Gravitational sorption method for extraction of vanadium-containing oil from reservoirs with the use of redox polymers

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Abstract: The article considers the possibility of extraction of residual oil reserves, based on the use of previously drilled wells and creation of conditions for drainage of formation fluid into production wells due to gravity forces and sorption processes of vanadium interaction in oil with injected redox polymers. The article makes a significant contribution to world science when studying the processes of extracting residual oil reserves from reservoirs and metals from liquid media, including oil. As a result of the analysis of the proposed method of extraction, the authors for the first time prove that the technology under consideration allows increasing the oil recovery factor and expand the scope of redox polymers when extracting oil from seams and associated metals. The proposed redox polymers have improved physico-chemical, oxidation-reduction and sorption-kinetic properties. Their application will allow solving the actual problem of import substitution of expensive foreign products for oil production. This makes it possible to implement integrated development of such oil fields as Buzachi and others with the extraction of associated metals and to improve the quality of oil and oil products.

Keywords: oil; mining; gravity; sorption; vanadium; redoxpolymer.

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1 Introduction

With the fall in world oil prices at the present stage one of the main tasks of the oil industry development is to reduce the cost of production and to extract more complete hydrocarbons in developed and equipped fields that are at a late stage of development and contain large volumes of residual oil reserves. Significant progress in the oil industry of oil-exporting countries is associated with the widespread use of polymer reagents as water thickeners in the technology of secondary oil recovery (polymer flooding) (Surgushev, 1985). In the case of polymer flooding, gels are formed that clog the paths of the intensive flow of injected water, thereby increasing the zone of formation coverage and increasing the oil recovery of the reservoirs. However, a large amount of oil remains in the cracks sealed by the polymer gel and therefore the oil recovery factor will generally be low.

It is possible to pump out no more than 20–30% of the balance reserves of oil in the fields by often practiced method in Kazakhstani oilfields to increase in-house pressure by injecting seawater or formation water without appropriate additions of chemical reagents. The remaining 70–80% of geological reserves of oil, as a rule, contains a large number of metals. Moreover, reagentless water flooding creates serious environmental and economic problems, namely, water cut and contamination of the near-wellbore territory, the costs of separating water from oil (the creation of sedimentation tanks, the destruction of water-oil emulsions), soil and surface water pollution with oil, metals and formation water. In this regard, the problems of enhanced oil recovery (EOR) with the extraction of associated metals (vanadium) and prevention of environmental pollution for oil companies in Kazakhstan are becoming particularly relevant. To do this, it is necessary to find new environmentally safe and economically profitable ways of EOR and extraction of associated metals, which will significantly reduce the cost of oil production and obtain additional profits from the sale of associated metals.

The use of polymers as water thickening agents is one of the methods for increasing oil recovery (http://www.newseconomic.com; Slatvinsky-Sidak and Soskind, 2014; Ahmedzhanov et al., 2012).

Known methods of increasing oil recovery from the reservoirs by hydrolysed polyacrylamide, copolymers of acrylamide, and modified starch do not entice metals from oil. The main disadvantage of the proposed methods is also the low salt resistance of polymer reagents, in particular, their precipitation in formation water, which contains a high concentration of salts.

It is clear that all the listed methods can not be used for simultaneous increase of oil recovery of reservoirs and extraction of metals from oil in reservoir conditions (USA Patent, 2014; http://www.npckbadra.ru; Maksimov et al., 2014; Klyamkin et al., 2014; Ivanov et al., 1998).

Polymers exported from abroad and used in the oil and mining industry of Kazakhstan are characterised by their high cost and insufficient extraction efficiency of oil from reservoirs and metals from liquid media (oil, leach solutions).

In this regard, the method of influence on oil layers with the introduction of aqueous solutions of domestic polymers is of considerable interest.

Vanadium is contained in a number of oil fields in Kazakhstan (northern Buzachi, Karazhanbas, Kalamkas, Zhalgiztobe, Karaturun, Besoba, Bozoba, Sinelnekovskoye, Karaarna, Tortai, Kumshety, etc.), which concentration ranges from 10 to 300 grams per ton of oil produced. However, up to now, the technology of vanadium extraction from these oils has not been developed (Mendebaev and Nukenov, 2001).

The extraction of useful valuable components, for example, vanadium and other metals, produced by oil, will allow increasing profitability and reducing the cost of oil production (http://www.newseconomic.com; Ageev et al., 2015; Slatvinskij-Cidak and Soskind, 2014). So, for example, by allocating 80 t of vanadium and 60 t of porphyrins from oil with a volume of 200 thousand tons of the Buzachi deposit (Republic of Kazakhstan), with the realisation of vanadium and porphyrins it is possible to obtain additionally up to US$1.6 and US$4.8 bln per year. If we consider that there are many such deposits in Kazakhstan, the profitability of their exploitation will be even greater. However, up to now, the technology of vanadium extraction from these oils has not been developed.

