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METHODS AND ENVIRONMENTAL ASPECTS OF UTILIZATION OF ASPHALTENE SEDIMENTS AS A HARD WASTE OF THE OIL PRODUCING INDUSTRY

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ABSTRACT

In this paper, possible methods for the prevention and disposal of waste asphaltene sediments (AS) are systematized. The practical importance of the rational use of existing methods for prevention of AS sediments occurrence, as well as the recycling methods are represented. The practical value is considered by the example of the Unvinskoye oilfield, enterprises of the Russian Federation and the USA. The formation of wastes from asphaltene sediments is possible during the drilling of wells, as well as in the course of operation during the overhaul of wells and cleaning of drainage tanks. This type of waste is mostly paraffinic, so a mechanical method of prevention (scrapers) is adopted. This paper summarizes the existing technologies for utilization and processing of sludge using them as alternative energy sources. The problem of their utilization is now solved by processing in the existing scheme for the preparation of commercial oil. Full utilization of liquid petroleum wastes, even at a single enterprise, ensures a reduction in the total amount of petroleum wastes by more than 70% and the return of marketable oil to resource turnover. The paper presents the results of calculations of waste generation during construction and operation. We also considered classification of hazardous waste to the environmentally dangerous. Promising areas of processing asphaltene sediments are presented.

INTRODUCTION

The most important environmental problem at present is the management of waste contaminated with oil and oil products [1].

The output of oil sludge in refineries is about 7 kg / ton of refined oil. These heavy oil residues contain on average 10-56% of petroleum products, 30-85% of water, and 1.3 - 4.6% of solid impurities. Based on the list of wastes it follows that the problem of handling such wastes as oil sludge is relevant for enterprises of many industries. The problem is compounded by the fact that industrial wastes containing petroleum products are toxic and flammable, and there are practically no efficient technologies for their processing or disposal. Due to their high danger they are not accepted for burial at city dumps. Therefore, sludge is accumulated in the territories of enterprises, is stored in sludge caps, earth storages, etc. being a permanent, chronic source of environmental pollution (EP). Processing and disposal of oil sludge is an important environmental and economic challenge [2]. Considering the problem of oil sludge utilization, it should be noted that oil sludge is also a valuable secondary material resource [3], a potential source of additional raw materials that can be processed to extract useful products or used as fuel. Using it as a raw material is one of the rational ways of its disposal, since it achieves a certain environmental and economic effect [4]. According to the state of aggregation, oil waste can be divided into liquid and solid ones [Fig. 1].

Of the greatest commercial interest is liquid oil waste which represents water-oil emulsions with an oil content of up to 90% wt. The problem of their utilization is now solved by their reprocessing in the existing scheme for commercial oil treatment. Full utilization of liquid oil waste, even at a single enterprise, ensures a reduction in the total amount of oil waste by more than 70% and the return of marketable oil to resource turnover [5].

All solid oil waste generated at the stages of production, treatment and transportation of oil and gas can be divided into three types: repair waste, asphaltene sediments (AS); ground oil waste. The composition of oil waste directly depends on the result of what operation they are formed [Table 1].

In practice, most often all types of waste, regardless of their state of aggregation and composition, are jointly collected in accommodation facilities (excluding some liquid oil waste disposed of at special facilities) [2]. Therefore, traditionally, the processing of oil waste is carried out by technologies "at the end of the pipe", which do not contribute to the differentiation of waste streams at the stage of formation and increase the proportion of the oil that can be used as secondary resources.

METHODS

The methods used to control deposits in oil field equipment are determined by the specific conditions of the field and suggest two directions: prevention of formation and removal of already formed sediments [6]. The classification scheme for methods for controlling asphaltene sediments is presented in [Fig. 2].

KEY WORDS

asphaltene sediments,
ecology, waste, sludge,
disposal, methods.

