Application of Cement-based Sealants for Prevention and Remediation of Environmental Impact of Submarine Resource Mining

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Application of Cement-based Sealants for Prevention and Remediation of Environmental Impact of Submarine Resource Mining

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Abstract— Recurrent studies on submarine hydrothermal deposits have been directed toward the practical mine development and the corresponding environmental impacts. Even after the extraction of submarine resources, the original environment shall be maintained in order to prevent harmful effects on the marine ecosystem. Nonetheless, relatively little research about mineral exploitation on the seafloor has been focused on how to prevent its environmental disturbances and rehabilitate the mining site. The author invented an environment-friendly underwater mining method that aims to control the dispersion of seabed surface sediments and fill the extracted areas by sealing a submerged mine site with an anti-washout cement-based material. This work investigates technological properties and environmental impacts of sealants with different cementitious binders and anti-washout agents on a laboratory scale. Using the remotely operated vehicle Hyper-Dolphin, field trials were conducted in the marine submerged Wakamiko crater. The results indicate that a sealant with particular types of cement and anti-washout agent showed superior anti-washout, filling and hardening properties under submarine hydrothermal conditions. Less dispersion of surface sediments was observed after covering the seafloor surface with the sealant during the field-scale experimental exploitation. Sealants had less negative effects on the seafloor ecosystem.

Keywords: Submarine resource mining, cement, sealant, environmental remediation, hydrothermal deposit

1. Introduction

As cement is one of the most energy- and carbon-efficient of all man-made materials on a volume basis, the use of cement-based materials contributes to development of the sustainable society. Cement is manufactured by using wastes and by-products such as fly ash, plastic waste and surplus soil etc. The Japanese cement industry consumed 28 million tons of wastes and by-products in 2015 in order to produce cement [1]. As a sustainable construction material "cement" has been utilized for cavity supports and backfills of underground mining as well as buildings and bridges.

This work aims to examine and advance the application of cement-based materials for mining methods of submarine hydrothermal deposits. Studies on submarine hydrothermal deposits have been repeatedly directed toward the practical development of mines (i.e. the process of constructing a mining facility and its supporting infrastructure) and the corresponding environmental impacts [2]. Even after the extraction of submarine resources, the original environment shall be maintained to safeguard the habitat for a huge variety of species living in the submarine hydrothermal system and support the biological diversity. Depression contours formed by the extraction could create dysoxic conditions that have harmful effects on the marine ecosystem. Surface sediments in and around submerged mine sites, which occasionally contain mercury and arsenic etc. derived from volcanic activities, can be dispersed by the extraction and bioaccumulate in fish and aquatic invertebrates. Nonetheless, relatively little research about the exploitation of submarine resources has focused on how to prevent its environmental disturbances and rehabilitate the mining site.

The author invented an environment-friendly underwater mining method that aims to control the dispersion of seabed surface sediments and fill the extracted areas by sealing a submerged mine site with an anti-washout cement-based sealants. Figure 1 illustrates the idea of the underwater mining method. When the underwater mining method is put into practical use, submarine hydrothermal deposits such as rare earth elements that are absorbed on clays can be vacuumed up without dispersing the harmful surface sediments.

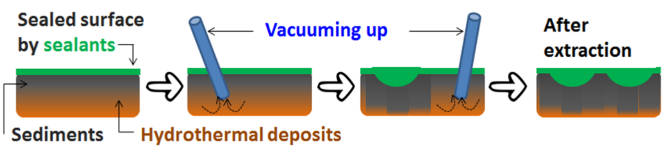

Figure 1. Environment-friendly submarine mining

This study measured and investigated technological properties and environmental impacts of sealants with different cementitious binders and anti-washout agents on a laboratory scale. Using the remotely operated vehicle (ROV) Hyper-Dolphin, field trials were conducted with the support of Japan Agency for Marine-Earth Science and Technology (JAMSTEC) in the marine submerged Wakamiko crater.

2. Background

2.1. Underwater concreting

Anti-washout concrete was developed to improve the reliability of concrete placed underwater and has been employed in the construction of bridge foundations and underwater walls etc. Compared to conventional concrete (CVC) using traditional methods such as tremie and concrete pump placing, anti-washout concrete is highly resistant to the washing action of water and rarely separates even when it is dropped into water. Thanks to specific viscosity modifying admixtures called anti-washout agents, e.g. hydroxyethyl cellulose and hydroxypropyl methylcellulose (HPMC), the components of anti-washout concrete never segregate and its flowability is excellent due to the concrete's low yield value and high viscosity [3].

