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ANALYSIS OF MODERN METHODS FOR OIL SLUDGE PROCESSING

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The problem of the negative impact on the environment of accumulated waste generated during the production, transportation, and storage of oil and petroleum products has not yet been resolved. As a result of the migration of harmful substances, environmental pollution occurs. It should be noted that all processes of transformation of NS hydrocarbons are activated in a hot climate - due to a decrease in viscosity and an increase in the reaction rate.

Mechanical methods include physical separation of NR by gravitational settling, in a centrifugal field, or filtration after averaging.

Dewatering is the use of a thickener to compactly settle solids. The thickener can increase solids concentration from 3% to 10-15%, and also allows the operator to control the settling tank for optimal effluent separation and plan further sludge treatment. The compacted sludge is then further dewatered by filtration or centrifugation.

Filtration

Filtration is a sludge dewatering technique suitable for treating sludges with low concentrations of hydrocarbons, as they may clog or dissolve the filter fabric. After filtration, the sludge contains less water, resulting in lower fuel costs, lower transportation costs, and therefore lower disposal costs.

Filtration using a press divides the filter into two parts - it separates solid impurities from the liquid component, but is characterized by low productivity. In addition, this method does not solve the problems of solid phase disposal and water purification.

Centrifugation

Centrifugation is advisable when the oil content in the sludge is higher than 10%. Centrifugation units reduce waste to a minimum and also allow for additional profit from the sale of recovered oil. To collect sludge from the required depth, a special slurry intake device is used. The pump for pumping is mounted on a floating pontoon; if necessary, the NS is heated with steam. The collected sludge is processed as trap oil: heated after the addition of flocculants or demulsifiers and separated into three component phases: solid sediment, water and oil.

Mechanical extraction of hydrocarbons from drill cuttings includes the following technological operations: removal of large mechanical impurities, phase separation by centrifugation or sedimentation. The method is applicable when the sludge contains liquid hydrocarbons, which can cover the costs of processing. Disadvantages - the formation of " oil-contaminated " mechanical impurities and a contaminated liquid phase, which require further neutralization.

1.3.1.1 Physico-chemical methods of oil sludge neutralization

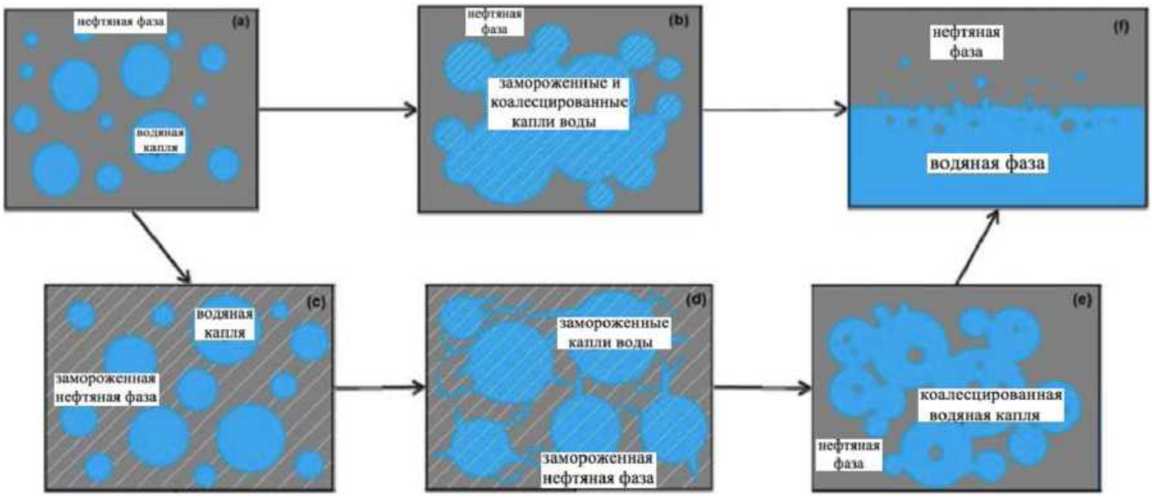
Physicochemical methods include electrochemical, electrokinetic and electromagnetic. Electrochemical processes include electrolysis, electroflotation , electrocoagulation,
electrodestruction , electrochemical disinfection, ion exchange, electrochemical oxidation and leaching, electrodialysis, electrochemical oxidation and leaching, ion exchange. The efficiency of a number of methods reaches 99%, however, significant energy costs and hardware complexity create difficulties for use in installations larger than pilot ones [41].