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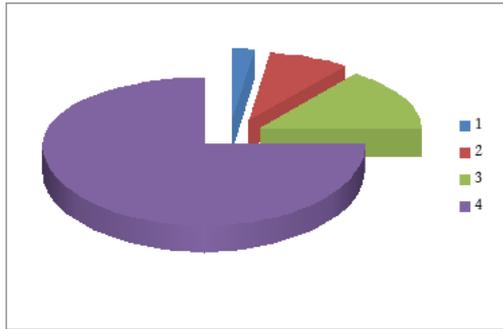


Fig. 1: The structure of oil waste oil and gas companies: 1 - maintenance waste; 2 - asphaltene sediments; 3 - ground oil waste; 4 - liquid oil waste.

Table 1: Classification of oil waste of an oil and gas production enterprise

Waste name	Technological process which generates waste	Composition of oil waste	% by weight
Solid Oil Waste			
Maintenance waste (asphaltene sediments + ground oil waste)	Well repair. Stripping of oil storage tanks	Organic substances Mechanical impurities Water	25-35 20-45 30-45
Asphaltene sediments	Repair of a well with steam cleaning of production tubing	Organic substances Mechanical impurities Water	50-93 5-49 1-5
Ground oil waste	Cleaning the area after a pipeline rupture in a warm season. Oil spill	Organic substances Mechanical impurities Water	15-20 45-65 20-35
Liquid oil waste			
Intermediate layer	Storage of oil in tanks	Organic substance Mechanical impurities Water	80-90 0-10 1
Oil polluted snow	Pipeline ruptures	Organic substance Mechanical impurities Water	2-10 40-60 38-50

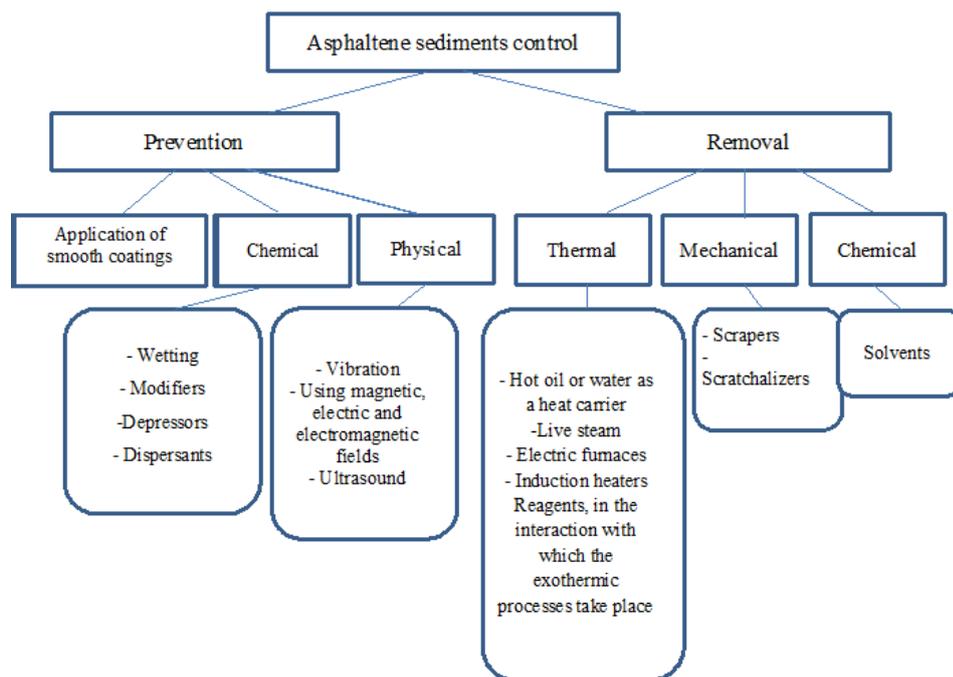


Fig. 2: Scheme for classification of asphaltene sediments control methods.

