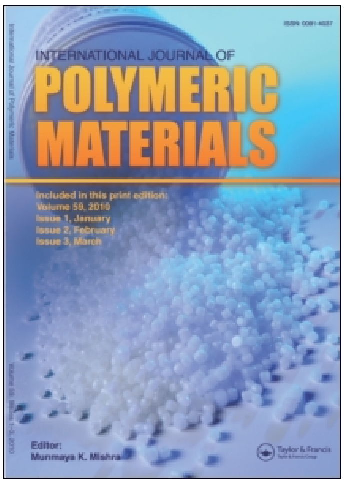

**International Journal of Polymeric Materials**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713647664

# Degradation and Stabilization of Polyacrylamide in Polymer Flooding Conditions

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**To cite this Article** Tolstikh, L. I. , Akimov, N. I. , Golubeva, I. A. and Shvetsov, I. A.(1992) 'Degradation and Stabilization of Polyacrylamide in Polymer Flooding Conditions', International Journal of Polymeric Materials, 17: 3, 177 — 193
**To link to this Article: DOI:** 10.1080/00914039208041113
**URL:** http://dx.doi.org/10.1080/00914039208041113

*Intern. J. Polymeric Mater.*, 1992, Vol. 17, pp. 177–193
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Printed in the United Kingdom

# Degradation and Stabilization of Polyacrylamide in Polymer Flooding Conditions

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*(Received November 17, 1991)*

This review presents some aspects of mechanical, thermal-oxidative and biological degradation of polyacrylamide in aqueous-saline solutions and methods of its prevention.

KEY WORDS Polyacrylamide, degradation, stabilization.

From the large number of water-soluble polymers, high molecular weight polyacrylamides, polyethylene oxides and polysaccharides (including xantanic resins) may be used as mobility control agents for water injected in the reservoir for stimulating oil production processes.

Employing polymer flooding for enhancement of oil recovery, has major advantages, but also considerable drawbacks. One of such drawbacks is the lack of stability in viscous and viscoelastic properties of water-soluble polyacrylamides (PAA) caused by the polymer flooding conditions when PAA macromolecules are subject to mutual effect of temperatures, pressures, shear stresses, water-dissolved salts, oxygen, hydrogen sulfide as well as bacterial action. Most common obvious results of such effects are, reduced viscosity of PAA solutions, decline in their performance properties, reduced efficiency of polymer flooding in enhancement of oil recovery. Views of investigators concerning the problem of PAA degradation in different conditions are quite contradictory and in most part based on speculative conclusions often insufficiently confirmed by experimental data.

## MECHANICAL DEGRADATION OF PAA

Mechanical degradation of PAA significantly affects filtration characteristics of PAA solutions resulting in their substantial deterioration[1] and in reduced efficiency of polymer flooding, especially in heterogenous reservoirs. Irreversible changes in the structure of PAA macromolecules are induced by mechanical loads on the stage of PAA production (drying and cutting) as well as on the stage of its practical application (stirring during the preparation of PAA aqueous solutions, injection into the reservoir, and movement in porous medium).

Mechanical or shear-induced degradation tendency of partially hydolyzed PAA is a serious problem which determines the possibility of its extensive application in the secondary and tertiary processes of oil production.

Mechanical degradation of polymer solutions takes place in the cases when fluid stresses which develop in the process of deformation or plastic flow become sufficiently high to destroy the polymer molecular chain.[2-5] It has become a common opinion that the chain breakage is induced by shear stresses in laminar shear flow or in turbulent intracapillar flow.

The obtained results,[3] however, testify that degradation of viscoelastic polymer solutions in capillary tubes is caused primarily by high tensile or normal stresses which occur at the capillary inlet. Such stresses occur as a consequence to unsteady Langrange's flow or longitudinal deformation at the capillary inlet.[6]

The flow through porous media induce as well the velocity fields which are, according to Langrange's concept, unsufficiently stable to allow to suggest the presence of high viscoelastic normal stresses.[7,8]

It has been proposed[9] that degradation of partially hydrolyzed PAA solutions in porous media is caused by significant viscoelastic normal stresses, mainly, in longitudinal deformation zones. The degree of mechanical degradation increases as function of growth of rate and dimensionless length of the flow and as function of permeability reduction of the reservoir around the well bore. Additionally, it is pointed that mechanical degradation, obviously, does not practically depend on the PAA concentration in the range of 300–600 mg/l in aqueous solutions when the total concentration of dissolved solids equals 3.0–3.3%. It is also stated that typical conditions of injection of PAA solutions into the reservoir may lead to large losses in mobility of oil-displacing fluid. Any physical changes in the well bore geometry which enlarge the sand bottom area will lessen the degree of mechanical degradation.

The possible means to reduce mechanical PAA degradation by improving the technology of preparation and injection of PAA solutions in the oilfield are discussed in the paper.[10]

Investigations of polyacrylamide degradation (degree of hydrolysis, 20%; mol mass, $10^7$) while stirring by a double-arm stirrer revealed[11] that at rates of 4000 l/min and beyond the polymer in the solution (0.05%) degraded rapidly (the screen factor decreases 6 times and more), while at stirring rate of 2000 l/min the screen factor decrease after 5 minutes of stirring equaled 50%. It was shown that the process of PAA solution degradation as influenced by stirring could serve as a model of mechanical degradation processes for PAA solutions in porous medium. On this base a method was proposed for the assessment of the basic technological qualities of PAA solutions which accounted for the mechanical degradation consequences.

