

Feature Article

Exfoliated Graphite for Spilled Heavy Oil Recovery

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Abstract

Exfoliated graphite was found to sorb selectively a large amount of heavy oil, about 80 g of heavy oil floating on water per 1 g of exfoliated graphite, which is highly possible to be applied to recovering spilled heavy oil. Sorption capacity, selectivity and kinetics of exfoliated graphite were reviewed. The possibility of recovery of heavy oil from exfoliated graphite and recycling of both recovered heavy oil and exfoliated graphite was also discussed. Its sorption performance was compared with other materials which were reported to show sorption of heavy oil.

Keywords : Exfoliated Graphite, Heavy Oil, Sorption, Recovery, Recycling

1. Introduction

There have been a number of oil spill accidents in the world. On January 6, 1997, the oil tanker Nakhodka spilled almost 6,200 kL of oil in the coast on the Japan Sea. Spilled oil moved along the coastline, extended over about 250 km and gave serious contamination on the shoreline. Common treatment techniques were applied for this oil spill accident; manual skimming from the spilled oil confined with large floating barriers, dipping up the spilled oil by using ladles to some containers to burn out Fig. 1(a) and (b), respectively, taking off contaminated sands and rocks, etc. These treatment activities at the site lasted up to 3 months. However, this disaster is expected to give certain influences on the environment during a long period.

Although such disastrous accidents gave massive oil spill, it was pointed out that the principal loss of oil occurred during its transportation and transfer [1]. A continuous leaking of oil through pipe joints, for example, may give a serious contamination of soil and sometimes subterranean water, which give important effects on life of human beings through various plants, fishes and also water [2]. These oil spills, not so much massive as tanker accidents, have occurred frequently and resulted in not only a great deal of damages to environment, such as sociological cycles, but also a great loss of energy source, heavy oil.

One of the possibilities for skimming massive spilled oil is the use of absorbents with high capacity and rate, the preferential absorption of oil being desired in the case of oil spill in the water. For leakage of oil during transportation, absor-

bents with large capacity and also easy manipulation may work to avoid serious pollution. So far, some of porous polymers, such as poly(propylene) and poly(ethylene terephthalate), have been used for the absorption of spilled oil, of which maximum absorption capacity is 10~20 g of heavy oil per 1 g of polymer [3]. However, most of polymers absorb water, as well as heavy oil, no special selectivity for heavy oils, and so effective absorption capacity of the polymers for heavy oils must be lower than the figures mentioned above.

In 1979, a patent proposal for sorption of heavy oil by exfoliated graphite was presented in Japan [4]. However, it did not attract the attentions and no more detailed studies had been carried out. A short report on the sorption of heavy oil onto exfoliated graphite was presented by Chinese group in 1996, the reported capacity being about 25 g/g [5]. In 1998, just after the Nakhodka accident in Japan sea, our group followed the previous works on exfoliated graphite and found that it was able to sorb a large amount of heavy oil floating on water at room temperature very quickly, more than 80 g/g within 1 min [6, 7]. Based on our results, a new research project on recovery and recycle of spilled heavy oils by using carbon materials was started in 1998. The principal purposes of our project were summarized into the following two; 1) recovery of spilled or dispersed heavy oils by using carbon materials and 2) recycle of both heavy oils and carbon materials. The promising results were obtained on exfoliated graphite, which were reported in a series of our papers [8-14]. Heavy oil suspended in water was also able to sorb into exfoliated graphite [15]. Pore structure in exfoliated graphite was studied by measuring exfoliation volume

