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# METHOD FOR EXTRACTION OF VANADIUM FROM OIL DURING PREPARATION

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## ABSTRACT

Many fields of high heavy oil and bitumen, both in Kazakhstan and abroad, include industrial concentration of vanadium, nickel and other metals. To enhance the efficiency of fields containing high viscosity oil, widely used thermal methods of stimulation. The use of various modifications can significantly increase oil recovery and expand the development of hard-to-hydrocarbon reserves. However, with proven technological efficiency of thermal methods remain the integrated development of deposits of metal-heavy oil and bitumen, including the associated extraction of vanadium and nickel. In particular, there were, until recently, industrial development projects viscous oils Peninsula Buzachi (Karazhanbas North Buzachi, Zhalgiztyube) extraction of vanadium was not provided. Economic damage from uncleared vanadium pentoxide contained in these oils may exceed a billion tenge.

**Key words**: Extraction, Heavy oil, Bitumen, Metals, Oil fields, Vanadium, Crude oil.

## INTRODUCTION

In order to study the effect of different thermal design methods for the degree of metal extraction studies have been conducted to analyze the concentrations of vanadium and nickel in oil from wells in the experimental-industrial fisheries Karazhanbas field, in this model, starting from the following changes in the concentration of vanadium and nickel in oil in the implementation of *in situ* combustion technology. In forming the combustion front metals should be concentrated in the coke residue from burning fuel. As you move the flame front and the formation of a zone of steam and hot water and a shaft of light hydrocarbons should see a sharp decrease in the concentration of vanadium and nickel in the produced product than oil produced outside the areas respond. Next, in an area not covered by the heat, there was a relative decrease in viscosity and density of the oil should also be reflected in a

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decrease in the concentration of asphalt-resinous components and associated metals. This model is well supported by the results of the research, which are based on the analysis of 89 samples of oil production well. Concentrations of vanadium and nickel in oil are without ashing samples by fluorescent X-ray radiometric analysis using a semiconductor spectrometer and X-ray tube by the technique developed in VNIGRI (V. Ponomarev, AR Nazarov), based on the analytical data were maps of the distribution of concentrations of vanadium and nickel, and the losses of metals delineated areas which should correspond to zones of varying the intensity of exposure. The direction of the combustion front can probably be traced to the minimum value of the concentration of metals in the oil prisoners. However, the grid 200 x 200 m wells are generally not possible to trace the dramatic changes in the content of metals from injection to production wells as combustion sources and condensation zone do not reach the latter. In general, the fishing in-situ combustion is a result in permanent loss of metals in crude oil, which accounts for an average vanadium 36.3% of the recoverable reserves, reaching in areas of severe exposure of 70-75%. Average content (% of initial) vanadium and nickel in oil in implementing HS in strong impact is 39.5 and 38.6, average - 64.2 and 77.2, the weak - 81.5 and 91.7, with no impact - 100 and 100, respectively. Relation to the area of distribution of these zones include high impact-11%, average - 61, low – 28[4].

Thus, taken as we do, and how to develop overseas heavy viscous oils, enriched with vanadium, do not provide a comprehensive and highly efficient exploitation, were therefore carried out theoretical and experimental research in the search for new ways to develop the vanadium-oil fields. For example, the method of thermal viscous oil using process oil produced. The method is based on the territorial and technology combining the extraction and processing of viscous oil. It includes its processing directly in the fishery on the installation of thermal processing of oil (USP), the selection of a plant and injection of oil-based coolant. With some additions and changes, this method allows extracting useful and associated components, in particular vanadium. The research and technical-economic calculations show that the implementation of technology and process spatial combining production, processing and associated metals recovery enables more integrated use of mineral resources in an economically viable basis, sparing environmental regime. The proposed technology can be extended to other fields of highly industrialized oil and bitumen[6]. At the same time, the metal - it is the only component of commercial oil, which is not desirable, or at least indifferent to any and all oil products, as they reduce the proportion of selection of light products (i.e. oil refining), poison many refining catalysts, lower the quality of many commodity oil, causing in some cases, the failure of refinery equipment (due to corrosion of vanadium) and, finally, are the main native ash boiler fuels. On the other hand, the compounds of oil, which include the bulk of the metal, are the main sources of viscosity and natural emulsifiers. Thus, the development and introduction of technology into our reality demetallization not only can significantly improve the quality of commercial oil, but will get a considerable number of highly deficit metals. However, this is not an easy process, because range of petroleum compounds containing metals, extremely broad and include organometallic compounds, salts of carboxylic acids, intramolecular complexes (such as porphyrins) as well as resins and asphaltenes. Till date many technologies have been developed for extracting oil from metals, but they are all used as raw material, as a rule, only the heaviest components of oil - mostly tar and asphalt - where metal concentrations are highest. Below is a list of fields in Kazakhstan, where possible application of the proposed method with the characteristics of these oil fields[5].