The paper[12] also presents results of investigations of mechanical stirring influence on PAA aqueous solution stability (mol mass, $7.91 \times 10^6$; concentration in the solution, 0.5% mass; stirrer's rate, 25 rps). In experimental conditions the molecular mass of the PAA decreased to $1.34 \times 10^6$.

The paper[13] disclosed data on the results of investigation of the PAA mechanical degradation impact on the efficiency of oil displacement in conditions of a heterogenous reservoir model. A 0.1-percent aqueous solution of PAA with molecular mass 10 mln. and hydrolysis degree 16% was used in the experiments. The data were given which indicated substantial reduction in ultimate oil recovery growth rate caused by the polymer degradation as compared to conventional flooding. Especially inefficient the degraded PAA solution was in tight formation layers. In the same paper[13] the authors proposed a means of "salt addition" to PAA solutions using alkali salt to increase their resistance to mechanical degradation. The authors hold the opinion that reduction of the size of the PAA macromolecules and their elastic reversible deformability in mineralized solvents reduce the probability of mechanical destruction of the polymer. Additionally, the degree of oil recovery increases by 16%, t.i. two times more than that when the degraded PAA solution is used.

A number of latest papers is dedicated to study the stability of PAA aqueous solutions in hydrodynamic field. Conclusions drawn by different authors are quite contradictory. Partially this can be explained by variations in experimental methods of investigation. The authors[15-17] who used viscometry and gel permeation chromatography (GPC) techniques considered that reduction of intrinsic viscosity and the GPC-curve displacement pointed to breakage of polymer molecules under the influence of hydrodynamic forces. However, the viscosimetry and GPC techniques provide information concerning effective hydrodynamic volumes but not molecular mass data. Since direct methods of molecular measurement have not been employed, conclusions about the destruction of the PAA macromolecules are not convincing[18] and the results obtained may as well be explained by a change in conformation of macromolecules and their association. Meantime, under the influence of hydrodynamic field, other physical/chemical transformations, besides degradation, up to phase separation[19,20] may take place. As described in the paper,[18] investigations have been performed on a commercial linear PAA sample with molecular mass, determined by sedimentation, $M_s = 4.5 \times 10^6$ and hydrolysis degree equal to 26%. The PAA solution concentrations varied from 0.005 to 0.01%. High-speed stirring of the PAA solutions was performed in the thermostatically controlled chamber at temperature 30°C. Viscosity of solutions was measured using the viscosimeter VPJ-1 with the capillary diameter $0.34 \times 10^3$ m. Macromolecule conformation of the hydrolysis PAA, considered as polyelectrolyte, was changed by varying the medium pH value. The least sizes the PAA molecules had in acidic medium. The higher pH resulted in increase of the number of ionized carboxyl groups, and the macromolecules grew in size affected by electrostatic interactions. At high pH the charged carboxyl groups were screened by sodium counter ions and macromolecules to some extent decreased in size. Relative changes in macromolecule sizes were judged from the reduced viscosity of diluted solution since it was not possible to determine intrinsic viscosity because of polyelectrolytic effects during nonisoionic dilution.

The authors of the paper[14] conducted a comparative study of different methods used to assess the degree of mechanical degradation and came to the conclusion that the most valuable information about the proceeding processes could be acquired by determining the molecular-mass distribution using the high-rate sedimentation method.

Application of absolute methods of molecular mass determination such as sedimentation in conjunction with diffusion and light scattering, is substantially complicated by the low concentration of initial solutions, macromolecule aggregation, etc. Nevertheless, the comparative study conveyed using the light scattering method for solutions before and after the exposure to hydrodynamic field permitted to draw the conclusion that polymer degradation in hydrodynamic field was not the critical factor that determined the hydrodynamic PAA solution instability. The assumption was made that under the influence of hydrodynamic field the thermodynamic affinity between the polymer and the solvent deteriorated and that, in turn, promoted creation of intra- and intermolecular polymer-polymer bonds. That leads to conformation freezing and reduction in size of separate macromoleules as well as to their aggregation. These views are more developed further in the paper.[21]

Intramolecular interactions in the form of electrostatic forces and hydrogen bonds change not only the size and the shape of macromolecules but also their deformability when subject to hydrodynamic field. Experimental data reviewed in this and other[22,23] papers testify that at equal degree of polymerization the more stable in the hydrodynamic field are the largest size macromolecules, although this contradicts with the obvious belief that the breakage of macromolecules would proceed the easier the larger are the polymer tangles.