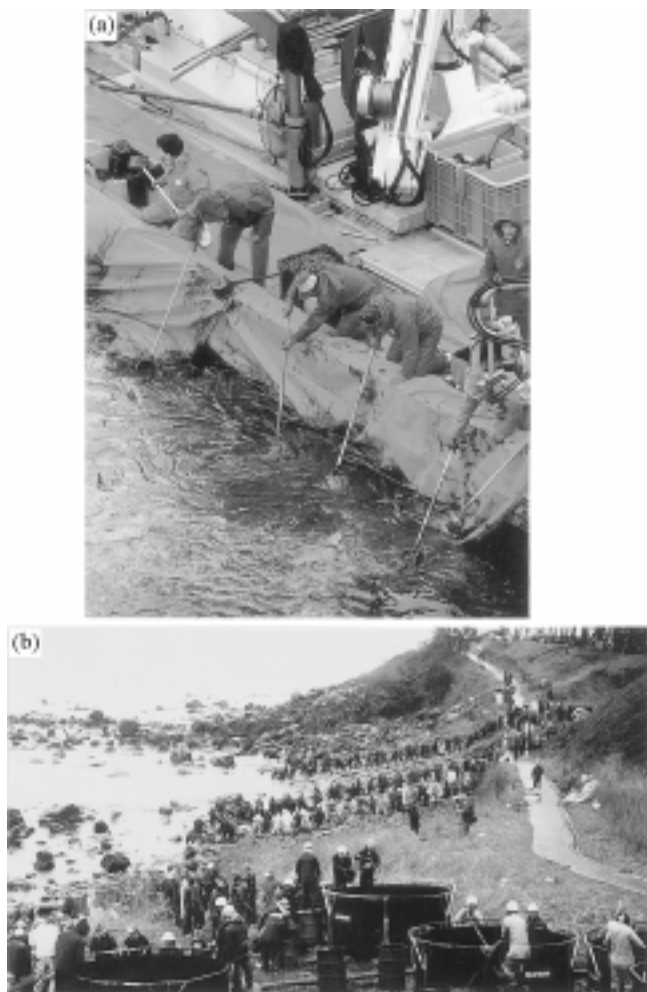


Fig. 1. Skimming of spilled heavy oil (a) and its dipping out by ladles (b).

[16] and also by image analysis technique [17].

Here, the experimental results on sorption capacity of a number of exfoliated graphite samples with different bulk density, recovery of heavy oil from exfoliated graphite and also recycling performance of exfoliated graphite were reviewed.

2. Sorption Capacity for Heavy Oils

By the addition of exfoliated graphite onto the heavy oil floating on the water, the characteristic brown color of heavy oil was disappeared by its sorption into exfoliated graphite. Typical photographs of the water with A-grade heavy oil floated are shown in Fig. 2(a) and (b) before and after the addition of an exfoliated graphite, respectively. In this case characteristic brown color of A-grade heavy oil disappeared within only 1 minute after the addition of exfoliated graphite. After taking out of exfoliated graphite, no contamination

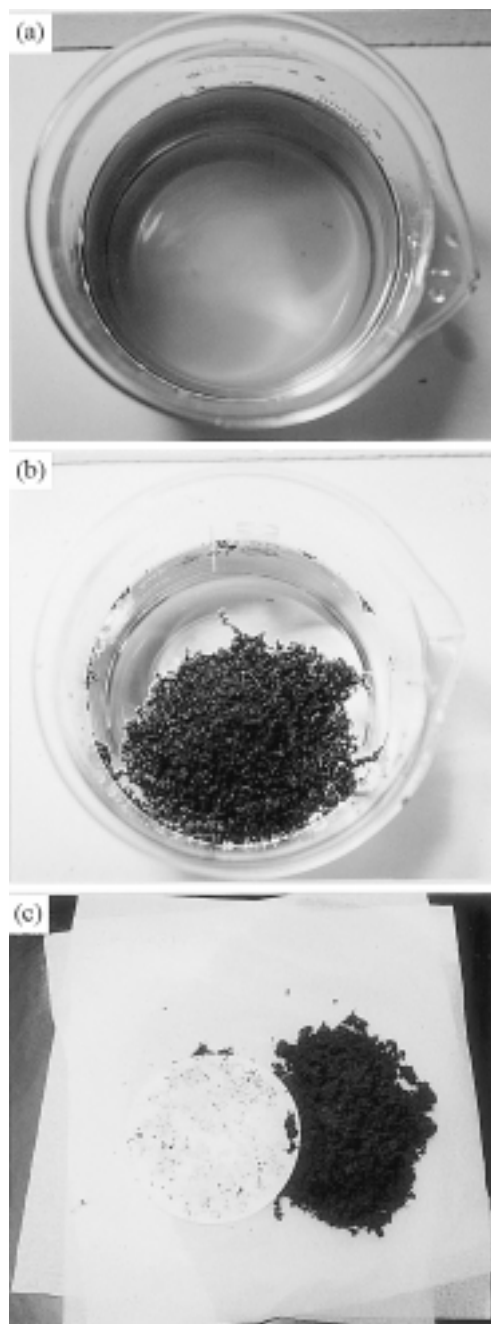


Fig. 2. Crude oil floating on water (a), its sorption by exfoliated graphite (b) and no transformation sorbed onto exfoliated graphite to filter paper (c).

was appeared in water. When the amount of heavy oil sorbed into exfoliated graphite was less than its maximum capacity, no contamination is not observed even if they are transferred onto a filter paper, as shown in Fig. 2(c).

