Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology.
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The detection of poly(acrylamide) flocculants in fresh water using fluorescent inter-polymer complex formation

Supporting Information

Water Sources

The detection method was tested in three environmentally sourced water samples. These three water sources were also analysed via ICP to reveal the elemental composition of all impurities in the water supply, in comparison with ultra-pure, deionised, tap and sea water (Table).

Table SI1 – ICP analysis of water sources, all results mg l^{-1}.

	Al	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn
U.P.	0.051	0.150	<0.002	0.002	0.150	0.051	<0.001	1.120	<0.01	0.010	0.030	<0.001
Deionised	0.019	0.078	<0.002	0.003	0.120	0.029	<0.001	0.820	0.030	0.040	0.030	0.002
Tap	0.056	4.920	0.005	0.040	0.980	2.470	0.004	27.400	1.130	14.200	2.690	0.009
Sea	0.410	390.0	<0.002	0.430	394.0	1180.0	0.008	9850.0	<0.1	811.0	1.270	<0.005
Y1	0.177	4.010	0.048	0.457	0.710	2.490	0.048	8.560	0.015	2.350	2.610	0.042
Y2	0.278	9.270	0.003	0.510	2.080	22.840	0.020	13.90	0.030	3.330	2.520	0.017
SA	102.0	47.10	0.210	80.00	32.00	15.200	1.170	25.10	3.650	15.500	216.0	0.920

Industrial Polymers

A range of anionic, cationic and non-ionic polyacrylamide flocculants were supplied by SNF (UK) LTD for testing. A full list of the flocculants supplied and details of the modifications are shown below.

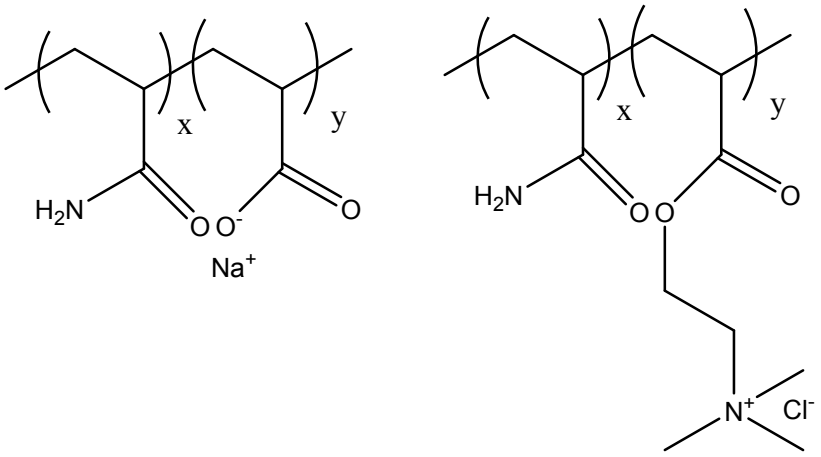

Figure SI1 - Anionic and Cationic modifications to SNF(UK)Ltd polyacrylamide flocculants

Table SI2 – List of polyacrylamide flocculants supplied by SNF (UK) LTD

Polymer	Comments
FloPam AN905	Anionic
FloPam AN905 SEP	Anionic
FloPam AN910	Anionic
FloPam AN910 SEP	Anionic
FloPam AH912	Anionic
FloPam AN913 SEP	Anionic
FloPam AN923 SEP	Anionic
FloPam AN934 BPM	Anionic
FloPam FA920	Non-ionic
FloPam FO4115	Cationic
FloPam FO4140	Cationic
FloPam FO4190	Cationic
FloPam FO4190 SEP	Cationic
FloPam FO4650 MPM	Cationic
FloPam FO4240	Cationic

Nomenculatire notes:

- AH912 is has a very small anionic charge that arises as a result of hydrolysis of the acrylamide during polymerisation.
- SEP grades are potable water approved,(ie free acrylamide <200 mg l^{-1}.)
- BPM and MPM are low molecular weight compared to other polymers.