The paper[24] is devoted to the investigation of the degradation mechanism of polyethylene oxide and polyacrylamide aqueous solutions in hydrodynamic field. The acquired experimental data provide additional information in favour of the view that the PAA solution instability in hydrodynamic field is not associated with molecular mass reduction and may be explained by generation of intermolecular cross-links of chemical or physical nature. Chemical changes suggest homolytic breakage of bonds in macromolecules associated with generation of macromolecules which enter into further chemical reactions. The presence of free macroradicals during stirring of polymer solutions was confirmed using the radical trap technique. The acquired experimental data showed that, in case of polyethylene oxide, one radical was gene-rated per 40 polymer links. In case of polyacrylamide in similar conditions of stirring, one PAA macroradical was generated per 12 monomeric links. That means that PAA generates more macroradicals than polyethylene oxide. This is explained by the possible stabilization of the generated radicals owing to combination with the carboxyl group. However, to generate such a large number of radicals, the macromolecules would destruct to molecular mass of about $(1-2) \times 10^3$ while the determined experimental values of hydrodynamic efficiency and intrinsic viscosity correspond to substantially higher mass values ($10^6$). Earlier light scattering data[18] testify that molecular mass of polymers in such conditions does not lower. In this respect, the authors suggest that such a large number of radicals was generated mostly by the process of breaking hydrogen off the carbon chain. The generated macroradicals would stabilize by secondary recombination and disproportionation reactions or reactions with acceptors. The latter could be represented by oxygen or stable radicals used in the radical trop technique (2,2, 6,6-tetramethylpiperidyl-1-oxyl).

As a result of disproportionation reaction and interaction of two macroradicals, one of them is oxidized producing a double bond while the other is reduced. Double bonding is energetically advantageous for the case of PAA because of its combination with the amidic fragment's carboxyl group. These transformations may be inter- and intramolecular, as a consequence of the radical's migration in the chain. Presence of double bonds in the macromolecular PAAs is conformed by qualitative reactions with aqueous solutions of $KMnO_4$, bromine and $AgNO_3$. Crosslinkage resulting from the recombination reaction leading to reduction in size and flexibility of macromolecules and causing steric complications in the process of interaction of macromolecule polar groups with solvent molecules is confirmed by indirect data of the light scattering experiments. Crosslinkage may serve as an explanation to dehydration of polyethylene oxide and PAA macromolecules in hydrodynamic field identified by the ultraviolet spectroscopy and ultraacoustic methods. "Crosslinking" of PAA molecules under the action of oxidation-reduction systems and metal salts may be used as a method of improving the resistance of the polymer to mechanical degradation (in cases of real breakage of the chain). However, it should be born in mind that "crosslinking" may have negative effect from the point of view of enhancing oil recovery.

To prevent mechanical PAA degradation, the so called method of "salt adding" to the hydrolyzed PAA solutions using sodium chloride is proposed.[25,26] Results of the assessment of this method tested under conditions of the Sosnovskoye field are given in the report.[27] The major effect of adding salt to polymer solution reveals an increase of the residual resistance factor as water injection is resumed when gradual sodium chloride removal results in "swelling" of the absorbed macromolecules.

## THERMAL-OXIDATIVE DEGRADATION OF PAA SOLUTIONS

In dry condition polyacrylamide is relatively stable, its degradation is accompanied by nitrogen generation and cross-polymerization at adequately high temperatures.

The study of thermal degradation of dry and hydrolyzed polyacrylamides[28] led to the conclusion that polymer destruction resulting in molecular mass reduction and structural modification was observed at temperatures beyond 120°C. It should be noted that in the temperature range of 220–335°C polyacrylamide is typically inclined to imidization reactions which follow the process of nitrile generation; to a lesser extent, typical in these conditions are dehydration reactions; generation of imides, nitriles, and C=C bonds takes place. At temperatures beyond 335°C the essential reactions include splitting of imides and amino-groups, splitting of the basic carbon chain, nitrile generation.

As to hydrolyzed polyacrylamide, the essential reactions in the temperature range of 220–320°C are imidization and dehydration of amido-groups, generation of imides, nitriles and isocyanides; at the same time the carbonyl-groups in the acid and amide fragments are preserved. In the temperature range 320–400°C the essential reactions are splitting of imides and amido-groups while the carboxy group disappears from the amide fragments but still remains present in the acid fragments.

At temperatures beyond 400°C the essential reactions include final decarboxylation of the acid fragments and breakage of the basic polymer chain.

PAA degradation in aqueous solutions during storage has been revealed quite long ago.[29] The authors postulated that the PAA molecular tangles in fush solution are mutually interlaced and that the reason of viscosity reduction during ageing of solutions is the following unlacing of the tangles but not their chemical transformations or the intramolecular bond breaking which are accompanied by molecular mass reduction. Kulike, W.-M. and Klein, G.[30] also neglect the molecular mass reduction as provoked by PAA degradation and explain the viscosity reduction as a result of changes in macromolecule conformation owing to the formation of intramolecular hydrogen bonds. On the contrary, in the paper [31] the viscosity reduction is explained as a result of the PAA molecular bond breakage in the weak points.

Existence of quick and slow PAA ageing stages may be also explained by narrowing of molecular-mass distribution during statistical degradation of the polymers. As to PAA, this is shown in the papers[32,33] where the authors have studied the kinetics of PAA degradation in the presence of potassium persulfate using the viscosimetry technique.

