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How the Environment of Marine Sediment Changes when Calcium Dioxide is Added

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Abstract: We investigated the changes in a contaminated bay sediment when some oxygen releasing compounds (ORC) were put in it: it was found that the ORCs such as MgO_2 , CaO_2 , and $Mg(OH)_2$ were good at suppression of H_2S and removal of phosphorus by changing the neutral pH into weak alkaline pH. In particular, performance of CaO_2 was the best of all probably because of the faster establishment in O_2 generation and weak alkaline condition. Consequently, it was concluded that ORCs instead of sea cultivation or red clay spreading would promote the conditions better in which O_2 was kept being generated and active microbial population for bioremediation should be maximized.

Keywords: Biodegradation, Oxidizing agent, Organic Compounds, Contaminated Sediments, Phosphorus Removal

1. INTRODUCTION

Marine contamination has been becoming severe as seashore development and land originated contaminants boom around the marine area. Especially marine sediment is a base for aquatic ecological system along with water layers [1]. Thus sedimental contamination greatly affects on water quality and furthermore destroys bio-species [2]. And that contamination consumes lots of oxygen while decomposing organic matter, resulting in a reductive environment. Additionally it could generate hydrogen sulfide and ammonia gases, which are very toxic to living organism [3].

In order to decontaminate the sediment, though dredging, sea bottom cultivation, spreading yellow soil and iron oxide, microbial agents have been tested, secondary contamination or economic problems still remain. Another way for natural remediation is putting more oxygen in the sites. Properly processed/treated Mg or Ca can be used as tool for oxygen release. ORCs raise dissolved oxygen in water and convert the anaerobic environment into more oxic one, which is more favorable for marine eco system. It has been reported that ORCs such as MgO , $Mg(OH)_2$, MgO_2 , CaO , and CaO_2 are being applied to soil and groundwater cleanup targeting

for TPH, BTEX, and TCE [3-4]. However, they are limited and have not been actually extended to sea sediment or seashore remediation.

This study is on experiments for testing MgO_2 , CaO_2 , and $Mg(OH)_2$ as oxygen suppliers. Efficiencies and relative characteristics of those agents are investigated and compared for possible application to sea remediation.

2. EXPERIMENTAL

2.1 MATERIALS

ORCs (Oxygen Release Compounds) such as magnesium peroxide(MgO_2), calcium peroxide(CaO_2), magnesium hydroxide($Mg(OH)_2$) were used in powder as received. MgO_2 and CaO_2 are insoluble but react with water to form magnesium hydroxide and calcium peroxide along with oxygen. Additionally phosphates block water permeation into crystal structures of MgO_2 and CaO_2 in order to control the degree of hydration of the crystals, resulting in continuation of O_2 generation. In addition, $Mg(OH)_2$, the hydrated form of MgO_2 was used in the experiments. During the experiments all reagents were protected from the moisture in air.

2.2 SAMPLE PREPARATION AND METHOD

2.2.1 SAMPLING

Sediment, 10 cm below the sea surface was sampled around Tongyong seashore. One kilogram of the sediment was placed in each basin. Four basins were prepared for control, MgO_2 , CaO_2 , and $Mg(OH)_2$. All basins were agitated three times a day under the anaerobic condition and maintained 60% of water content with supply of filtered seawater once per day.

3. ANALYTICAL METHOD

pH was directly monitored from the sediment using an ORION model 210A. COD (Chemical Oxygen Demand), AVS (acid-volatile sulfides) were analyzed in accordance

with the standard methods. TN and TP were also analyzed with some chemical treatments and UV/Vis spectrometry.

