Study on Addition of Surfactants Agents to Improve the Behavior of High Water Content Sediment for Rare Earth Mining in Deep Sea

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Abstract

Importance of rare mineral metal resources is increasing currently. Therefore, the rare earth elements rich mud which exist on the deep-sea floor has the potential to be developed to fulfill their demand. As one of the effective mining method, a suction mining method is expected to apply to seabed mining. The seabed sediment containing rare earth element shows the very high water content, more than 100%. And the sediment movement during the suction is greatly affected by the water content (W_C) and liquid limit (W_L) of the material. Therefore, it is important to modify the liquid limit by adding a chemical agent to control the behavior of sediment. We selected eight different surfactants which can be divided into three types. They are dispersant type, water retention type, and thickener type. We carried out a liquid limit test and viscosity measurement of the sediment mixed with the agents. It is found that the water-absorbing polymer and the hydroxyethyl cellulose increase the liquid limit and viscosity. Whereas, the alkyl ammonium salt surfactant and the alkyl ammonium salt, alkyl aryl sulfonate blend decrease the liquid limit and viscosity. It is possible to control sediment behavior by adding suitable surfactants.

Keywords: *deep sea mining, high water content sediment, rare earth, surfactants agent*

Introduction

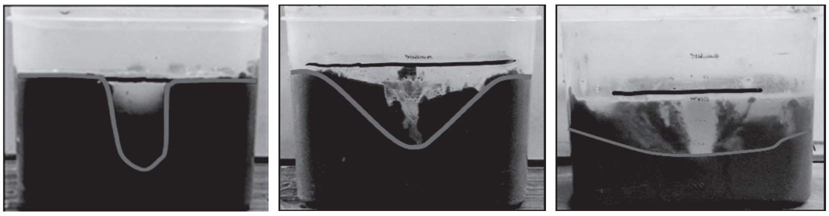
In recent years, the demand for rare mineral resources has grown and a lot of investigations have been conducted to discover new ore deposits all over the world. As a result, it was discovered that abundant rare-earth elements-rich mud exists on the deep sea floor (Kato et al., 2011, Hirai, 2014, Agency for Natural Resources and Energy, 2016). In recent years, some seabed mining method by using road header, drum cutter, or suction pump were developed all over the world (JOGMEC, 2010). Especially, suction pump mining is considered as one of effective methods for rare-earth elements-rich mud mining because it needs smaller-scale machine and less cost than other mining methods. However, it is required to evaluate the deformation behavior of rare-earth elements-rich mud in seabed mining because it will cause suspension and topographic variation (Ministry of the Environment, 2011) though there are some researches to minimize the environmental disturbance by adopting cement-based sealants (Sakamoto et al., 2016, Takahashi et al., 2017). For this reason, it is important to control the deformation behavior of rare-earth elements-rich mud in order to evaluate environmental impact in seabed mining. In the previous study, Tagami et al. (Tagami et al., 2017) reported that the deformation behavior of the mined seabed sediments is classified based on the ratio of water content and liquid limit as shown in Figures 1 (a)~(c). Therefore, if the liquid limit of the sediment can be varied by adding materials such as surfactants agents, the deformation behavior of the sediment can be controlled in order to obtain more suitable behavior for mining. This paper discussed the deformation behavior of seabed sediment by adding several different types of surfactants agents and measure the liquid limit and viscosity to evaluate the effectiveness.

Material and methods

Preparation of simulated sediment sample

Rare-earth elements-rich mud is classified as clay on soil classification. However, liquid limit and water content of rare-earth elements-rich mud are different depending on the place and it is expected that these difference change the deformation behavior of rare-earth elements-rich mud on suction mining. The geotechnical properties of rare earth rich mud are shown in Table 1. The simulated sediment samples which had the liquid limit and water content were prepared and used in the laboratory test. Those soil samples were prepared by blending two types of bentonite clay in different mixing ratio. Liquid limit and water content of the sample are 120% and 130% respectively.