Araltobe field is located in Zhylyoi area 70 km from Kulsary area, this field is opened in 1926. The presence of vanadium and nickel are 0.0045% 0.0030% in the field. Kolzhan field is located in Zhylyoi area, this field is opened in 1957. The presence of vanadium and nickel are 0.0041% and 0.0041% in the field. Esenzhol field is located in Zhylyoi rayona area 65 Km from Kulsary area, this field is opened in 1957. The presence of vanadium and nickel are 0.0038% 0.0022%. Zhubantam field is located in Zhylyoi district, 90 Km from Kulsary, this field is opened in 1972 to the development in 1980-1981. Soderzhit large amount of vanadium (15.3 x 10%), which largely prevails over nickel (0.26 x 10%). Oilfield Karaarna is located in Zhylyoi area, 180 Km south-east of Atyrau city. The field was discovered in 1960. Vvedeno in 1974. Karazhanbas field is located in the Caspian oil and a gas province, this field is opened in 1974. Technological support by 70% of vanadium North Buzachi is located at 175 North km. from Aktau city, this field is opened in 1974. Shilikty field is located in Alga district, 65 Km from Aktobe city, this field is opened in 1979. The presence of vanadium and nickel are 0.0019% and 0.0032%. Karamurut field is located in Zhylyoi area of 205 Km away from the mountain Imanқara. This field is opened in 1981. The presence of vanadium and nickel are 0.014% 0.029%. Қyryқmyltyқ field is located in the area in Zhylyoy 60 Km North-East of Kulsary. Mestorozhdenie discovered in 1988. The presence of vanadium is (7-54 g/t), and nickel is (up to 76 g/t). Karaturun field is located 270 Km from Aktau. This field is opened in 1988. The presence of vanadium is 3580 x 10%. When determining the activation of neutral nickel in an amount of 941 x 10%[1,2].

Due to the high temperature and pressure applied during ashing at high pressure, it is possible to achieve complete decomposition of organic samples even problematic. The risk of contamination is minimized by the use of closed vessels, and small quantities of reagents. Very low content of residual carbon after ashing gives sample solution that is suitable for analysis, even using highly instrumental techniques. Microwave digestion, used for comparison, was performed in a microwave digestion system at high pressure of Anton Paar with vessels made of quartz glass, designed to work at high pressure. In microwave systems with low operating rates Digestion of crude oil is not enough. In terms of safety and reliability, ashing at high pressure is the preferred method, since fluctuations in weight of the sample or reaction progress are not having much impact on the results of analysis. Vanadium is the rare representative of ferrous metals, the main application of vanadium-production of vintage cast iron and steel. The addition of vanadium provides high performance titanium alloys for the aerospace industry. It is widely used as a catalyst in the production of sulfuric acid. In nature, is found in the vanadium titanium magnetite ore, rare rock phosphate, as well as uranium-bearing sandstones and siltstones, where its concentration is less than 2%. The main ore minerals of vanadium in these fields are carnotite and vanadium muscovite-roskoelit. Significant amounts of vanadium are sometimes also present in bauxite, heavy oil, brown coal, bituminous shales and sands. Vanadium is usually obtained as a by-product of the extraction of the principal components of mineral raw materials (such as titanium slag processing titanomagnetite concentrate, or ash from the combustion of oil, coal, etc.)[7,8].

The vanadium is found in South Africa, U.S., Russia (mainly the Urals) and Finland, on discounted stocks vanadium lead South Africa, Australia and Russia.