There is already a practical experience of direct extraction of vanadium from oil in the world. Foreign experience in the industrial development of vanadium-containing oils confirms the economic feasibility of using oil as raw material for the production of vanadium with its content of 200 g and higher per 1 ton of raw materials, mainly ores. Apparently, economic efficiency can be further enhanced by using oil as a raw material for vanadium extraction with its preliminary concentration in the high molecular weight.

In foreign countries, the small-scale extraction of vanadium from the products of oil and petroleum products combustion has been going on for a long time. Semi-industrial works on vanadium extraction from bitums and heavy oils are carried out in England, Venezuela, Mexico, Italy. In the United States, a method of extracting vanadium from Venezuelan oil, containing 0.03% V (USA Patent, 2008), is tented.

Canada Petrofina Company extracts vanadium from oil residues of heavy Venezuelan oils since 1965. The process of vanadium extraction includes the following technological stages: desalination of oil, atmospheric distillation of oil, coking of the residue, coke oxidation, removal of vanadium from the ashes by sulphuric acid, oxidation of vanadium to a five-valent state by sodium pechlo-rate and precipitation with ammonia. The hydrated vanadium oxide is then melted and cast into granules. There have been developed methods for the extraction of vanadium and other metals from soot deposits.

In this regard, it is interesting to note that the extraction of vanadium from soot obtained by burning oil in the area of Lake Maracaibo in Venezuela has evolved into an industrial process. In petroleum coke, Wells reports that 0.22% of V_2O_5 is present in the breccia bitumen from Terlingua (Texas); 0.043% V_2O_5 (equivalent to 61% ash) in asphalt from Baoba (well 1) (Lake Bermudas, Venezuela); 12.2% in the ash of gragamite from the vicinity of Page (Oklahoma); 45% in asphalt ash from Nevada.

For example, Canada, the USA and Italy extract vanadium from Venezuelan oil for decades, and there is no more vanadium in it than in Buzachi oil in Kazakhstan. According to our scientists, in 1 million tons there are 440 tons of vanadium pentoxide. Given the scale of oil production and consumption in today's world this is not so small.

Here it is necessary to note that the so-called heavy and superheavy oils differ in the metals containing. The ones whose production is currently limited due to processing difficulties. In general, its geological reserves in Buzachi Peninsula oil at a depth of 300–600 metres, are estimated at hundreds of thousands of tons. It is not difficult to imagine what benefit the country would derive from extracting this scarce metal from its oil.

Mainly known methods for extracting vanadium from petroleum are associated with the thermal treatment of petroleum and petroleum products and can not be used to extract vanadium directly from oil and petroleum products (Imangaliev et al., 2017). By heat treatment of oil and petroleum products, the bulk of vanadium can be released into the atmosphere and may pollute the environment.

The most interesting is the method (http://www.npckbadra.ru), which allows the extraction of metals (vanadium and others) directly from oil and petroleum products. However, this method requires the creation of special equipment for the electrolysis of oil in conditions of thin films in flow-through electrolytic reactors.

The elucidation of mechanism of solution ingredients influence on the sorption of metals is of scientific and practical interest (Ergozhin et al., 2003). Successful introduction of redox polymers for the simultaneous extraction of metals from oil and metal-containing oil from seams can be realised through a comprehensive study of the processes taking place in a complex ion-solution system. Knowledge of the regularities of various factors influence on the state of metal ions in the phase of ion exchangers is important for a deeper understanding of not only sorption, but also catalytic, and oxidation-reduction processes involving 'complexed' ion exchangers. For practical purposes, systems containing metals that are capable of varying degrees of oxidation are of particular interest. Taking into account the prospects of using metal-containing raw materials in the mining and oil and gas industries, the study of the complexation of redox polymers with such metals as vanadium seems to be practically justified.

This problem can be solved by introducing the technology of vanadium extraction from oil and solutions of leaching of ores by sorption processes. In this regard, it is of interest to create promising ion exchangers for the recovery of vanadium from oil and leach solutions to obtain high quality V_2O_5. Wherein, the quality of oil will improve at the same time, which remains topical nowadays. Taking into account the proposed, the sorption capacity of new redox polymers with respect to vanadium ions in solutions has been studied. When developing a sorption technology for the extraction of vanadium from oil, one of the main tasks is the choice of a sorbent characterised by high capacity and selectivity with respect to vanadium ions.

