Experimental research of reagent capsulation process at various methods of carbon dioxide supply

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Abstract. The article considers some features of the reagent encapsulation method at low temperatures. A setup layout has been created to measure temperature of the encapsulated material while reagent encapsulating. During the experiment, the duration of maintaining the temperature for preparing the next portion was determined. Methods for supplying carbon dioxide to the unit during reagent encapsulation were compared. As a result of the experiment, a more profitable way of supplying carbon dioxide to the unit was determined.

1. Introduction
The widespread use of petroleum products in the world, and Russia, in particular, is followed with their getting on the soil. These can be broken car crankcases, accidents while transporting petroleum products by vehicles on a road or by rails, spills during the oil extraction, transshipment and transportation, etc.

Currently, there are many methods developed to remove or mitigate the effects of oil spills [1-3]. Most of the developed methods are based on extractants (special solvents) or on washing the soil with aqueous solutions adding surfactants [4-7]. The disadvantage of these methods is that they are effective in summer and mostly are time-expended.

Considering the climatic conditions of the Russian Federation, especially Siberian regions, where the average daily temperature is below zero for a significant period of the year, the issue of rapid removal of oil pollution of the territory is an urgent issue, since temperature increasing can lead to future pollution spreading over significant distances, its getting into groundwater, into open water with surface runoff, etc.

The elimination of the effects of pollution at low temperatures requires special technologies and equipment. At the same time, the main problem with neutralization is that oil-contaminated soil is in a frozen state, which requires additional energy costs in the form of thermal energy.

2. The statement of the problem
The objective of the present research is to determine the optimal mode of carbon dioxide supply at low temperatures, while neutralizing soil contaminated with oil products using reagent encapsulation method.

3. Theory
Under below-freezing temperature conditions for the oil-contaminated soil neutralizing, the technology of reagent encapsulation is one of the most promising. This technology is based on reagent encapsulation. The reagent encapsulation technology is described in [8-9], the technology is a complex process, but in a simplified form it can be described using two chemical equations (1)(2) [10]:

$$CaO + H_2O \rightarrow Ca(OH)_2 + Q_1,$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O + Q_2.$$  

The technology is based on a cheap alkaline reagent on calcium. Quicklime is the most suitable reagent for this technology (building lime, GOST 9179-77). In this case, the final product of the oil-contaminated soil neutralizing is encapsulated material, which looks like a finely divided mixture similar to ordinary sand (Fig. 1) [8]. The main advantage of this technology from the point of eliminating pollution is its efficiency.
At low temperatures the advantage of this method is the heat generated (the reaction by-product). When implementing equation (1) the heat dissipates quickly in the environment. The final formation and hardening of the shell of microcapsules made of calcium carbonate (2) takes place at the test sites under ordinary conditions (Fig. 2) for several years, since the concentration of carbon dioxide in the atmosphere does not exceed 0.05%, and in practice, this process remains unnoticed.

Energy potential evaluation of the exothermic process of chemical reactions showed that when the CO$_2$ supply is intensified, the amount of heat generated is sufficient to ensure the heating of frozen soil. That is why the next portion of contaminated soil in winter can be brought to the required temperature. Based on this principle, a number of standard sizes of units with heat recovery in a jacket containing non-freezing liquid have been developed (Fig. 3) [11]. The heat transferred to the jacket is used subsequently to prepare the next portion of contaminated soil. The units carry out the soil neutralization process at the place of formation in winter without additional energy sources.
However, this design complicates the unit, moreover, a sealed jacket makes it heavier and makes it vulnerable to transportation and operation. Moreover, a decrease in ambient temperature leads to an increase in heat loss to the environment and a reduction in heating of the mixture in the unit reactor. As a result, additional heat treatment is required to prepare the next portion.

