CLEANING OF WATER AND SAND BEACHES FROM OIL AND OIL PRODUCTS WITH GRAPHITE SUPERSORBENT. METHODS AND EQUIPMENT.

ОЧИСТКА ВОДНОЙ ПОВЕРХНОСТИ И ПЕСКА, ЗАГРЯЗНЕННЫХ НЕФТЬЮ И НЕФТЕПРОДУКТАМИ ГРАФИТОВЫМ СУПЕРСОРБЕНТОМ. МЕТОДЫ И ОБОРУДОВАНИЕ.

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Abstract: *Elaboration of effective ways of elimination of spilled oil and oil products are very actually now. One of the most effective methods for solving this problem is the absorption of the oil by sorbents. Supersorbent on the basis of thermally expanded graphite has unique characteristics. It is a special modification of the graphite obtained by multi-stage thermo-chemical treatment of natural flakes graphite. We have developed different methods of preliminary preparation and subsequent application of this sorbent considering a specificity of emergency spill, properties of spilled liquid, the nature of cleaning surface and weather conditions. Also, question of spent sorbent utilization has been studied. The recycling process involves the desorption process up to 85% with subsequent use of the sorbent to 10 cycles of regeneration. Obtained while desorption liquid can be used for another purpose or as an additive to fuel oil. Technology and equipment for liquidation of emergency oil spills on water surface and coastal sand have been developed and tested.*
KEYWORDS*: SUPERSORBENT, THERMALLY EXPANDED GRAPHITE, OIL SPILLAGES, REGENERATION OF SPENT SORBENT, STABLE AND MOBILE UNITS*

1. Introduction

At the present time to eliminate pollutions on the water surfaces and sand beaches from oil, petroleum and other organic fluids spills as rule porous substances of natural and artificial origin are used. They are: peat, sawdust, shredded twigs, perlite, polystyrene foam, various fibrous materials. Sorbents are applied to the contaminated area after that the major part of spilled product is collected more often by mechanical means. Also, special bacteria that decompose organic matter into the neutral substance is used [1].

2. Objective and research methodologies

At liquidation of emergency spills of oil and oil products by the method of sorption the most promising method is the use as oil-absorbing sorbent termoexpanded graphite (TEG). TEG represents by itself a special modification of the graphite obtained by multistage natural graphite thermochemical processing. This kind of graphite found in the literature also under the names of exfoliated graphite, foamed graphite and thermografenite. This product is characterized by very low bulk density (2-5 kg/m^3) and high specific surface which in combination with its selectivity for oil causes a high absorption capacity relative to oil and other organic liquids. One gram of this substance can absorb 30-60 grams of oil (see Table 1). An important feature of this sorbent is its inertness, the ability to desorption up to 90% of absorbed liquids and the possibility of thermochemical regeneration for repeated use [2-4].

Table 1. *TEG sorption characteristics for some organic liquids*

The name of the substance	Sorption capacity, g/g sorbent
Acetone	30
Turpentine	30
Benzene	35
Diesel fuel	40
Kerosene	40
Vegetable oil	45
Machine oil	50
Crude oil	55

Actually liquidation process of emergency spills of oil, oil products and other organic liquids on the water surfaces and sand of coastal zone with sorbent on the basis of thermoexpanded graphite includes such stages:
- sorbent obtaining – thermo expanded graphite (if it required directly on the place of emergency spill);
- pre-treatment (preparation) of the sorbent;
- applying of a sorbent on contaminated surface;
- collecting of a saturated sorbent;
- separation and recycling of on absorbed liquid;
- regeneration of a waste sorbent and its reuse.

