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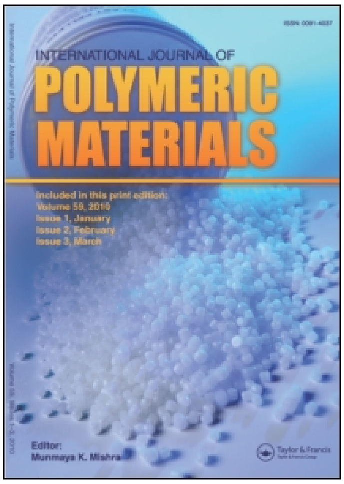

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Degradation and Stabilization of Polyacrylamide

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The thermooxidizing stability of aqueous solutions of polyacrylamide in the temperature range of from 20°C to 70°C in water with different degrees of mineralization containing H_2S and Fe^{2+} is researched. The affect of some of the above-mentioned factors on the change in molecular weight and molecular weight distribution is studied. Some aspects of the mechanism of thermooxidative destruction of polyacrylamide are investigated. To stabilize aqueous polyacrylamide solutions a number of water-soluble antioxidants phenolic, aminophenolic and amine types, metal-deactivator, containing phosphorus, nitrogen and sulfur, are studied. The optimal proportion of components and their total concentration in aqueous solutions is established for composite stabilizers. For aqueous polyacrylamide solutions, containing the most effective stabilizers, rheological characteristics and oil-driving ability are studied in an oil-stratum model. The applications of stabilizers considerably increases the resistance factor, residual resistance factor and oil-driving ability of polyacrylamide solutions.

KEY WORDS Degradation, stabilization, polyacrylamide.

This paper is devoted to the problem of destruction and stabilization of water-soluble polymers used to enhance oil recovery. Today polymer flooding to enhance reservoir oil recovery is used increasingly in the processes of oil production. The polyacrylamide most widely used for this purpose has a number of advantages: high conformance factor coupled with high displacement efficiency, low toxicity, explosion safety and good water solubility. However, in reservoir conditions, polyacrylamide water solutions begin to lose their viscous and viscoelastic characteristics. This phenomenon is caused by a combined effect of several factors during the polymer flooding process: high pressures, high temperatures, shear stresses, dissolved metal salts in water, oxygen, hydrogen sulphide.[1–7]

The viscous and filtration properties (concerning screen-factor values) of commercial polyacrylamide products supplied by foreign companies are presented in Table I. These properties are investigated when storing 0.1% solutions of polyacrylamide in strong brine (90 gpl of NaCl, 20 gpl $CaCl_2$) at 45°C. While storing the solutions for three weeks, especially when adding hydrogen sulphide and iron ions to the solution, a considerable decrease of screen-factor takes place. This may be caused by mechanical, thermal or oxidation-induced destruction of polyacrylamide, by its conformational transformations or by other complicated, little studied changes.

The extraordinary nature of the occurring changes was revealed, for instance,

TABLE I

Screen-factor's change of aqueous solutions of commercial PAA-samples

N	H_2S	Fe^{2+}	PAA-samples	Screen-factor 0 day	Screen-factor 7 days	Screen-factor 14 days	Screen-factor 21 days
1	—	—	PDA-1020	26.29	11.67	7.5	5.90
2	5.0	—	—"—	17.0	18.36	17.06	14.0
3	—	10.0	—"—	23.41	4.47	6.84	5.25
4	5.0	10.0	—"—	14.38	9.57	4.23	4.40
5	—	—	DKS-ORP-40F	54.75	58.09	46.27	35.60
6	5.0	—	—"—	27.88	26.40	44.89	35.50
7	—	10.0	—"—	40.63	14.77	8.04	10.50
8	5.0	10.0	—"—	13.5	7.18	6.40	7.62
9	—	—	CS-35	49.0	53.75	125.34	42.70
10	5.0	—	—"—	22.04	15.82	19.57	22.0
11	—	10.0	—"—	38.09	15.24	6.05	15.60
12	5.0	10.0	—"—	12.90	9.09	8.40	8.60
13	—	—	Accotrol-628	62.44	65.23	60.39	26.40
14	5.0	—	—"—	12.0	5.38	3.05	3.11
15	—	10.0	—"—	52.89	40.50	8.10	5.60
16	5.0	10.0	—"—	42.11	11.50	4.00	4.35

in the course of our study of molecular characteristics of polyacrylamide in water solutions subjected to the effects of temperature and iron ions.

