Which Technology Could be Suitably Applied for the Remediation of Deep-Sea Mining Tailings?

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ABSTRACT: Remediation technologies for deep-sea mining tailings were mainly evaluated in this research in order to derive candidate technologies for the future development of practical remediation technologies required for commercial deep-sea mining to respond to strengthening of international marine environmental standards. Polymetallic nodules which were collected at the Clarion-Clipper zone in the Pacific Ocean consist of mostly inorganic materials such as manganese (Mn, 61.0%), silicate (Si 10.3%), iron (Fe, 5.57%), heavy metals and other tiny elements. It is assumed that deep-sea mining tailings may be slurry mixed with fine solid materials having a particle diameter of several tens to 100 μm which are originated from crushing of polymetallic nodules and liquid substance produced from selection process on vessel connected with lifting and collecting procedures. Fine particles as well as harmful components eluting from deep-sea mining tailings may adversely affect marine environment including marine life. A new modular remediation treatment system in which physical separation and chemical treatment are repeated several times in a single treatment flow should have to develop in order to overcome various limitations (space, energy, process water, vibration, corrosion, weather conditions, etc.) at sea area.

KEYWORDS: Deep-sea resources, polymetallic nodules, mining tailings, remediation, candidate technologies

INTRODUCTION

Since natural mineral resources on land have been depleted in proportion to increasing human activities, demand for the development of deep-sea mineral resources is rapidly increasing inevitably. The Republic of Korea (South Korea) has acquired exclusive exploration licenses at four areas which are the Clarion-Clipperton zone in the Pacific Ocean (2002), Tonga (2008), Fiji (2011) and Indian Ocean (2014) since 1994. Both Nautilas minerals (Canada) and Lockheed martin minerals (USA) are already ready for commercial mining in 2018 and 2020, respectively. Hence, The London Protocol 1996 (LP) under International Maritime Organization (IMO) is working with the International Seabed Organization (ISA) to set up international environmental guidelines for deep-sea mining tailings until the early 2020s, in order to protect marine environment including marine life (ISBA/23/LTC/CRP.3, 2017). Deep-sea mining tailings may be treated by suitable treatment methods. Otherwise deep-sea mining tailings should be transported to land and disposed followed by adequate treatment. Therefore, for commercial mining of deep-sea mineral resources from the early 2020s, on-site remediation technologies including treatment, beneficial use and disposal are essentially required. Deep-sea polymetallic nodules may include a wide range of sediments considering their origin and contents. Similar commercial technologies have been commonly used for the remediation of sediments and soils, because remediation mechanisms of sediments are similar to that of soils. Unfortunately, these conventional land-based remediation technologies could not be directly applied at ocean, sea area without development of new technologies that may overcome various restrictions such as marine weather, vibration and limitation of infrastructures (space, energy, process water, etc.).

The objectives of this research are to evaluate appropriate remediation technologies for deep-sea mining tailings and to draw candidate technologies as preliminary data in order to develop practical remediation technologies in the near future.