2.2. Geology of Wakamiko crater

The Wakamiko crater, which contains submerged calderas and two active volcanoes, is located in the eastern portion of the innermost coastal section of Kagoshima bay. The maximum water depth over the crater floor is approximately 200 m. A huge hydrothermal deposit of antimonite with a diameter of 1500 m and a thickness of 5 m, which is estimated 1 million tons of antimony, was discovered in 2011 [4]. Figure 2 shows a calcareous chimney and gravel of antimonite photographed at the Wakamiko crater. A maximum of 80 m-thick layer of surface sediments have accumulated on the antimonite deposit, which contains a maximum of 260 ppm of mercury and 500 ppm of arsenic derived from volcanic activities [5]. For this reason, the deposit must be extracted without dispersing the sediments and having any impacts on fish and aquatic invertebrates.

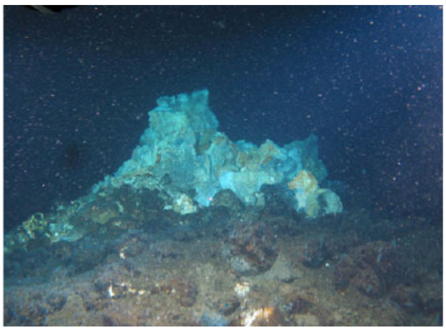

Figure 2. Chimney (white) and gravel of antimonite (dark)

3. Experimental

3.1. Mix designs

For the purpose of sealing a submerged mine site and filling the extracted area, cement-based sealants need to have excellent self-leveling and anti-washout properties as well as moderate hardening properties. Table 1 shows the mix proportions of the experimental sealants consisting of cementitious binders, aggregate and chemical admixtures. Polycarboxylic ether (PCE) is a dispersant that disperses binder particles and improves fluidity of suspension. HPMC and the tube-like micelle forming agent are anti-washout agents that increase the viscosity of sealants and prevent the component materials from separating in water. To prepare the sealants, 10 kg of all components were mixed with 3 kg of water for 2 min using a hand-held mixer.

Table 1. Proportions of the experimental sealants

	Cementitious binders	**Admixtures**
A	Portland cement	PCE, HPMC
B	Portland cement, gypsum, calcium aluminate cement	PCE, HPMC, retarders
C	Portland cement	PCE, tube-like micelle forming agent

3.2. Laboratory tests of technological properties

Density, flow value, suspended solids content as an index of anti-washout, setting time and compressive strength of the experimental sealants were measured based on JIS A 1116, EN 12706, JSCE D 104, JIS R 5201 and JSCE F 504, respectively. Plastic viscosity of the sealants was measured under the pressurized condition and was determined from the Bingham plot using the measured share stress–share rate curve. The pressure values were predetermined at 0.1 MPa (standard atmosphere) through to 10 MPa (hydraulic pressure at 1000-m depth).

3.3. Field tests of technological properties

Self-leveling, anti-washout and hardening properties of the experimental sealants were investigated at a field scale through the dive expedition number 1691–1694 of the ROV Hyper-Dolphin of JAMSTEC. Sealants that were loaded onto the ROV were pumped by a peristaltic pump at a discharge rate of 10 L/h and poured into a polyvinyl chloride (PVC) frame set on the seafloor at 200 m below the surface. This 5-cm high PVC frame has a base area of 50 cm^2. Turbidity and seawater temperature were measured during the pouring of sealants into the frame. Leveling and washout (spreading) of sealants were monitored by the camcorder equipped with the ROV. Figure 3 depicts the ROV with testing equipment.

After the sealants were hardened, sediments under the sealants were vacuumed using a suction sampler in order to observe sealing behavior of the sealants. Specimens for the compressive strength test were casted at the same site where the PVC frames were set (Fig. 4).