Ways to prevent formation of deposits

Under conditions of intensive formation of paraffin deposits, the inter-cleaning operation period of a well is significantly reduced (less than 30 days), the number of washes with heated agents or hydrocarbon solvents increases, what leads to an increase in oil production costs and a negative impact on the bottom-hole formation zone [7]. In such operating conditions, the best method to control asphaltene sediments is to prevent them by application of protective coatings, physical methods or special chemicals [8], [9], [10].

Methods of asphaltene sediment removal

The removal of asphaltene sediments can be carried out by a variety of methods, among which there are:

- thermal methods: flushing the downhole equipment with hot oil, creating a local heat flux using submerged electric heaters, heating cable lines or high-frequency electric field;
- chemical methods: removal with solvents and technical detergents;
- physical methods: destruction by ultrasonic action;
- biological methods: elimination using aerobic and anaerobic bacteria.

This classification of methods for controlling paraffin deposits is based on practical methods for removing or preventing the formation of deposits.

RESULTS

To consider the formation of oil waste and their disposal in practice, the calculation of the formation of asphaltene sediments during the well construction and infrastructure development at the multiple-well platform of the Unvinskoye oilfield (at the stage of developing project documentation) [11], [12] was made.

To prevent the formation of asphaltene sediments in the wellbores, semi-automatic dewaxing mechanisms of the SDU-80 type are provided. When drilling wells of the multiple-well platform, the formation of asphaltene sediments may occur during the process of cleaning the drainage tank. In the course of operation, asphaltene sediments may be formed as a result of workover of wells. The calculation of waste generation is presented in [Table 2].

Table 2: Calculation of waste generation during construction and operation

Item. No	Waste name	Oil slime quantity, t / year
For the period of drilling		
1	Sludge from cleaning pipelines and tanks (barrels, containers, cisterns, road aids) from oil	13,500
For the period of construction and operation		
2	Waste from the extraction of oil and gas (asphaltene sediments, fuel oil contaminated soil)	1,062
3	Sludge from pipelines and tanks (barrels, containers, cisterns, road aids) from oil	0.162

In order to reduce the environmental impact of a waste, this waste has to be disposed of. According to the contract of a contracting organization, they are transferred to an enterprise that is capable of utilizing this type of waste. According to the norms and rules of transportation, waste is transferred to the organization with a passport for the type of asphaltene sediment waste in a certain amount specified in the contract.

To prevent the formation of asphaltene sediments, at the Unvinskoye field in the Perm region of the Russian Federation (RF) [11], semi-automatic mechanisms for dewaxing of wells were provided (mechanical method). The waste generated during the repair of wells and the cleaning of drainage tanks were transferred to the technological site, where the work technology provided for their saturation with commercial oil and their further use. This solution made it possible to avoid the release of hazardous waste into the soil and water bodies, and emissions from the source of pollution were minimized, too.

An example of the enterprise that can utilize, recycle and neutralize this type of waste is "Priroda-Perm" LLC. One of those technologies is the saturation of asphaltene sediments with commercial oil (microbiological remediation technology). The technology has already been introduced at the Yarino-Kamenolozhskoye oil field in the Perm Territory.

[Fig. 3] presents a diagram of the main possible ways on processing and using wastes of asphaltene sediments.