The polyacrylamide solution with molecular mass equal to 8.10^6 is selected as the object of the investigation. The following methods are used to investigate the molecular characteristics:

—Determination of intrinsic viscosity and calculation of molecular mass on the basis of the determined intrinsic viscosity;

—Determination of molecular mass by the absolute method of light diffusion;

—Sedimentation-diffusion analysis and determination of sedimentation constants followed by molecular mass calculation on the basis of these constants.

The intrinsic viscosity and screen-factor variation-in-time relationship for 0.05% solutions in distilled water at 20°C and 45°C in the presence and absence of iron ions is shown in Figures 1 and 2.

The reported data point to a considerable worsening of viscous characteristics of polyacrylamide water solutions under the conditions of temperature increase and in the presence of iron ions.

The molecular mass characteristics of polyacrylamide samples acquired by different methods are presented in Table II. They show good convergence when measured in distilled water at 20°C.

The temperature increase to 45°C and curing of the samples for 28 days lead to considerable decrease of intrinsic viscosity from 14.6 to 3.1, and, consequently, result in substantially underrated molecular mass values which have been calculated by this method.

Molecular mass determination by the absolute method of light diffusion reveals quite a different situation—that of preservation of a constant molecular mass. Similar results are acquired when iron ions are added to the solution. The sedimentometric analysis allows us to distinguish two polymer fractions with the corresponding molecular mass values of $3-5.10^6$ and $23-20.10^6$. This permits us to

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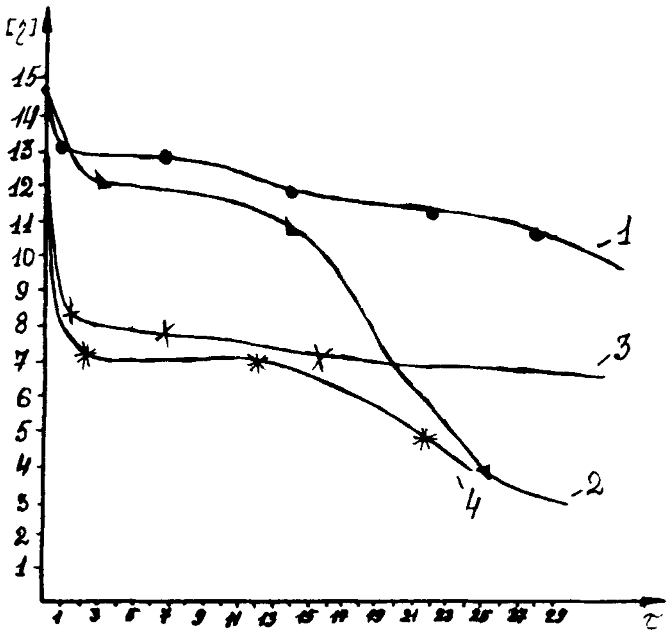

FIGURE 1 Change of PAA-viscosity by the storage. (1) PAA-solution in distillate water, t = 20°C. (2) PAA-solution in distillate water, t = 45°C. (3) PAA-solution in distillate water +10 mg/l Fe^{3+}, t = 20°C. (4) PAA-solution in distillate water +10 mg/l Fe^{3+}, t = 45°C.

suggest the proceeding of both partial polymer chain destruction and cross-linking processes.

As to enhanced oil recovery conditions, under the influence of the affecting factor, there may proceed other, more complex, structural changes in the polymer which result in a worsening of the viscosity characteristics of its water solutions. It is known that under the conditions of oxygen deficiency these processes are substantially inhibited, while in the presence of iron ions their rates accelerate. This indicates the proceeding of oxidizing processes which are catalized by metals.

In this respect, it is of particular interest to investigate water-soluble antioxidants and their compositions with metal deactivators for polyacrylamide stabilization.