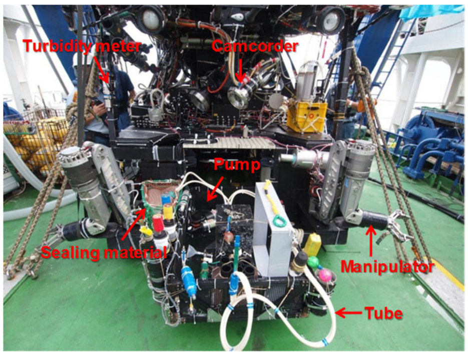

Figure 3. ROV set-up

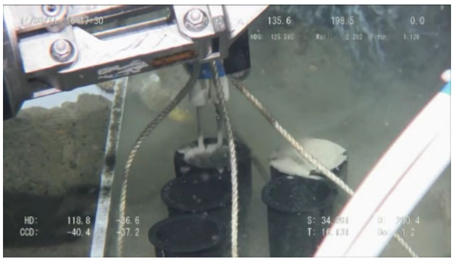

Figure 4. Casting of specimens for strength tests

3.4. Laboratory tests of environmental impacts

A huge variety of species, e.g. bacterium as a primary producer and gastropoda as a primary consumer etc., live in the seafloor hydrothermal system. There is a similar ecosystem in the coastal sea area. Diatoms, which are primary producers, are fed by gastropods such as *Omphalius rusticus*. On a laboratory scale, this study monitored the diatom breeding performance and population on the surface of hardened sealants A and B, and of CVC with/without seashell repellent applied to these. In addition, the gastropod feeding behavior on the diatoms was monitored. Diatoms were bred for a month on hardened samples (13 cm by 10 cm) in seawater and its breeding success was quantified by the value of chlorophyll a [6]. An *Omphalius rusticus* was placed for 12 h on the hardened samples in seawater where the diatoms were bred, and subsequently the hardened samples were air dried for 12 h to detect visually the trail of *Omphalius rusticus*.

Marine biofouling in the coastal area of Seto Inland Sea was investigated by placing cubic hardened sealants in the littoral zone for 6 months (May–November in 2015).

4. Results and Discussion

4.1. Technological properties of experimental sealants

Table 2 shows density, flow value, suspended solid content, setting time and compressive strength of the experimental sealants. The suspended solid content of ordinary anti-washout concrete is defined as less than 50 mg/L [3]. As the suspended solid content of sealants A–C were less than 50 mg/L, sealants A–C have a good anti-washout characteristic at standard atmosphere. Flow-ability of sealants A and B were higher than that of sealant C. Compared to sealants A and C, setting was earlier and strength development was accelerated in sealant B.

Figure 5 shows the plastic viscosity as a function of the applied pressure. Plastic viscosity of sealants B and C was drastically decreased when 0.5 MPa of pressure was applied and further decreased with the increase of applied pressure. Effects of pressure on plastic viscosity were less pronounced in sealant A. Figure 6 represents the relationship between plastic viscosity and suspended solid content under pressurized conditions. The suspended solid content was increased in direct proportion to the decrease of plastic viscosity due to the applied pressure (the coefficient of determination was 0.7).

Table 2. Technological properties of the experimental sealants

Sealants		A	B	C
Density	g/cm^3	1.9	1.9	1.9
Flow value	mm	183	185	152
Suspended solid content	mg/L	9.0	15.9	4.2
Setting time	min	630	220	730
3 h strength	N/mm^2	0.0	6.2	0.0
1 d strength	N/mm^2	8.0	19.1	5.6

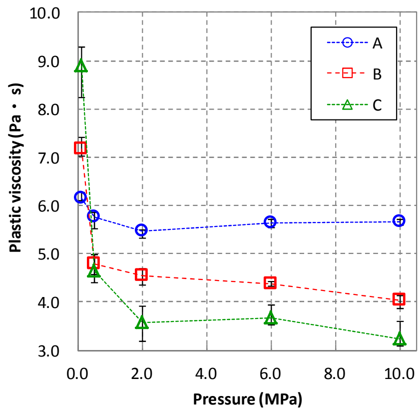

Figure 5. Plastic viscosity as a function of the applied pressure

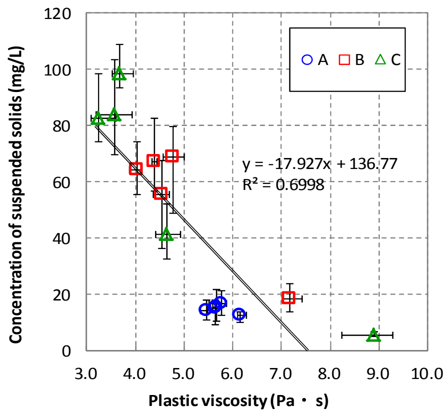

Figure 6. Relationship between viscosity and suspended solid under the pressurized condition