The flowability of the particles suspended in the liquid generally depends on the dispersion and aggregation of the suspended particles. When a strong attractive force is generated between the particles and strongly aggregated primary aggregates or secondary aggregates due to the weak attraction are formed, the water restrained between the particles increases and the free water involved in the fluidity decreases and the fluidity decreases. On the other hand, when a strong repulsive force acts on the particles, the particles are dis-



(a) W_C/W_L <1.3 (sharp) (b) W_C/W_L <1.3~1.6 (cone-shape)(c) W_C/W_L >1.6 (circular arc)

Fig. 1. Classification of deformation behavior of simulated soil based on the water content (W_C) amd the liquid limit (W_L)
Rys. 1. Klasyfikacja deformacji dla symulowanej charakterystyki gleby na podstawie zawartości wody (W_C) oraz limitu cieczy (W_L)

Tab. 1. Properties of sample of rare-earth elements-rich mud (Agency for Natural Resources and Energy, 2016)
Tab.1. Właściwości próbki podłoża z pierwiastkami ziem rzadkich (Agency of Natural Resources and Energy, 2016)

	A-1	A-2	A-3	A-4	B	C
Density (g/cm^3)	2.850	2.831	2.792	2.792	2.833	2.821
Liquid limit (%)	116.3	111.1	98.7	105.4	117.1	109.8
Water content (%)	124.1	138.9	156.3	140.3	128.8	146.1

Tab. 2. Surfactants used in this study
Tab. 2. Odczynniki powierzchniowe zastosowane w badaniu

Group	Surfactant	Addition ratio (%)		
Dispersant	Low molecular weight polycarboxylic acid ethers	0.2	0.5	1.0
	High molecular weight polycarboxylic acid ethers	0.2	0.5	1.0
	Alkyl ammonium salt	0.2	0.5	1.0
Water retention agent	Hydroxypropylmethylcellulose	0.2	0.5	1.0
	Water-absorbing polymer	0.2	0.5	1.0
Thickener	Hydroxyethyl cellulose	0.2	0.5	1.0
	Alkyl ammonium salt, Alkyl aryl sulfonate blend	0.2	0.5	1.0
	Polyacrylamide	0.2	0.5	1.0

persed, restrained water is reduced, and fluidity is improved. Considering those mechanisms above, the surfactants agents which are classified as three groups as shown in Table 2 were added with 0.2~1.0% by the weight of the simulated sediment samples in order to control the dispersion and aggregation of the suspended particles.

Liquid limit and viscosity were measured to evaluate the properties of the sediment samples. Liquid limit tests were conducted according to the test method for liquid limit and plastic limit of soils (JIS A 1205:2009). Soil sample is put in a brass dish with a thickness of 1 cm and cut a groove in the sample in the cup. Turn the handle of the device at a ratio of 2 drops per second. Count the number of blows until the two halves of the soil sample come in contact along a distance of 1.5 cm. Adding or evaporating water to collect the data. The viscosity of the sample was measured by B type viscometer. One cycle of changing the rotational speed in the order of 0.3, 0.6, 1.5, 3.0, 6.0, 12, 30, 60, 30, 12, 6.0, 3.0, 1.5, 0.6, 0.3 rpm. The cycle is repeated for a total of 4 times. The interval of each speed is 30 seconds. The average viscosity of the 60 rpm from the 2nd to 4th cycle was calculated as the viscosity during suction pumping.

Suction pump test

In order to evaluate the deformation behavior of simulated soil samples, suction quantity and influence range were measured by a suction pump test. Conceptual diagram of a suction pump test is shown in Figure 2. The suction force of the pump was adjusted in 4.0 kPa (maximum suction force of the pump is 21.4 kPa). The caliber of a suction pump was 10 mm and the suction time was 8 seconds. The suction area was 50 mm depth from the simulated soil surface. After the suction pump test, deformation behavior of simulated soil was observed and the maximum vertical length (V) and horizontal length (H) of the deformation area were measured. Influence range was defined as H/V. Furthermore, the ratio of water content and liquid limit (W_C/W_L) was defined in order to evaluate the fluidity of simulated soil samples quantitatively.

