Production of Hard-to-recover and Non-recoverable Oil Reserves by means of Binary Mixtures Technology

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Abstract. The paper discusses the results of the enhanced oil recovery by means of binary mixtures containing mineral (ammonium) and/or organic (mono-ethanolamine) nitrate and initiators of their decomposition. Calculations and large-scale field experiment show that resource-saving technology of binary mixtures can be considered as an alternative to the well-known thermal steam technology (Canada, USA). Designed and tested by the authors monitoring system of temperature and pressure in the reaction zone of the well, which provides conversion depth and efficiency coefficient of binary mixtures reaction that are close to 1 is a necessary and sufficient condition for the successful application of this method for the purpose of enhanced oil recovery.

Keywords: heat of formation, ammonium nitrate, organic nitrate – mono-ethanolamine, binary mixtures, oil production technology, reaction control mode at the bottomhole, thermochemical gas lift.
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Introduction

At the initial stage of hydrocarbon deposits exploitation, oil is generally extracted using high pressure in the formation that exceeds the bottomhole pressure of production wells. Oil production during the development falls in synchronization with the lowering of the reservoir pressure. In order to maintain production rate for increasing reservoir pressure through injection wells water is pumped into the formation under pressure. Now in Russia from wells, on average, about 90% of water and 10% of oil is extracted (Aleksandrov, Kuznetsov, 2007). In the depths about 60% of proven, but 'non-recoverable' oil remains. Mass of non-recoverable oil is more than mass of oil extracted from the subsoil throughout its production history.

In recent years, there has been a decision to extract non-recoverable reserves using thermochemical technology of binary mixtures. Binary mixture is an aqueous solution of ammonium nitrate (ammonium or organic) and their decomposition reaction initiators (metal hydrides or sodium nitrite) (Aleksandrov, Koller, 2008; Merzhanov et al., 2010). Aqueous solutions of binary mixtures reactants are pumped into the well through different channels. They come into contact in the bottomhole formation zone and react, generating heat and gas that go into a pressurized reservoir, created by the reaction.

History

Before 2011, injection of binary mixture solutions in wells was produced in unmanaged mode, and Rostekhnadzor allowed using small doses of binary mixtures. Typically, it was not permitted to inject into the well more than one ton of explosive nitrate. In the reaction about a ton of hot gas was produced, which was affecting formation near the well and ensured growth of recoverable oil, usually sufficient to payback the operation (Aleksandrov, Kuznetsov, 2007; Aleksandrov, Koller, 2008; Merzhanov et al, 2010;. Aleksandrov, et al, 2012; 2013).

When implementing the project, International Science and Technology Center No.985 of the Institute of Biochemical Physics of the Russian Academy of Sciences conducted R&D activities in the laboratory and on the field (Chernogolovka, Moscow region). Operating formulations have been developed on the basis of ammonium and organic nitrate (mono-ethanolamine nitrate) and conducted their tests on well No. 21 of Razumovsk field, Saratov region (Aleksandrov, Kuznetsov, 2007). These formulations were then successfully applied in the fields of the Perm region and the Komi Republic (Usinsk deposit) (Aleksandrov et al 2012;. Aleksandrov, Kuznetsov, 2007; Merzhanov et al, 2010; Aleksandrov, Koller, 2008).

The amount of heat introduced into the reservoir by the technology of binary mixture for injection into the well of one ton nitrate, is three times less than the amount of heat introduced into the formation in the next cycle of steam injection according to Canadian steam technology. Therefore, the technology of binary mixtures (TBM) of 2001 (ISTC project No. 985) did not seem able to compete with leading thermal technology of the World SAGD (Merzhanov et al., 2010).

In 2010 the Institute of Biochemical Physics of RAS has developed and tested a system of continuous monitoring and optimization of BM reaction in the wells, and obtained the permit of Rostekhnadzor authorities No. 25-ID-19542-2010 to pump into the subsoil of nitrate without limiting its mass. In the oil fields 2-level explosion-proof system was used of decomposition of tens of tons of ammonium nitrate, injected into the well (Aleksandrov et al. 2012).