Anisotropy Fitting details:

The full details of the fit from Fig. 3 are displayed below. These contain both the individual correlation time components T_1 and T_2, B1 and B2 from equation 2, and the final correlation time calculated via equation 3, with the standard deviation and goodness of fit values.

From Figure 3 – 1 : 1 mixture of PAA + SNF (UK) FloPam polymers

FloPam Flocculent	pH	T_1 / ns	A	T_2 / ns	B	T_c / ns	S.d / ns	ChiSq
FA920	3.99	1.20	0.04	12.58	0.05	11.71	0.19	1.40
	2.62	1.20	0.04	124.97	0.05	123.97	2.46	0.97
	1.26	1.20	0.04	119.03	0.05	128.04	2.43	1.16
	6.75	1.20	0.04	4.88	0.04	4.08	0.27	1.04
	5.05	1.20	0.04	9.60	0.01	7.10	1.23	1.05
	2.07	1.20	0.04	115.60	0.07	121.90	1.75	1.33
	2.42	1.20	0.04	121.18	0.07	120.49	2.71	1.13
	3.30	1.20	0.04	106.59	0.07	105.90	2.33	1.10
	3.09	1.20	0.04	122.70	0.06	121.81	4.04	1.19
	5.42	1.20	0.04	2.53	0.08	2.27	0.08	0.94
	2.50	1.20	0.04	131.50	0.05	130.56	5.94	1.02
AN934BPM	5.54	1.20	0.04	2.42	0.08	2.16	0.02	1.01
	3.62	1.20	0.04	7.01	0.10	6.61	0.11	1.49
	7.37	1.20	0.04	0.16	0.08	1.00	0.01	1.14
	2.02	1.20	0.04	139.64	0.06	138.84	0.29	1.80
	4.55	1.20	0.04	2.16	0.14	2.02	0.02	0.97
	5.79	1.20	0.04	1.80	0.07	1.63	0.02	0.94
	2.34	1.20	0.04	37.22	0.07	36.51	0.42	1.92
	3.04	1.20	0.04	2.79	0.15	2.62	0.03	1.03
	2.5	1.20	0.04	34.79	0.04	18.44	0.48	0.99
	4.1	1.20	0.04	5.98	0.06	2.32	0.02	1.27
	1.01	1.20	0.04	173.79	0.03	143.53	2.39	1.23
	2.14	1.20	0.04	50.06	0.03	28.21	0.44	1.38
	7.76	1.20	0.04	5.12	0.08	2.12	0.02	1.60
	1.52	1.20	0.04	172.58	0.02	133.35	3.59	1.26
FO4650 MPM	2.91	1.20	0.04	240.12	0.06	239.25	0.06	1.09
	2.08	1.20	0.04	242.37	0.06	241.52	6.02	1.04
	0.49	1.20	0.04	11.10	0.04	9.98	0.36	1.09
	2.38	1.20	0.04	241.39	0.08	240.74	4.26	1.21
	0.88	1.20	0.04	9.54	0.05	8.67	0.56	0.96
	2.01	1.20	0.04	234.24	0.07	233.51	2.72	0.95
	1.46	1.20	0.04	18.19	0.08	17.60	0.67	1.61
	4.53	1.20	0.04	241.09	0.07	240.36	3.58	1.21
	4.93	1.20	0.04	21.30	0.04	20.09	1.81	1.17
	1.76	1.20	0.04	177.34	0.08	176.69	6.26	1.10

3.94	1.20	0.04	262.20	0.05	261.12	9.08	1.18
6.81	1.20	0.04	28.76	0.05	27.75	2.19	1.34
1.68	1.20	0.04	39.01	0.05	38.02	2.37	1.16
2.07	1.20	0.04	207.38	0.05	206.31	3.49	1.45
1.87	1.20	0.04	34.35	0.07	33.64	1.97	1.75
1.97	1.20	0.04	71.65	0.05	70.74	2.80	1.21
3.21	1.20	0.04	259.48	0.05	258.4	10.66	1.61
4.79	1.20	0.04	168.89	0.04	167.5	6.44	1.44
5.62	1.20	0.04	26.33	0.05	25.4	3.15	1.40
7.90	1.20	0.04	26.97	0.05	16.04	3.36	1.52