The range of known industrial redoxionites is limited. The ways of their synthesis differ in complexity, multistage, duration, the need to carry out reactions under harsh conditions, i.e. at elevated pressure and temperature, corrosive environments, and that is why difficult to implement. In addition, the poorly satisfactory kinetic characteristics of oxidation-reduction polymers, a small assortment of monomers suitable for the synthesis of redoxionites, substantially limits their use. In connection with this, the question of finding new affordable and cheap reactive redox monomers is currently acute.

This is possible with the use of locally available raw materials, such as vinyl monoethanola-mine ether. As the analysis of patent and periodical literature shows, compounds with valuable properties for various purposes were obtained on their basis, however, redox polymers were not synthesised. This work is aimed at developing simple, convenient and affordable, economically viable and environmentally friendly, non-waste methods for the synthesis of redox and ion-exchange polymers based on new redox monomers.

The possibility of solving a wide range of various problems with the help of ion-exchange, complexing and oxidation-reduction polymers attracts much attention. The need for science and technology in such materials for special purposes is constantly growing and is considerably ahead of the pace of their production. In this regard, the study of the effectiveness of a number of domestic polymers in the field of ion-exchange, including oxidation-reduction and complexing properties of macromolecules are promising and necessary from the point of view of improving their performance and creating new promising technologies for extracting oil from reservoirs, vanadium From oil and metal leaching solutions. Such studies are relevant, both from a scientific and a practical point of view, and are undeniably new.

Increasing the efficiency of oil deposits development can also be achieved by extracting metals from oil. The extraction of associated valuable components, for example, vanadium, is also one of the directions to increase profitability from natural bitumens as well (Waters, 1977; US Environmental Protection Agency, 2007; Aboulafia et al., 2010).

2 Experimental part

On the territory of Kazakhstan, many fields on land reached the IV stage of development and their operation is almost completed in the coming years. These deposits include the Emba Group in Atyrau region, the Mangistau field and a number of deposits in the Aktobe and Kyzylorda regions. After the extraction of oil from such fields, more than half of the reserves remain in the bowels, and their territories are practically completely equipped. Closing and preserving such facilities is not profitable either from the economic point of view (large losses of oil, liquidation of equipped production facilities), or from social points of view (loss of jobs, degradation of regions, the need to resettle a huge mass of the working population).

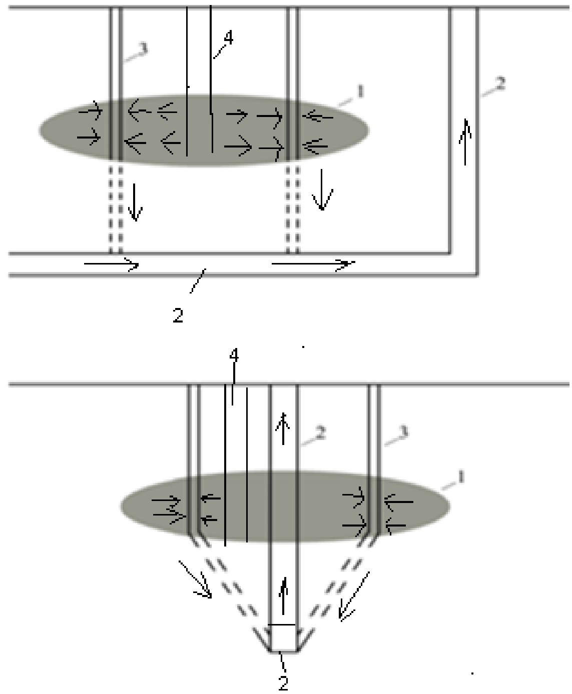
Increasing the efficiency of oil fields development can also be achieved by gravitational-sorption method of oil recovery from the reservoirs, using redoxpolymers, especially at the stage of depletion of the reservoir energy.

To extend the life of the oilfields at the final stage of development, it is proposed to use the new technological scheme of production, residual oil reserves on the spent oil fields, the essence of which is as follows (Ahmedzhanov et al., 2012). On the site of the deposit, additional horizontal wells of large diameter 2 are conducted, which are connected to drilled existing production wells 3 and through them the gravitational extraction of the remaining part of the oil is carried out (Figure 1).