System of nitrate controlled injection and initiator of its decomposition into the well can be regarded as a thermochemical gas generator (TG), with which the whole nitrate injected into the formation is converted into gas and heat by the reaction: $NH_4NO_3 \rightarrow N_2 + 2H_2O + 0{,}5O_2 + Qr$. The reaction heats the formation and creates conditions for the gas lift, which works mainly due to the energy of oil oxidation with

oxygen, precipitated in the reaction of nitrate decomposition. Live crude after the pressure rise and opening of valves at the wellhead usually gushes.

TG is a new engine of borehole type – in situ combustion engine of oil. TG, as experience has shown, can provide pumping out of hot fluid from the wellbore at a temperature much higher than the limit for operation of commercial motor pumps.

In November 2011, the pilot tests were performed of the technology of binary mixtures (managed by E.N. Aleksandrov). In the wells No.1242 and 3003 of Usinsk field (LLC LUKOIL-Komi) an aqueous solution was injected containing 20 tons of ammonium nitrate, and 9 tons of sodium nitrite.

In 2012 the yield of these wells increased by an average of 4.95 and 8.44 t/d, respectively (Table 1). Weight of additional oil in 2012 amounted to 3400 tons, an average of 1.7 thousand tons per well. At the end of 2011 – beginning of 2012 on the Usinsk field using the BM technology the following wells were treated: 6010,600,1283,7169,8198 (managed by E.N. Aleksandrov, V.B. Zavolzhsky). In 2012, 13232 tons of additional oil was obtained using the BM, on average 2646 tons per well (Table 2).

Therefore:

- The system of regulated non-hazardous injection on seven wells of Usinsk field was created and tested in 2011-2012.

- It has been shown that the system is functioning effectively both technically and economically, providing a ratio of income/expenses not lower than 5;

- Advertising the features of the binary mixtures technology on the Internet led to negotiations with foreign companies and to the proposal from the company ViscosEnergy Ltd. to hold pilot testing in the United States.

Technology of binary mixtures in the development and competition with the world's leading technologies

In June 2013 products of the binary mixtures reaction treated unprofitable wells No. 8 and No. 10 on the Eastland field, Texas, United States (managed by E.N. Aleksandrov) (Aleksandrov et al., 2012). The field was abandoned by oilfield workers in 1994 as a fully worked out. Prior to treatment from wells No. 8 and No.10 during the week (June 1-8, 2013) formation fluid was pumped out, consisting of water (99.99%) with a film of oil (0.01%). Prior to injection of reagents, the static level of surface water in the well No. 8 was detected at a depth of 210 m.

In the evening, the 9th of June 2013 in wells No. 8 and No. 10 55 tons of aqueous solutions of ammonium nitrate and sodium nitrite was injected into wells No. 8 and No. 10.

Well No.	Pump brand	Month	Operational date	Base flow rate	Number of days	Average flow rate, t/d	Incremental oil production, t	Specific flow rate, t/d	Planned specific flow rate
1242	EVNT-25-1500	November 2011 December 2011 January 2012 February 2012 March 2012	09.11.2011	0	22.00 30.83 31.00 29.00 31.00	5.82 5.50 4.63 4.94 3.98	128.00 169.57 143.00 143.26 123.38		1
		Total			**143.83**		**707.73**	**4.92**	**8.5**
3003	EVNT-25-1500	January 2012 February 2012 March 2012	04.01.2012	1.93 t/d	28.00 23.00 30.75	10.6 10.60 9.98	242.90 199.60 247.60		
		Total			**81.75**		**690.10**	**8.44**	**6.5**

Table 1. The results of pilot tests of the BM technology in wells No. 1242 and No. 3003 of Usinsk field in November 2011,

Effectiveness analysis of experimental program Ltd. «NTRS-Komi» on Permo-Carboniferous deposit of Usinsky filed, 2012