In the fitting of these models all T1 and A are kept constant using values determined previously which represent uncomplexed polymer probe. ***See T. Swift, L. Swanson and S. Rimmer, RSC Advances, 2014, 4, 57991-57995.***

From Figure 4: - Low concentration test of FloPam FA920

mg l^{-1} PAA	pH	mg l^{-1}	T_c / ns	SD / ns	ChiSq
70	2.00	162.2	101.48	8.06	1.18
		81.1	94.70	7.86	1.22
		38.9	94.24	6.49	1.09
		16.2	86.64	9.59	1.20
		8.51	85.31	8.21	1.23
		6.70	45.36	4.03	1.84
		3.33	10.48	2.40	0.95
		0.30	4.96	0.41	1.08
		0.00	8.29	1.62	1.15
700	2.00	518.0	180.21	8.06	1.31
		179.3	110.16	7.86	1.23
		103.6	100.45	6.49	1.32
		52.0	88.28	9.59	1.44
		33.0	37.91	8.21	1.38
		10.0	15.13	4.03	0.98
		1.0	14.89	2.40	1.20
700	4	0.02	3.34	0.41	1.06
		518.0	2.30	0.97	0.97
		179.3	7.94	7.05	1.90
		103.6	5.87	1.70	1.16
		51.8	3.96	1.39	1.05
		33.0	3.48	0.70	1.04
		10.0	5.30	1.60	0.98
		1.0	5.71	1.14	0.98
		0.02	8.89	3.74	1.19

From Figure 5: Low concentration test of FO4115 with 0.113 mg ml^{-1} probe

mg l^{-1}	Tc / ns	Sd / ns	ChiSq
0	8.40	0.71	1.24
0.8	15.69	2.03	1.16
1.6	11.87	1.63	1.16
2.4	16.51	1.70	1.28
2.8	16.41	1.38	1.23
3.2	17.91	2.02	1.30
7.1	36.41	7.74	1.23
10.7	59.24	6.47	1.24
16.9	104.73	10.06	1.32
27.14	113.86	11.55	1.28
33.9	124.90	10.64	1.34
50.9	122.25	17.58	1.30
53.7	122.51	9.51	1.58
61.1	122.78	10.10	1.24
64.4	117.42	9.88	1.11
67.8	133.22	12.28	1.17

From Figure 6:

Flocculant	Water Source	pH	T_1 / ns	A	T_2 / ns	B	T_c / ns	SD / ns	ChiSq
None	Sea	3.28	1.20	0.04	6.61	0.08	6.14	2.03	1.13
		4.23	1.20	0.04	6.82	0.07	6.26	2.64	1.49
		1.54	1.20	0.04	4.96	0.09	4.58	0.82	1.45
		9.87	1.20	0.04	0.78	0.36	1.03	2.50	0.98
		1.97	1.20	0.04	5.12	0.08	4.67	1.06	1.00
		3.58	1.20	0.04	4.76	0.08	4.34	1.87	1.01
		6.4	1.20	0.04	1.00	0.21	1.04	1.63	0.91
FA920	Sea	1.70	1.20	0.04	145.78	0.03	145.09	4.94	1.00
		2.35	1.20	0.04	73.80	0.04	73.18	3.13	1.02
		5.00	1.20	0.04	19.74	0.04	18.37	0.70	1.22
		3.19	1.20	0.04	6.12	0.07	4.95	0.24	0.99
		2.70	1.20	0.04	7.25	0.05	6.67	0.14	1.22
		3.64	1.20	0.04	6.03	0.08	5.44	0.16	0.91
		2.95	1.20	0.04	5.08	0.08	4.59	0.25	0.97
		2.20	1.20	0.04	35.30	0.07	33.62	1.15	1.03
		0.96	1.20	0.04	198.16	0.03	196.64	4.15	0.99
		0.64	1.20	0.04	215.60	0.04	214.38	4.39	1.04
		1.56	1.20	0.04	182.79	0.05	181.77	4.85	1.24
		2.30	1.20	0.04	121.78	0.02	119.17	5.33	1.32
		7.21	1.20	0.04	3.18	0.06	2.75	0.09	1.04
		6.15	1.20	0.04	3.54	0.08	3.19	0.11	1.18
None	Tap	1.49	1.20	0.04	40.17	0.06	4.02	0.75	1.30
		1.65	1.20	0.04	34.53	0.06	3.45	0.77	3.89
		2.20	1.20	0.04	82.60	0.04	8.26	1.58	1.42
		2.33	1.20	0.04	72.26	0.04	7.23	1.57	1.55
		2.60	1.20	0.04	34.53	0.06	3.45	1.21	4.20
		2.64	1.20	0.04	30.29	0.06	3.03	1.15	2.05
		2.83	1.20	0.04	67.70	0.04	6.77	1.84	11.39
		3.07	1.20	0.04	29.63	0.06	2.96	1.32	4.38
		3.13	1.20	0.04	2.80	0.09	2.80	1.31	1.16
		3.23	1.20	0.04	42.62	0.04	4.26	1.67	1.20
		3.75	1.20	0.04	41.85	0.04	4.19	1.92	1.39
		4.36	1.20	0.04	94.06	0.04	9.41	3.34	1.37
		4.37	1.20	0.04	103.23	0.03	10.32	3.51	1.23
		6.01	1.20	0.04	125.05	0.03	12.51	5.31	1.48
		6.6	1.20	0.04	111.82	0.03	11.18	5.52	1.55
		6.80	1.20	0.04	53.31	0.04	5.33	3.93	1.34
		8.10	1.20	0.04	18.02	0.07	1.80	2.72	3.83
		9.58	1.20	0.04	92.12	0.04	9.21	7.27	4.10
		9.64	1.20	0.04	85.61	0.04	8.56	7.05	1.07
		8.10	1.20	0.04	18.02	0.07	1.80	2.72	3.83

		7.60	1.20	0.04	17.62	0.04	1.76	2.52	1.22
		4.75	1.20	0.04	7.90	0.05	0.79	1.06	1.07
		1.60	1.20	0.04	87.95	0.02	8.80	1.19	1.25
		1.92	1.20	0.04	22.17	0.02	2.22	0.71	1.06
FA920	Tap	4.6	1.20	0.04	12.04	0.02	9.97	0.19	1.19
		3.1	1.20	0.04	114.64	0.05	113.57	1.25	0.99
		3.92	1.20	0.04	15.73	0.04	14.06	0.84	1.16
		3.45	1.20	0.04	45.04	0.07	44.07	0.76	1.04
		2.25	1.20	0.04	136.37	0.06	135.49	1.29	0.97
		6.24	1.20	0.04	1.20	0.05	1.20	0.57	1.06
		2.63	1.20	0.04	126.83	0.05	125.91	1.68	1.19
		4.57	1.20	0.04	3.39	0.07	2.99	0.16	1.06
		3.1	1.20	0.04	63.45	0.01	59.23	6.78	1.20
		1.59	1.20	0.04	187.90	0.01	184.52	11.03	1.17

Additional Comments

An increase in turbidity was noticed when the polymer probe was added to the sea water sample at high pH (Fig. SI2) although no response was observed in the correlation time.

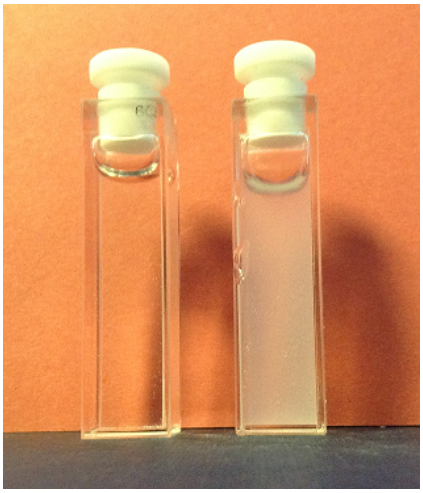

Figure SI2 – Sea water sample response to pH adjustment by NaOH addition
(left pH 3, right pH 8)

