37	1.26	1.32	1.61	2.93
V	1000	98	10.07	9.17	5	2.76	2.54	2.65	2.21	4.86
VI	1000	123	12.64	11.26	5	4.80	4.41	4.61	2.70	7.31

[a] Percent total solids 1.34; percent suspended solids 1.10; pH 6.0. [b] Calibration and quantitation were performed with 30 ppm (method A) and 100 ppm (method B) Separan MG 700 solution in distilled water as external calibration standards. The average of the two quantitations was taken as the residual flocculant concentration. [c] After correction of 24% loss of flocculant in double-pass/triple-wash UF cycles. This average loss was determined by flocculant spiking and recovery studies in distilled water (see Table II). [d] ND = none detected.

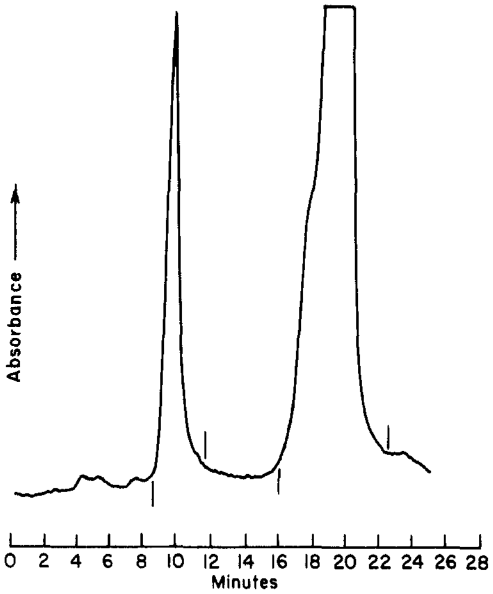

Figure 3. Size-exclusion chromatogram of ultrafiltration retentate of a coal washery effluent sample flocculated with 6.7 ppm anionic polyacrylamide (Separan MG 700). Chromatographic conditions same as in Figure 1.

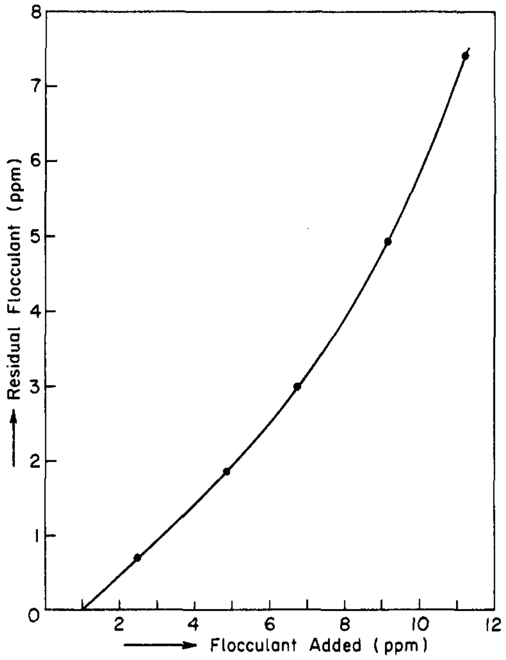

Figure 4. Variation of residual flocculant concentration with increasing dosage in flocculation of a coal washery effluent sample.

during the flocculation and UF sample preparation steps prior to SEHPLC analysis.

The results of flocculation and analysis of residual flocculant are presented in Table III, and a plot of residual flocculant concentration against increasing flocculant dosage is presented in Figure 4. As expected, an increase in residual concentration is observed with an increase in flocculant dosage. This demonstrates the utility of the combined UF/SEHPLC–UV procedures in the determination of residual PAM flocculants in coal washery effluent water.

Conclusions

The methodologies combining ultrafiltration for sample preparation and TSK gel SEHPLC–UV detection for analysis as described allow measurement of residual polyacrylamide flocculant in dilute waste effluents. Analysis of flocculants is achieved by chromatography on 5000 PW type TSK gel packings of appropriate pore size (molecular weight exclusion limits 3×10^4–8×10^6) with a mobile phase of proper ionic strength (0.05 M Na_2SO_4) and a compromise UV wavelength (208 nm) for detection. This analytical method is chosen over other chromatographic methods because of better resolution with no adsorption effects, improved sensitivity, and longer column life. An ultrafiltration sample preparation step required for the isolation of a salt-free retentate concentrate fraction prior to analysis is accompanied by some loss of polyacrylamide during the wash cycle. A correction of the observed residual flocculant concentration for this loss is therefore necessary. A case study with a coal washery effluent flocculated with an increasing dosage of an anionic polyacrylamide has demonstrated the applicability of the methods. It is concluded that the methodologies described offer considerable promise as a simple, rapid, and sensitive method with a fairly high degree of precision for the determination of residual polyacrylamides in flocculated coal washery effluents, petroleum oil process water, and tailings from mineral processing plants.