Wherein to injection wells 4 it is proposed to pump solutions of redox polymers which, on the basis of ionic interaction with metals in the remaining oil, will facilitate its movement towards the production wells. At the same time, it is necessary to use oriented directional drilling of production wells at the drill, the mouth of which remains open and pumping into solutions of redox polymer solutions through injection wells 4 in order to improve the drainage conditions of oil and maximally minimise the volume of horizontal wells. As a rule, large volumes of colour, noble and rare metals are concentrated in the rest of the oil. Therefore, when extracting and processing such oil, it is necessary to apply effective methods of extracting and preparing oil, with the extraction of associated minerals (vanadium, gold, etc.), which will compensate for the costs of additional horizontal wells.

To obtain new domestic redoxpolymers based on vinyl ether monoethanolamine (VEMEA), the following technology was used (Nuranbaeva, 2003; Ergozhin et al., 2002).

Figure 1 Technological scheme of working off residual oil reserves in the seams using the gravity regime



Note: 1 – oil reservoir, 2 – horizontal wellbore, 3 – drilled production wells, 4 – injection well.

3 Results and its discussion

The elucidation of mechanism of solution ingredients influence on the sorption of metals is of scientific and practical interest. Successful introduction of redoxpolymers for the simultaneous extraction and metalliferous oil from reservoirs and metals from oil can be realised through a comprehensive study of the processes taking place in a complex ion-solution system. In this connection, it is of scientific and practical interest to create promising ion exchangers for extracting metal-containing oil from reservoirs and vanadium from oil and ore leaching solutions to obtain high quality V2O5. Wherein, the quality of oil will improve at the same time, which does not remain less ugent these days. Taking into account the proposed research, the sorption capacity of new redoxpolymers with respect to vanadium ions in solutions was studied.

When developing a sorption technology for the extraction of vanadium from oil, one of the main tasks is the choice of a sorbent characterised by high capacity and selectivity with respect to vanadium ions.

When developing the sorption technology of vanadium extraction, one of the main tasks is the choice of a sorbent characterised by high capacity and selectivity with respect to metal ions, for example, vanadium. The best properties are possessed by vinyl pyridine anion exchangers; therefore, the sorption properties of not only homopolymers based on quinoid VEMEA derivatives, but also copolymers based on 2- and 4-vinylpyridines are investigated.

In this work, the sorption of vanadium ions of new rare polymers based on quinoid derivatives of VEMEA was studied by polarography. When developing a sorption technology for vanadium extraction, one of the main tasks is to select a sorbent with a high capacity and selectivity for metal ions, for example, vanadium. Vinylpyridine-based anionites have the best properties, so the sorption properties of not only homopolymers based on quinoid derivatives of VEMEA, but also copolymers based on 2- and 4-vinylpyridines have been studied.

Polarograms were taken in a thermostatic cell at 25 ± 0.5°C using a PU-1 polarograph on a mercury dripping electrode with a capillary characteristic at open circuit: $m^{2/3}t^{1/6}$ = 4.38 $mg^{2/3}$ $sec^{-1/2}$. A saturated calomel electrode was used as the reference electrode. Oxygen was removed from the polarographic solutions by purging argon.

An important role in the sorption of metal ions is played by the pH environment, which affects the dissociation of polyelectrolyte functional groups and the ionic state of certain polyvalent metals, including vanadium.

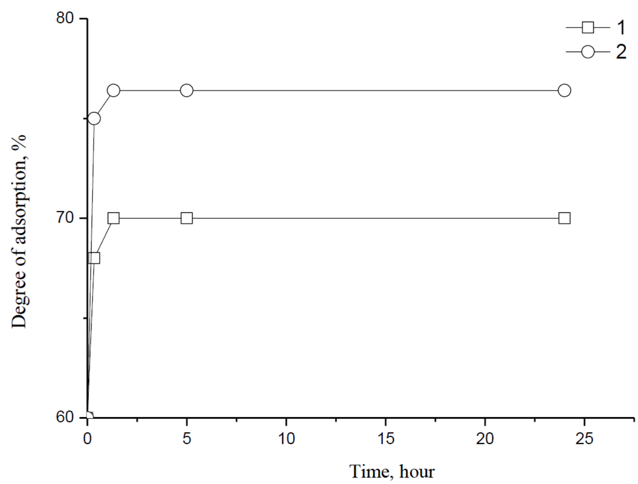
Numerous data (Ergozhin et al., 2004; Sakharov and Turpida, 1980; Strakhov, 1950; Astashkina et al., 1990; Dzhabarov and Gorbachev, 1964; Goncharenko, 1969; Tr. Institute of Chemistry of the USSR Academy of Sciences, 1971; Muzgin et al., 1981) on the ionic composition of Vanadate solutions are contradictory. The variety of ionic forms of vanadium (V) is due to both the concentration and acidity of the solution. Ergozhin et al. (2004) provide data on the presence of various vanadium ions in solutions depending on the pH:

	VO_4^{3-}	HVO_4^{2-}	$V_3O_9^{3-}$	$V_{10}O_{28}^{6-}$	$HV_{10}O_{28}^{5-}$	$H_2V_{10}O_{28}^{4-}$	VO_2^+
pH	>13	8–3	8–6.6	6.5–6.6	6.0–3.5	3, 2 – 2	<2

Astashkina et al. (1990) point out the existence of a wide range of easily polymerised and hydrolysable vanadium ions in aqueous solutions, the balance between which is determined mainly by the pH value of the medium and the concentration of vanadium in the solution. In the area of moderately acid solutions of pentavalent vanadium formed numerous isopolyvanadate. It is noted that in aqueous solutions in a wide range of acidity, the compounds of pyativalent vanadium are most stable, and vanadates and isopolyvanadates are highly hydrated. The vanadan ion VO^{2+} is formed only in strongly acidic solutions. Five-valent vanadium, having amphoteric properties, can be present in aqueous solutions in both anionic and cationic forms (Goncharenko, 1969). In addition, depending on the pH of the medium and the total concentration of vanadium in the solution, the degree of ion condensation also changes. In strongly alkaline and strongly acidic environments, as well as at low vanadium concentration in solution (less than 10^{-4} g-atom/l), there are monomer forms. The maximum degree of condensation is observed in a weakly acidic medium, where the Vanadate ion contains 10 vanadium atoms. Within the concentration range of 10^{-1}–10^{-4} g-atom/l vanadium in the form of mononuclear particles exists only in acidic (pH > 2) and strongly alkaline (pH < 13) solutions. Decavanadicic acid $H_6V_{10}O_{28}$ in aqueous solutions easily cleaves off four protons, it exists in the pH range 2–6. At a pH of 5–7, decavanadate ions coexist with metavanadate ions. In Tr. Institute of Chemistry of the USSR Academy of Sciences (1971), the authors also note that the question of the state of vanadium ions often remains unclear. This is especially true for vanadium (V), whose ionic composition is very complex.

Despite the fact that the polarographic behavior of vanadium is also highly dependent on pH, polarographic method has been successfully used for the quantitative determination of compounds of vanadium in solutions, but also allows you to penetrate deeper into the complex field describing the status of vanadium in aqueous solutions (Astashkina et al., 1990; Dzhabarov and Gorbachev, 1964; Goncharenko, 1969; Tr. Institute of Chemistry of the USSR Academy of Sciences, 1971; Muzgin et al., 1981). Sorption of vanadium ions by different redox polymers was studied under static conditions depending on the pH of the medium, the concentration of solutions, and time. The initial and equilibrium concentrations of ammonium and sodium vanadates were determined by polarographic method (Antonovich et al., 1997; Ryabchikov and Tsitovich, 1962).

Figure 2 Kinetic curves of vanadium sorption by copolymers VEMEA-X with 2-VP (1) and 4-VP (2)



The study of the kinetic curves of vanadium sorption with VEMEA-X copolymers with 2- and 4-*VP* (Figure 2) at pH 2, the concentration of a solution of ammonium vanadate $2.5 \cdot 10^{-2}$ mol/l (2.27 g/l V_2O_5 or 1.27 g/l V) showed that the ion-exchange equilibrium occurs in both cases in 10 minutes, a further increase in the contact time up to 24 hours does not lead to significant changes, which indicates a high permeability of the obtained ion exchangers.

Tables 1 and 2 show the sorption capacity of new redox polymers for vanadium and the distribution coefficient calculated by the formula:

$$C_{distr} = \frac{M_r \cdot V}{M_s \cdot m};$$

where M_r and M_s – equilibrium concentration of metal in the resin phase and solution, g; V is the volume of the solution, ml; m - resin weight, g.

Table 1 Dependence of the distribution coefficient and sorption capacity on pH during vanadium sorption from a solution of ammonium metavanadate ($C = 2.5 \cdot 10^{-2}$ mol/l) by homopolymers from redox monomers

pH	*C distr.*			*CE, mg V_2O_5/g*		
	VEMEA-X	*(VEMEA)$_2$-X*	*VEMEA – 1,4-NPH*	*VEMEA-X*	*(VEMEA)$_2$-X*	*VEMEA – 1,4-NPH*
0.9	35.61	35.61	35.61	59.63	59.63	59.63
2.0	100.00	100.00	100.00	113.54	113.54	113.54
3.0	134.69	134.69	59.80	130.32	130.32	85.00
4.0	59.80	59.80	35.61	85.00	85.00	59.63
6.1	35.61	47.91	24.95	59.63	73.55	45.34