Results and discussion

Properties of sediment sample by addition of surfactant agents

Figures 3 (a)~(c) show the relationship between the liquid limit and addition ratio. When water retention agents were added, liquid limit increased, whereas, dispersant type agents tend to reduce the liquid limit. For the thickener type agents, a specific trend was not observed. Further, when the hydroxyethyl cellulose and the water absorbing surfactant were added, a larger effect of increasing the liquid limit was obtained as compared with other surfactants. On the other hand, the alkyl ammonium salt and the alkyl ammonium salt, alkyl sulfonate blend was used, the liquid limit decreased significantly. Figures 4 (a)~(c) show the relationship between the ratio of water content to liquid limit (W_C/W_L) and the addition ratio of each surfactant when the water content of sediment sample is 130%. As the water content is constant, the trend of the variation of the ratio is similar to the trend of liquid limit variation.

The viscosity test was conducted on each sample under the same conditions of W_C/W_L indicated in Figure 4. Figures 5 (a)~(c) show the relationship between the viscosity and the addition ratio of each surfactant. As shown in the figure,

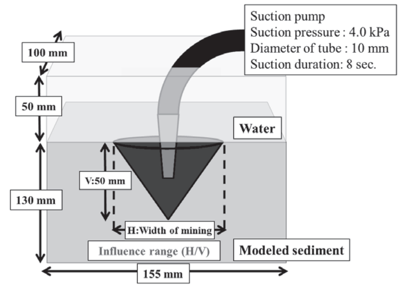
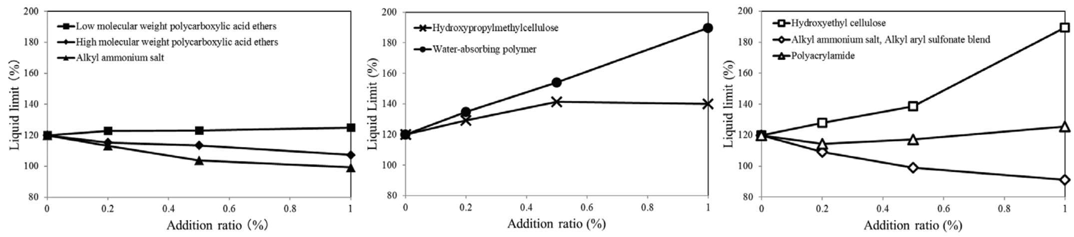


Fig. 2. Conceptual diagram of suction pump test

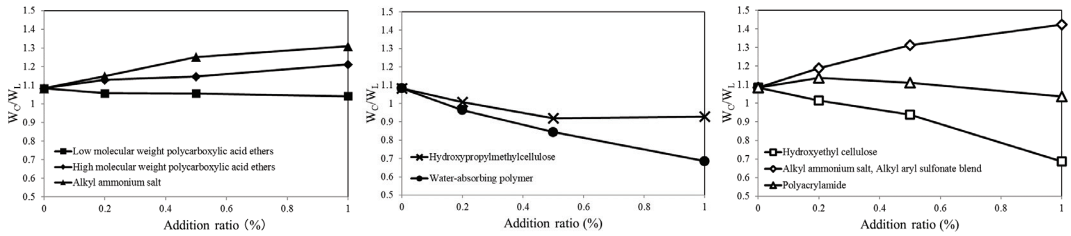
Rys. 2. Diagram koncepcyjny testu pompy ssącej



