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USE OF THERMAL ENERGY OF THE FORMATION

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Abstract: The physicochemical principles of selection implemented in ICH compositions have been further developed in the development of physicochemical reservoir stimulation methods, in which the thermal energy of the reservoir or injected coolant is used for the in-situ generation of alkaline buffer systems, CO2, and for the formation of freely and cohesively dispersed systems (inorganic gels and sols) that enhance oil displacement and formation coverage by flooding. The scientific basis for these methods is the results of studies on the kinetics of hydrolysis and gelation in the aluminum salt, urea, surfactant, water, and rock system.

Keywords: organic solvents, ionic associates, cation, tetraphenylarsonium, tetraphenylphosphonium, triphenyl lead, ionic association, benzene, toluene, xylene.

Introduction: Urea and ammonium nitrate are practically not sorbed by oil field rocks, which led to their use as indicators and tracers of filtration flows in the formation. When oil was displaced by the compositions, the mobility of the filtered core significantly increased, and core permeability increased by 6-60%. The increase in the displacement efficiency during oil flushing was 13.2-21.9% with a primary displacement of 17.2-23.2%. A method has been developed for enhancing oil recovery in highly heterogeneous formations by regulating filtration flows and increasing formation coverage by flooding with thermoreversible polymer gels [1-2], which are formed from polymer solutions with a lower critical solution temperature. The factor causing gelling is the thermal energy of the formation. The main feature of the method is that at low temperatures the solutions are low-viscosity, and at high temperatures they turn into gels.

Methods: IHNKA compositions with adjustable alkalinity and viscosity were developed for high-temperature formation conditions. They consist of an aqueous solution of a mixture of nonionic and anionic surfactants, urea, and ammonium nitrate. In the formation, under the influence of high temperature, urea hydrolyzes to form carbon dioxide and ammonia (Fig. 1).

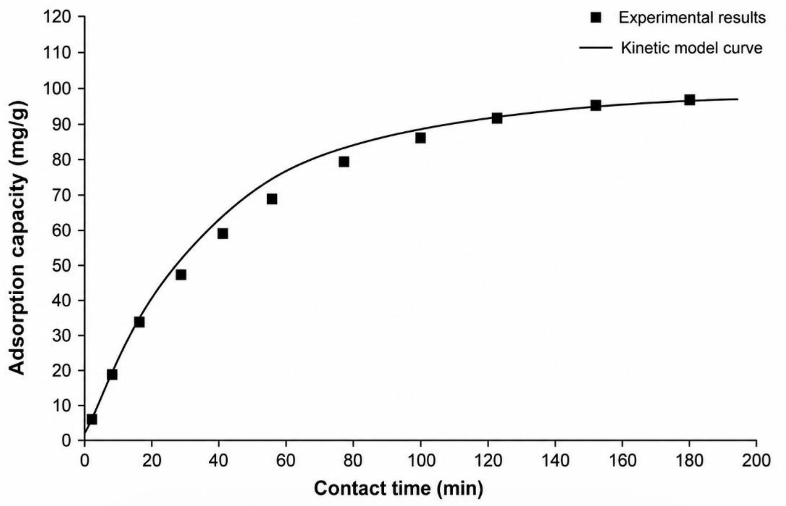

Fig. 1. Effect of temperature on the kinetics of urea hydrolysis in the IHN-KA composition. Temperature, °C: 80 (1), 100 (2), 120 (3).

Several beneficial effects are observed. Dissolving carbon dioxide in oil leads to a decrease in its viscosity. Carbon dioxide and ammonia reduce the swelling of clay minerals in the reservoir rock, thereby helping to maintain the initial permeability of the formation. The ammonia buffer system, formed by dissolving ammonia in an aqueous solution of ammonium nitrate (Fig. 2), also plays a similar role. Furthermore, due to its alkalinity (pH 9–10) and the presence of surfactants, it promotes intensification of countercurrent imbibition and oil displacement.

To optimize the composition of the compositions, the effects of temperature, component concentrations, and

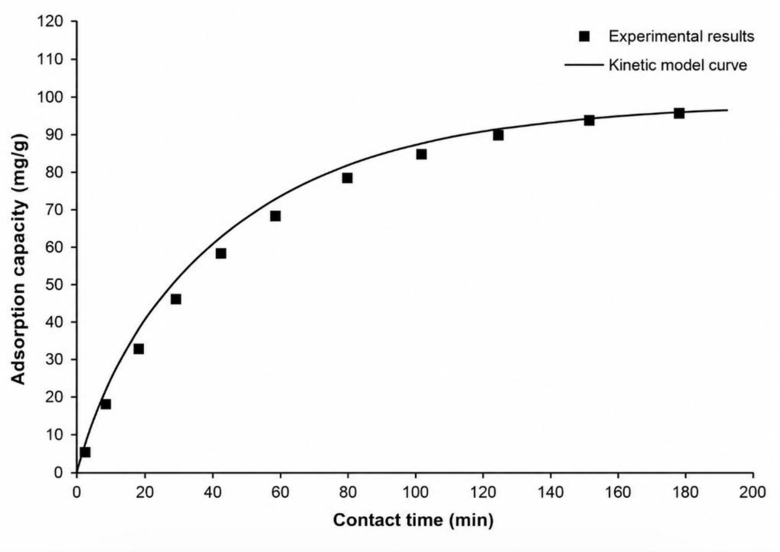

Fig. 2. Dependence of buffer capacity on pH for the composition after thermostatting for 15 days at 100 °C.