Table 2 Dependence of the distribution coefficient and sorption capacity on pH during vanadium sorption from a solution of ammonium metavanadate ($C = 2.5 \cdot 10^{-2}$ mol/l NH_4VO_3 or 1.27 g/l V) with copolymers based on VEMEA-X and VEMEA-X-VEMEA with 2- and 4-vinylpyridines

pH	*C distr.*					*CE, mg V_2O_5/g*				
	VEMEA-X		*(VEMEA)$_2$-X*			*VEMEA-X*	*(VEMEA)$_2$-X*			
	2-VP	*4-VP*	*CT*	*2-VP*	*4-VP*	*2-VP*	*4-VP*	*CT*	*2-VP*	*4-VP*
0.9	47.91	59.80	24.95	35.61	35.61	73.55	85.00	45.34	59.63	59.63
2.0	232.98	321.19	134.69	232.98	321.19	158.99	173.17	130.32	158.99	173.17
3.0	100.00	175.32	100.00	100.00	175.32	113.54	144.60	113.54	113.54	144.60
4.0	59.80	100.00	81.71	59.80	100.00	85.00	113.54	102.12	85.00	113.54
6.1	35.61	59.80	59.80	35.61	59.80	59.63	85.00	85.00	59.63	85.00

From the data in Tables 1 and 2, it can be seen that these characteristics also depend on the pH of the solutions. The maximum value of C_{distr} and *CE* are observed for all copolymers and homopolymers based on VEMEA-1,4-NPH at pH 2, and for homopolymers from VEMEA-X and VEMEA-X-VEMEA at pH 3.

Figure 3 shows isotherms of vanadate ions sorption from solutions of NH_4VO_3 with pH 2.0 homopolymer from VEMEA-X and its copolymers with 2- and 4-vinylpyridines, removed under static conditions at a ratio of ionite: 1:100 solution, sorption time – 24 hours.

The initial concentration of vanadium ions has a significant effect on the sorption capacity of redox polymers. Copolymers based on vinyl pyridines extract vanadate ions better than homopolymer, especially from more dilute solutions. At pH 6.7–7.0 of initial solutions of NH4VO3with a concentration of 1.5 g/l V, the extraction degree of vanadate ions for the homopolymer is 10.87%, and for copolymers for 2- and 4-VP it is 21.48%. Of neutral solutions of NH_4VO_3 with a higher content of vanadium, no sorption occurs.

Figure 3 Sorption of vanadium ions from solutions of NH_4VO_3 with the homopolymer of VEMEA-X (1) and its copolymers with 2-VP (2) and 4-VP (3)

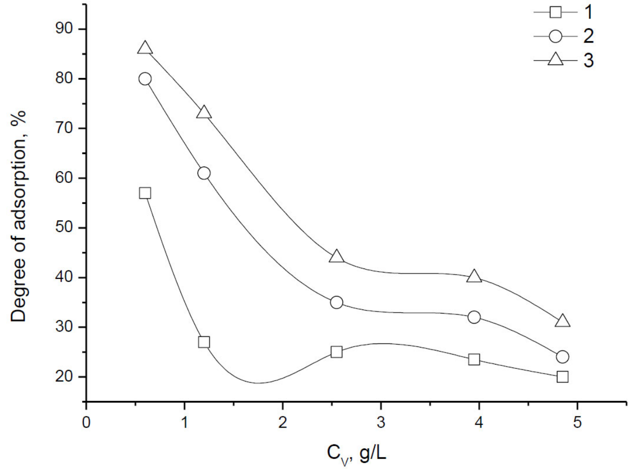
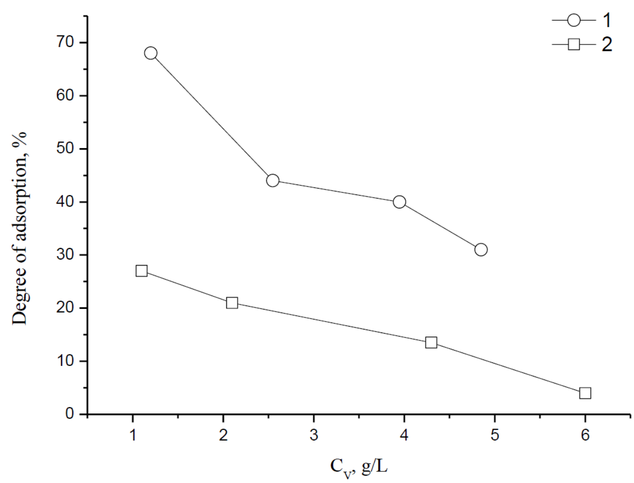