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Registry No. PAM, 9003-05-8; Separan MG700, 54578-21-1; Percol E-10, 106946-89-8; Superfloc 127, 39393-20-9; Hercofloc

1021, 106946-84-3; Percol 352, 106946-88-7; H_2O, 7732-18-5.

Literature Cited

(1) Hamza, H. A. *CIM Bull.* **1979**, *72*, 116.
(2) Vreugde, M. J. A.; Poling, G. W. *CIM Bull.* **1975**, *68*, 54.
(3) Chow, C. D.; Jewett, G. L. *J. Liq. Chromatogr.* **1980**, *3*, 419.
(4) Beazley, P. M. *Anal. Chem.* **1985**, *57*, 2098.
(5) Hasimoto, I.; Sasaki, H.; Airua, M.; Kato, Y. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1789.
(6) Skelly, N. E.; Husser, E. R. *Anal. Chem.* **1978**, *50*, 1959.
(7) Singh, B. K. *Glueckauf* **1978**, *114*, 513 (in German). Available from National Research Council, Ottawa, Ontario, Canada.

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Wind Dispersal of Metals from Smelter Waste Tips and Their Contribution to Environmental Contamination

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■ Results from a detailed investigation of metal concentrations in soil and house dust in the Lower Swansea Valley, based on work done in Swansea as part of a nationwide survey, showed that contamination of garden soils by wind erosion from waste tips had taken place. However, house dusts showed considerably higher levels than the corresponding soils, and there was no evidence for a similar route of contamination. Multiple-regression models indicated that only a small number of factors explained a large proportion of the variability in metal concentrations in soil; similar models could not explain the variability in house dust.

Introduction

In recent years, much attention has been focused on the possible subclinical health effects of heavy metals, particularly lead (*1*), and especially in relation to areas of soft water (*2*) or to children with pica (*3*). It has been suggested that the dust-to-hand-to-mouth route is of primary importance in the exposure of children (*4*). A number of prospective studies are currently investigating this route, and preliminary results from a major study of hand-to-mouth activity in 2-year olds in an inner city area of the U.K. have recently been published (*5*). For cadmium, it has been suggested that it would be prudent to contain intakes within currently acceptable tolerance limits, as the metal serves no known useful biological function, accumulates in the body throughout life, and is acutely toxic in very low doses (*6*). Only quite recently has information become available for the U.K. on the concentrations of lead and other metals in soils and house dusts across the country (*7*). As a part of this survey, paired samples of house dust and garden soil were collected from the town of Swansea in Wales. This paper reports the results of an investigation into the metal concentrations of 80 such samples.

At the beginning of the industrial revolution Swansea was ideally situated, as a port at the head of a valley leading deep into the Welsh coalfield (Figure 1), to refine metal ores and export the finished product. The basis of much of the manufacturing wealth was copper production, which continued from 1717 until the turn of the century. Zinc, produced by a sublimation process, was also refined from 1738 until World War II. These processes led to prodigious quantities of waste slags and furnace ashes being discarded to form the bulk of the non-ferrous metal waste tips on the floor of the valley (*8*). Since eventual restoration of the land on termination of working was not proscribed by legislation, the Swansea valley contains a number of non-ferrous metal tips, as large mountains of unsorted and often uncemented materials scattered over a marshy, waterlogged valley plain and overlooked by around 70% of the local housing situated in terraces along the valley sides. The metal content is apparent from the strong colors predominating in both the fresh and weathered materials and the general toxicity of the substrate, which has prevented the development of soils. Only a few sparse areas of metal-tolerant grasses (*9*) were found to be binding the surface, and the greater extent was obviously subject to erosion and transport by wind.

Methods

The soil and house dust samples analyzed in this study were obtained as part of a survey into the nationwide concentrations of heavy metals in garden soils and house dusts, carried out by the Applied Geochemistry Research Group of Imperial College (University of London) on behalf of the Department of the Environment between 1980 and 1983 (*7*). The sample localities were selected to give as even a coverage as possible over each chosen urban area. Each garden soil sample (0–5-cm depth) was dried, sieved (2-mm mesh), and ground to −80 mesh. Samples (0.25 g) were digested in concentrated nitric acid for 1 h at 105 ± 5 °C before dilution and analysis. The contents of the vacuum cleaner bag were sieved twice (1-mm mesh) to remove carpet fluff and large objects. Samples (0.25 g) were carefully heated to 185 ± 5 °C with a mixture of concentrated perchloric and nitric acids until dryness. The samples were then refluxed for 1 h at 60 ± 5 °C with 6 M hydrochloric acid followed by dilution and analysis, which was carried out on a Perkin-Elmer SP 5000 atomic absorption spectrophotometer.

In addition to soil and house dust samples taken at each house in the national survey, a questionnaire was completed by the householder. A simplified version of that questionnaire was used in this study and covered the occupation of the adult occupants, number of preschool children, smoking habits, foam-backed carpets, age of house, type of heating, distance of house from road, road

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