MATERIALS AND METHODS

Polymetallic nodules were collected using free fall grab and box corers at the Clarion-Clipper zone (Location: 131°22.68′W~131°17.22′W, 10°27.3′N~10°32.7′N) of the Pacific Ocean in March 2018 (Figure 1). Collected polymetallic nodules were dried naturally in the research vessel during the survey period. After the survey cruise, dried polymetallic nodules were stored at room temperature in a laboratory. Dried polymetallic nodules were initially crushed by a jaw crusher and secondly crushed by a ball mill. Crushed nodules were then separated as three particle sizes (larger than 63 μm, 20~63 μm, smaller than 20 μm) using two vibratory sieve shakers (Analysette 3 pro, Fritsch, Germany). This procedure was repeated several times. These materials were used as samples in this research.
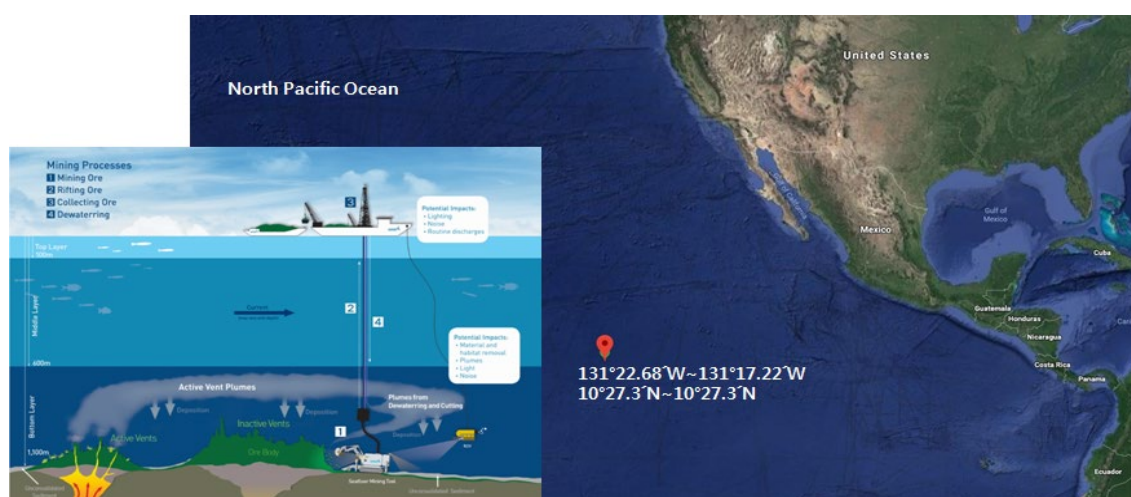

FIGURE 1. Schematic diagram of deep-sea mining process and collecting area map of polymetallic nodules.

The constituents of samples were determined by X-ray fluorescence spectrometer (XRF-1800, Shimadzu, Japan). The material structures of samples were evaluated by scanning electron microscope (SEM) (S-2400, Hitachi, Japan). Carbon components of samples were determined by total organic carbon (TOC) analyzer (TOC-Vcph, SSM, Shimadzu, Japan). Heavy metals were determined by inductively coupled plasma-mass spectrometer (ICP-MS) (Thermo X series, ThermoFisher, USA). The recovery ration of heave metals was also verified using standard reference materials, MESS-3 (National Research Council, Canada). The magnetic property of samples was evaluated by magnetic property measurement system (MPMS-7, Quantum design, USA). All chemical reagents used in this research were extra pure (EP) grade.

RESULTS AND DISCUSSION

Characteristics of samples. The constituents of samples for each particle size are shown in Table 1.

TABLE 1. Constituents of sample at each particle size.

Element	Smaller than 20 μm	20~63 μm	Larger than 63 μm	Nodules*
		Contents (%)		
Mn	27.1	30.5	28.1	27.0~30.0
Si	13.2	10.3	11.4	
Fe	8.66	5.57	6.91	6.00~8.00
Na	3.00	3.59	3.53	
Al	4.04	3.07	4.11	
Ni	2.80	2.96	3.53	1.25~1.5
Ca	3.06	2.71	3.32	
Mg	3.00	2.65	3.61	
Cu	1.98	2.59	2.61	1.00~1.40
Cl	2.03	2.01	1.68	

K	1.76	1.85	2.05	
Ti	0.581	0.475	0.415	
Co	0.375	0.399	-	
Zn	0.296	0.348	-	0.20~0.25
P	0.391	0.302	0.363	
S	0.259	0.264	0.317	
Ba	0.509	-	-	
Sum	73.0	69.5	71.9	

*(Kuhn, 2017)

Samples at each particle size were composed of the following five major components: manganese (Mn), silicate (Si), iron (Fe), aluminum (Al) and sodium (Na). Harmful heavy metals were nickel (Ni) 2.80~3.53%, copper (Cu) 1.98~2.61% and zinc (Zn) 0.296~0.348%, respectively. Concentrations of heavy metals were found to increase with increasing particle size until 63 μm.