In Fig. 3, sorption capacities of two exfoliated graphite samples with a little different bulk density are compared on four grades of heavy oil (Table 1), as histograms. In the case of A-grade heavy oil, up to 83 g was sorbed into 1 g of the

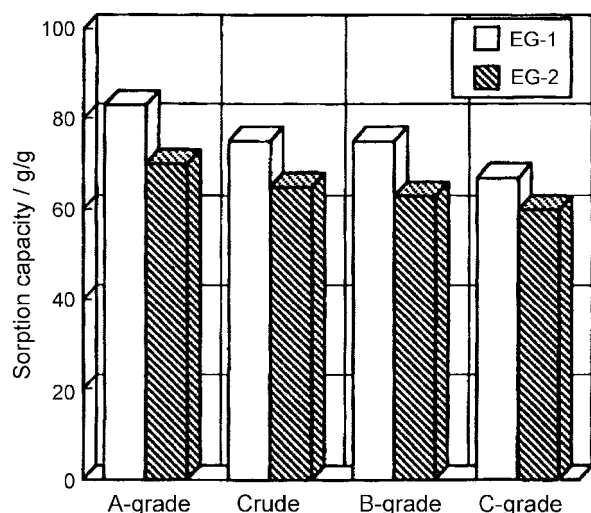


Fig. 3. Sorption capacity of two exfoliated graphite for four different grades of heavy oil at room temperature.

Table 1. Characteristics heavy oils used

Heavy oil	Specific gravity (kg/m^3)	Viscosity at room temperature (Pa·s)
A-grade	864	0.004
B-grade	890	0.27
C-grade	945	0.35
Crude	826	0.004

exfoliated graphite with bulk density of 6 kg/m^3 at 25°C . When a little larger amount of heavy oil than this maximum sorption capacity was used, a characteristic brown color of floating heavy oil was completely disappeared, but the lump of graphite was trimmed by a transparent oily material. Used more amount of oil, a small amount of oil with brown color remained floating on the water surface even after sorption by exfoliated graphite. This sorption capacity in weight is much higher than that of polypropylene and polyurethane mats which have ever been used. Sorption rate of A-grade oil was so quick as to complete within 1 min. The exfoliated graphite with the bulk density of 10 kg/m^3 has a little less sorption capacity (about 70 g/g).

The sorption capacity for a crude oil was similar to that for A-grade heavy oil, as the viscosities for these two oils are comparable (Fig. 3). Its sorption rate was also as high as in the case of A-grade oil, finishing within 2 min. The sorption capacity of these two exfoliated graphite samples for crude oil are 75 and 65 g/g , respectively.

In the case of C-grade heavy oil which has relatively high viscosity, sorption capacity of exfoliated graphite is a little smaller than the case of A-grade oil, but still 67 and 60 g/g for these two exfoliated graphite samples (Fig. 3). Sorption of C-grade heavy oil proceeded very slowly, about 8 hours being needed for the completion of sorption. B-grade heavy

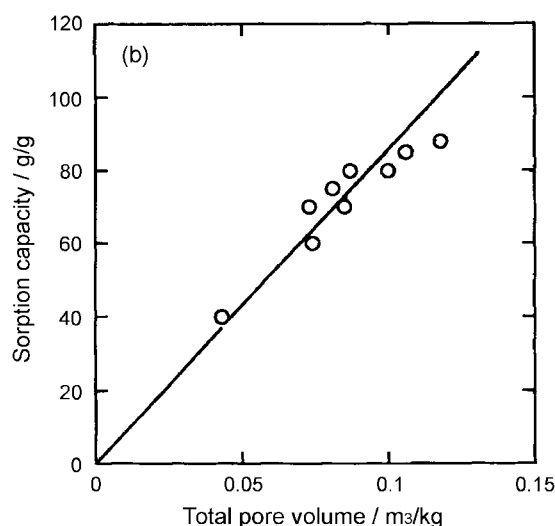
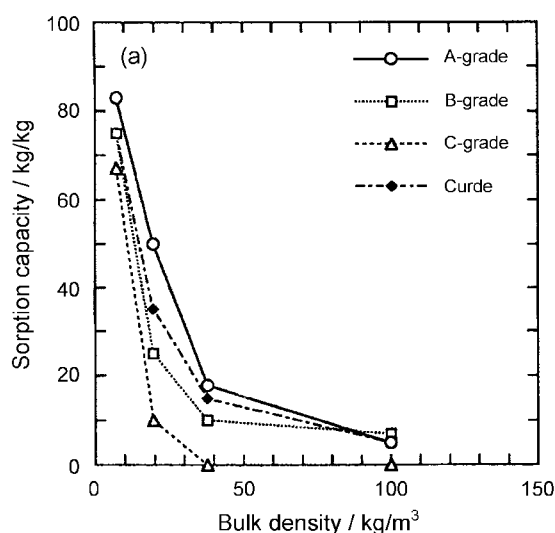