4. The experiment
A setup layout was created to conduct experiments (Fig. 4). The installation is a tank with mixing elements, temperature sensors and a carbon dioxide supply tube. Two augers rotating in opposite directions act as mixing elements. The entire encapsulation process from mixing the components to the finished encapsulated material takes place directly in the installation. Recording of temperature sensors is carried out automatically using a PC.

There are three temperature sensors in the installation, two of them are immersed into the encapsulated mixture, and one is located directly at the wall of the installation. This arrangement of sensors determines the temperature inside the encapsulated mixture and the temperature at the wall-mixture level, which allows not only to obtain data on the reaction temperature, but also the temperature transmitted to the jacket. The CO₂ supply pipe has a number of holes and is located at the bottom of the unit, which evenly
supplies CO₂ to the mixture. CO₂ is supplied continuously or in batches, the period and time of the supply are manually adjusted, maintaining the average temperature in the installation within 70°C. As the average temperature, we use the average temperature of the mixture recorded by the sensors inside the mixture. In this case, the sensor readings near the wall are not taken into account.

The experiment starts by loading the components into the installation. First, oil-contaminated soil and quicklime are loaded. These components are mixed, then it is necessary to add water. As a result of water adding, a chemical reaction begins and microcapsules form. In this case, the temperature rises. The duration of the first stage depends on the ambient temperature. The lower the ambient temperature, the faster the encapsulated material cools. The end of the first stage is the moment after reaching the maximum temperature the temperature of the mixture is 50-55 °C.

Cooling the encapsulated mixture to a lower temperature is impractical. This is due to the fact that the temperature at the installation wall differs from the temperature inside the mixture, the temperature difference on average is 10°C, i.e. non-freezing liquid will have a temperature of less than 40 °C and the process of preparing the next portion will slow down significantly. Also, if the encapsulated mixture has a lower temperature, then it is more difficult to start the second stage, while a repeated increase in temperature will occur, but with a lower speed and lower heat output.

The second stage is to add carbon dioxide to the encapsulated mixture. When carbon dioxide is added, microcapsules are strengthened and the encapsulation process is completed. In this case, a repeated increase in temperature is observed.

5. The experiment results
At the first stage of the experiment, there was estimated the time for reducing the temperature in the reactor at a constant CO₂ supply. The research was conducted at positive and negative ambient temperatures (Fig. 5). The graphs show that when the ambient temperature decreases from +20°C (Fig. 5a) to -5°C (Fig. 5b), the time we can maintain the necessary temperature to heat a portion of the soil in the second stage decreased by 23 minutes (the duration of the second stage at +20 °C was 50 min., at -5 °C it was 27 min.).
Figure 5. Temperature graphs of the mixture state in the reactor, when CO₂ is supplied until the carbonization process is completed:

a) at +20°C (constant CO₂ supply);
b) at -5°C (constant CO₂ supply);
c) at -5°C (partial CO₂ supply).

Another design option is proposed, in which carbon dioxide is supplied in portions with controlled regulation of the lower and upper temperatures in the installation. This design option will allow
maintaining the average temperature more effectively, prolonging the process of increased temperature in
the reactor of the installation.
At the second stage of the experiment, the time for reducing the temperature in the reactor with a partial
CO₂ supply was estimated. The research was conducted at a below-freezing ambient temperature (Fig.
5c).
The graphs show that when CO₂ is supplied at the second stage in portions, the process time increases,
provided that the average temperature is kept at 70 °C for 9 minutes. (from 27 min. to 36 min.). The
addition of CO₂ occurs until the temperature ceases to rise; on average, 3-5 minutes of CO₂ addition is
required. Thus, for the entire period of the encapsulation process, it is possible to add 3 portions of CO₂,
whereafter CO₂ no longer reacts with the encapsulated material and the temperature does not increase.

6. Conclusion
The partial supply of CO₂ to the installation developed to overcome the consequences of soil pollution
with oil products increases the average temperature in the reactor (by 15-25% depending on the ambient
temperature) and provides the necessary time to heat up the next portion of oil-contaminated material at
low temperatures.

7. References
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