The reason for changes in the plastic viscosity of the pressurized sealants could be explained by the different thickening mechanisms of binders and anti-washout agents. HPMC adsorbs on the binder particles and forms net-like structures [7], which prevent component materials from separating in water. On the other hand, the tube-like micelle forming agent does not adsorb on the binder particle. When pressure is applied to the sealant with tube-like micelle, the tube-like micelle in the water phase might be agglomerated or its net-like structures might be deformed, and subsequently the anti-washout properties of the sealant degrade. The hydration (reaction) of cementitious binders also causes net-like structures among the binder particles to form and increases the viscosity of sealants [8]. Retarder regulates the hydration rate and delays the formation of the structures at the early hydration period. The net-like structures of sealant B including retarder might be broken easily under the pressurized and shared condition.

4.2. Field tests

Leveling and anti-washout behavior of sealants A–C during the pouring of sealants into the PVC frame were shown in Figs. 7–9, respectively. Sealant A showed superior self-leveling and anti-washout behavior, however, sealants B and C were washed out. The spreading of sealant C was more pronounced. Changes in turbidity and seawater temperature (Fig. 10) that were provoked by the pouring of sealant A were small. These results indicate that the sealant with Portland cement and HPMC (sealant A) showed superior anti-washout and filling properties under submarine hydrothermal conditions.

Table 3 shows the compressive strength of sealants A and B casted and cured under submarine hydrothermal conditions. There was little difference in compressive strength of sealant A cured under laboratory and submarine conditions. As sealant B was washed out during the casting, the compressive strength of the sample cured under submarine conditions was about half of the sample cured in lab.

Figure 11 shows that less dispersion of surface sediments was observed after covering the seafloor surface with sealant A during the field-scale experimental suction.

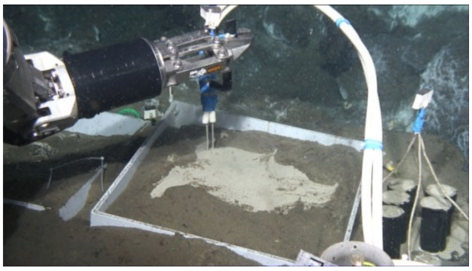

Figure 7. Sealant A poured into the frame

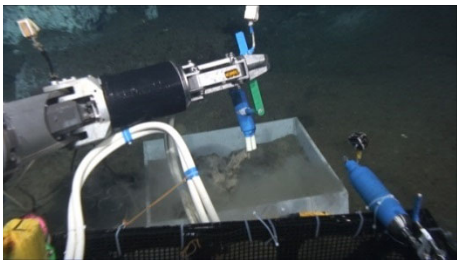

Figure 8. Sealant B poured into the frame

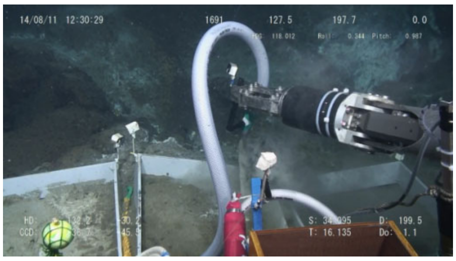

Figure 9. Sealant C poured into the frame

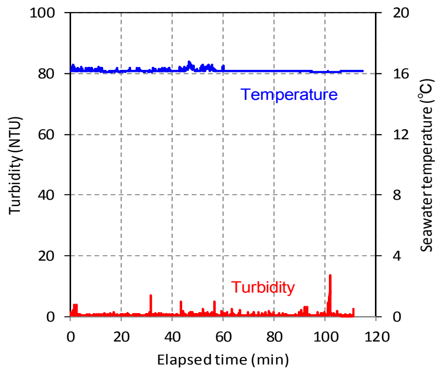

Figure 10. Changes in turbidity and seawater temperature

Figure 11. Field-scale experimental suction

Table 3. Strength of sealants A and B (unit; N/mm^2)