Scientists from Gas Institute of National Academy of Sciences of Ukraine have designed, manufactured and tested series of units with different performance, autonomy and automation for TEG manufacturing.
– pilot unit with a capacity of 8.5 m^3/h (35 kg/h by raw material). One example of the unit was manufactured and put into operation at the Argonne National laboratory, Chicago, USA (Fig. 1);
– autonomous automatic unit of a local destination with capacity of 1-2 m^3/h (5 kg/h by raw material (Fig. 2);
– TEG autonomous knapsack generator with a capacity of 0.8 m^3/h (3 kg/h by raw material) (Fig. 3) [5];

Fig. 1. *Pilot unit for TEG generation with a capacity of 8.5 m^3/h Simulation (left). In metal (right)*

The last three types of installations can work offline and used in liquidation of oil spills in difficult to access places. As well as the autonomous car based unit was designed (Fig.4)

Significant technical obstacle when using oil-absorbing sorbent on the basis of expanded graphite is its extremely low bulk density, resulting in low profitability of the technology as a whole with TEG delivery to the place of emergency spill. Spreading of the sorbent in the form of a dry powder to the contaminated surface is also associated with its entrainment (losses), which causes an increase in specific consumption of sorbent and contamination of the surrounding area. In the Gas

Institute of NAS of Ukraine various methods of preliminary TEG treatment have been investigated and tested on a pilot scale. Different modifications of the sorbent have been elaborated. They are:

-granulation by mechanical method with some binder (Fig. 5) [6, 7];

-pressing of TEG to obtain the sorption elements using a binder and without them, as well as using reinforcing interlaying and without them, followed by applying mechanical methods (Fig. 6) [8-10];

- preparation of the water-graphite suspension with subsequent application by means of a centrifugal pump (Fig. 7) [11, 12];

- preparation of the water-graphite foam suspense followed by the application of air-foam jetting [13].

Fig. 2. *Autonomous automatic aggregate of a local destination with capacity of 1-2 m^3/h by TEG*

Fig. 3. *TEG autonomous knapsack generator with a capacity of 0.8 m^3/h (3 kg/h by raw material).*

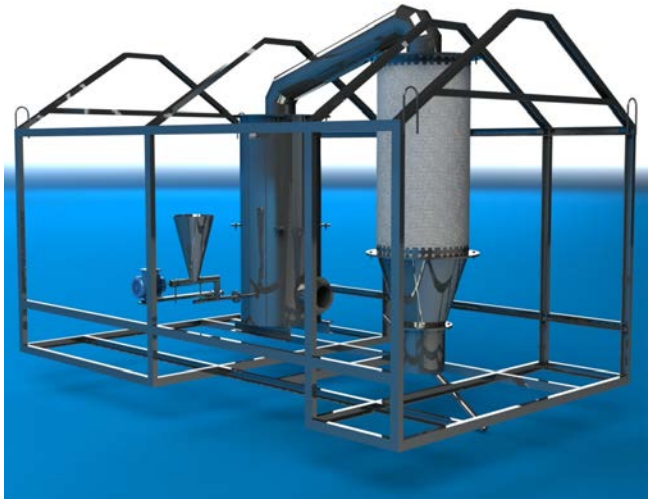

Fig. 4. *Mobile unit in a container mounted on a wheeled chassis (truck GAZ-66-02).*

a)

b)

Fig. 5. *The granular adsorbent of expanded graphite obtained by extrusion (a) and clumping (b)*

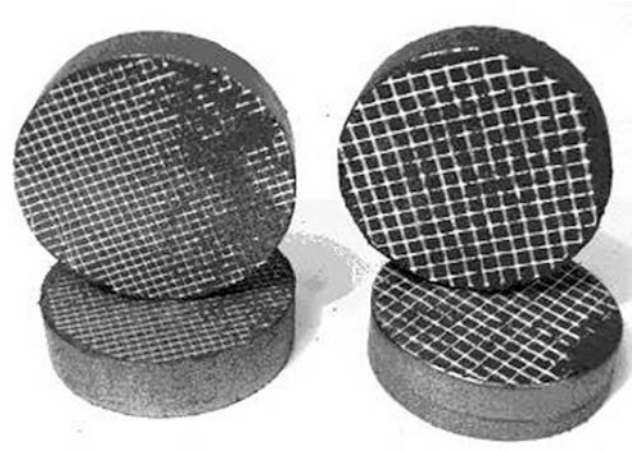

Fig. 6. *Extruded sorption elements, reinforced by polymer mesh*

Fig. 7. *Experimental unit for the preparation and application of a graphite-aqueous suspension*

Choosing the method of sorbent preparation on the basis of TEG is accomplished taking into account a specificity of an emergency spill, properties of adsorbed liquid, the nature of the polluted surface and surrounding area conditions (e.g., availability of water sources for the preparation of water-graphite suspension).