Figure 4 Sorption of vanadate ions with VEMEA-X copolymer: 4-VP from solutions of NH_4VO_3 (1) and $NaVO_3 \cdot 2H_2O$ (2) with pH 2.0 (24 hours)



As shown in Figure 4 and Table 3, the extraction of vanadate ions depends on the nature of the vanadium salt cation. From solutions NaVO3·2H2O with pH 2.0 sorption goes much worse than from a solution of NH4VO3 with pH 2.0. From solutions $NaVO_3 \cdot 2H_2O$ with pH 7.8 vanadate ions are slightly extracted only by the homopolymer of VEMEA-X, and its copolymers with 2- and 4-vinylpyridines in the concentration range 1-6 g/l V do not sorb them at all.

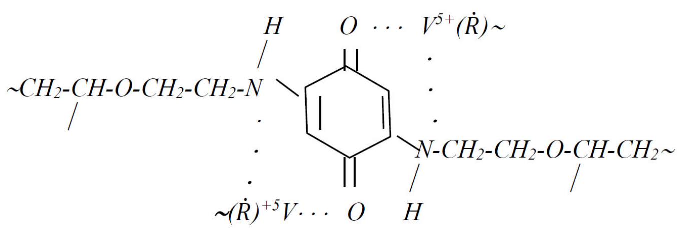
Table 3 Sorption of vanadate ions by a homopolymer from VEMEA-X and its copolymers with 2- and 4-VP, depending on the concentration and pH of $NaVO_3 \cdot 2H_2O$ solutions

pH	*CV ucx., g/l*	*Extraction rate, %*		
		–[–VEMEA-X–]n–	*–[–VEMEA-X-2-VP–]n–*	*–[–VEMEA-X-4-VP–]n–*
2	1	65.75	56,50	78.50
	2	26.59	50.80	50.70
	4	0.00	25.80	25.40
	6	0.00	15.20	15.40
8	20.00	0.00	0.00	0.00
	10.30	0.00	0.00	0.00
	10.55	0.00	0.00	0.00
	2.50	0.00	0.00	0.00

Thus, the best sorption properties with respect to vanadate ions are copolymers of VEMEA-X and VEMEA-X-VEMEA with 4-VP when they are extracted from acid dilute solutions of ammonium vanadate.

The complexation of (co)polymers based on the quinoid derivatives of VEMEA occurs, apparently, both as a result of the oxygen atoms of the ether bond and the nitrogen of the amino group of VEMEA, and also due to the carbonyl group of quinones and metal ions (Figure 5).

Figure 5 Scheme of complexation of (co)polymers based on quinoid derivatives of VEMEA



As can be seen from Figure 4, together with vanadium, a redoxpolymer based on quinoid pro-induction VEMEA will extract oil from the pores and cracks of the seams.

In addition, the nitrogen atoms of the heterocycles 4-VP and 2-VP are ‘turned’ in the process. Unlike ion-bound metal of donor nitrogen atoms, donor oxygen atoms of coordinated ligands are usually easily protonated and lead to the destruction of chelate cycles.

Thus, synthesised redox (co)polymers based on VEMEA can find practical application, for example, in oil production and hydrometallurgy.

The practice of exploitation of oil and gas fields shows that in addition to the main useful components, i.e. hydrocarbons, oil and gas contains such associated minerals as sulfur, vanadium, Nickel, uranium, nitrogen, helium, etc. When estimating the cost of oil and gas, up to now only the presence of hydrocarbons has been taken into account, without taking into account the cost of other associated minerals included in oil and gas. In case of complex development of oil and gas fields, the price of oil and gas should be determined by the formula:

- For oil:

$$C_o = C_{HO} + \sum\nolimits_{i=1}^{n} C_i, \qquad (1)$$

where

C_{HO}	cost hydrocarbons in the oil
$\sum\nolimits_{j=1}^{m} C_j$	the total value of minerals included in the composition of commercial oil.
i = 1 … n	minerals that are part of oil.

- For gas:

$$C_g = C_{hg} + \sum\nolimits_{j=1}^{m} C_j, \qquad (2)$$

where

C_{hg}	value hydrocarbons in the gas
$\sum\nolimits_{j=1}^{m} C_j$	the total value of minerals included in the composition of the gas
j = 1 … m	along the way-produced gas that is part of the gas.