(a) Dispersant (b) Water retention agent (c) Thickener

Fig. 3. Relationship between liquid limit and addition ratio of each surfactant

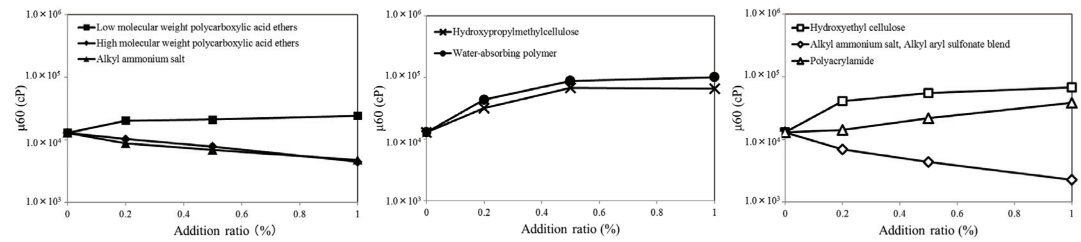
Rys. 3. Zależność pomiędzy limitem cieczy a stopniem dodania każdego odczynnika powierzchniowego



(a) Dispersant (b) Water retention agent (c) Thickener

Fig. 4. Relationship between the ratio of water content to liquid limit (W_C/W_L) and addition ratio of each surfactant

Rys. 4. Zależność pomiędzy zawartością wody a limitem cieczy (W_C/W_L) oraz stopniem dodania każdego odczynnika powierzchniowego



(a) Dispersant (b) Water retention agent (c) Thickener

Fig. 5. Relationship between viscosity and addition ratio of each surfactant

Rys. 5. Zależność pomiędzy lepkością a stopniem dodania każdego odczynnika powierzchniowego

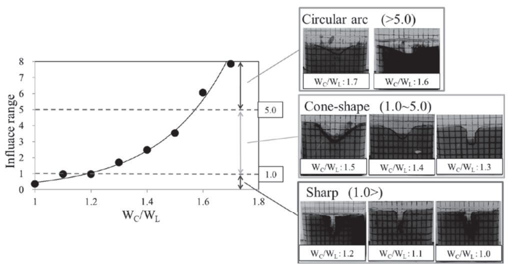
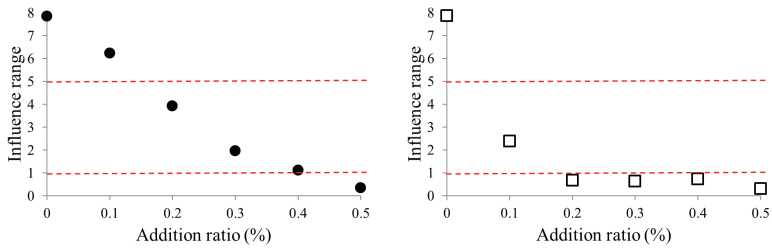


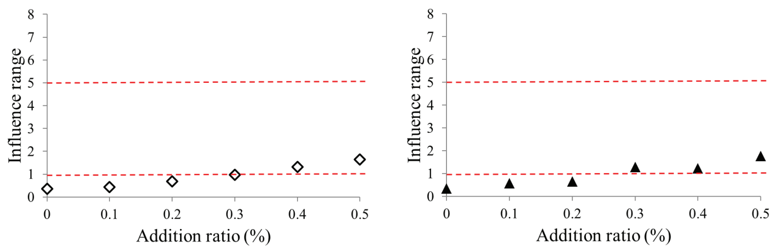
Fig. 6. Definition of influence range for 3 types based on W_C/W_L : circular arc, cone-shape, and sharp

Rys. 6. Definicja stopnia wpływu dla trzech typów na podstawie WC/WL: łuk kolisty, kształt stożkowy oraz łuk ostry



(a) Water-absorbing polymer (b) Hydroxyethyl cellulose

Fig. 7. Modification effect by suction test: circular to cone-shape
Rys. 7. Wpływ modyfikacji typu łuku kolistego na kształt stożkowy w teście ssania



(a) Alkyl ammonium salt (b) Alkyl ammonium salt, Alkyl aryl sulfonate blend

Fig. 8. Modification effect by suction test: sharp to cone-shape
Rys. 8. Wpływ modyfikacji kształtu ostrego na kształt stożkowy w teście ssania

when the water absorbent polymer, hydroxypropyl methylcellulose, and hydroxyethyl cellulose were added, the viscosity increased more than the other surfactants. In addition, when the alkyl ammonium salt, high molecular weight polycarboxylic acid ethers, and the alkyl ammonium salt, alkyl sulfonate blend surfactants were added, the viscosity decreased. These results agree with those of the relationship between the liquid limit.