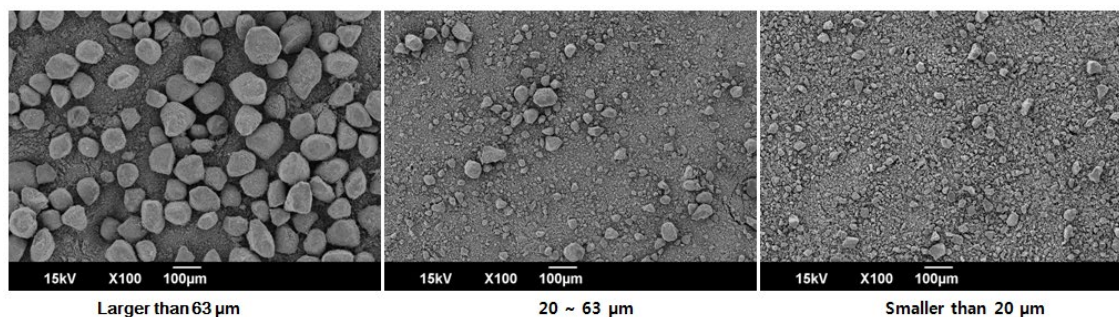The material structures of samples at each particle size are represented in Figure 2.

Larger than 63 μm   20 ~ 63 μm   Smaller than 20 μm

FIGURE 2. Material structure of sample at each particle size.

Samples larger than 63 μm were mixed with large amounts of coarse particles and small amounts of fine particles, unevenly. Its composition was not dense due to a large number of voids between particles. On the contrary, samples smaller than 63 μm were mixed with mostly fine particles and a tiny amount of coarse particles, evenly. In case of larger than 63 μm particles, physical separation / detachment, chemical washing / extraction might be easily applied based on the results of SEM. On the other hand, these kinds of technologies may not be easily applied to particles less than 63 μm.

Carbon contents of samples at each particle size are represented in Table 2. There was no significant difference in carbon contents depending on the particle size of the sample. Since total organic carbon (TOC) of samples was 0.33%, organic matters were only slightly proportional in the total constituents of samples.

TABLE 2. Contents of total carbon and total organic carbon at each particle size.

Specification	TC (%)	TOC (%)
larger than 63 μm	0.36	0.33
20 ~ 63 μm	0.34	0.33
smaller than 20 μm	0.34	0.33

Heavy metals concentrations of samples at each particle size is summarized in Table 3.

TABLE 3. Heavy metal concentration of sample at each particle size.

Specification	Al wt%	Fe wt%	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Cd mg/kg	Pb mg/kg
Larger than 63 μm	1.89	3.13	8.62	15,004	13,606	1,578	43.3	24.3	247
20 ~ 63 μm	2.38	4.17	7.85	15,131	12,932	1,462	55.3	18.0	254
Smaller than 20 μm	2.72	5.53	12.4	13,471	10,993	1,238	65.5	15.9	333

Korea's environmental standards for marine sediment remediation are represented in Table 4.

TABLE 4. Environmental standards for marine sediment remediation (KOREA).

Environmental standard, KOREA	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Cd mg/kg	Pb mg/kg
Level 1	80	23	24	200	9.0	0.68	50
Level 2	370	52	108	410	41.6	4.21	220

There are two environmental standards for the remediation of marine sediments in Korea. The meaning of Levels 1 and 2 are similar to that of US EPA's ERL and ERM. However, the concentration of each item is a little different due to Level 1 and 2 set according to the background concentrations of marine sediments and marine environmental conditions in Korea. The concentrations of all heavy metals were increased proportionally as particle size decreased. Nickel (Ni), copper (Cu), cadmium (Cd) and zinc (Zn) exceeded Level 2 by 259, 102, 3.77 and 3.02 times, respectively. Arsenic (As) and lead (Pb) also exceeded Level 2 by 1.57 and 1.51 times, respectively. Therefore, Ni, Cu, Cd and Zn were selected as primary target materials for prioritized remediation; then As and Pb were selected as secondary target materials for remediation.