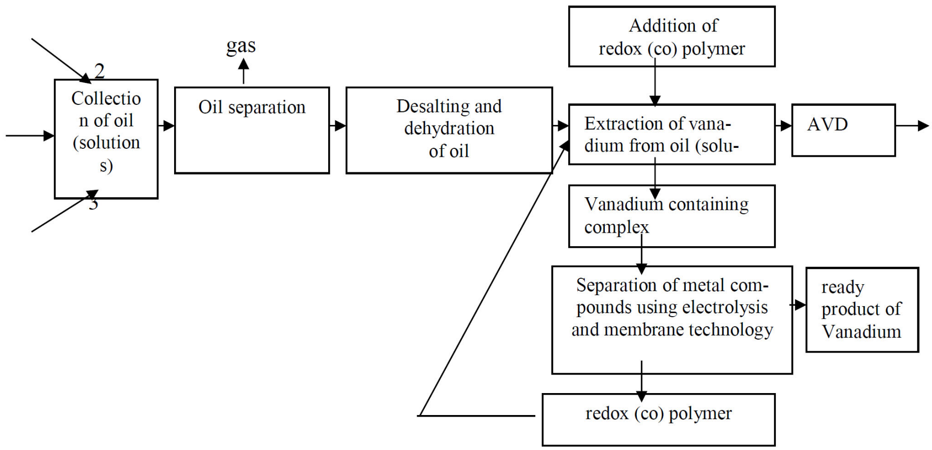
As is known, more than 60 different trace elements and metals have been found in oil, the concentration of which varies very widely: from traces to hundreds of grams per ton of oil. Increased content of trace elements of metals is usually characteristic of high-viscosity heavy oils and natural bitumens.

By vanadium content (0.02–0.6 wt.% or 440 tons of vanadium pentoxide per 1 million tons of oil) buzachinskaya oil competes with many types of vanadium-containing ores. Taking into account the constant growth of demand for vanadium – a strategic metal-research on its separation from buzachin oil is very relevant and is of both theoretical and practical interest. the high profitability of vanadium extraction processes was noted: when processing 200 thousand tons of buzachinsky oil per year, it is possible to obtain about 80 tons of vanadium with the achievement of an economic effect when selling vanadium – up to $1.6 billion a year. Below is the proposed method for extracting vanadium from high-viscosity oils, which consists in territorial and technological combination of the processes of extraction, processing and extraction of vanadium and other associated components.

At the same time, practice shows that under existing technological schemes of oil refining, a large number of useful components (Au, Zn, Cu, Ni, V, etc.) that are extracted with oil are lost. This also leads to a decrease in the quality of oil and undesirable environmental shifts in the natural balance when metals get into oil products. In this regard, the search for innovative schemes for the preparation and processing of oil with the extraction of associated metals is an urgent scientific problem of the modern oil and gas industry, and in particular, oil refineries.

For practical use of the obtained results in the processes of vanadium extraction from oil and ore leaching solutions, a new technological scheme for the collection and treatment of oil (solutions) is shown in Figure 6 (Nuranbaeva, 2013; Ahmedzhanov et al., 2011).

Figure 6 Innovative technological scheme for the collection and treatment of oil (solutions) with the extraction of vanadium



Note: 1, 2, 3 – vanadium-containing oil (solutions) deposit, AVD – atmospheric-vacuum primary distillation of oil.

4 Conclusions

1. To develop residual oil reserves, a new technological scheme of production is developed, which consists in creating such conditions for drainage of liquid fluids, under which they will be collected under the action of gravity forces in a horizontal well and pumped out by pumps.
2. To improve the drainage conditions, it is proposed to pump a solution of redox polymers into the formation through injection wells, which will involve metal-containing oil in the moving liquid stream due to the sorption of metals.
3. It is proven that redox polymers are capable of extracting vanadate ions from acid dilute solutions, for example, oil. At the same time, it has been established that copolymers based on quinoid VEMEA derivatives of vinyl pyridines sorb ions of vanadium more efficiently than other redoxions.
4. The results of studies of complex-forming and redox-properties have shown the possibility of developing new waste-free, environmentally friendly import-substituting sorption technologies that can be used in the oil and gas and mining industry of the Republic of Kazakhstan to extract oil from reservoirs and vanadium from solutions.

5 The use of cheap Kazakhstani raw materials - vinyl ether monoethanolamine (VEMEA) will significantly simplify the synthesis and reduce the cost of redox polymers, allows their multiple regeneration, involves multiple operation, reducing the cost of transportation of raw materials will pay for the costs of their receipt. In addition, the presence of an amino group in the structure of VEMEA eliminates the additional stage - amination, imparts hydrophilicity to polymers and improves kinetic characteristics, due to complexing and redox properties.

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