To solve this task, several water-soluble antioxidants of phenolic, aminophenolic and amine types are synthesized and selected from a number of market-grade products. The polyacrylamide solution at 0.06% mass concentration, prepared on water model containing 124.6 gpl NaCl, 11.4 gpl $CaCl_2$, and 11.4 gpl $MgCl_2$, is selected as the object of the investigation.

The stabilizers' efficiency is estimated on the basis of measured screen factor and viscosity variations of stabilizer containing polyacrylamide water solutions while storing them at 25°C subjected to the effect of hydrogen sulphide and iron ions, as well as to their combined effect. Stability factors K_{st} and K'_{st} are selected as criteria to assess the stabilizers' efficiency:

$$K_{st} = \frac{S_{f_{st}}}{S_{f_{PAA}}}, \qquad K'_{st} = \frac{S_{f_{st}}}{S'_{f_{PAA}}}$$

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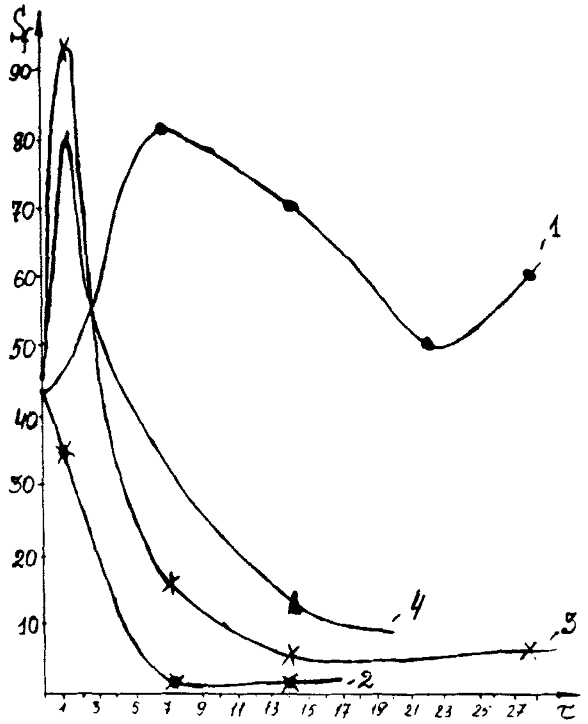

FIGURE 2 Change of PAA-screen-factor by the storage. (1) PAA-solution in distillate water, t = 20°C. (2) PAA-solution in distillate water, t = 45°C. (3) PAA-solution in distillate water +10 mg/l Fe^{3+}, t = 20°C. (4) PAA-solution in distillate water + 10 mg/l Fe^{3+}, t = 45°C.

TABLE II

Determination of molecular weight of polyacrylamide by different methods

N	t, °C	Fe^{3+}	M_η $[\eta] = 7.9 \times 10^{-5} M_\eta^{0.76}$	M_w	M_s $S_0 = 2.4 \times 10^{-15} M_s^{0.42}$	$M_{\eta s}$ $M_{\eta s}^{2/3} = \frac{\sqrt[3]{[\eta]} \cdot \eta_0 \cdot RS_0}{(1 - \nu\rho_0) \cdot A_0}$
1	20	—	$\tau = 0$ $\eta = 14.6$ $M_\eta = 8.5 \times 10^6$	$\tau = 0$ $M_w = 7.4 \times 10^6$	$\tau = 0$ $S_0 = 19.3 \times 10^{-13}$ $M_s = 8.27 \times 10^6$	$\tau = 0$ $\eta = 14.6$ $S_0 = 19.3 \times 10^{-13}$ $M_{\eta s} = 8.54 \times 10^6$
2	45	—	$\tau = 28$ $\eta = 31$ $M_\eta = 1.1 \times 10^6$	$\tau = 28$ $M_w = 8.84 \times 10^6$		
3	20	10	$\tau = 16$ $\eta = 7.0$ $M_\eta = 3.2 \times 10^6$		$\tau = 16$ $S_0' = 15.5(2/3)$; $M_s' = 4.9 \times 10^6$ $S_0'' = 29.8(1/3)$; $M_s'' = 23.10^6$	$\tau = 16$ $\eta = 7.0$ $M_{\eta s}' = 5.4 \times 10^6$ $M_{\eta s}'' = 15 \times 10^6$
4	45	10	$\tau = 12$ $\eta = 7.0$ $M_\eta = 3.2 \times 10^6$	$\tau = 12$ $M_w = 5.43 \times 10^6$		