Technology	Well No.	Production facility	Date of procedure conducting		Well input date after experimental program	Mode of working before procedure			Mode of working after procedure			Current mode of working			Costs, thous. rub		Increment Q_o, t/day	After-production, thous.t	Active days after procedure	Brief characterization of experimental program results	Comment
			Beginning	End		$Q_ж$, т/сут	$Q_н$, т/сут	%	$Q_ж$, т/сут	$Q_н$, т/сут	%	$Q_ж$, т/сут	$Q_н$, т/сут	%	Plan	Fact					
Injection of silicon inorganic compounds	6010	P-C	15.05.2012	16.05.2012	27.05.2012	22,9	3,6	84,4	20	6,8	67	17,5	12	33	780	780	10,2	5,566	547	effective	
	600	P-C	03.05.2012	04.05.2012	12.05.2012	-	-	-	21	5,9	70	21	5	76	780	780	5,0	1,05	81	effective	non-operating well
	1283	P-C	12.05.2012	15.05.2012	17.05.2012	9	4,5	50	25	13	46	22	13	42	780	780	9,6	2,16	225	effective	
	7169	P-C	12.12.2012	12.12.2012	14.01.2012	49,4	5,6	88,6	62	15	76	21,7	1,3	94	780	780	8,4	1,644	194,9	effective	effect till August, 2013
	8198	P-C	25.12.2011	04.01.2012	10.02.2012	49,2	0,8	98,3	41	13	68	22,6	6,1	73	780	780	9,1	2,812	307,7	effective	
Total																	9,8	13,232	1356		

Table 2. The treatment results of five wells on the Usinsk field in late 2011 - early 2012 (Managed by E.N. Aleksandrov, V.B. Zavolzhsky).

According to the work plan, half of the reagents reacted in the well by providing approximately 25 tons of gas heated, an average of 300 ° C, which went to an adjacent layer under the pressure generated by reaction. The other half of the BM, stopping the reaction in the well was injected into the heated reservoir. In the reservoir slow decomposition reaction of nitrate continued for more than 3 days (Fig. 1, graph of pressure change in the well No. 8 for 09-12 June 2013, Table 3). The pressure at the wellhead No. 8 increased to 15 atmospheres. Given that the liquid level in the well increased to 210 meters due to the pressure increase by 21 atm, the total pressure increase due to the decomposition reaction of ammonium nitrate, mainly in the formation was 36 atmospheres.

After the cessation of pressure rise at the wellheap, valves were opened. Figure 2 shows a picture of the gush from well No. 8. The well No. 8 selected in the center of the field gave fluid with composition: oil – about 30%, water – about 70%. Well No. 10 chosen on the edge of the field gave fluid with composition: oil – 10% water – 90%.

The contracting company in the United States ViscosEnergy Ltd. placed an online advertising with the heading "Comparison of technologies" about the successful revival of oil production in the abandoned Eastland field using the revolutionary technology of binary mixtures. In the ad it was written: "Scientists based in Russia have developed and tested a technology of output stimulation by heat from reactions of binary mixtures (BM)".

ViscosEnergy Ltd. presented the stimulation results by BM reaction products, oil production from wells No. 8 and No.10 for the Eastland field (Texas, USA) (Table 3). These results are compared in the advertisement with the results of stimulation by leading technologies of the West: fracturing technology (hydraulic fracturing, the United States) and thermal steam technology (SAGD, Canada).

The second row of Table 3 shows that the BM technology as opposed to Western technologies, waters the subsoil much less (i.e. negligible). The third row of the table specifies the potential of technologies for their ability to maximize the beneficial share of proven reserves:

- SAGD 30%;
- hydrofractures 35%;
- BM is not less than 50%.

The eighth row of Table 3 contains the cost of a barrel of oil extracted from the subsoil: SAGD (50-60) &/BBL; hydraulic fracturing (40-60) &/BBL; BM (10-35) &/BBL. The BM technology, which value is determined by market competition, until 2012, held the third place in the world and was inferior to hydraulic fracturing technology (US) and thermal steam SAGD technology (Canada). In 2012-2014 BM technology, ensuring oil production by cost (10-35) &/BBL, is ahead in terms of profitability of both leading Western technologies.

It should be emphasized that the published in the advertising cost of oil barrel, extracted from the subsoil by the existing profitable fields using SAGD – (50-60) &/BBL and hydraulic fracturing – (40-60) &/BBL is compared with the cost of oil (10-35) &/BBL, extracted from the subsoil by means of BM in unprofitable field left without the protection 19 years ago. Modern technology of BM, being developed by the authors from 1997 is different from other technologies by optimized heat generation during injection, which ensures high efficiency of the reaction close to 1. With the BM technology