Freeze/Thaw Cleaning

Freeze/thaw treatment for sludge dewatering in cold regions has been proposed as an effective method for separating emulsions. As shown in Figure 3, separation of emulsions can occur through two different mechanisms. The first occurs when the aqueous phase in the emulsion solidifies before the hydrocarbon phase. Increasing the volume of frozen water droplets causes them to stick together and causes internal breakdown of the emulsion, and the aqueous phase gradually freezes as the temperature decreases (Figure 3b) . During the thawing process, the oil phase comes together as a result of surface tension forces, and the oil-water mixture can thus separate into two bulk phases under the influence of gravitational force (Figure 3 f) . The second mechanism occurs when the hydrocarbon phase solidifies before the aqueous phase. It forms a strong lattice that encapsulates water droplets during the freezing process (Figure 3c) . These water droplets gradually freeze as the temperature decreases, and the increase in volume of the frozen droplets breaks the resulting lattice. This can lead to the formation of small cracks that allow unfrozen water droplets to penetrate the lattice and merge with each other, forming an extensive network of microchannels (Figure 3d). During the thawing process, water droplets coalesce , which leads to phase inversion (Figure 3e), and such an unstable oil-water mixture can separate into two bulk phases under the influence of gravitational force (Figure 3f) .

Figure 3 - Schematic diagram of the freezing mechanism /
defrosting, to separate the water/oil emulsion:
(a) original emulsion,

(b) water droplets freezing, expanding and coalescing ,
(c) solidification of the oil phase with the formation of a solid cell,
(d) freezing drops of water that break the lattice during expansion,
(e) emulsion solidifies, water droplets coalesce ,
(e) gravitational delamination.



Overall, freeze/thaw purification is a promising method for dewatering and recovering oil from oil sludge . However, for its industrial application, the required freezing time and associated costs should be studied. Chun et al suggested that 8 hours was sufficient for freezing at minus 20° C . Additionally, freezing can be a relatively slow process that is energy intensive and therefore expensive. Thus, freeze/thaw refining to extract oil from oil sludge may be more promising in cold regions where natural freezing is possible. In addition, the effectiveness of the method is inversely proportional to the content of suspended solid phase in oil sludge , that is, the method can be used mainly for separating tank oil sludge containing a small amount of solid impurities .

Extraction methods.

Liquid-liquid extraction is widely used to remove organic compounds from soil-water matrices. To carry it out, oil-containing waste is mixed in the required proportion with the extractant to ensure complete homogeneity. After settling, the extractant-oil mixture is sent for distillation to separate the oil from the solvent.

Obviously, the efficiency of extraction depends on a number of factors - temperature, pressure, ratio of solvent to slurry, miscibility and solubility of various compounds. As a rule, mixing during heating is required to improve the dissolution of organic components in the solvent. High temperature can speed up the extraction process, but can also lead to the loss of petroleum hydrocarbons and solvents through evaporation, and also increases fire and explosion hazards. At the same time, lowering the extraction temperature can reduce the cost of the process - while simultaneously reducing the efficiency of oil extraction. Lower distillation pressure helps lower the distillation temperature; This can not only save heating costs, but also prevent thermal degradation of solvents. In addition, the quantity and quality of the recovered oil fraction changes with increasing solvent-sludge ratio. For example, it was found that the ash content and tar and asphaltenes content of collected oil decreased with increasing solvent ratio.

Typically, solvent extraction is a simple but effective method for separating hydrocarbons from solid or semi-solid sludge and reducing its volume. The extraction method can be completed in a relatively short period, and is potentially suitable for treating large volumes of oil sludge ; The determining factor in this case is the volume of the mixer. In order to prevent loss of solvent vapors, it is desirable to use a closed and continuous process. Solvent distillation also requires heating, so a heat exchanger unit is needed to reduce energy costs. One of the main obstacles to the use of extraction for oil sludge processing is the large volume of organic solvents required. This can lead to significant economic and environmental problems. Some alternative methods have been developed to increase extraction productivity. For example, the supercritical fluid extraction method can extract petroleum hydrocarbons in a soil matrix faster than conventional solvent extraction, and more importantly, it can eliminate the use of organic solvents. However, the use of this method for extracting oil from a large volume of oil sludge may be associated with low efficiency and instability of technological parameters.