Fig. 4. Dependences of sorption capacity of exfoliated graphite EG-1 for A-grade heavy oil at room temperature on its bulk density (a) and total pore volume (b).

oil showed a behavior to be sorbed into exfoliated graphite similar to that of C-grade heavy oil in sorption capacity (Fig. 3) and also in sorption rate.

Figure 4(a) indicates the dependence of sorption capacity for different heavy oils on bulk density of exfoliated graphite. Sorption capacity of exfoliated graphite is found to depend strongly on its bulk density; the capacity decreases drastically with the increase in bulk density of exfoliated graphite.

In Fig. 4(b), sorption capacity of the exfoliated graphite samples for A-grade heavy oil at 20°C is plotted against total volume of pores in the range of 1 to $600 \mu\text{m}$ in radius measured by a mercury porosimeter. From the consequence that sorption capacity is linearly related to the total pore volume of exfoliated graphite, it can be concluded that an effective pore size for sorption of heavy oil is in the range of $1\sim 600$

μm . It is reasonable to suppose that most of the heavy oils are sorbed into the space formed among the worm-like particles of exfoliated graphite with capillary condensation, because of their large molecular sizes. It has to be mentioned however, total pore volume of exfoliated graphite had to be determined by mercury porosimeter using a special cell [18].

3. Selectivity of Sorption

Exfoliated graphite was able to sorb relatively small amount of water, its capacity measured on the present exfoliated graphite EG-1 was about 1.8 g/g; no difference in sorption capacity for water was detected among distilled, tapped and sea water. Even after saturation with water, the exfoliated graphite floated on the water surface and did not sink. When A-grade heavy oil was dropped onto a lump of this water-saturated exfoliated graphite, water was found to come out first, as shown in Fig. 5. By continuing the dropping of heavy oil, finally heavy oil came out. The sorption capacity of the exfoliated graphite which was saturated either by sea and tapped water in advance for A-grade heavy oil was 70 g/g, and the time for the sorption was about 4 h, which were a little lower and much longer than the case of the exfoliated graphite without saturation by water (83 g/g and within 1 min), respectively.

Consequently, heavy oil was found to replace the water sorbed into exfoliated graphite, but not completely. The reason for lowering of sorption capacity and increasing the time for sorption seemed to be the followings; water which had sorbed in advance into the small pores, possibly the pores inside of and/or crevices on the surface of worm-like particles of exfoliated graphite, could not be exchanged by heavy oil.

The same experiment was carried out on the polypropylene (PP) mats which were commercially available. The PP

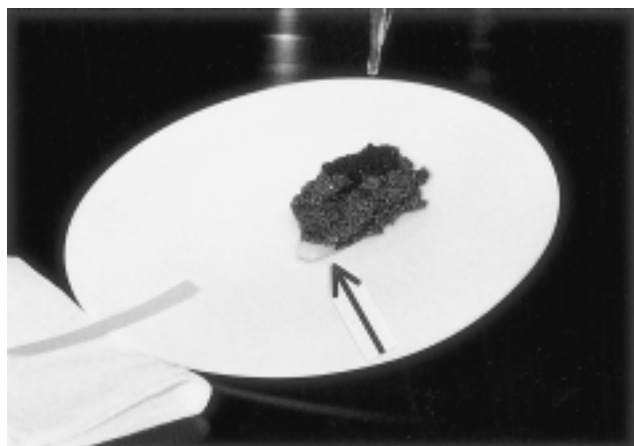


Fig. 5. Water exclusion from saturated exfoliated graphite by dropping heavy oil. (a) In the beginning and (b) after dropping a large amount of heavy oil.

Table 2. Content of water in heavy oils

Sample A-grade heavy oil	Water content (vol%)
Original	0.00
Oil sorbed onto exfoliated graphite from its floating on water surface	0.05
Oil stirred in water for 20 hours and then sorbed into exfoliated graphite	0.05

mats could sorb rather large amount of water, saturated amount of water sorbed being about 4 g/g. When A-grade heavy oil was dropped onto the water-saturated PP mat, water was not recognized to come out from the PP mat. Therefore, the PP mats which have been commercialized for oil absorption and used in practice could not sorb the heavy oils preferentially.