Criteria	SAGD	Hydrofractures	Binary mixture
Principle	**Heats the formation with steam to lower viscosity**	**Pacal's Law: Cold liquids requiring strong pumps fracture formation**	**Heats the formation to lower oil viscosity. Uses reactions to increase energy and gas lifting**
Damage to well	**Rapid water-logging**	**Rapid water-logging**	**No irrigation or any other damage**
Production over time	**non-economical after appx. 30% of oil is extracted**	**non-economical after appx. 35% of oil is extracted**	**Can extract 50-80% of all oil from the well over its lifetime**
Energy loss	**+/- 25% to heat water and to transfer it to well**	**strong pumps (>10.000 HP), proppants**	**Negligible loss**
Depth limits	**800-1000m (more, if costly thermo-insulated tubing is used)**	**Depends on well construction and strength of pumps available**	**Unclear; deepest wells at 15,000 ft**
Temperature reached	**250°C**	**N/A**	**From 100-500°C, fully regulated**
Investment	**Large upfront investment**	**Moderate**	**Moderate**
Production costs	**$50-60/BBL**	**$40-60/BBL**	**$10-35/BBL depending on geological/market conditions**
Environment-friendliness	**Water pollution and exhaust gases in athmosphere**	**High water consumption**	**Limited; by-products are nitrogen, water, and C02. All other solid materials (if indeed any) remain down in the well.**
Repeatability	**Increasing water content lowers economical effect**	**Repeated stimulation has lesser effect**	**Can be repeated many times or can run permanently**

Table 3. The treatment results of wells No. 8 and No. 10 on the Eastland field, USA (managed by E.N. Aleksandrov).

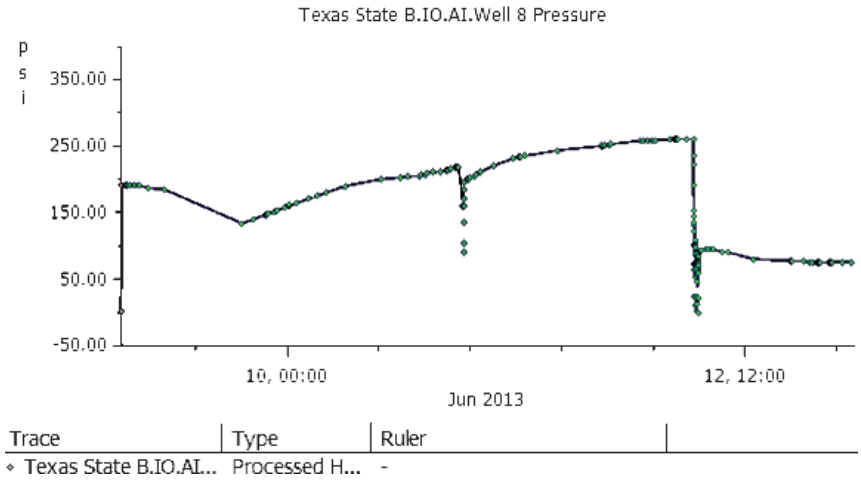

Fig. 1. Graph of pressure change in well No. 8 during June 9-12, 2013, with the valve closed at the wellhead during 3 days with the fourth day after injection of BM into the well and formation.

Fig. 2. Picture of mixture gush (water – 70%, oil – 30%) from the well No.8.

we managed to find the real possibility of complete removal of the skin layer around tens of thousands of currently uneconomic wells in Russia, which has accumulated over several decades of their not resource-saving operation. This layer seems to be the main cause of the 'shortage' from of 60% proven oil reserves in Russia. The skin layer is comprised of heavy viscous oil particles that are more sorbed by pore and crack walls than light oil. Cooling fluid contributes to the sorption greatly during its exit from the formation into the borehole (Joule-Thomson effect).

Binary mixtures technology perspectives

From a number of perspective 'branches' of TBM we will consider, for example, the possibility of using the binary mixtures in the wells of the Canadian tandem (Fig. 3). Steam replacement in wells tandem to the BM solutions is planned to make in the following manner.

BM solutions must be pumped into the lower horizontal shaft, wherein it is easy to organize the continuous reaction of BM fed into the well via the installation of low-power pumps CA-320. Capacity of BM reaction, generating hot gas in the well at a temperature of about 300 °C, must exceed the capacity of hydraulic fracturing pumps (10 thousand liters a second). Thus for a few hours we can arrange a discharge drainage of hot gases from the low horizontal shaft to the upper horizontal shaft of tandem, in which the conditions will be created for continuous operation of thermochemical gas lift. It is capable of continuous delivery of hot fluid to the surface, containing a mixture of oil and water at a temperature close to 100 °C. As a result of replacement of production mode SAGD to the BM mode, we can expect an increase in the speed of heavy viscous oil production by an order of magnitude.