Microwave irradiation

The frequency of microwave radiation ranges from 300 MHz to 300 GHz, but industrial applications are typically associated with radiation with a frequency close to either 900 MHz or 2450 MHz, due to a number of technical reasons . Radiation energy can be directly transferred to the material when interacting with an electromagnetic field, and provide a rapid heating process, more efficient than conventional methods. This effect can be used to separate an emulsion by rapidly increasing its temperature, which leads to a decrease in viscosity, therefore accelerating separation. A rapid increase in temperature can also provoke cracking of heavy hydrocarbons with an increase in the proportion of light fractions. When materials with low dielectric constant are used, microwave radiation can pass through them with little energy absorption; for materials with high dielectric constant, microwave energy will be absorbed depending on the electric field strength and dielectric loss factor. When processing a mixture of materials with different dielectric properties, selective heating can occur. For a water/oil emulsion, when the dispersed phase is water with a relatively high dielectric constant, it will absorb more energy than oil. In this case, a decrease in surface tension at the water-oil interface may occur, facilitating separation. In addition, microwave radiation can cause a change in the polarity of the electrical charges surrounding the water molecules, that is, destroy the electrical double layer at the oil/water interface, resulting in a decrease in the zeta potential. In this case, droplets of water and oil in the emulsion can move more freely and collide with each other in the process of coalescence . The above mechanisms can lead to emulsion separation .

The performance of microwave irradiation when demulsifying oil sludge depends on many factors: the power of the microwave radiation source, the duration of treatment, the presence of surfactants, the pH of the aqueous phase, salinity and other properties of oil sludge , for example, the water-oil ratio. Increasing the pH of the aqueous phase can reduce the stability of the water-oil emulsion by increasing hydrophilicity. On the other hand, increased efficiency of microwave radiation was noted due to the increased conductivity of the aqueous phase, which increases the heating rate. However, the use of microwave irradiation in industrial-scale oil sludge treatment is limited due to the specific equipment involved and the possible high operating costs.

1.3.1.2 Chemical methods for neutralizing oil sludge

Chemical methods for processing sludge include the following technologies: washing, chemical oxidation, extraction and encapsulation. Washing hydrocarbons from sludge using new generation technical detergents. Application is limited due to the formation of contaminated mechanical impurities and liquid phase. It is advisable to use the method in combination with others (for example, mechanical, etc.). The washing process includes loading oil-contaminated soil, supplying heated water and adding a surfactant with further mixing. After this, liquid containing petroleum products is collected from above, and the soil is sent for drying. The liquid can be purified using sorbents or centrifuges. And the soil is drained using hydrocyclones and centrifuges.

Chemical methods for processing NS include extraction with selective extractants, encapsulation using plasticizers and additives, treatment with water repellents based on slaked and quicklime or other materials. The general idea is to treat NS with a chemical reagent to form a structure that immobilizes pollutants and prevents their release into the environment.

Such methods of neutralizing oil waste can dramatically reduce damage to the environment and obtain marketable products for various industries. Cleaning the surfaces of reservoirs from spilled oil is carried out using emulsifiers that decompose bacterially . Oil slicks on the surface of water bodies contribute to the spread of waste and possible subsequent biochemical oxidation. It is also known to use magnetic fluids, which are complex polydisperse colloidal systems, including water, an oil phase and solid impurities . When such a liquid is mixed with hydrocarbons, a mixture is obtained, which is collected using a magnetic device.

The following reagents can be used : top ash and fly ash, gypsum, clay, Portland cement, class “ F ” fly ash, class “C” fly ash (lime), calcination powder (from kilns), fine slag from blast furnaces, phosphogypsum, slaked and quicklime, thermoplastic organics (asphalt), organic polymers, sand.

Lime encapsulation

Encapsulation involves mixing NPs with a solid additive to obtain a matrix within which petroleum products and metals are fixed and will not be washed out. The use of lime for this purpose is known and practiced; it has been shown that the addition of lime produces physical and chemical changes in NS that facilitate the adsorption of hydrocarbons and the immobilization of metals in the form of insoluble salts. The high pH level is ensured by the addition of lime, which is important. When obtaining a hydrophobic matrix, some additives can be introduced to prevent contamination by acidic percolation sediments.