Samples of FloPam FA920 (2 mg ml^{-1}) were prepared in a range of 0.1 M salt impurities, mixed with an stoichiometric equivalent amount of probe (Fig. SI3Figure SI3). In the case of ammonia, sodium phosphate, sodium chloride and calcium chloride complexation was clearly observable below pH 2, although it should be noted that the calcium chloride had a marked effect on the correlation times at higher pHs. In the presence of magnesium sulphate the increase in correlation time was clearly diminished although still distinct from the uncomplexed polymer. When the concentration of magnesium sulphate was reduced to 0.01 M a full complexation response was observed (Fig. SI4).

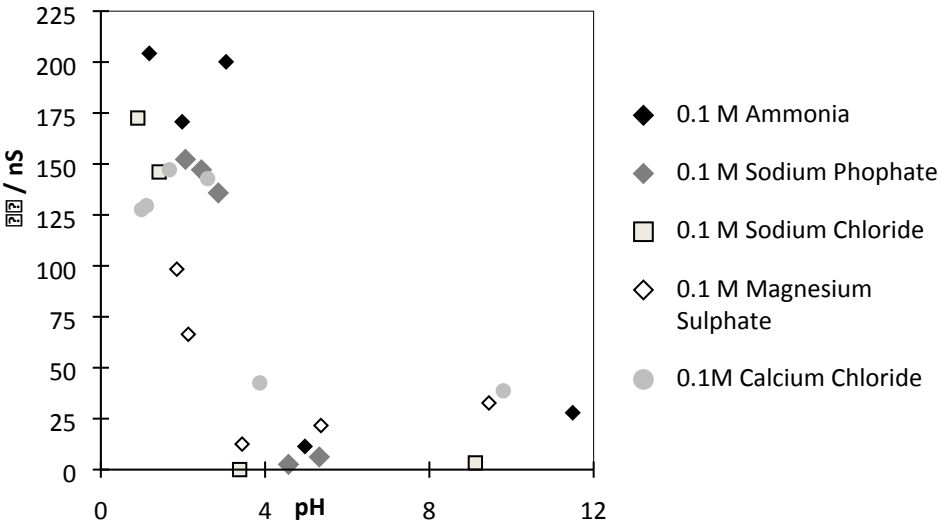

Figure SI3 – Correlation time of probe and FloPam FA920 samples
in 0.1 Molar impurities

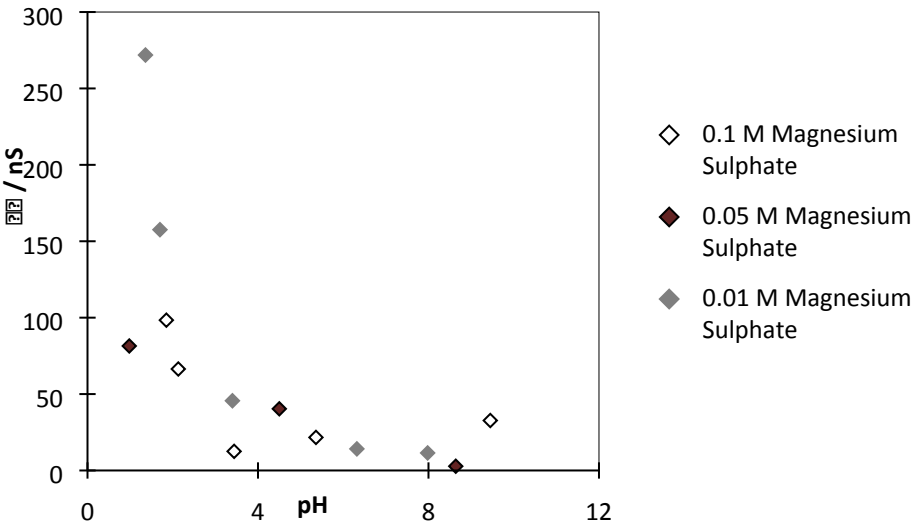

Figure SI4 - Correlation time of probe and FloPam FA920 samples in magnesium sulphate