This method permits to calculate the mean number of macrobond breaks. As shown in the paper,[34] the curve of the inverse mean numerical molecular mass value as function of degradation time represents a straight line with a slope that determines the degradation content. Assuming that the equation of Marc-Kuhn-Hauvink is known for the polymer system studies, which ties the values of intrinsic viscosity and molecular mass, the number of breaks may be determined using the formula:

$$S = \frac{\bar{M}n(o)}{\bar{M}n(y)} - 1 = \left(\frac{[\eta]o}{[\eta]g}\right)^{1/\alpha} - 1$$

where $[\eta]o$, $[\eta]g$ = the intrinsic viscosity values for the solution before and after degradation; $\alpha$ = Marc-Kuhn-Hauvink's constant.

This equation is applicable if molecular-mass distribution does not change during the degradation process.

$$\frac{\bar{M}y(o)}{\bar{M}y(g)} \approx \frac{\bar{M}n(o)}{\bar{M}n(g)}$$

Haas, H. C. and McDonald, R. L.[35,36] also explained macrobond degradation by the action of traces of the initiator $K_2S_2O_8$ which is often used when producing PAA and microorganisms multiplying during storage of solutions. In papers[37–39] it is noted that during prolonged storage in the presence of the bactericide $NaN_3$ the viscosity of PAA aqueous solutions does not decrease.

Tests on samples of solution of the linear polyacrylamide with molecular mass $8.4 \times 10^6$ which did not contain $K_2S_2O_8$ and was prepared in bidistillate showed that they remained unchanged for 62 days without any bactericidal additives.[40]

Presence of dissolved oxygen is the most critical factor negatively affecting the stability of PAA solutions. It is suggested that oxygen acts as a specific initiator of reaction of the free radical with residues of different reducers also present in the solution.

It has been shown in the paper[43] that reduction of dissolved oxygen concentration from 5 to 1.2 mg/l markedly lowers degradation at temperatures 30° and 70°C (Figure 1).

Quite opposite results have been acquired by Knight, B. who studied the impact of oxygen on the PAA solution stability in freshwater at 50°C.[41] The PAA solutions were prepared in water with unseparated oxygen and were stored in oxygen-free medium at 50°C. Viscosity, screen-factor and the value of pH were measured at different times in oxygen-free and ambient air media. Measurement results did not show any major variations in the values (Figure 2).

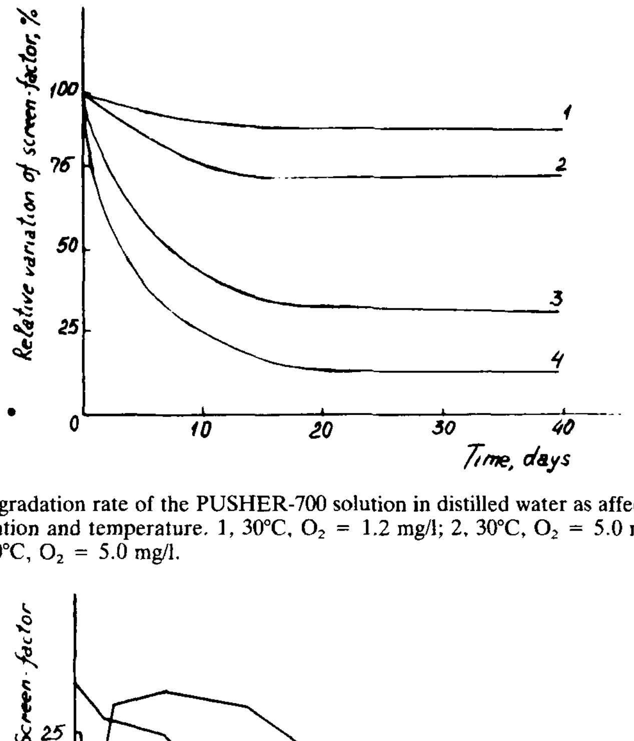


FIGURE 1 Degradation rate of the PUSHER-700 solution in distilled water as affected by dissolved oxygen concentration and temperature. 1, 30°C, $O_2$ = 1.2 mg/l; 2, 30°C, $O_2$ = 5.0 mg/l; 3, 70°C, $O_2$ = 1.2 mg/l; 4, 70°C, $O_2$ = 5.0 mg/l.

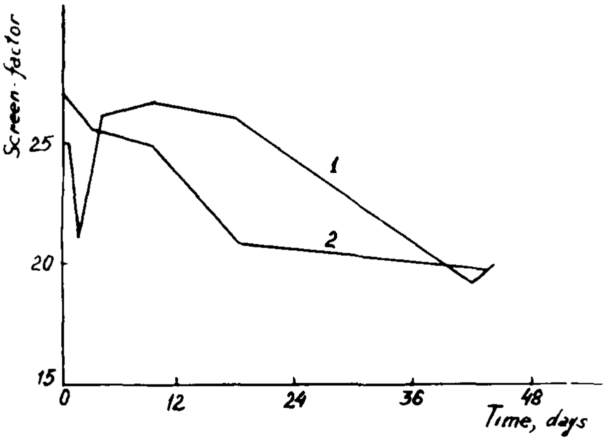


FIGURE 2 Degradation rate as affected by storage condition of PAA solutions at 50°C. 1, storage in nitrogen medium; 2, periodic exposure to air.