Magnetic susceptibility of samples at each particle size is shown in Table 5. The magnetic susceptibility of samples at each particle were very low values which represent the properties of paramagnetic materials. Thus, magnetic separation technology may be very limited for the remediation of these samples, deep-sea mining tailings without additional improvement treatment to selectively bind with ferromagnetic materials.

TABLE 5. Magnetic susceptibility of sample depending on particle size.

Specification	Magnetic susceptibility(χ)
Larger than 63 μm	9.7×10^{-7}
20 ~ 63 μm	7.0×10^{-7}
Smaller than 20 μm	6.0×10^{-7}

In the leaching test, 0.01 g, 0.1 g and 1 g samples were mixed with surface sea water and low-layer sea water at 1,000 m as 1 ℓ and stirred for specific time (0 ~ 12 h) under dark (without light) conditions. Leaching test were conducted at 4 ℃ for only low-layer sea water conditions. Based on leaching tests, the elution concentrations of Ni, Cu, Cd and Zn were higher than the background concentrations of sea water. On the contrary, the elution concentrations of As and Pb were lower than the background concentrations of sea water. The maximum leaching ratios of Ni, Cu, Cd and Zn were 0.22%, 0.19%, 5% and 2.83%, respectively. Even though the leaching concentration of heavy metals was low, it may be considered that heavy metals may accumulate in ocean and also give a negative effect on the marine environment.

From the results of biotoxicity tests using plankton (Zoo- / Phyto-), the growth of plankton was possible at all concentration ranges from 0.2 sample g/ℓ to 1.0 sample g/ℓ, but the growth rate was lower as the concentration of the sample increased. In addition, plankton may intake

sample and then the growth rate decrease at the particle size lower than 63 µm. Therefore, not only leaching concentrations of harmful heavy metals but also the size of fine particle can affect the growth of plankton.

Consideration of existing commercial remediation technologies. Generally, physical, chemical and complex technologies are widely used for the remediation of sediments, soil or mining tailings. Physical treatment technology is a treatment technique to remove or separate pollutants from base materials such as mining tailings, sediments or soil based on physical properties such as particle size, specific gravity, hydrophilic, hydro-phobic and magnetic property. Since various research results of which treatment devices are most effective have been reported for decades, adequate treatment technologies and devices may easily be selected followed by the determination of particle size and range of target materials (Dermont, 2008). Nevertheless, it is very difficult to optimize physical treatment depending on the amount of target materials, the degree of contamination, the content of fine particle lower than 75 µm, the presence of liquid phase, slurry state, etc.

Chemical treatment technology is a treatment technique to remove pollutants selectively from base materials throughout chemical reactions with a chemical reagent such as oxidants, surfactants, chelating chemicals, solvents, acids, and bases (Mulligan, 2001 a). According to target materials, reagent required chemical treatment may also easily select. Considering the remediation of deep-sea mining tailings, remediation treatment needs to be set up on site in sea area. Especially, the impact of all treated products such as final products and mid-products and produced waste including solid and liquid on marine environment should have to be minimized and meet environmental standards for marine disposal. Since, toxic chemicals, strong acids or bases could not be used it is also extremely difficult to treat deep-sea mining tailings under mild conditions using environmentally safe chemical reagents.
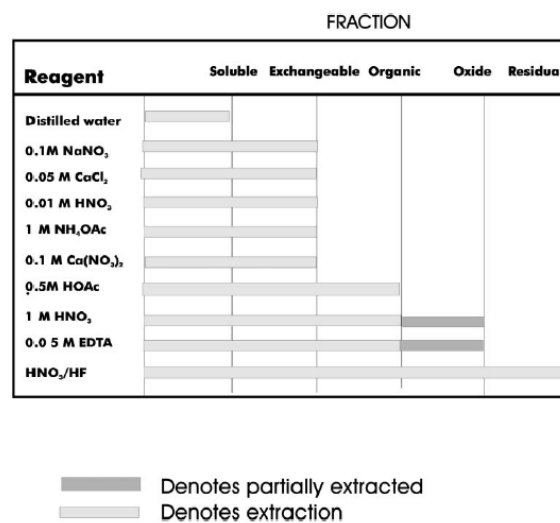

FIGURE 3. Feasibility of chemicals as extracting agents for different metal fractions (Mulligan et al, 2001 a).