4. RESULTS AND DISCUSSION

4.1 PH CHANGE WITH DIFFERENT ORCS

As shown in Fig. 1, when 10% of MgO_2 , CaO_2 , and $Mg(OH)_2$ were added to the basins, pH maintained in the range of 7.4~7.51 for 3 days. After that, pH grew in all treated basins to finally reach 9.27~9.57. With addition of the ORCs chemical reactions such as (1) and (2) occur to form the metal hydroxides at first. And then followed reactions (3) and (4) generate OH^- to turn the environment into weak alkalinity, which mainly depends on the solubility of the hydroxides. For example, solubility of $Mg(OH)_2$ is 0.009 g/L while that of $Ca(OH)_2$ is 1.85 g/L[5], The lowest solubility of $Mg(OH)_2$, therefore, resulted in the lowest pH. However, Scavenger effect of the generated oxygen on OH^- ions might suppress further pH rise.

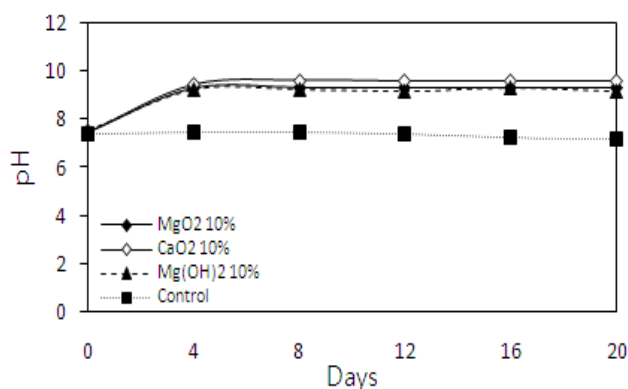
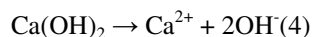
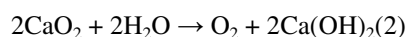
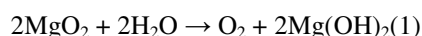


Fig. 1. Changes in pH for 20 days at inputs of 10% MgO_2 , CaO_2 , $Mg(OH)_2$.

4.2 COD CHANGES WITH DIFFERENT ORCS

COD changes with the ORCs input were shown in Fig. 2. As in ignition loss the pattern of COD reduction was similar. When 10% of CaO_2 was added the COD reduction was 35.8%; meanwhile MgO_2 and $Mg(OH)_2$ produced 27.5% and 7.25% of removal rate, respectively. Nitrous and phosphorus compounds could increase biomass (microbial population) thus leading to higher COD in the sediment with ORC producing oxygen. However, increased microbial population in the highly oxidic environment would decompose organic matter (COD) more rapidly thus resulting in COD decrease[6].

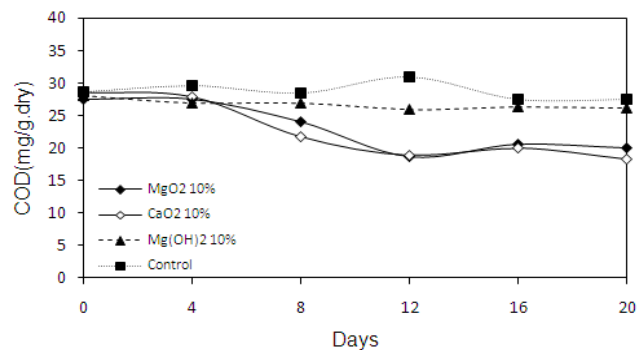


Fig. 2. Changes in COD for 20 days at inputs of 10% MgO_2 , CaO_2 , $Mg(OH)_2$.

4.3 AVS CHANGES WITH DIFFERENT ORCS

AVS as toxic compounds deserves to be monitored in the marine sediment. In Fig. 3 the changes in AVS concentration of the ORC treated sediment were shown. Natural attenuation of AVS in the control was not trivial (from 1.4 to 1.1 $\mu\text{g/g.dry}$). The AVS was completely consumed in 12 days with addition of CaO_2 . Addition of MgO_2 or $Mg(OH)_2$ reduced the AVS concentration by 61.5% or 76.9%, respectively.