Similar results were obtained by Matide Ceisi.[42] Investigations of polyacrylamide degradation in aqueous solution revealed that at first viscosity sharply decreased and after that slow-down of degradation rate took place. Essentially, this process is similar both in oxygen and nitrogen media.

In the papers[44–46] it was noted that laboratory samples purified from residual impurities remained stable in presence of oxygen and at high temperatures. On the contrary, commercial samples containing residual impurities, when exposed to oxygen and high temperatures, rapidly degraded with substantial reduction in molecular mass.

When laboratory experiments are carried out at low concentrations of dissolved oxygen, serious difficulties arise in storing the solutions. Many papers describe the efforts made to achieve the zero level of oxygen content using various methods. Many of them did not prove to be efficient. Most promising results were obtained by those authors[47] who utilized soldered ampules in combination with antioxidizer and used the glove-box vented by extra pure nitrogen. Residual concentration of oxygen was $10^{-3}$ mg/l. Reproducibility of experiments appeared to be excellent. Similar methodology was used in experiments described in the paper.[48]

It is observed that increase in temperature causes acceleration of degradation rate accompanied by worsening of viscous and, especially, viscoelastic properties of polymer solutions. In the paper [49] the reaction of polymer oxidation by dissolved oxygen resulting in degradation of the polymer is viewed as the first-order reaction where the measure of degradation rate is represented by the so called half-life period, t.i., the time of two-fold decrease in the screen-factor value of the polymer solution. The most rapid polymer degradation is observed in the temperature range of 40–55°C. However, in some fields (Mishkinskoye field, the "Udmurtneft" Production Association) terpolymer flooding is conducted injecting 0.1% PAA solution heated to 80–90°C into the formation. Laboratory investigations performed on samples of polyacrylamide, grade PDA-1020, with hydrolysis degree 15% and molecular mass $9 \times 10^6$, in solutions containing 0.5–7.8 mg/l of dissolved oxygen and aged at 55°C for 7 days, revealed high degradation of polymer resulting in screen-factor decrease and deterioration of filtration properties of the PAA solution.

In the paper[50] results are presented testing thermaloxidative degradation of partially hydrolyzed PAA in aqueous solutions in the temperature range from 30° to 60°C. Changes in technological properties were assessed by screen-factor variations. 67% of polymer's initial activity were lost at temperature 30°C in 30 days while at temperature 60°C the efficiency of polymer solution decreased to zero in 10 days.

Investigation of the effect of temperature and pressure on viscosity of PAA solutions[51] revealed that increase of pressure in the range of 0.1–20 mPa followed by decrease to 0.1 mPa did not greatly affect viscosity of polymer solutions while increase of temperature from 20 to 60°C led to viscosity reduction by more than 50%. Most significantly temperature affected PAA solutions of lower concentrations with higher pH values (Table I).

Tests at higher temperatures, as shown in the paper,[43] lead to full destruction of polyer in 40 days at temperature 100°C and in 12 days at temperature 130°C, in spite of the fact that dissolved oxygen content did not exceed 1 mg/l. Mungan, N.[52]

TABLE I

Thermal degradation values for different PAA grades (temperature = 20–60°C)

| Pressure, mPa | Thermal degradation values, % | | | | | |
|---|---|---|---|---|---|---|
| | Accotrol-623 | | DKS-OKPF-49NT | PDA-1020 (conc. in sol. = 0.1%) | | |
| | conc.in sol.,% | | conc.in sol.,% | solution pH | | |
| | 0.1 | 0.3 | 0.1 | 4 | 6.5 | 8.5 |
| 0.1 | 6.70 | 3.85 | 9.96 | 4.90 | 13.10 | 32.50 |
| 10 | 15.80 | 3.83 | 9.70 | 4.80 | 13.00 | 33.50 |
| 15 | 16.40 | 4.15 | 10.10 | 4.75 | 12.80 | 35.60 |
| 20 | 16.40 | 4.85 | 10.20 | 4.25 | 12.40 | 35.70 |
| 0.1 | 14.60 | 4.65 | 9.10 | 4.90 | 12.60 | 37.00 |

showed that PAA solutions at temperature 135°C degraded in absence of oxygen in just 6 hours.

The authors[52] hold the view that thermal PAA degradation begins at 121°C and essentially is completed at 149°. Since in most cases PAA use temperature does not fit this range, such form of degradation presents no practical interest.

When studying the effect of temperature on stability of commercial PAAs, Müller, G.[44] concluded that increase of temperature could have a double effect:

1. Molecular mass, which strongly depends on presence of oxygen and residual impurities, decreases;
2. Degree of hydrolysis of amido groups increases.