Quicklime is most often used because of its disinfectant properties. When wet waste is mixed with it, the reagent is quenched with water and, interacting with carbon dioxide in the air, forms calcium carbonate:

$CaO + H_2O \rightarrow Ca(OH)_2 + Q$;

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3\downarrow + H_2O$.

In this case, the temperature rises to 60-100°C, the mixture evaporates excess water and, after some time, the sludge turns into solid granular material. Particles of this material are covered with a waterproof hydrophobic shell. The hydrocarbons inside the capsule do not affect the environment due to the high strength and tightness of the capsule. The micropores of the capsule shell filled with liquid hydrocarbons contribute to the hydrophobization of its surface and greatly reduce the wettability of particles, exposure to the aquatic environment (including groundwater, acid rain), and increase resistance to cyclic freezing. The possibility of the capsule contents transferring into an aqueous solution is reduced by several orders of magnitude. Over time (within 1-3 months), due to the ongoing carbonization of the capsule surface, the strength of the shell increases significantly. The encapsulated material can withstand volume pressure up to 5 MPa without noticeable destruction, repeated cyclic freezing, and exposure to a slightly acidic environment [45].

Treatment of NS with fly ash from thermal power plants

NS, which contains petroleum products in the form of an aqueous emulsion, mechanical impurities and other polluting agents, can be processed using a mixture of an aqueous suspension of fly ash and a small amount of polymer.

Light NSH is thickened in a tank with stirrers. And NS, including heavy oil products and mechanical impurities , after separation in a centrifuge, is processed with fly ash from thermal power plants in a screw mixer.

The settled thickener products and mixer products are transported to waste disposal sites. These landfills must be waterproofed to reduce leaching. The short curing time during the hot season makes it possible to transport it and further use it for road construction. After covering with a layer of soil, the burial site can be used to grow grass and trees. This method can be quite expensive as the process requires equipment, energy and operating facilities.

Reagent method encapsulation

Known abroad as " DKR technology ", in Russia the method of treating sludge with quicklime with the addition of various modifiers is called " reagent encapsulation ."

The completeness of sludge processing is determined by its composition, the properties of lime: in particular, the size of granules, chemical purity and activity, as well as the quality of mixing. A fundamentally important indicator of the reagent process encapsulation is the ratio of the amounts of sludge and reagents.

Reagent technology encapsulation , due to sealing and not destruction of pollutants, in addition to NS, drill cuttings, is also applicable to other waste - sewage sludge, livestock waste. In this case, an increase in the temperature of the mixture to more than 60 °C as a result of lime slaking entails the death of pathogenic microflora.

AKTOR company S. _ A. _ (Greece) as of 2009 on the island. Psythallium using the reagent method The encapsulation plant processed about half a million tons of sludge sludge, but this was preceded by a lengthy selection of the hardener reagent formulation. The following conclusions of Greek researchers are fundamental:

- the dose of quicklime must be more than 9% of the sludge mass to achieve a pH value > 11 of the resulting product.
- the amount of quicklime must be more than 18% of the sludge mass to achieve a temperature of the resulting product of at least 55 ° C.
- the dose of quicklime must be more than 25% of the mass of oil waste to achieve a temperature of the resulting product of at least 55°C, maintained for at least two hours, and to obtain the values of physical and chemical indicators that ensure its safe disposal [50].

In the work of N.G. Yagudin shows: the required amount of binder reagent added to drilling rigs is about 14% by weight. The ratio of encapsulating reagent and water for oil waste of various compositions was determined in the dissertation of Yu.V. Logunova. For NS formed during cleaning of main oil pipelines, during transportation and storage of oil, the share of the reagent is about 80-100% of the mass of the feedstock. It follows that data on reagent curing formulations vary depending on the source of information.

Equipment for implementing the encapsulation method

An example of highly efficient equipment for implementing the encapsulation method is a mobile block unit manufactured by Voest -Alpine GmbH (Austria), the productivity of which can reach 20 t/h, consisting of a homogenizer, a hydration reactor, a reagent dispenser and various components for loading raw materials and outputting the product. . The installation neutralizes at the final stage of the process (tested after leaching for 24 hours), %: hydrocarbons - 94-98; dissolved organic matter - 80-95; salts of heavy metals - up to 99.

Developers and patent holders do not disclose the design features and technological parameters of the processes.

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