The influence of formation rock on the kinetics of urea hydrolysis was studied. Temperature and ammonium nitrate concentration were found to have the greatest influence on the rate of hydrolysis. The effect of surfactants was less pronounced. In the presence of surfactants, and especially ammonium nitrate, urea hydrolysis slows. With increasing temperature, the inhibitory effect of surfactants and ammonium nitrate is significantly reduced. The maximum pH is achieved at a degree of hydrolysis of 10–20%, while maximum buffering capacity is achieved only in the presence of ammonium nitrate. At 353 K, formation rock has no effect on the rate of hydrolysis, and at 373 K and above, it decreases it slightly.

The kinetics of the overall urea hydrolysis reaction in solutions of the composition in the temperature range of 353–373 K and at a urea mass fraction of 0.5–20% obeys a first-order equation:

$$\ln(1 - a) = kt$$

where k is the hydrolysis rate constant, s^{-1}; t is time, s. At 373 K, the reaction order is higher than the first order. The hydrolysis reaction rate constant of urea increases from 1.4×10^{-7} s^{-1} at 353 K to 36×10^{-7} s^{-1} at 373 K. Based on the temperature dependence of the rate constant, the parameters of the Arrhenius equation, namely the activation energy (E) and the pre-exponential factor (A), for the hydrolysis reaction of urea were determined ($E = 134$ kJ/mol, $A = 1.51 \times 10^{-13}$ s^{-1}).

Thus, CO2 and oil-displacing fluids such as IHN compositions with high buffering capacity in the pH range of 9.0–10.5 are formed directly in the formation. The physicochemical technology of IHNKA compositions for the formation combines the advantages of flooding with alkali and surfactant solutions with the effect of CO2.

The process is reversible: upon cooling, the gel liquefies, becoming a low-viscosity solution again, and upon reheating, it gels again, and so on, repeatedly. The most promising polymers are cellulose ethers (CEs). The dependence of CE solution viscosity on temperature in the range of 20–95°C is extreme: at the beginning of heating, viscosity decreases, then increases (Fig. 2) until the solution turns into a gel. The temperature and gelation time in the range of 40–120°C can be controlled using inorganic and organic additives, adjusting the temperature and salinity of the water to specific formation conditions. The gels are stable at temperatures up to 200–250°C and can be used as an effective means of limiting water influx, preventing gas breakthrough, and eliminating gas cones.

The effect of complexing agents was studied for thermoreversible polymer gels formed in a cellulose ether with a lower critical solution temperature (LCST)–aqueous phase system.

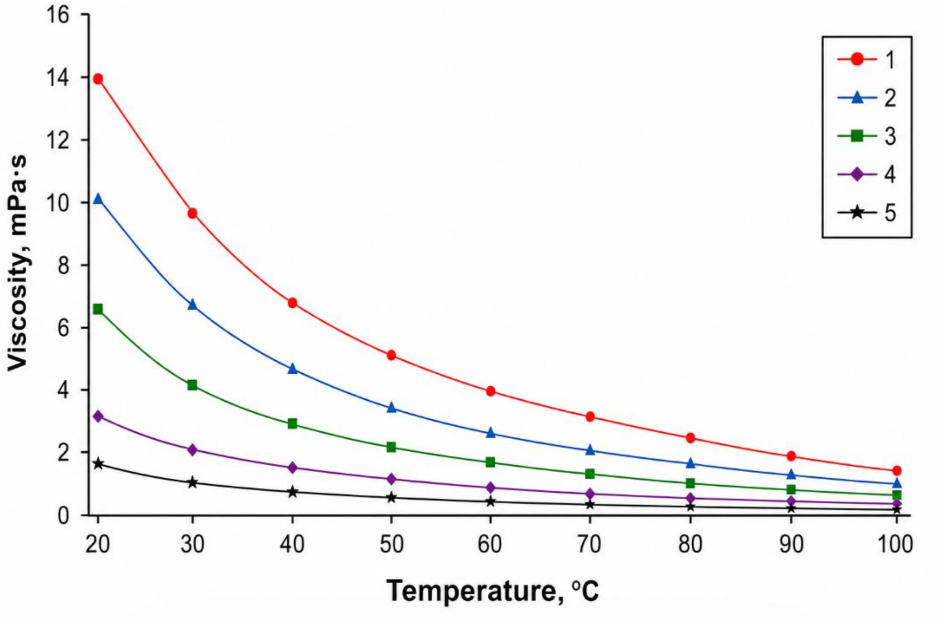

Fig. 3. Dependence of the viscosity of 1% cellulose ether solutions on temperature at different mineralization of formation waters of electrolytes and non-electrolytes on phase equilibria and gelation kinetics.