It should be noted that the sorption capacity of any sorbent modification obtained after preprocessing of the original TEG is lower than sorption capacity of dry powder due to increasing of its density. For example, at granulation of TEG powder with the use as a binder 2.5% solution of the glue – "PVA", sorption capacity of the pellets, sufficient for reliable manipulation strength (0.15 kg/cm^2) is 23.9 g/g for diesel fuel, i.e., 40% lower than the original TEG. Sorption capacity of pressed sorption elements with density of 12.5 kg/cm^3 is 12-14 g/g, i.e. three times less than that of the original TEG. However, considering the high degree of adaptability of cleaning operation of contaminated area on the whole a significant reduction of costs for sorbent delivery to the place of an accidental spillage – the economic feasibility of pre-treatment and preparation of initial TEG is justified. A little decrease in sorption capacity compared to original sorption capacity of TEG – 8.5-20% is observed when oil-absorbing sorbent from the TEG in the form of water-graphite and foam-graphite suspension is used. Thus, a high degree of cleaning of water surface and coastal sands is provides. Also, pollution of an environment by sorbent is prevented. In addition, this technology is characterized by relative simplicity and does not require the development of special technological equipment. Regardless of the type of pre-processing the original TEG and the method of its application on contaminated surface collecting the saturated sorbent is produced by any known and proven in practice methods: a perforated material or grid with a mesh size of up to 12 mm [14, 15] or vacuuming [1]. When emergency spillage is small collecting of saturated sorbent can be effected by any suitable means at hand. As noted above, a significant advantage of oil-absorbing sorbent compared to known is the possibility of desorption of absorbed liquid and regeneration of a "pressed" sorbent for reuse [4]. Up to 85% of absorbed oil is separated when desorption occurs by centrifugation. After appropriate treatment this product can be used for its intended purpose**.** Developed at the Gas Institute of NAS of Ukraine the technology of thermochemical regeneration of the spent sorbent provides for a high-temperature treatment of the waste and subjected to a desorption of a sorbent in the furnace of the cyclone type (Fig. 8) [16]. Wherein the content of residual oil in the pressed sorbent allows accomplish a thermo-chemical regeneration in the autothermal regime [17]. Experimentally it was proven a principle possibility of 10 regeneration cycles with maintaining an acceptable sorption capacity of the regenerated sorbent (Fig. 9).

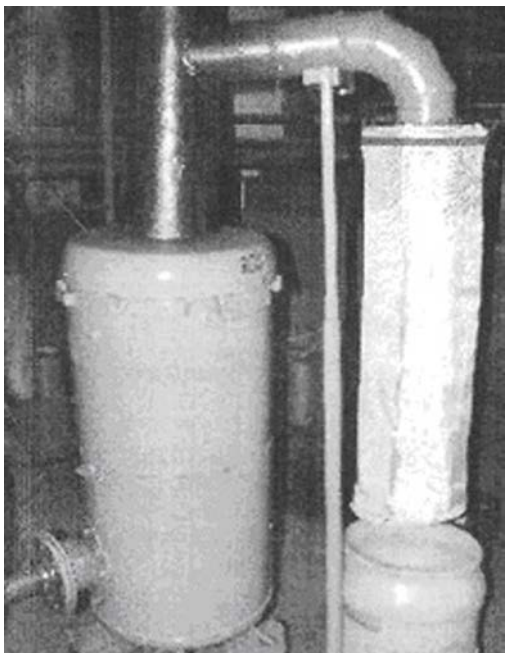

Fig.8. *External view of the experimental unit for the regeneration of a spent sorbent in a furnace of "cyclone" type*