In petroleum are found more than different 60 minerals and metals, the concentrations of these metals are very varies widely in the petroleum: from traces to hundreds of grams per ton of oil. High levels of trace metals are a main characteristic of extra-heavy oil and natural bitumen. In petroleum are found more than different 60 minerals and metals, the concentrations of these metals are very varies widely in the petroleum: from traces to hundreds of grams per ton of oil. High levels of trace metals are a main characteristic of extra-heavy oil and natural bitumen[9].

The aims of researchers interest to create a selective ion-exchange resin, selectively sorbing ions of noble, non-ferrous and rare metals. In Kazakhstan, the main industrial source of metal ores is for the extraction of which often use foreign sorbents, so the problem of synthesis of selective ion exchangers relevant.

However, the practice shows that the existing technological schemes refining lose more of produced oil-mineral components (gold, zinc, copper, nickel, vanadium, etc.), this leads also to a decrease in oil quality, and undesirable environmental shifts the balance of nature in contact with metals in petroleum products. In this regard, the search for innovative schemes of preparation and processing oil to the recovery of produced metal is an actual scientific problem in modern oil and gas industry and in particular, oil refineries (refinery)[3].

Upon receipt of the quantitative characteristics of the composition of petroleum in the Atyrau field, refinery complexes of various metal ions were studied by hromotomass the spectrometer (Fig. 1). From the calculated data, the number of fields in the oil refined at the Atyrau field refinery presence of metals such as zinc, copper, nickel (Table 1) etc.

**Table 1: Results of the study on the gas chromatograph mass spectrometer**

| S. No. | Name of sample | Cobalt (Co) | Zinc (Zn) | Nickel (Ni) |
|---|---|---|---|---|
| 1 | Mangyshlak oil | - | - | $C_4NiO_4$ 0.172 |
| 2 | Zhanazhol oil | $C_{14}H_{19}Co$ 0.005 | $C_{18}H_{34}Zn$ 0.337 | |
| | | $C_{22}H_{21}B_2Co$ 0.008 | - | - |
| 3 | Petroleum. ELOU-AT-2 Time of selection 08.00 date of selection18.11.2009 | - | - | $C_4NiO_4$ 0.826 |
| 4 | Oil after desalting. ELOU-AT-2 Time of selection 08.00 Date of selection 18.11.2009 | $C_{10}H_{13}Co$ 0.002 | - | - |
| 5 | Petroleum. installation CDU VDU-3 Time of selection 08.00 Date of selection 18.11.2009 | - | - | $C_4NiO_4$ 0.337 |
| 6 | Oil after desalting. ELOU-AVT-3 Time of selection 08.00 Date of selection 18.11.2009 | $C_{10}H_{13}Co$ 0.001 | $C_{12}H_{14}Cl_2N_2$ Zn 0.008 | $C_4NiO_4$ 0.784 |

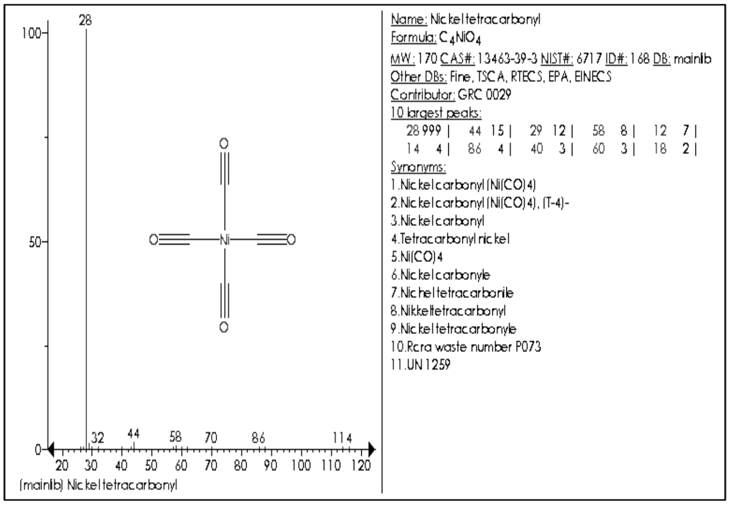


**Fig. 1: Oil after desalination, ELOU-AT-2, chromatogram and the nickel compound**

A large number of rare metals-vanadium also marked in the high-oil and bitumen (Table 2 and Table 3). One of the trace elements in the oil composition as mentioned above is vanadium. Vanadium is used in heavy and light industry, livestock, for preparing medicines. From the studies of petroleum in Kazakhstan fields in Table 2 that showed the vanadium are present in almost all oils.