Detection of Flocculated Samples

Y1 Water Treatment Plant

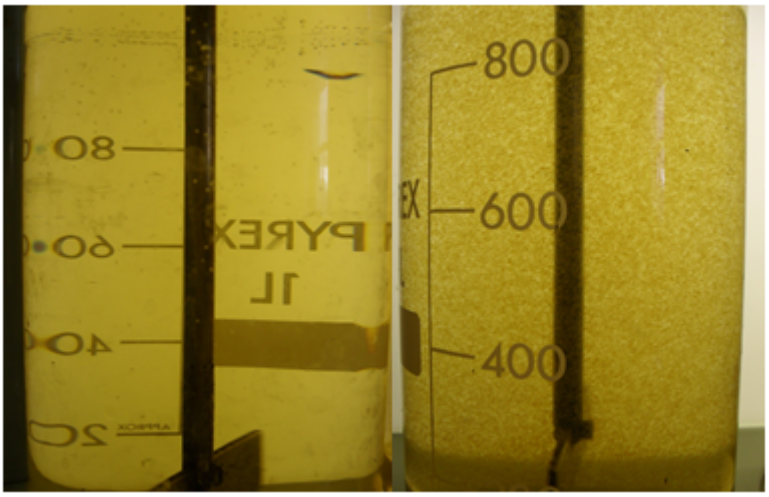

Figure 2 – Comparison between reference beaker (L) and flocculated sample (R)

Y2 water treatment plant

In the absence of poly(acrylamide) there is no increase in the correlation time of the polymer probe. At very low PAM concentrations there is a small increase, the limit of detection being determined by the concentration of probe polymer. At low ppm loading (< 10 ppm) there is an increase in the correlation time of flocculated Y2 water over the unflocculated Y2 fresh water, an increase visible as low as 0.8 ppm. Though this is a small increase relative to the total potential rise of the probe polymer this warrants further examination of the lower limits of detection available.

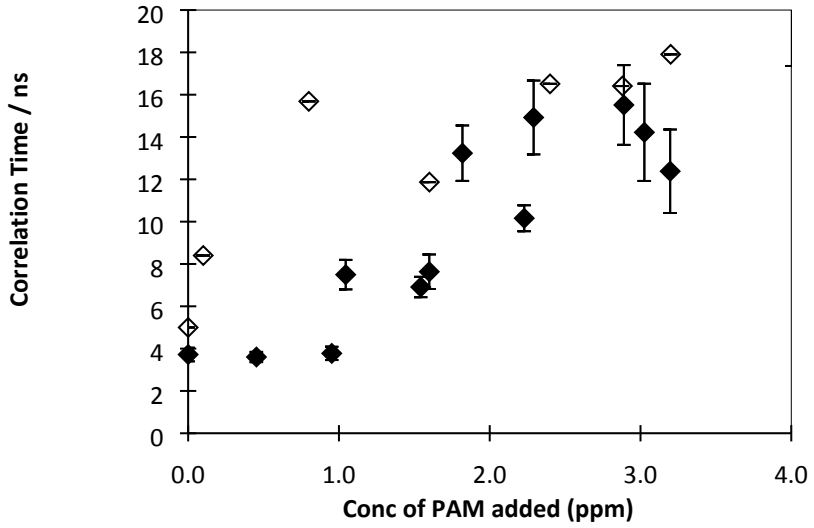

Figure SI6 – Comparison of detectior response of PAM in ultrapure water (Fig. 13) (clear samples) vs detector response of flocculated PAM (Fig. 12) (black samples)

Coagulation Test of Floc Sizes

Visual identification of floc sizes following coagulation of dissolved organic matter (see Fig. 9, 10, 13) were made with reference to a UK industry standard reference chart. Visual comparisons were made at a fixed timepoint to the suspended floc particles and the reference chart copied below.