If successful, lowering of SAGD production costs will be ensured by costs reduction to almost zero in the creation of the steam generator plants. (Injection of BM in Russia is usually done with 'wheels' of installations CA-320, applied for cementing, and always available in the fields). Production accelerating is also expected by eliminating the steam injection periods, during which the production in SAGD system is not conducted. Thus the opportunity to use the advantages of steam tandem that is not applied deeper than 1 km due to heat losses steam towards the bottomhole area, also in wells with horizontal shafts at any depth. Considering planned by us continuous process, in which an order of thermochemical gas lift capacity exceeds the capacity of mechanical pumps, we should expect a radical production stimulation of both heavy and light oil.

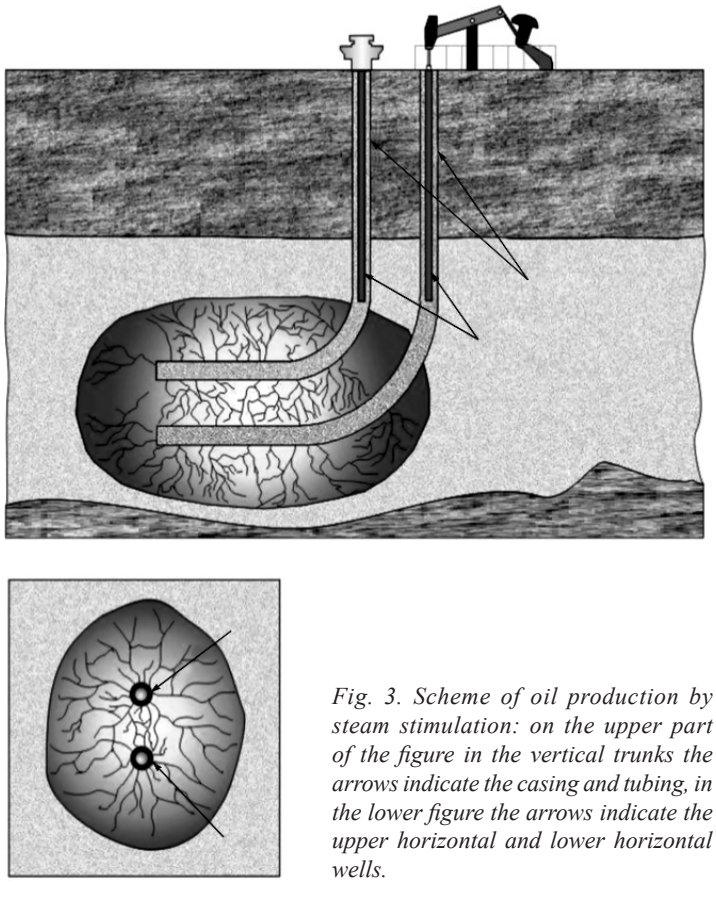

Fig. 3. Scheme of oil production by steam stimulation: on the upper part of the figure in the vertical trunks the arrows indicate the casing and tubing, in the lower figure the arrows indicate the upper horizontal and lower horizontal wells.

During the pilot testing on the Usinsk field we discovered previously unknown heat wave of nitrate decomposition in the formation initiated by heat of the heated portion via the BM reaction in the well. The heat wave moved from the well into the formation to almost complete decomposition of nitrate injected into the formation. This wave is displayed in the graph of pressure changes in the well No.8 (Eastland field) during 09-12 June 2013 with the pressure build-up at the beginning of nitrate decomposition reaction at a closed valve in the wellhead (Fig. 1, the pressure drop in the evening of 10 June there due to short-term leaks of wellhead, the cause of which quickly liquidated).

It should be emphasized that due to the complete explosion of heat by expanding any mass of nitrate in the formation, giving the bulk of the heat to formation rocks, the use of this heat wave becomes the main focus of the BM application to a massive stimulation of oil production (Calculation of heat wave movement of nitrate decomposition is shown in the paper (Kuznetsov, 2016)).

Technology of binary mixtures as an alternative to SAGD technology

We believe that in the future the BM technology should replace the SAGD technology. We believe that (at least initially) in the BM technology we can use well tandem characteristic for SAGD technology.