**Table 2: The vanadium content in the oil fields in Western Kazakhstan**

| Field | Content, g/t | Field | Content, g/t |
|---|---|---|---|
| **Mangistau region** | | **Aktobe area** | |
| North. Buzachi | 100-300 | Bozoba | 50-120 |
| Karazhanbas | 70- 300 | Sinelnikovskoye | 5-50 |
| Kalamkas | 60- 300 | Zhanazhol | 1- 10 |
| Zhalgyztobe | 60- 200 | Kenkiyak | 1- 10 |
| Karaturun | 70- 140 | Ostansuk | 1-5 |
| Besoba | 70- 140 | **Atyrau area** | |
| Uzen | 0.5-5 | Karaarna | 40-70 |
| Asar | 0.5-5 | Tortay | 10-80 |
| North. Rakushechnoe | 0.5-5 | Kumshety* | 10-60 |

Cont…

| Field | Content, g/t | Field | Content, g/t |
|---|---|---|---|
| **Mangistau region** | | **Aktobe area** | |
| Zhetybai | 0.1-1 | Biikzhal | 5-40 |
| Shinjiro | 0.1-1 | Tengiz | 0.1-1 |
| Tasbulat | 0.05-0.5 | **West Kazakhstan region** | |
| Oymasha | 0.01-0.1 | Gremyachinskoye | 20-50 |
| North. Karagie | 0.01-0.05 | Zap. Teplovsko | 1-10 |
| Uylyuk | 0.001-0.01 | Karachaganak | 0.05-0.5 |
| Zhilindy | 0.001-0.01 | | |
| Aschisor | 0.001-0.01 | | |

Not only in oil but also in the bitumen and shale are different types of these trace elements, the Table 3,4 that showed the concentration of vanadium in bitumen and shale rocks in Western Kazakhstan.

**Table 3: The vanadium content in the oil and bituminous rocks of the Western Kazakhstan**

| Field | Content, g/t | Field | Content, g/t |
|---|---|---|---|
| **Aktobe region** | | **Atyrau region** | |
| Akbulak | 50-400 | Imankara | 20-80 |
| Dongeleksor | 20-70 | Akshoky | 10-70 |
| Mortuk | 10-70 | Kolzhan | 30-50 |
| Field | Content, g/t | Field | Content, g/t |
| Shilikty | 20-50 | Karamurat | 20-50 |
| Copa | 1-20 | Munayly | 10-30 |
| **Mangistau region** | | Karasaj | 5-30 |
| Tyubedzhik | 10-70 | | |
| Karasyaz-Taspas | 5-30 | | |
| Beck-Taspas | 5-30 | | |
| Tyubkaragan | 1-20 | | |

**Table 4: The vanadium content in carbonaceous shale deposits in South Kazakhstan**

| Field | Content, g/t | Field | Content, g/t |
|---|---|---|---|
| Коксу | 500-1200 | Karatal Valley | 50-200 |
| East. Valley of Tekeli Kyuel 150-300 50-250 | 150-300 | Kyuel | 50-250 |
| Yablonovskaya | 80-300 | Kokkus | 50-100 |

Vanadium content in the oil depends on the age of the rock layer Table 5.