The negative effect of salt components of natural waters on visous characteristics of PAA solutions during long-term storage at elevated temperatures is predominantly associated with increase in degree of hydrolysis of amido groups and precipitation of polymer in presence of calcium and magnesium salts. Many authors[53-56] have studied the effect of cations $Ca^{2+}$ and $Mg^{2+}$ on stability of PAA solutions. In this respect, the paper[53] deserves special attention. It points that in absence of oxygen polyacrylamide solutions remain stable at 90°C for 20 months. However, in real conditions, along with elevation of temperature, amido groups are to a growing extent subject to hydrolysis. That results in increase of carboxyl group content in polymer which, in its turn, affects solution properties, particularly, because hydrolyzed polyacrylamide interacts very intensively with bivalent metal ions $Ca^{2+}$ and $Mg^{2+}$. This interaction may lead to gelation and even precipitation of polymer at adequately high content of Ca and Mg salts in the solution. At the same time, it is noted that dissolved NaCl inhibits formation of polymer-bivalent cation complexes and their precipitation. The results of investigations permitted to draw the conclusions that at temperatures exceeding 70°C, when hydrolysis process of amido groups proceeded quite intensively, polyacrylamide could be used at less than 200 ppm concentration of Ca ions. At 50°C hydrolysis of polyacrylamide proceeded so slowly that PAA solutions remained stable for a long period regardless of composition and content of dissolved salts. In the temperature range of 60–70°C solution stability is determined by polymer's molecular mass, by concentration of bivalent ions, and by duration of storage. Reproduced on figures are plots of changes in viscosity of PAA saline solutions as function of time and temperature (Figures 3 and 4), and as function of degree of PAA hydrolysis (Figure 5).

Negative effect of hydrogen sulfide and ferric salts, found as components of different natural waters, on technological properties of polymers is currently quite a complicated problem.

The mechanism of hydrogen sulfide effect on PAA solutions is not yet clear, but there are indications that $H_2S$ in amounts exceeding 0.9 mg/l provokes dete-

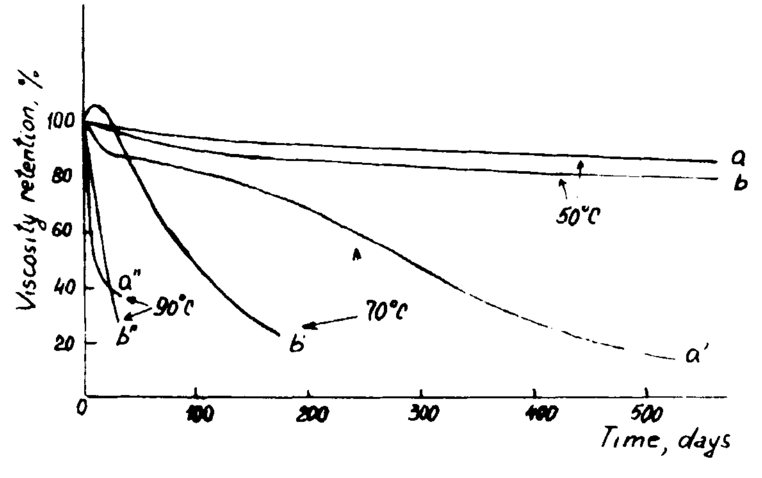


FIGURE 3 Thermal stability of PAA in 9.0% NaCl, 1.0% $CaCl_2$. a, a', a'', polyacrylamide A; b, b', b'', polyacrylamide B.

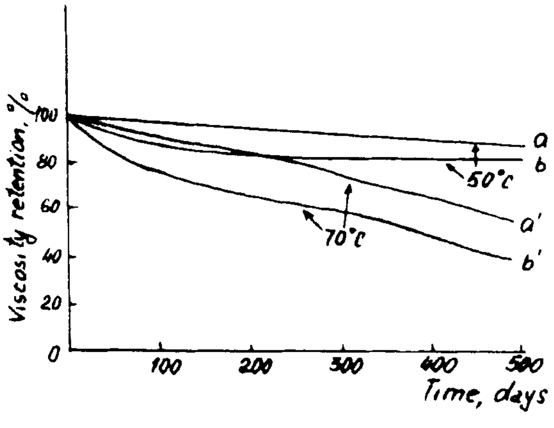


FIGURE 4 Thermal stability of PAA in 9.0% NaCl, 0.856% $MgCl_2$ (polymer concentration 2000 ppm). a, a', polyacrylamide A; b, b', polyacrylamide B.

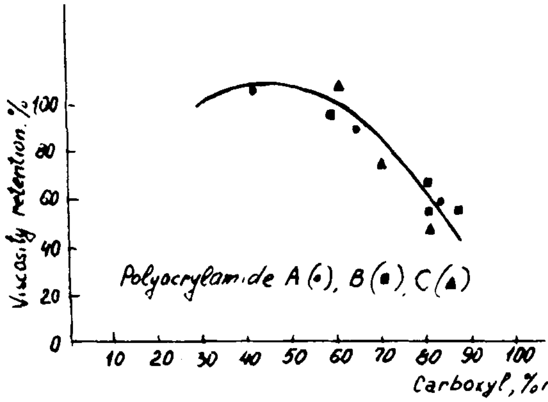


FIGURE 5 Thermal stability of PAA as a function of hydrolysis at 90°C in 2.0% NaCl, 200 ppm $Ca^{++}$ (polymer concentration 1000 ppm).

rioration of viscous properties of polymers. This, however does not give ground to consider that as polymer chain breakage. Perhaps, this is the process of change in conformation of PAA macromolecules and elevation of degree of hydrolysis at changing of the solution pH.