Considering the modification of liquid limit and viscosity, the surfactants of water-absorbing polymer and hydroxyethyl cellulose seem to be effective to change the deformation behavior from circular arc to cone-shape while alkyl ammonium salt and alkyl ammonium salt, alkyl aryl sulfonate blend seem to be effective for the changing the behavior from sharp to cone-shape. Therefore, the actual deformation behavior owing to the suction mining is discussed in the next section.

Deformation behavior of sediment sample in suction pump test

In order to confirm the effectiveness to control the deformation behavior by adding surfactants, the suction pump test was carried out. The deformation behavior was evaluated by using the influence range defined as 3 types: circular arc, cone-shape, and sharp. Figure 6 shows a definition of influence range in this study for 3 types based on W_C/W_L.

Figures 7 (a) and (b) show the results of deformation behavior when water-absorbing polymer and hydroxyethyl cellulose are added. From these results, both surfactants are effective to change the deformation behavior from circular arc to cone-shape because the influence range is reduced with the increase of addition ratio. Additionally, the hydroxyethyl cellulose is more effective to control the deformation behavior of sediments because the less adding of the surfactant is enough to change the deformation behavior. This result is inconsistent with the fundamental properties of the sediment sample; the WC/WL is higher and the viscosity is smaller in the sediment sample added hydroxyethyl cellulose compared to that of water-absorbing polymer. Therefore, a more detailed study will be needed to conduct the quantitative evaluation of the effects to change deformation behavior such as viscoelasticity properties and the viscosity under the different rotational speed.

Figures 8 (a) and (b) show the results of deformation behavior when alkyl ammonium salt and alkyl ammonium salt, alkyl aryl sulfonate blend are added. These results indicate the effectiveness of the addition of both surfactants to change the deformation behavior from sharp to cone-shape. Additionally, both surfactants have an almost similar effect to change the deformation. However, the addition of alkyl ammonium salt and alkyl ammonium salt, alkyl aryl sulfonate blend is less effective to control the deformation behavior that that of water-absorbing polymer and hydroxyethyl cellulose. This can be explained by the fundamental properties of the sediment samples; the changing of liquid limit, viscosity, and WC/WL are less compared to the surfactants of water-absorbing polymer and hydroxyethyl cellulose.

From the above results, in the modification of the suction behavior of the simulated sediment, it is possible to select the suitable surfactants agents. For example, if the behavior have to be modified from a circular arc structure to a cone-shape one, it is considered that the water-absorbing polymer and hydroxyethyl cellulose are applicable. When the behavior have to be modified from a sharp structure to a cone-shape one, it is preferable to use an alkyl ammonium salt surfactant and an alkyl ammonium salt, alkyl aryl sulfonate blend.

Conclusion

In order to investigate the modification method of rare earth sediment fluidity, a series of laboratory experiments were conducted. We selected 8 different surfactants which can be divided into 3 types. They are dispersant type, water retention type, and thickener type. The fundamental properties of the sediment mixed with the surfactants were measured by the liquid limit test and viscosity measurement. Additionally, the suction pump test was carried out to confirm the effectiveness to control the deformation behavior during suction mining. As a result, proper selection of surfactants can modify the liquid limit and viscosity and lead to control the deformation behavior of the sediments. In order to conduct the quantitative evaluation of the effects to change deformation behavior, a more detailed study has to be needed such as viscoelasticity properties and the viscosity under the different rotational speed.