**Table 5: The content of vanadium and nickel in crude oils from the various sediments, $10^4$ wt. %[4]**

| Age of the sediments | Interval of occurrence, m | V | | | | The average V |
|---|---|---|---|---|---|---|
| | | Terrigenous | | Carbonate | | |
| | | Measurement limit | Average | Measurement limit | Average | |
| 1 | 2 | 3 | 4 | 5 | 6 | |
| Oil with a high content of metals | | | | | | |
| Cainozoe | 0-1000 | 7.0-413.0 | 109.1 | 2.5-180.0 | 86.6 | 94.0 |
| | 1000-2000 | 2.4-348.0 | 86.2 | 7.0-600.0 | 160.1 | 146.1 |
| | 2000-3000 | 5.0-937.0 | 167.5 | 0.3-23.0 | 12.1 | 128.7 |
| | 3000-4000 | 21.0-179.0 | 127.4 | — | 4.1 | 102.6 |
| The average | | 2.4-937.0 | 113.5 | 0.3-600.0 | 138.1 | 131.0 |
| Mesozoic | 0-1000 | 1.9-251.0 | 55.7 | — | 120.0 | 57.4 |
| | 1000-2000 | 0.4-146.0 | 44.8 | 1.9-95.0 | 39.8 | 43.7 |
| | 2000-3000 | 1.1-170.0 | 41.4 | 1.5-206.0 | 68.2 | 44.6 |
| | 3000-4000 | 1.6-57.0 | 23.7 | 15.0-147.0 | 72.0 | 38.5 |
| The average | - | 0.4-251.0 | 44.2 | 1.5-206.0 | 57.9 | 46.1 |
| Paleozoic | 0-1000 | 13.3-106.3 | 44.9 | — | — | 44.9 |
| | 1000-2000 | 1.3-222.0 | 84.5 | 18.0-448.0 | 62.0 | 67.9 |
| | 2000-3000 | 15.0-90.0 | 36.2 | 5.6-237.5 | 82.9 | 66.2 |
| | 3000-4000 | 3.7-48.0 | 19.5 | 21.4-50.0 | 35.5 | 26.4 |
| | 4000-5000 | 73.6-100.0 | 86.8 | — | — | 86.8 |

Cont…

| Age of the sediments | Interval of occurrence, m | V | | | | The average V |
|---|---|---|---|---|---|---|
| | | Terrigenous | | Carbonate | | |
| | | Measurement limit | Average | Measurement limit | Average | |
| The average | - | 1.3-222.0 | 74.9 | 5.6-448.0 | 62.7 | 66.3 |
| Phanerozoic | 0-1000 | 1.9-413.0 | 66.2 | 2.5-180.0 | 88.0 | 73.1 |
| | 1000-2000 | 0.4-348.0 | 67.8 | 1.9-600.0 | 92.0 | 83.7 |
| | 2000-3000 | 1.1-937.0 | 49.9 | 0.3-206.0 | 66.9 | 52.9 |
| | 3000- 4000 | 1.6-179.0 | 50.2 | 4.1-147.0 | 47.1 | 49.2 |
| | 4000-5000 | 73.6-100.0 | 86.8 | — | - | 86.8 |
| The average | - | 0.4-937.0 | 59.6 | 0.3-600.0 | 88.3 | 73.3 |
| Cainozoe | 0-1000 | 0.01-1.6 | 0.72 | — | — | 0.72 |
| | 1000-2000 | 0.0-13.4 | 0.67 | — | — | 0.67 |
| | 2000-3000 | 0.0-2.5 | 0.88 | — | — | 0.88 |
| | 3000-4000 | 0.15-3.2 | 0.72 | — | — | 0.72 |
| | 4000- 5000 | — | 5.0 | — | — | 5.0 |
| The average | - | 0.0-13.4 | 1.2 | - | - | - |
| Mesozoic | 0-1000 | 0.0-27.0 | 1.8 | 0.26-4.3 | 2.28 | 1.82 |
| | 1000-2000 | 0.01-15.0 | 4.23 | 6.0-14.3 | 8.36 | 4.67 |
| | 2000-3000 | 0.02-53.0 | 7.79 | — | — | 7.79 |
| | 3000- 4000 | 0.11-2.24 | 1.18 | — | 8.1 | 3.49 |
| The average | - | 0.0-53.0 | 2.28 | 0.26-14.3 | 7.6 | 4.38 |
| Paleozoic | 0-1000 | 0.05-0.37 | 0.21 | 0.84-7.04 | 4.05 | 2.51 |
| | 1000-2000 | 0.52-1.8 | 1.16 | 0.07-83.7 | 5.52 | 5.2 |
| | 2000- 3000 | 0.6-10.0 | 5.3 | 0.0-13.6 | 1.86 | 2.05 |
| | 3000-4000 | 0.0-24.0 | 4.53 | 0.06-9.3 | 2.88 | 3.98 |
| | 4000- 5000 | 0.15-1.0 | 0.58 | 0.06-15.0 | 7.53 | 4.06 |
| | 5000- 6000 | — | 9.4 | — | — | 9.4 |
| The average | - | 0.0-24.0 | 3.64 | 0.0-83.7 | 3.03 | 3.55 |
| Phanerozoic | 0-1000 | 0.0-27.0 | 1.47 | 0.26-7.04 | 3.34 | 1.6 |
| | 1000-2000 | 0.0-15.0 | 76 | 0.07-83.7 | 5.99 | 2.52 |