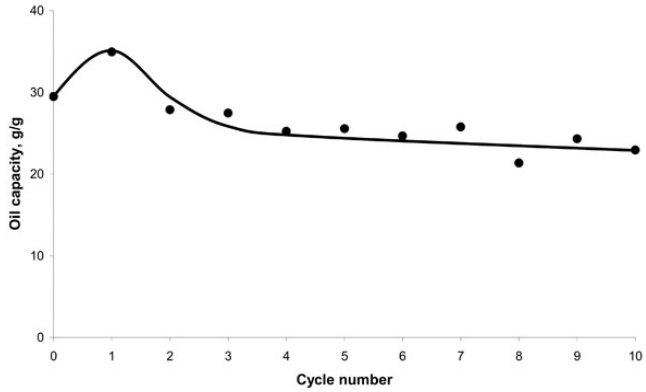

Fig. 9. *Dynamics of changes in the sorption capacity of the regenerated sorbent depending of regeneration cycle's number*

3. Conclusion

Proven technologies and technical solutions can be used as a basis for the creation of technical units in ministries and departments, responsible for the effective and rapid elimination of consequences of emergency spills of oil and oil products on water surface and sand beaches.

4. Literature

1. Kormak D. Struggle against pollution of the sea by oil and chemical substances / Dmitriy Kormak; - M., Transport, 1989 – 365 s.
2. E.V. Strativnov., A.P. Kozhan., V.M. Dmitriev., A.A. Sergienko., A.S. Vavrish., "A study of regeneration process of thermal expanded graphite" // Energotechnologii i resursozberezhenie. - 2012.-№1.- p. 47-52
3. Pat. 104098 Ukr., IASC (2012) B09C1/00. Method of cleaning water and soil from oil and oil products by graphite sorbent. / Dmitriev V.M., Kozhan A.P., Ryabchuk V.S., Strativnov E.V., Bondarenko O.B.., – Publ. 12.08.2013.
4. Pat. 79769 Ukr., IASC (2012) B09C1/00. Method of cleaning water and soil from oil and oil products oil-absorbing by sorbent based on expanded graphite. / Dmitriev V. M., Kozhan A. P., Bondarenko O. B., Strativnov E.V., Ryabchuk V.S., Pisarenko A.I. Publ. 25.04.2013.
5. Pat. 85362 Ukraini, MPK^7 B 01 J 20/00. Portable autonomous apparatus in order to receive and application of sorbent / Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Raybchuk V.S., Sergienko O.A. – Opubl. 12.10.2009, Byul. № 1.
6. Method of granulation of carbon sorbent: Pat. 23972 Ukraini, MPK^{7}B 01 J 20 / 00, B 09 J 20 / 20 / Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Sergienko O.A., Moskalik L.D. (Ukraini) – Zaaivnik i vlasnik: Institut gazu NAN Ukraini. - № u200701849; zayavl. 22.02.2007; opubl. 11.06.07, Byul. № 8. – 8 s.
7. Method of granulation of oil absorbing sorbent on the basis termoexpanded graphite: Pat. 31784 Ukraini, МПК7 B 01 J 20 / 00, B 09 J 20 / 20 / Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Hohulay I.M., Raybchuk V.S. (Ukraini) – Zayaivnik i vlasnik: Institut gazu NAN Ukraini. - № u200713038; zaaivl. 26.11.2007; opubl. 25.04.08, Byul.№ 8. – 7c.
8. A.P. Kozhan, V.M. Dmitriev, E.V. Strativnov, V.S. Ryabchuk, O.B. Bondarenko. "Cleaning surface of water basins and soil at oil outflow with using a sorbent on thermoexpanded graphite basis" // Ecologiya i promishlennost 2012, no. 4, pp. 33-42.
9. Method of water cleaning from oil and oil products with the help of carbon sorbent: Pat. 31783 Ukraini, МПК7 E 02 B 15 / 04, C 02 F 1 / 28 / Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Hohulay I.M., Aleksandrov V.V. (Ukraini) – Zayaivnik i vlasnik: Institut gazu NAN Ukraini. -№ u200713037; zaaivl. 26.11.2007; opubl. 25.04.08, Byul. № 8. – 7c.
10. Cleaning method of water surface from hydrophobic pollution: Pat. 82819 Ukraini, МПК7 E 02 B 15 / 04, C 02 F 1 / 28 / Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Hohulay I.M., Aleksandrov V.V. (Ukraini) – Zayavnik i vlasnik: Institut gazu NAN Ukraini. -№ u200713037; zayvl. 26.11.2007; opubl. 25.04.08, Byul.№ 8. – 7c.
11. A.P. Kozhan, V.M. Dmitriev, E.V. Strativnov, V. S. Ryabchuk, O. B. Bondarenko. "Purification of water surface and soil from accidental spills of oil and oil products by sorbent based on thermally expanded graphite", in: "Innovative solutions of actual problems of basic industries, environment, energy and resources": proceedings of the international scientific-practical conference / Kazantip – ECO – 2012/ June 4-8, 2012, ShChelkino, Crimea/ Ukrgt "Energostal": in 3 volumes - Kharkov: NTMT, 2012. – volume 3.p. 73-84.