Complex treatment technologies are a combination of two or more treatment technologies such as physical and chemical treatment. In the most remediation sites of sediments, soil or mining tailings, complex treatment technologies are commonly used (Mulligan, 2001b). As a result of reviewing related remediation technologies, problems that may arise when existing commercial remediation technologies may be directly applied to the remediation of deep-sea mining tailings in sea area, on-site, are followings.
- Limitation of space (surface area and height)
- Limitation of energy and process water

- Ocean weather such as storm or wave, vibration, rust due to salt
- Need to minimize discharge wastewater and reduce liquid ratio depending on solid
- Need to make modular treatment system

The required modular treatment system may consist of complex treatment technologies in a simple treatment flow.

Deriving candidate remediation technologies. The concept of development plan for the remediation of deep-sea mining tailings is represented in Figure 3. The direction for the development of remediation treatment technologies were derived as followings.

- Evaluation of the characteristics of more various deep-sea mining tailings and then make database.

- Separation technology for fine particles lower than 75 μm may need to develop and optimize in a single complex treatment flow.

- A new chemical treatment technologies for deep-sea mining tailings may need to develop using environmentally friendly chemical reagents under mild conditions.

- A new modular remediation treatment system may need to develop in a single treatment flow in order to overcome various limitations in sea area, on-site.

- New water treatment technologies without settler or dewatering process may also need to develop in order to apply in sea area, on-site.

- New remediation treatment technologies may need to develop on the basis of recent research results such as biological surfactants.
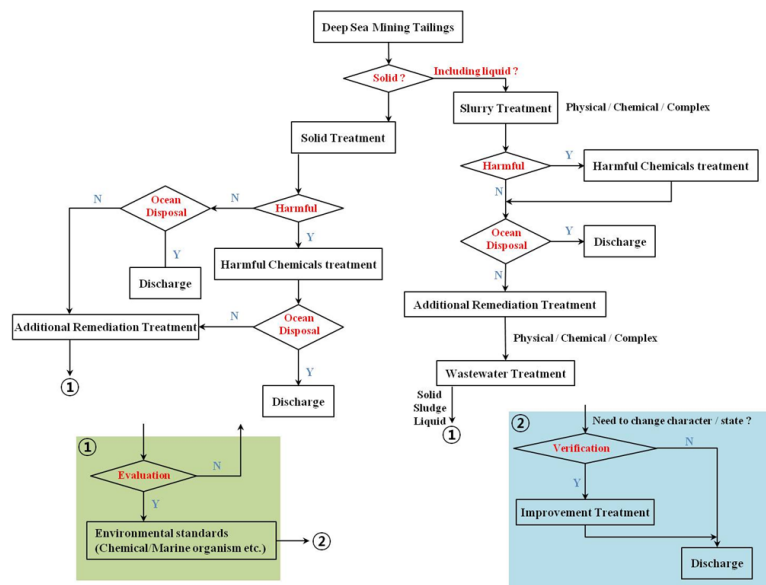

FIGURE 4. Concept of development plan for the remediation of deep-sea mining tailings.

CONCLUSIONS

Following conclusions were drawn from this research.

1. Since deep-sea mine tailings have fine particles lower than 75 μm and harmful heavy metals affecting marine environment, these materials should have to be treated with appropriate remediation technology and then finally disposed in sea area.
2. A new remediation treatment system should have to develop in order to overcome the limitations of land-based treatment technologies consideration of on-site conditions.
3. There is no need to develop highly precise remediation technology in considering of required time, money and efficiency.

4. A modular treatment system which selectively separates and washes according to the degree of contamination and particle size need to be developed.
5. It is also necessary to develop a treatment technologies for improving the property of treated materials connected with remediation process, for safe ocean disposal.
6. In the near future, the actual development results of remediation technologies will be reported continuously for deep-sea mining tailings.

ACKNOWLEDGEMENTS

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