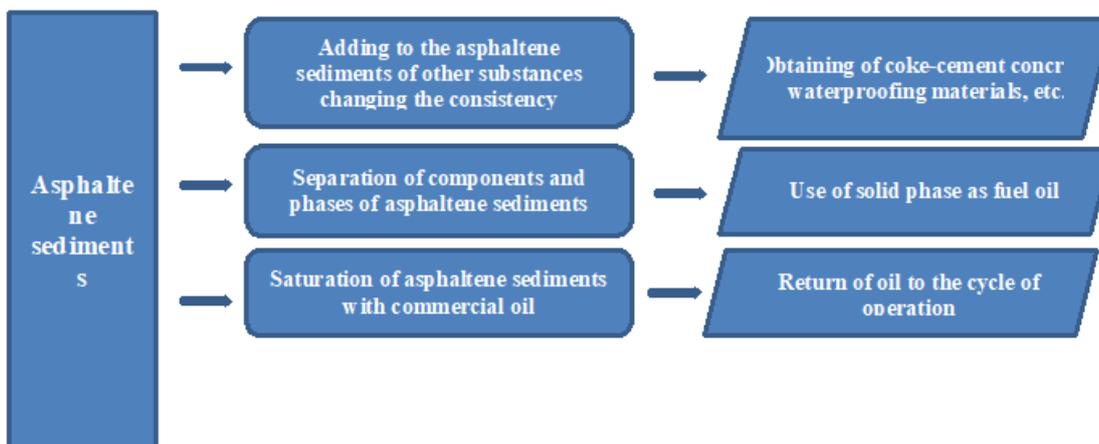


Fig. 3: Possible ways of reprocessing of asphaltene sediments.

At present, it is known, for example, that in the Republic of Tatarstan in the Russian Federation the JV Tatoiilgaz has built for the processing of oil waste an installation using the technology in which the waste was divided into water and solid sludge. The latter contains up to 5% of oil, the rest is dry black powder, which is used as a road surface.

Experimental studies have shown that the use of ground oil waste with asphaltene sediments and lime in certain proportions allows obtaining a waterproofing material for covering solid waste landfills with high physico mechanical properties [11], [13]. New schemes and technologies are being developed for processing this waste and methods of its secondary use, reducing its negative impact on the environment.

DISCUSSION

The currently existing numerous methods of dealing with paraffin deposition can significantly increase the inter-cleaning period for a well, but it is not possible to completely avoid the formation of deposits. Therefore, when carrying out routine and capital repairs of wells and pipelines or other technological operations, a mechanical sweeping (or steaming) of oilfield equipment is a necessary condition. As a result, a significant amount of solid oily waste is generated. As a rule, asphaltene sediments make up about 80% of the total amount of solid oil-contaminated waste generated [14].

From an environmental point of view, the chemical aggressiveness of deposits against environment is determined by the resins and asphaltenes contained in it. Carcinogenic polycyclic aromatic hydrocarbons containing sulfur, oxygen, nitrogen and trace elements are concentrated in asphaltene sediments. The latter can be divided into 2 groups: non-toxic (silicon, iron, calcium, magnesium, phosphorus, etc.) and toxic (vanadium, nickel, cobalt, lead, copper, molybdenum, etc.), affecting living organisms as poisons. Accordingly, the use of a single integral indicator relative to asphaltene sediments may affect the results of the obtained calculations of the hazard class, distorting them to lower values. Therefore, the determination of the hazard class of asphaltene sediments, taking into account the expanded list of indicators, is an urgent task both in terms of the correctness of hazard class calculations and for choosing a rational and safe temporary storage, disposal or recycling of this type of waste.

The organic component of asphaltene sediments can be considered as an alternative source of raw materials for petrochemical products. So, in the USA, the technology of cleaning asphaltene sediments was implemented according to the scheme: deasphalting and tertiary treatment at a refinery with obtaining high-quality white paraffins and high-melting ceresins or paraffin-ceresin compositions. However, the processes of isolating individual components or a mixture of substances are complex, time consuming, lengthy and costly. In this case, of the greatest interest is the possibility of using the purified heavy oil deposits without separation as a component of various industrial products or, realizing the principle of asphaltene sediments recovery, the return of some materials for reuse in the same process [6], [15].

Of particular interest in this context is the possibility to return of previously cleaned asphaltene sediments to commercial oil, which, on the one hand, increases the likelihood of re-precipitating heavy components of oil during its transportation through main pipelines. On the other hand, depending on the mass of the asphaltene sediments introduced into the oil, its quantitative yield increases and, accordingly, the financial benefit for a production enterprise increases. But the most important thing is the circulation of these substances is thus carried out, without the formation of asphaltene sediments as oil waste.