In Table 2, water content in A-grade heavy oils is listed, which has been stirred in water for different periods and then recovered by using exfoliated graphite. Since the limit of this determination is supposed to be 0.05 vol%, the water content in the recovered oils even after stirring in water for 20 hours can not be differentiated from that of the original. These results show clearly that exfoliated graphite sorbs heavy oils preferentially.

These experimental results show that exfoliated graphite could sorb heavy oils preferentially even though water was coexisted with heavy oils, heavy oil being floating on the water surface and also water being mixed into heavy oil. Even if exfoliated graphite was saturated with water, most of water could be replaced by heavy oil, though not completely.

4. Sorption Kinetics

Sorption rate of heavy oils, A- and C-grade, was evaluated by applying the so-called wicking method [19]. Weight increase by capillary suction of heavy oil into exfoliated graphite packed with different densities from its bottom with a cross-sectional area of 314 mm² at room temperature was measured by using a load cell as a function of time. The height of exfoliated graphite column was kept at a constant value of 10 mm. The experimental details were reported elsewhere [20].

Representative sorption curves for A- and C-grade heavy oils were shown in Fig. 6, as a function of packing density of exfoliated graphite. Sorption rate evaluated from the initial slope of sorption curves depends strongly on the packing density of exfoliated graphite; very gradual suction of heavy oil is observed for the exfoliated graphite column with a packing density of 7 kg/m³, not reaching the saturation even after 50 s, though very rapid suction and reaches saturation within 10 s by the one with 20 kg/m³. Very similar dependence on the packing density of exfoliated graphite column was also observed for the sorption of much viscous C-grade

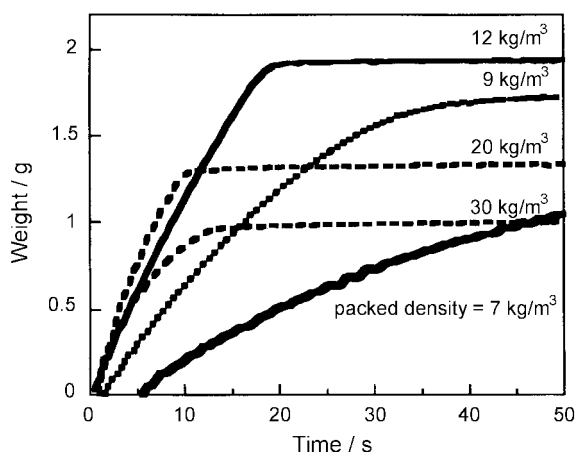


Fig. 6. Sorption curves measured by wicking method on exfoliated graphite column with different packing density.

heavy oil, but, the saturation, it needed much longer time than A-grade heavy oil.

In order to characterize the sorption rate more quantitatively, half time $t_{1/2}$ for the time needed to reach a half weight increase of the saturation (inserted in Fig. 7) was determined [20]. Half time $t_{1/2}$ for the sorption of A- and C-grade heavy oils is plotted against packing density of exfoliated graphite column in Fig. 7(a) and (b), respectively. By densifying the exfoliated graphite column from 7 to 20 kg/m³, the value of $t_{1/2}$ reduces to one-fourth for both grades of oil. However, the densification of the exfoliated graphite to more than 20 kg/m³ seems to have almost no effect on the sorption rate.

A large difference in sorption rate evaluated by $t_{1/2}$ is clearly shown between A- and C-grade heavy oils, that for the former being quicker by more than two orders of magnitude than that for the latter. Such difference in sorption rate between two grades of heavy oil was expected to be due to the large difference in viscosity of oils.

In Fig. 6, the saturated weight increase is found to depend also on the packing density of exfoliated graphite column. It shows a maximum at packing density around 12 kg/m³. In the case of the sorbed oil weight per unit weight of exfoliated graphite (sorption capacity), however, the maximum point shifted to the lowest packing density, 7 kg/m³. For the reason why the maximum of saturated weight increase was shown at 12 kg/m³, it was assumed that a large amount of pore volume with an effective size for heavy oil sorption (1 to 600 μm) was formed in the exfoliated graphite column packed at 12 kg/m³.