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where $S_{f_{st}}$ is the screen factor for the polyacrylamide solution in the presence of the stabilizer, iron ions and hydrogen sulphide, $S_{f_{PAA}}$ is the same, but in the absence of the stabilizer, $S'_{f_{PAA}}$ is the same, but in the absence of the stabilizer, iron ions and hydrogen sulphide.

The results of the study are presented in Table III. As can be seen, some antioxidants significantly improve the viscous and viscoelastic properties of polyacrylamide brine solutions affected by hydrogen sulphide and iron ions.

Table IV presents the results of the study of antioxidant and metal deactivator compositions that display high performance efficiency. An optimal ratio of components is determined for these compostions. As an example, the results of this study are shown in Figure 3. It is seen that addition of some metal deactivator to the stabilizer enables us to improve its performance significantly.

For the most efficient compositions, relationship of stability factor to storage time is determined. An example of such a relationship is shown in Figure 4.

TABLE III

Efficiency of antioxidants by the stabilization aqueous PAA-solutions

	One day		One week	
Stabilizer	K_{st}	K'_{st}	K_{st}	K'_{st}
PK	0.797	0.982	0.031	0.038
FPK	0.663	0.817	0.030	0.037
GH	0.279	0.334	0.032	0.039
KF_k	0.884	1.065	0.839	1.075
FK	0.654	0.806	0.621	0.076
M-3	0.400	1.640	0.230	0.734
PA-1	0.530	1.430	0.321	0.564
AN	1.078	1.328	1.045	1.289
D	0.977	1.204	0.933	1.15
FD	1.66	2.340	0.630	1.10
AOM	0.703	0.838	0.549	0.754
SOM	1.101	1.313	0.864	1.187
OOM	0.980	1.169	0.922	1.267
ADOM	0.26	0.725	0.10	0.389
AM	0.707	0.843	0.639	0.878
F-16	0.458	0.547	0.423	0.581
	0.330	—	0.03	—

TABLE IV

Efficiency of the composition of antioxidants with metal deactivators by the stabilization of aqueous PAA-solutions (10 mg/l Fe^{2+}, 5 mg/l H_2S)

AO	MD	AO:MD	K'_{st}	K_{st}
AN	TG	5:1	1.76	0.85
AN	LG	5:1	1.35	0.69
AN	GMD	5:1	1.73	0.88
D	TG	5:1	2.12	1.01
D	EDTA	5:1	1.65	0.79
D	LG	10:1	2.59	0.92
FD	TG	5:1	2.97	0.98
FD	LG	10:1	3.30	0.90
	TG	5:1	1.79	0.90

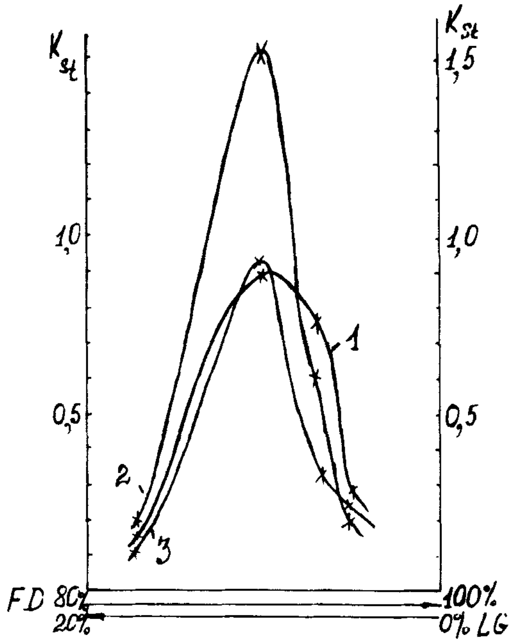

FIGURE 3 Influence of proportion of stabilizer-components on the stabilizer-efficiency. (1) In one day. (2) In 3 days. (3) In 7 days.