Acknowledgements

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Literatura – References

1. KATO, Yasuhiro et al. Deep-sea mud in the Pacific Ocean as a potential resource for rare-earth elements. Nature Geoscience, 4, 2011, p. 13-24, 2011, ISSN 1752-0894.
2. HIRAKI, Koji. Trends in Metal Resource Development and Strategies for Resource Security, Surface Science for Resource, 35(2), 2014, p. 114-115, ISSN 1881-4743.
3. Agency for Natural Resources and Energy, Report of Resource Potential Assessment for Rare Earth Sediments, [online]. c2016 [cit. 2019-04-02]. Dostupný z WWW: < https://www.meti.go.jp/press/2016/07/20160706004/20160706004-2.pdf>. (Japanese).
4. JOGMEC, Study of Mining System of Seafloor Hydrothermal Deposits [online]. c2010 [cit. 2019-04-02]. Dostupný z WWW: < http://mric.jogmec.go.jp/kouenkai_index/2010/briefing_100527_5.pdf>. (Japanese).
5. Ministry of the Environment, Report of Technology Assessment of Environmental Impact, [online]. c2011 [cit. 2019-04-02]. Dostupný z WWW: < http://warp.da.ndl.go.jp/info:ndljp/pid/11057318/www.neti.env.go.jp/policy/assess/4-1report/file/h23_08i.pdf>. (Japanese).
6. SAKAMOTO, Seiichi et al. Fundamental Study on Deformation Behavior of Seafloor Covered with Sealing Materials in Seabed Mining, Proc. International Symposium on Earth Science and Technology 2016, 2016, 74-78. ISBN 978-4-9902356-5-9.
7. TAKAHASHI, Keisuke et al. Application of Cement-based Sealants for Prevention and Remediation of Environmental Impact of Submarine Resource Mining, Proc. of 26th International Symposium on Mine Planning & Equipment Selection, 2017, 363-367. ISBN 978-91-7583-935-6.
8. TAGAMI, Taiko et al. Study on Deformation Behavior of Rare-Earth Elements-Rich Mud and Applicability of Sealing Materials in Seabed Mining, Proc. International Symposium on Earth Science and Technology 2017, 2017, 161-164. ISBN 978-4-9902356-6-6.

Badanie wpływu odczynników powierzchniowych na poprawę właściwości osadu pod kątem głębinowego górnictwa pierwiastków rzadkich

Złoża metali rzadkich są bardzo ważne a ich istotność wzrasta w ostatnich latach. Zatem, dno morskie, które zawiera duże ilości tego typu pierwiastków posiada potencjał do zaspokojenia potrzeb w tym zakresie. Jako jedną z efektywnych metod górniczych w tym aspekcie należy traktować ssanie. Osad denny z dna morskiego, który zawiera pierwiastki ziem rzadkich wykazuje bardzo dużą zawartość wody. Ruch osadu podczas ssania jest uzależniony w dużym stopniu od zawartości wody (W_C) oraz krytycznego limitu cieczy (W_L) materiału. Zatem, ważnym jest aby zmodyfikować limit cieczy poprzez dodatek odczynnika chemicznego w celu kontrolowania zachowania się osadu. Wybrano osiem różnych odczynników powierzchniowych, które mogą być podzielona na trzy typy. Są to odczynniki typu dyspergującego, typu retencji wody oraz typu zagęszczającego. Przeprowadzono test limitu cieczy i pomiaru lepkości osadu wymieszanego z odczynnikami. Stwierdzono, że polimer absorbujący wodę oraz hydroksyetyloceluloza zwiększają limit cieczy oraz lepkość. Z kolei, sól amoniowo-alkilowa oraz blenda alkiloarylosulfonianowa zmniejszają te wielkości. Możliwa jest kontrola zachowania się osadu poprzez dodatek odpowiednich odczynników powierzchniowych.

Słowa kluczowe: *górnictwo głębinowe, osad o dużej zawartości wody, pierwiastki ziem rzadkich, odczynniki powierzchniowe*