These results demonstrate that the sorption of heavy oil occurs due to capillary suction, for which large pores among worm-like particles of exfoliated graphite must be responsible, in order to explain such a large sorption capacity as 80 g/g, as mentioned in the previous section. The detailed studies on sorption performance of carbon materials, including

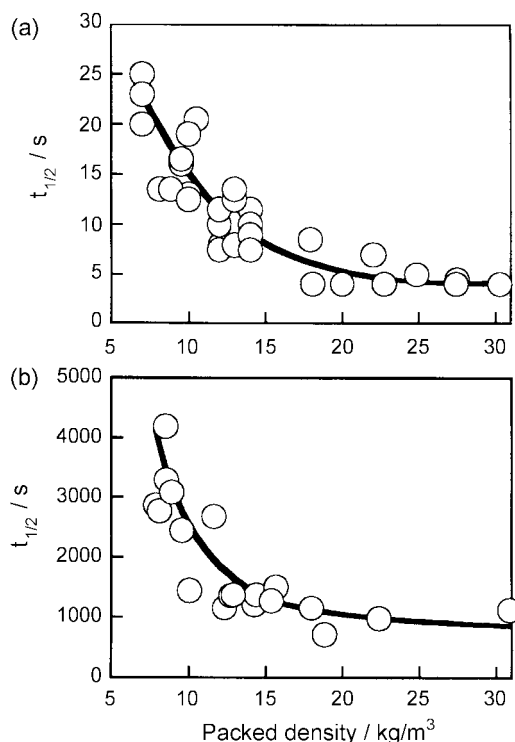


Fig. 7. Dependence of half time $t_{1/2}$ for the capillary suction of heavy oil on packing density of exfoliated graphite. (a) A-grade heavy oil and (b) C-grade heavy oil.

exfoliated graphite, were carried out on the bases of capillarity and diffusion [21].

5. Recycling Performance

By a filtration of sorbed exfoliated graphite, heavy oils

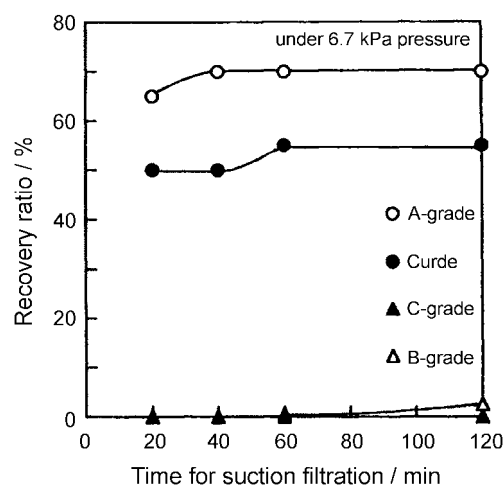


Fig. 8. Recovery of heavy oils sorbed on exfoliated graphite as a function of the time exposed for suction filtration.

were found to be recovered without marked change in the texture of exfoliated graphite. Figure 8 shows the dependence of the recovery ratio on the time of suction filtration under a pressure of 6.7 kPa. The recovery ratio for A-grade and crude oils with low viscosity was 70 and 55%, respectively. B- and C-grade heavy oils with high viscosity, however, could not be recovered by such a mild filtration. These results show that heavy oils with relatively low viscosity are easily recovered from sorbed exfoliated graphite without marked disruption of the bulky texture of exfoliated graphite.

In Fig. 9, changes of sorbed and recovered amounts of A-grade and crude oils, respectively, with recycling are shown on an exfoliated graphite with the bulk density of 6 kg/m³