During the reaction in the formation near well a zone of high pressure is created, in which the gas is produced. Formation fluid movement through the pores and cracks under the ga pressure is called the pressure drainage.

Unlike the gravity drainage of steam technology, pressure drainage, supported by the energy of the BM reaction, is a process controlled by the intensity and direction. In addition to the pressure drainage effect at the BM reaction in the well and formation, the gas evolved in the reaction is soluble in the formation fluid, making it less viscous and lighter. Gas lift is a movement of fluid saturated by gas upward the borehole. Artificial gas lift, supported by the energy of the BM reaction was found in the well No. 169 of Kurbatovsky field (Perm region) (Aleksandrov, Kuznetsov, 2007).

Conclusion

The recovery of the industrial oil production in the Eastland field (USA) in 2013 by means of BM reaction, which for 1994-2013 was considered unrecoverable, can be regarded as an opportunity to turn from more than a century of accumulation in the depths of non-recoverable oil reserves for their cost-effective production. In the depths there are hydrocarbons, the mass of which at times exceeds the reserves at fields developed currently. Finding the possibility of extracting 'uneconomic' oil reserves is equivalent to the discovery of new major fields with almost no costs for geological prospecting and exploration. This result has no analogues in the prior literature.

As is clear from the eighth row of Table 3, the leading Western technologies SAGD technology and hydrofractures, used now in active, i.e., cost-effective fields in terms of production profitability deposits ceded primacy to the BM technology applied at an abandoned unprofitable field. This result also does not have analogues in the prior literature.

Recovery of oil production with the BM technology on currently uneconomic fields is the new direction of the commercial thermochemistry, which can provide improvement for the economy of Russia as a great energy-producing nation.

Findings

1. The method of thermo-chemical stimulation of oil production is developed and mastered by means of new technological elements:

- System of adjustable safety heat up of oil reservoirs in the temperature range 200-700 °C;
- Thermochemical gas lift used for pumping out the formation fluid at high temperatures.

2. At identic production modes on Usinsk and Texas fields, technologies tested in the United States have paid off for two months.

3. Revival of oil production in depleted fields should be considered as a promising new direction of commercial thermochemistry.

References

Aleksandrov E.N., Aleksandrov .P.E. Kuznetsov N.M, Lunin V.V., Lemenovskiy .D.A. Rafikov R.S.,Chertenkov M.V., Shiryaev P.A., Petrov A.L., Lidzhi-Goryaev V.Yu. *Neftekhimiya = Oil chemistry.* 2013. V. 53. No. 4. Pp. 312-320. (In Russ.)

Aleksandrov E., Koller Z. Technology of oil and bitumen output stimulation by heat from reactions of binary mixtures (BM). TCTM limited. 2008. 76 p.

Aleksandrov E.N., Kuznetsov N.M. Masshtabnyy nagrev produktivnogo plasta i optimizatsiya dobychi nefti [Broad-scale heat of productive deposit and optimization of oil production]. *Karotazhnik = Well Logger*. 2007. No. 4. Pp. 113-127. (In Russ.)

Aleksandrov E.N., Varfolomeev S.D., Lidzhi-Goryaev V.Yu., Petrov A.L. Stimulirovanie dobychi nefti produktami reaktsiy binarnykh smesey (BS) kak al'ternativa tekhnologiyam, obvodnyayuschim neftyanoy plast [Stimulation of oil production by reaction products of binary mixtures as an alternative to deposit inundation technologies]. *Tochka opory = Reference point*. 2012. No. 158, November. Pp. 14-15. (In Russ.)

Kuznetsov N.M. K stimulirovaniyu neftedobychi na osnove binarnykh smesey [Stimulation of oil production based on binary mixtures]. *Gorenie i vzryv = Combustion and explosion*. 2016. V. 9. No. 2. Pp. 111-119. (In Russ.)

Merzhanov A.G., Lunin V.V., Lemenovskiy D.A., Aleksandrov E.N., Petrov A.L., Lidzhi-Goryaev V.Yu. Vysokotemperaturnoe stimulirovanie dobychi nefti [High-temperature stimulation of oil production]. *Nauka i tekhnologii v promyshlennosti = Science in technology and industry.* 2010. V. 2. Pp. 1-6. (In Russ.)

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