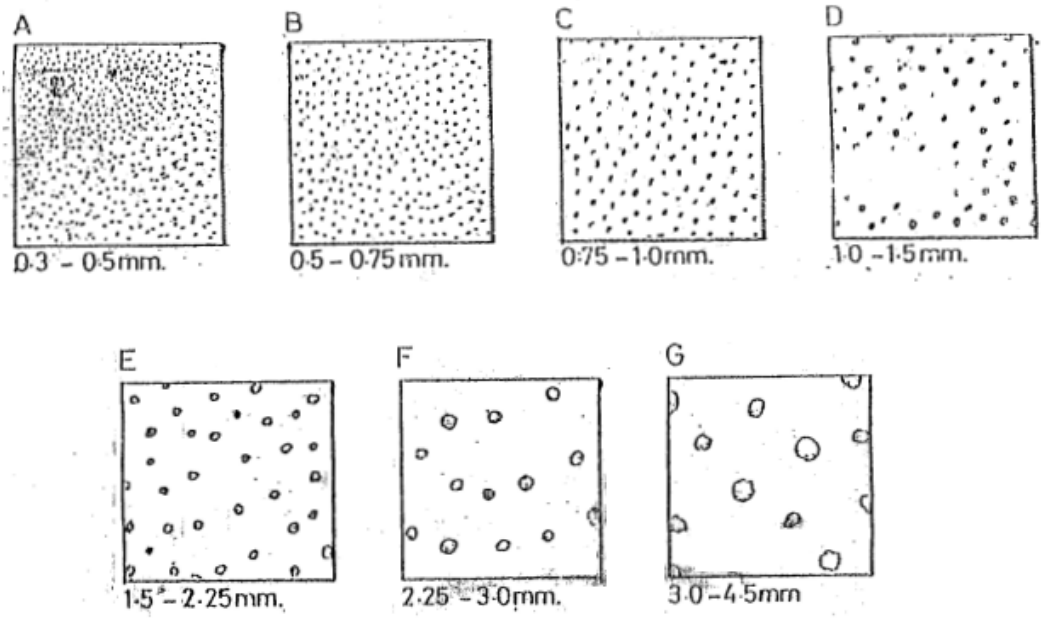

Fig. SI7 – Floc Comparator for the Classification of Floc Produced in Coagulation Tests, kindly supplied by SNF (UK) LTD.

Soil Aggregates

Table SI3 - ICP analysis of Quarry flocculated samples (by ppm) compared to raw effluent, results given in mg l^{-1}.

ppm	Al	B	Ba	Ca	Cr	Cu	Fe	K	Mg	Mn
0	102.00	0.70	0.78	47.10	0.15	0.21	80.00	32.00	15.20	1.17
15	13.20	0.52	0.18	21.20	0.03	0.04	12.70	9.38	3.55	0.13
20	12.40	0.24	0.17	19.20	0.02	0.03	12.40	8.83	3.45	0.13
25	27.70	0.18	0.29	24.80	0.05	0.05	24.40	12.90	5.65	0.30
30	18.30	0.33	0.20	21.90	0.03	0.05	16.00	10.50	4.32	0.18
35	32.10	0.72	0.30	24.60	0.05	0.06	26.80	14.00	6.09	0.32
40	18.60	0.44	0.22	21.60	0.03	0.05	16.90	10.10	4.35	0.19

ppm	Na	Ni	P	Pb	S	Si	Sr	Zn	Ti	V
0	25.10	0.10	3.65	0.65	15.50	216.00	0.24	0.92	5.31	0.24
15	23.40	<0.01	1.15	<0.05	14.70	34.10	0.08	0.13	0.81	0.04
20	23.20	<0.01	1.05	<0.05	14.40	30.50	0.07	0.15	0.75	0.03
25	23.30	0.03	1.55	0.15	14.80	62.50	0.11	0.27	1.56	0.07
30	23.40	0.02	1.20	0.15	14.90	43.50	0.09	0.18	1.03	0.05
35	24.60	0.02	1.65	0.12	15.30	72.50	0.11	0.30	1.69	0.09
40	25.20	0.01	1.30	0.10	15.40	48.10	0.09	0.19	1.14	0.05