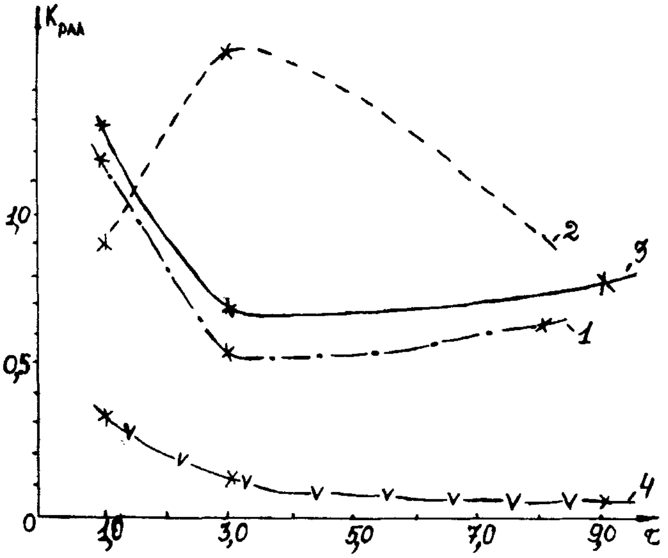

FIGURE 4 Efficiency of composite stabilizers by the storage of aqueous PAA-solutions. (1) FD : TG = 4 : 1. (2) FD : LG = 10 : 1. (3) FD : TG = 5 : 1. (4) PAA.

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TABLE V

Influence of filtration properties of aqueous PAA-solutions with composite stabilizers (10 mg/l Fe^{2+} · 5 mg/l H_2S)

Composite stabilizer	Proportion AO:MD	R_r	R_{rr}
Without stabilizer	—	5.0	1.5
D + TG	4:1	6.3	2.5
AN + GMD	4:1	5.8	1.3
NaFK + TG	4:1	6.1	2.8

R_r is the resistance factor.
R_{rr} is the residual resistance factor.

The data presented show that antioxidant composition containing metal deactivators may, at optimal component ratios, significantly improve the polyacrylamide stability in an aggressive environment for long storage periods.

Additionally, investigations are carried out to study filtration properties of polyacryamide water solutions in the presence of most effective compositions. The results of these investigations are presented in Table V.

The data presented reveal good filtration properties of all the compositions studied.

Thus, it has been found that in polymer flooding conditions polyacrylamide water solutions lose their viscous and viscoelastic characteristics which, however, can be significantly improved by adding antioxidant and metal deactivator compositions to the solution.

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References

1. W. Nagashira and T. Tsukoda, Degradation of polyacrylamide molecules in aqueous solutions by high-speed stirring, *J. Appl. Polym. Sci.*, **21**(4), pp. 1149–1153 (1977).
2. B. P. Makagon, M. M. Povelko, T. A. Bodnarenko, *et al.*, Influence of macromolecular conformation on hydrodynamic effectiveness of polyacrylamide. *IFZh*, **51**(1), pp. 47–52 (1986).
3. G. Müller, Thermal stability of polyacrylamide solutions, *Polymer Bulletin*, **5**(1), pp. 31–37 (1981).
4. R. G. Ryles, Chemical stability limits of water-soluble polymers used in oil recovery processes, *SPE*, **13585**, pp. 389–404 (1985).
5. W. M. Leung, D. E. Axelson and J. D. Van Dyke, Thermal degradation of polyacrylamide and poly(acrylamideoco-acrylate), *J. Polym. Sci., Part A., Polym. Chem.*, **25**, pp. 1820–1846 (1987).
6. D. K. Ramsden and K. McKay, Degradation of polyacrylamide in aqueous solution induced by chemically generated hydroxyl radicals. Part I. Polymer degradation and stability, **14**, pp. 217–229 (1986).
7. S. L. Willington, Biopolymer solution viscosity stabilization. Polymer degradation and anioxidant use, *Soc. Petrol. Eng. J.*, (SPE), p. 901, December (1983).