The reason of changes in polyacrylamide solution properties as affected by temperatures and dissolved oxygen lies not only in hydrolysis of amido groups and in associated effects (including salt effects). In the papers by Rämsden, D. K. and his colleagues[59–61] the mechanism of polyacrylamide degradation in presence of $Fe^{2+}$ ions is described. It is shown that polyacrylamide molecules degrade in aqueous solutions under the influence of the hydroxyl radical generated in the reaction of $Fe^{2+}$ with $H_2O_2$ as a result of autoxidation of $Fe^{2+}$ causing breakage of chain followed by viscosity reduction. It is also pointed that in the absence of dissolved oxygen breakage of PAA chains does not take place.

$$Fe^{2+} + O_2 \rightarrow Fe^{3+} + O_2^- \tag{1}$$

$$O_2^- + H^+ \rightarrow H\dot{O}_2 \tag{2}$$

$$Fe^{2+} + H\dot{O}_2 \rightarrow Fe^{3+} + HO_2^- \tag{3}$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \tag{4}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + \dot{O}H + \bar{O}H \tag{5}$$

$$Fe^{2+} + \dot{O}H \rightarrow Fe^{3+} + H\bar{O} \tag{6}$$

$$PH + \dot{O}H \rightarrow P\cdot + H_2O \tag{7}$$

$$P\cdot + O_2 \rightarrow PO_2^{\cdot} \tag{8}$$

$$2PO_2^{\cdot} \rightarrow P{-}O{-}O{-}O{-}O{-}P \tag{9}$$

$$P{-}O{-}O{-}O{-}O{-}P \rightarrow 2PO\cdot + O_2 \qquad (10)$$

$$PO\cdot \rightarrow F\cdot + F \qquad (11)$$

The reactions (1–11) represent variations of possible chemical transformations. The symbol P corresponds to the polymer macroradical while the symbol F, to the fragment of the macromolecule or that of the PAA macroradical.

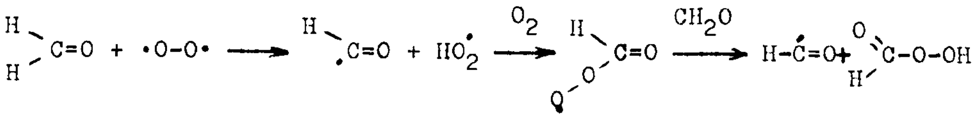
In the region of low pH values (<4.0) PAA degradation is so negligible that it does not cause any practical consequences. However, when the value of pH increases to 5–6, a rapid reduction of viscosity of the PAA solution is observed. It is pointed that rate of degradation increases significantly (up to twice) when a chelating agent is introduced into the system (e.g., ethylenediamine of tetraacetic acid).

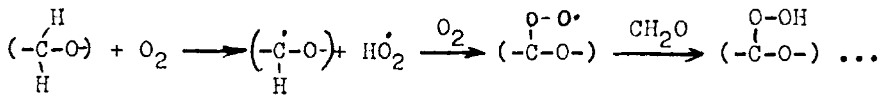
A similar point of view concerning the role of $Fe^{2+}$ ions in processes of oxidative degradation of biopolymers was expressed earlier[62]: possible application of antioxidants of different types was shown as means to prevent or inhibit radical oxidative processes at temperature of 97°C (thiourea, allyl alcohol, thiodiacetic acid, hydroquinone, ethylene glycol, paraformaldehyde, 2,2-thiodiethyl etc.). It was pointed that preventive antioxidants (those causing breakdown of peroxides) such as mercaptans, thioesters, etc. appeared more effective than antioxidants which broke the chain.

Taking into consideration the radical character of many chemical transformations which takes place in PAA molecules, it is proposed in patent literature to use different antioxidants and their compositions and, taking into account the negative effect of bivalent and trivalent metals, to introduce different complexing compounds.

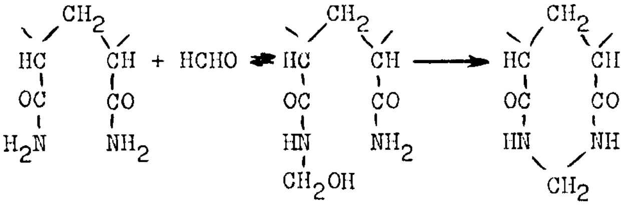
In the paper[63] data are given testifying that oxygen binders ($Na_2SO_3$) improve thermal stability of PAA, but do not prevent degradation. Application of substances which produce chelate compounds with metal ions (Trilon B) also does not provide sufficient increase in thermal stability. However, quite unexpected results were obtained when chelating and oxygen-binding agents were introduced in succession: the solution did not change its properties for 21 days at temperature 150°C. Investigation of mechanical stability in the temperature range of 25–90°C in presence of the same additives also revealed satisfactory results.

The authors of the paper[41] consider formaldehyde to expose equal inhibitive activity with sodium bisulfite. It is suggested that formaldehyde and the equal-in-weight polyoxymethylene suppress oxygen activity by generating stable radicals as shown in the following reactions:





Formaldehyde interacts directly with polyacrylamide producing methylol derivatives. Methylated polyacrylamide is characterized by higher viscosity and a higher screen-factor value as compared to conventional polymer solutions.[64] The authors of the paper[64] suggest that polyacrylamide and formaldehyde reaction may lead to formation of intermolecular cyclical structures. The methylol derivative may transform into the product of condensation between the final and another amido groups.