Existing to date developments on the involvement of the organic part of the deposits as raw materials for the production of a number of products are presented in [Table 4].

Table 4: Perspective directions of reprocessing the asphaltene sediments

Directions of reprocessing	Composition of the product	Application area
Preservative lubricant manufacturing	Petrolatum 10-20% in asphaltene sediments 80-90%, Anticorrosive additive MNI-7 0.9-1.1%	Protection of metal structures against corrosion
Rope grease	Plasticizer PN-6k-15-25%; ceroxone amide -3-7; asphaltene sediments - 20-40%; petroleum oil - up to 100%.	Lubrication of steel cables to reduce friction and wear between the individual strands of steel cables with friction mechanisms, as well as to prevent corrosion.
As a component in the production of insulation and construction bitumen	Additive 20-30% of asphaltene sediments to bitumen	Road, industrial and civil construction, the production of soft roofing and waterproofing materials, and other industries.
Waterproof roofing material	Water up to 15% wt.; Oil sludge (asphaltene sediments) - 50- 60% wt. and ceramsite cinder - 40-50% wt.;	As a material for soft roofs, as well as waterproofing basements and foundations
Waterproofing screen for landfills	Clay 45-50%, sand 15-20%, lime 10-15%, asphaltene sediments 20-25%.	Watertight material with hydrophobic properties that reduce the emission of seepage water
Waterproofing coating	Asphaltene sediments 40-50% LDPE waste 60-50%	Watertight material with hydrophobic properties
Solid carbon-containing fuel (composition for briquetting fuel)	Peat 1-10% coal, asphaltene sediments 1-40% coal 72-78%, asphaltene sediments 22-28%	For use in the fuel industry and for domestic needs

The presented directions for using asphaltene sediments are determined, first of all, by their specific properties due to their composition. Accordingly, asphaltene sediments have anti-corrosion properties and can be used as protective coatings, with good adhesion to the surface due to the presence of surfactants [6].

Therefore, a possible direction of disposal of asphaltene sediments that can be considered is using them as a basis for the preparation of special conservation coatings, for example, as alternatives to film-forming inhibited oil compositions.

CONCLUSION

In order for such type of waste as asphaltene sediments could not form, works are provided for to prevent the formation of deposits and their removal. Despite the numerous methods for controlling asphaltene sediments, there is no universal and effective one, since the deposits differ significantly by their properties and composition, what makes it necessary to constantly search for the best methods to prevent and remove asphaltene sediments. Considering the methods of waste disposal, we can say that most enterprises transfer waste to specialized organizations, and do not use it as a secondary raw material. The activities of enterprises engaged in the processing of asphaltene sediments are mainly aimed at turning this type of waste into commercial oil and its reusing.

In connection with the foregoing and with unfavorable trends associated with a decrease in oil reserves and the difficulties of its production, as well as a decrease in the raw material base of components for preservation materials, asphaltene sediments can be considered as valuable, affordable and cheap raw material due to their high organic content and useful properties.

The search for directions on reprocessing asphaltene sediments is particularly relevant in the context of expanding the resource base in the Russian Federation of heavy highly viscous and high-paraffinic oils, with a high content of resins, asphaltenes and paraffins prone to sedimentation, the production of which will be accompanied by the formation of substantial amount of asphaltene sediments.

The development and implementation of resource-saving technologies for the disposal of asphaltene sediments with the production of popular products is an important national economic task. Its solution will, on the one hand, reduce the technogenic load on natural geosystems by reducing the number or elimination of oily waste sites, and on the other hand, will ensure a more rational use of non-renewable natural resources by replacing primary raw materials with secondary ones.

CONFLICT OF INTEREST

The authors declare no conflict of interest relating to the material presented in this paper.

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