Sealants	Curing conditions	3 h strength	24 h strength
A	Laboratory	0.0	6.5
A	Submarine	0.0	6.2
B	Laboratory	5.7	19.6
B	Submarine	2.9	9.1

4.3. Impacts on seafloor ecosystem

Breeding success of diatoms on the hardened sealants A, B and the CVC with/without repellent is quantified in Table 4. Experimental seawater was obtained from Seto Inland Sea, where 28–120 mg/m^2 of diatoms naturally live [9]. Except for the case of CVC with repellent, diatoms established on the hardened samples in the lab at the same level as in the natural marine environment.

Figure 12 depicts the trails of *Omphalius rusticus* that were detected in sealants A, B and CVC without repellent.

Figure 13 shows the cube-shaped specimens used for marine biofouling in the littoral zone of Seto Inland Sea. The attachment of *botrylloides violaceus* was observed after one month. Two months later, diatoms covered whole specimens of sealants A and B. Balanomorpha, ascidians, porifera as well as diatoms were attached after 6 months. Figure 14 represents the amounts and species of biofouling after 6 months. Ascidians preferably attached to sealant A and porifera preferably attached to sealant B.

These results indicate that the negative effects of the experimental sealants on seafloor ecosystem could be minimized.

Table 4. Breeding of diatoms on sealants A, B and CVC

Sealants	Chlorophyll a concentration (mg/m^2)
A	59.2
B	59.5
CVC without repellent	68.8
CVC with repellent	24.3

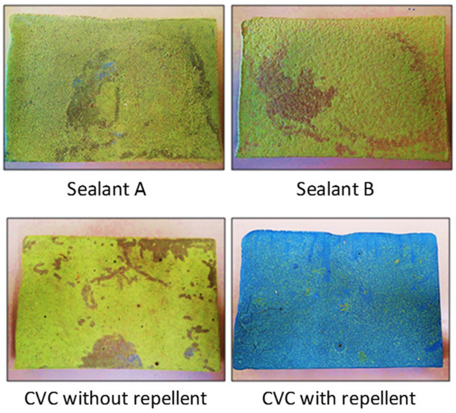

Figure 12. Trails of Omphalius rusticus

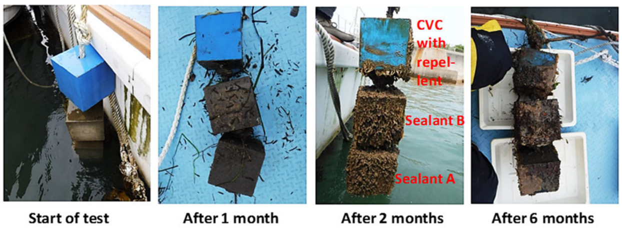

Figure 13. Specimens for marine biofouling

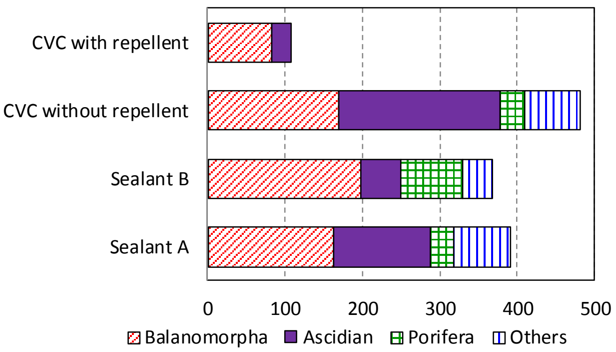

Figure 14. Amounts and species of biofouling

5. Conclusions and Perspectives

By examining the application of cement-based sealants for the mining of submarine hydrothermal deposits on both a field scale and a laboratory scale, it was evident that the sealant with Portland cement and HPMC showed superior anti-washout and filling properties and moderate hardening property under the submarine hydrothermal conditions at the Wakamiko crater. Few negative effects of the experimental sealants on the seafloor ecosystem were observed.

There is currently great emphasis on the practical mine development stage. Further research is necessary in order to carry out the next stage for prevention and remediation of environmental damage resulting from submarine resource mining, which would involve field trials in a deep-sea environment (over 1000-m depth) and optimization of the sealing method through simulations on a laboratory scale etc.

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