12. A.P. Kozhan, V.M. Dmitriev, E.V. Strativnov, V.S. Ryabchuk, O.B. Bondarenko/ "Oil-absorbing sorbent based on nano-layered thin films of graphite", in: "III international scientific conference "NANOSTRUCTURED MATERIALS 2012: RUSSIA – UKRAINE – BELARUS": proceedings of the international scientific-practical conference / NANO – 2012/ 19-22 November 2012, Saint-Petersburg, Russia Scientific center of Russian Academy of Sciences (spbsc RAS), Institute of silicate chemistry of the. I. V. Grebenshchikov: p. 274.
13. Method of cleaning of soil and coastal strip from hydrophobic pollution: Pat. 83181 Ukraini, МПК7 B 09 C 1 / 00 , B 01 J 20 / 20 /Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Raybchuk V.S., Komisarenko A.A. (Ukraini) – Zayavnik i vlasnik: Institut gazu NAN Ukraini. -№ u200701852; zaaivl. 22.02.2007; opubl. 25.06.08, Byul.№ 12. – 6c.
14. Cleaning method of water surface from oil and hydrophobic liquid: Pat. 92000506 Rossii, МПК7 C 01 B 31 / 04 Smirnov A.V. (Rossia) – Zayavitel i sobstvennik Smirnov A.V. - № 93000506/26; zayavl 15.10.1993; opubl.. 27.06.96, Byul. № 11. – 5 c.
15. Cleaning method of water surface from oil and oil products: Pat. 2140488 Rossii, МПК7 Э 02 B 15 / 04 / Samosadnii V.P. (Rossiya) – Zayavitel i sobstvennik: OOO Nauchno proizvodstvennoe obedinenie " Texnoprom" - № 98001306/32; zayavl 21.12.1998; opubl.27.10.99, Byul.. № 7. – 6c.
16. Cleaning method of soil from oil and oil products by graphite sorbent: Pat. 48026 Ukraini, МПК9 У 09 З 1 / 00 /Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Raybchuk V.S., Sergienko O.A., (Ukraini) – Zayavnik i vlasnik: Institut gazu NAN Ukraini. -№ u200811085; zaaivl12.09.2008.; opubl. 10.03.10, Byul.№ 5. – 6c.
17. Cleaning method of soil from oil products sorbent graphite: Pat. 83180 Ukraini, МПК7 B 09 C 1 / 00 , C 02 F 1 / 28 / Bondarenko B.I., Kozhan O.P., Dmitriev V.M., Raybchuk V.S., Sergienko O.A., (Ukraini) – Zayavnik i vlasnik: Institut gazu NAN Ukraini. -№ u200701850; zayavl 22.02.2007.; opubl. 25.06.08, Byul.№ 12. – 9c.