Anions have the greatest influence on the change in the gelling temperature of cellulose ether solutions; their effect correlates with their position in the lyotropic series. The influence of cations is significantly less. Salts containing the Cl– anion cause the greatest decrease in LCST, while the opposite effect—an increase in LCST—is observed.

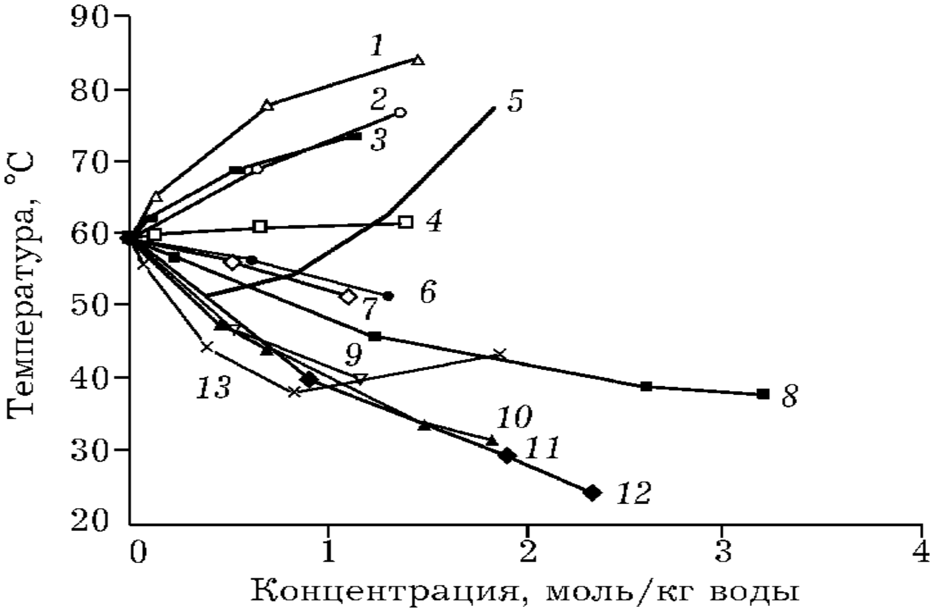

Fig. 4. Effect of electrolytes on the gelling temperature of cellulose ether solutions: 1 – NH4NCS, 2 – NaNCS, 3 – KNCS, 4 – NH4NO3, 5 – ZnCl2, 6 – NaNO3, 7 – KNO3, 8 – LiCl, 9 – MgCl2, 10 – CaCl2, 11 – KCl.

Thiourea, ethyl alcohol, and isopropyl alcohol significantly increase the LCST. It was established that the effect of electrolyte and non-electrolyte additives is additive. The conducted studies made it possible to select optimal gelling compounds for use in enhanced oil recovery technologies by limiting water influx during waterflooding and thermal stimulation of the formation.

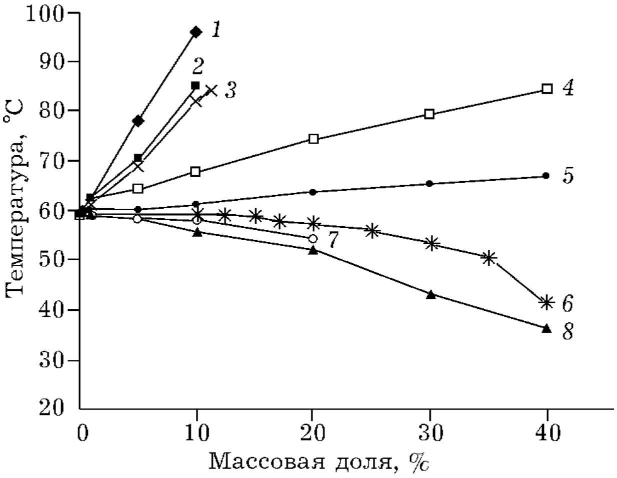

Fig. 5. Effect of non-electrolytes on the gelling temperature of cellulose ether solutions: 1 – thiourea, 2 – isopropyl alcohol, 3 – ethyl alcohol, 4 – urea, 5 – triethanolamine, 6 – ethylene glycol, 7 – polyglycol, 8 – glycerol.

Results: Gel-forming compositions and technologies for their use to increase reservoir coverage and limit water influx. A low-viscosity aqueous solution capable of forming gels under reservoir conditions at temperatures of 40–120°C is injected into the reservoir. In the highly permeable portion of the reservoir, where the bulk of the composition is injected, a gel screen forms, leading to a redistribution of filtration flows. Injecting the compositions into injection wells results in a smoothing of their injectivity profile, a reduction in water cut, and an increase in oil flow rates from production wells hydrodynamically connected to the injection wells. The compositions are easy to use, with the best polymer solubility in water achieved at temperatures of 0–10°C.

Technologies using these compositions are cost-effective and environmentally safe, implemented using standard oilfield equipment, and can be used to regulate filtration flows in heterogeneous oil reservoirs, limit water influx during water or steam injection, and eliminate gas breakthroughs. The environmental safety of the reagents and their absolute harmlessness to humans allow these technologies to be used in underground oil production.

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