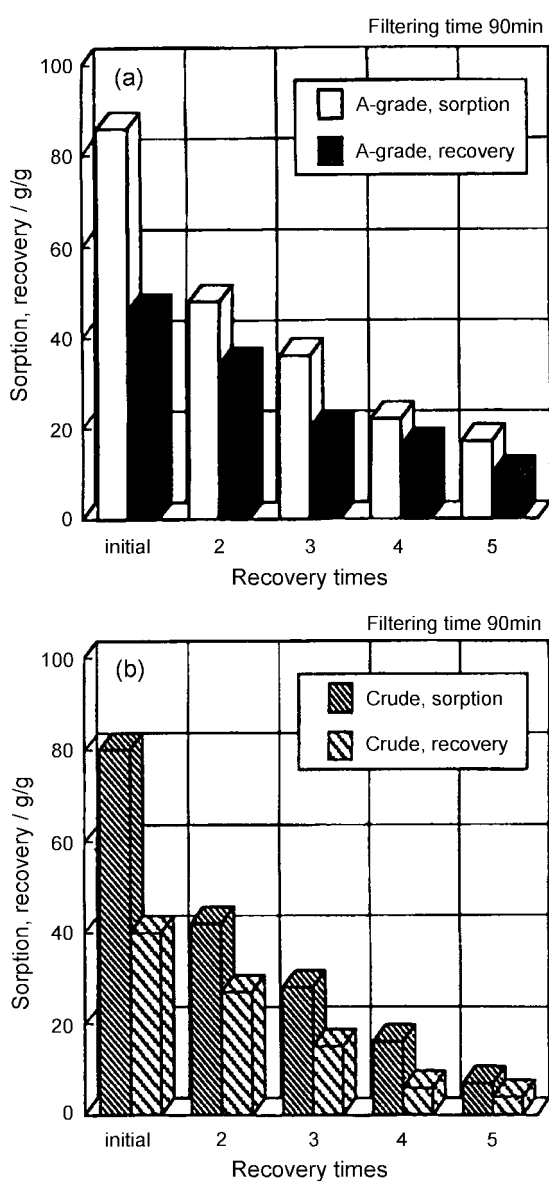


Fig. 9. Changes in sorbed and recovered amounts of heavy oil with recycling times by suction filtration. (a) A-grade heavy oil and (b) Crude oil.

after desorbing heavy oils by a filtration under suction for 90 min. For the first sorption and desorption cycle, sorption capacity is as high as 80 g/g and about 70% of sorbed oils is recovered. However, sorbed and recovered amounts of oils decrease rather markedly with increasing recycling times. The reason of drastic decrease in sorption capacity for heavy oil between the first and second cycle seems to be the retention of heavy oil in the pores and/or on the surface of the exfoliated graphite after filtration.

In Fig. 10, change in sorption capacity of the exfoliated graphite with the bulk density of 6 kg/m³ as a function of recycling times, where washing the exfoliated graphite with n-hexane (a) and heat-treating the exfoliated graphite at 400 °C for 7 h (b) were inserted in between 4th and 5th cycles. Sorption capacity with recycling by filtration decreases to a half up to the fourth cycle. By hexane washing and also by heat-treating, sorption capacity decreased, which was contrary to the anticipation of the authors. Shrinkage of exfoli-

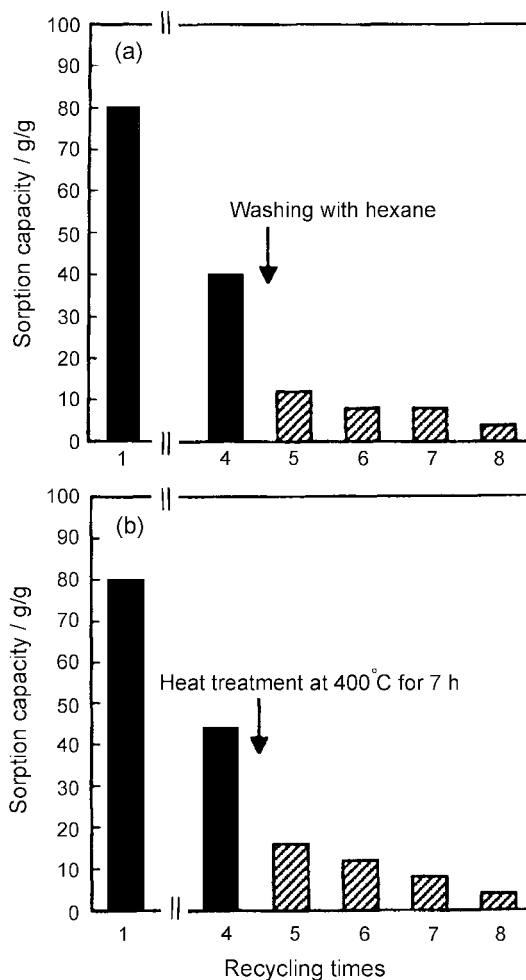


Fig. 10. Changes in sorption capacity of exfoliated graphite for A-grade heavy oil with recycling under suction filtration interrupted by washing with n-hexane (a) and heating at 400°C for 7h (b).

Table 3. Analytical data of original and recovered heavy oils

Sample oil	M_n	M_w	M_w/M_n	H_{al}	W_{sa}	W_{ar}	W_{resin}
Original A-grade oil	469	652	1.39	4.0	72.7	26.4	0.9
Recovered A-grade oil	428	546	1.28	4.2	71.5	27.3	1.2
Original C-grade oil	1071	1768	1.65	5.4			
Recovered C-grade oil	1207	1836	1.52	4.6			
Original crude oil	645	869	1.35	4.9			
Recovered crude oil	672	915	1.36	4.5			

M_n : Number-averaged molecular weight,
 H_{al} : Fraction of aliphatic hydrogen (wt%),
 W_{ar} : Aromatic hydrocarbons (wt%),

M_w : Weight-averaged molecular weight,
 W_{sa} : Saturated hydrocarbons (wt%),
 W_{resin} : Resinous hydrocarbons (wt%).