Cont…

| **Age of the sediments** | **Interval of occurrence, m** | **V** | | | | **The average V** |
|---|---|---|---|---|---|---|
| | | **Terrigenous** | | **Carbonate** | | |
| | | **Measurement limit** | **Average** | **Measurement limit** | **Average** | |
| | 2000- 3000 | 0.0-53.0 | 5.48 | 0.0-13.6 | 1.86 | 4.06 |
| | 3000- 4000 | 0.0-24.0 | 1.98 | 0.06-9.3 | 3.75 | 2.27 |
| | 4000-5000 | 0.15-5.0 | 2.05 | 0.06-15.0 | 7.53 | 4.24 |
| | 5000- 6000 | — | 9.4 | — | — | 9.4 |
| The average | - | 0.0-53.0 | 2.41 | 0.0-83.7 | 3.34 | 2.71 |

Based on these studies we proposed (Fig. 2), the following flow charts extraction of produced precious, non-ferrous and rare metals and allow for preparation and processing to extract them from the oil and oil products, thus improving the quality of these metals.

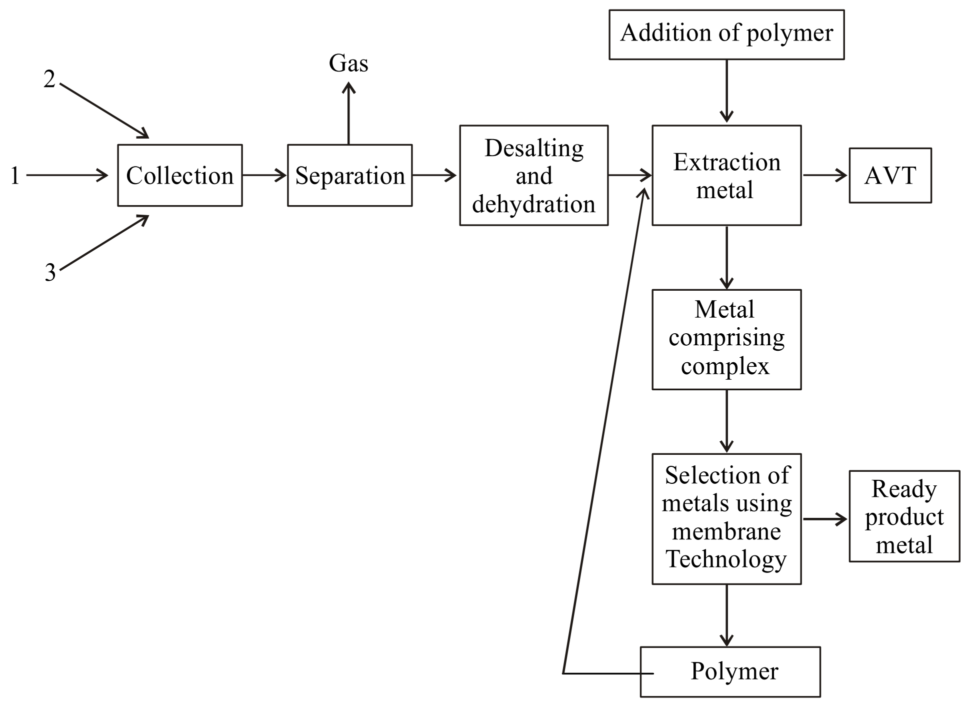


**Fig. 2: A new flow sheet gathering and treatment with extraction of produced metal (vanadium)**

1, 2, 3 – of produced metal-mine, AVT – atmospheric and vacuum distillation of the Oil.

Thus, these problems can be solved by implementing of the oil industry of sorption processes for the extraction of metals based on polymers with membrane technology. This corresponds to the integrated development of the oil fields.

## CONCLUSION

In this paper, the interest to create advanced ion exchange resins for the extraction of produced precious, non-ferrous and rare metals from crude oil and petroleum products. A general technological scheme of the collection and preparation of oil and oil products the extraction of precious and non-ferrous and rare metals, polymers and membrane technology.

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