As a result of intense dilution of polyacrylamide macromolecules, crosslinking of polymer chains is hardly probable. However, if certain favourable conditions are provided, the mixtures are capable of gelation.[64]

Simultaneous application of formaldehyde and sodium sulfite of bisulfite has been described in the patent.[65] The produced partially hydrolyzed sulfomethylated polyacrylamide of high molecular mass is hydrolphylic and contributes to higher efficiency of oil production.

In the patent[66] it is proposed to use spatially-impeded phenols as stabilizers of acrylamide polymers. More often these compounds are used in combination with sulfur-containing antioxidants for PAA solutions[67,68] or in combination with phenol derivatives.[69]

The patent application[70] describes use of hydoxalamine and hydrazine or their salts as stabilizers of PAA aqueous solutions.

To stabilize PAA aqueous solutions, application of 2-mercaptobenzimidazole and its salts has been proposed,[71] as well as its composition with phenolic type antioxidants,[72] mixtures of thiourea with ammonium or sodium salts of ethylenediaminetetraacetic acid,[73] composition of guanidine derivatives with mercaptobenzothiazole or with different acids.[74,75] Higher stability to the action of iron ions is peculiar to the composition containing 2.2-(1-methyl-2-butyl)phenylamino-2-oxyethylpyridinium chloride.[76] At moderate temperatures in fresh water thiourea may be used.[77] As to elevated temperatures, the authors[49] propose to use mercaptobenzothiazole, which is usually utilized as a stabilizer in rubber production. In contrast to thiourea, mercaptobenzothiazole reveals inhibiting properties both in fresh and mineralized water. At 60–80°C introduction of 2% concentration of PAA mercaptobenzothiazole permits to achieve approximately a 10-fold decrease in degradation.

Stable PAA aqueous solutions may be produced by introduction of formaldehyde aminourea and acid additives[74,78] as well as by introducing inorganic sulfur compounds (sulfites, hydrosulfites, thiosulfites) and complexing compounds (aminopolycarboxylic acids and their salts, organophosphoric acids, inorganic condensed phosphates).[79] As concerns stabilization, the main problem lies in search of new efficient synergistic compounds and their use in various conditions of PAA application.

## BIOLOGICAL DEGRADATION OF PAA

For a long time investigators focused their attention to the fact that PAA solutions "aged" during storage and were losing their viscous properties, grew turbid, sometimes precipitates. Addition of low-molecular electrolyte (NaCl) in concentration 1 mole/l to PAA solution inhibited viscosity changes in the solution during storage but did not prevent this phenomenon completely. However, introducing a bactericidal agent, such as $NaN_3$, provided complete suppression of solution degradation. That permitted to suggest presence of bacteria in the PAA solution. Indeed, yeast cells and their fission products were found in the PAA solution. However, it remains unclear whether microorganisms provoke destruction of the main polymer chain or they disturb only intermolecular hydrogen bonds. Assessment of PAA bidegradation in polymer flooding process and of means to prevent it has been presented in the papers.[80,81] It was shown that PAA degradation took place under the influence of biocenosis of microorganisms. The degree of degradation was 60–80% by the end of the 60-th day. A number of bactericides to protect PAA was investigated, their doses determined, and compatibilities with PAA and formation waters studied.

## BASIC CONCLUSIONS

Analysis of data discussed in literature has revealed that the main reasons of loss of technological properties of polyacrylamide aqueous solutions in the polymer flooding process lie in degradation of polyacrylamide which is caused by mechanical loads, temperatures, hydrolysis, aggressive environment and microorganisms, changes in salt content and pH values of the medium. Decrease in viscosity and deterioration of viscoelastic properties of PAA solutions are not always associated directly with polymer chain breakage and reduction of molecular mass of the polymer. In many cases the reason lies in change of conformation of PAA macromolecules at varying salt content and pH values of the medium, in increase of PAA hydrolysis degree and in influence of mechanical loads. At the same time, there exist quite convincing confirmations of PAA polymer chain breakage under the influence of thermal oxidative and bactericidal action. In most cases the mechanism of changes which take place in polyacrylamide during polymer flooding is yet unclear and requires deeper investigation.

The main means to prevent mechanical degradation involves improvements in technology of preparation and injection of polymer solutions. Reduction in the rate of thermal-oxidative PAA degradation is achieved predominantly by the method of chemical modification of PAA, by introduction of stabilizers of different types of the solutions as well as by water treatment to remove interfering impurities (oxygen, hydrogen sulfide, ferrous iron). The problem of biological degradation is to be solved by introduction of different bactericides to polymer solutions.

To our mind, the most expedient trend of research to improve polymer flooding efficiency involves the study of mechanisms of polyacrylamide degradation and ageing of its aqueous solutions in reservoir conditions, combined with purposeful development of efficient stabilizers and chemical modification of polyacrylamide in order to improve its stability, as well as investigation of other classes of water-soluble polymers and development of viscosifying systems based on these polymers to enhance oil recovery.

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