Table 4. Heavy oil sorption performance of various materials proposed

Materials	Heavy oil	Sorption Capa-city (g/g)	Sorption rate parameter $t_{1/2}$ (s)	Recycling performance	Ref.
Exfoliated graphite	A	87	ca. 25	by filtration	10 & 20
	C	67	ca. 4100	no recovery	
Fir fibers carbonized	A	78	ca. 10	by filtration	26
	C	66	ca. 4000	by washing	
Poly(propylene) nowoven web	Crude	11.3		by squeezing	23
Cotton fibers	Crude	33.2		by squeezing	23
Milkweed fibers	Crude	38.2		by squeezing	23
Kenaf heated up to 400°C	33			24	

ated graphite itself was apparently observed after hexane washing, which was reasonably supposed to reduce the sorption capacity. Washing by kerosene, xylene and heating in vacuum at 400°C for 2 h gave also the reduction in sorption capacity of exfoliated graphite.

In Table 3, analytical data on the original and recovered oils are summarized. From the FDMS analysis of three grades of heavy oils recovered from an exfoliated graphite, no pronounced differences from the original ones are detected in both number-averaged molecular weight M_n and weight-averaged one M_w . Only a slight decrease in M_w/M_n is observed on A- and C-grade heavy oils, suggesting a slight sharpening in molecular weight distribution. In recovered C-grade and crude oils aromaticity seems to increase slightly and in A-grade oil the relative content of saturated hydrocarbons seems to decrease in recovered oils. However, all of these differences in analytical data between original and recovered oils are very slight. Therefore, the oils recovered from exfoliated graphite can be concluded to have no difference from the original, in other words, they can be recycled.

6. Comparison with other materials for heavy oil sorption

There have been used poly(ethylene terephthalate) and poly(propylene) mats for the sorption of spilled heavy oil and also various materials, such as kenaf and cotton fibers,

have been proposed for the same purpose [22-24]. In Table 4, sorption performance of some of these materials is compared with exfoliated graphite and also fir fibers on which one of the present authors studied [25, 26].

Exfoliated graphite has extremely high sorption capacity in comparison with polypropylene mats and natural sorbents of fiber component of cotton, milkweed and kenaf. Fir fibers which were also fiber component of wasted fir tree and carbonized up to 900°C were found to have comparable sorption capacity for both A- and C-grade heavy oil [25, 26] with exfoliated graphite. In both exfoliated graphite and carbonized fir fibers, strong dependence of sorption capacity on their bulk density was observed. To keep high sorptivity, their bulkiness was shown to be essential, and so recycling performance of A-grade heavy oil by filtration under reduced pressure and that of viscous C-grade heavy oil by washing with some solvents, like n-hexane and less viscous A-grade heavy oil, were not so good. Though sorption capacity was not so high as exfoliated graphite and carbonized fir fibers, the recovery of heavy oil and recycling of some of natural sorbents were reported to be possible by squeezing, which could not be applied for exfoliated graphite and carbonized fir fibers.

7. Concluding Remarks

Exfoliated graphite has been industrially produced as a

raw material for flexible graphite sheets which have a wide application for sealing and gaskets at a high temperature and under a corrosive circumstance. It was pointed out that to prepare dense and flexible graphite sheets high degree of exfoliation, up to 300 times in volume, was essential when residue compounds of natural graphite flakes with sulfuric acid were rapidly heated up to about 1000°C, which resulted in very porous and fragile worm-like graphite particles entangled with each other. Such a network of worm-like particles in exfoliated graphite gave a possibility for so high sorption capacity as more than 80 g/g, thanks to hydrophobic nature of graphite surface. In a lump of exfoliated graphite, there are at least two kinds of pores, the ones inside of worm-like particles and the others among the particles; the former could be approximated by ellipsoids and analyzed with image processing of cross-section of the particle in our previous paper [17] and the latter are mostly responsible for their large sorption capacity for heavy oils. Recently, other possibility as sorbents for macro-bio-molecules, such as blood cells, was briefly reported [27]. Detailed studies on sorption of these macro-molecules and practical application in the field of surgery are going on in China.

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