As shown in reactions (1) and (2) the reaction products $Ca(OH)_2$ and $Mg(OH)_2$ may form covering film on the surface of sediment, thus resulting in not only suppression of phosphates release but deactivation of sulfate-reducing bacteria (SRB) for a long period of time[7]. The anoxic environment of sediment – low pH, generation of hydrogen sulfide gas – would be toxic to any living matter both in sediment and its vicinal water[7]. Yooet. al. report that sulfide-reducing bacteria could grow at pH 6.5-7.5 while they would not survive at pH 8.5 or higher. Normal seawater is weakly alkaline but that in contaminated region accumulates organic acids oxidized and produced by action of oxidic microorganism, thus turns to be acidic and to lack oxygen, in which SRB inevitably grows fast, generating hydrogen sulfide gas, a typical compound of AVS. With ORC treatment the sediment changes into alkaline (pH > 8.5), which deactivates SRB activity thus minimizes production of the sulfide gas.

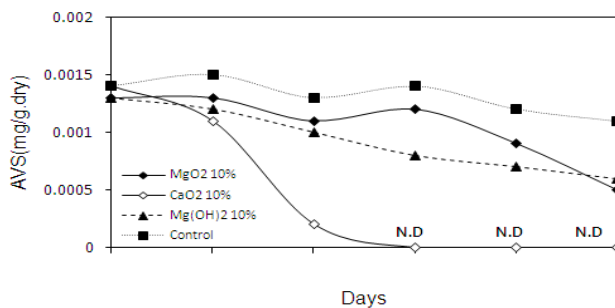


Fig. 3. Changes in AVS for 20 days at inputs of 10% MgO_2 , CaO_2 , $Mg(OH)_2$.

4.4 TN CHANGES WITH DIFFERENT ORCS

Initial total nitrogen in all the test sediment was about 1.6 mg/g and then slowly reached a maximum followed by a decline. Apparently final TN reduction was greatest for Mg(OH)₂(48.9%), lowest for CaO₂(18.3%). This surprising result may be explained with following two mechanisms: as shown in reaction (5) oxidation of ammonia or organic nitrogen with sufficient O₂ supply can facilitate release of nitrates and nitrites, resulting in higher TN. At the same time, the released nitrous compounds could be denitrified by microorganism activated in the anoxic environment[8]Oxidation of carbonic organic matter and nitrification compete each other with O₂ generation. That means higher oxygen producer cannot necessarily raise the rates of nitrification and followed nitrous release since C/N ratio is very critical in aerobic microbial activity. In 12th day biologically available organic content seemed to be used up. Therefore, Mg(OH)₂ treatment showed more drastic change in TN than that of CaO₂. Another possibility for that low TN reduction might be on fast, inevitable ammonia release via organic decomposition with O₂ supply (refer to reaction (6)).

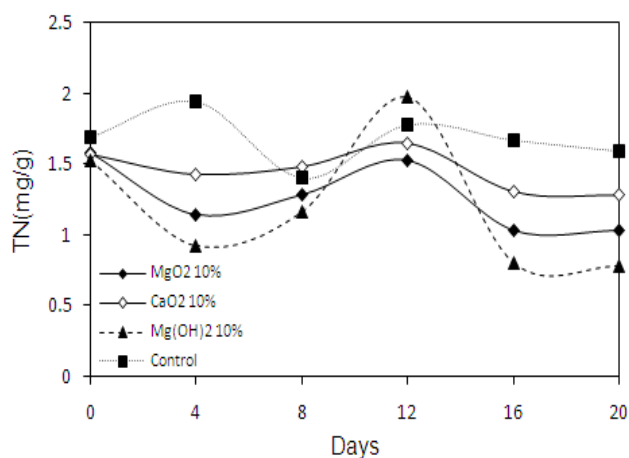
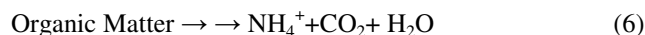
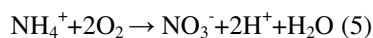


Fig. 4. Changes in TN for 20 days at inputs of 10% MgO₂, CaO₂, Mg(OH)₂.

4.5 TP CHANGES WITH DIFFERENT ORCS

Phosphorus as a limited nutrient is more crucial than nitrogen in a closed marine region. Fig. 5 shows TP changes over time with different kind of ORCs. TP reduction was the highest for CaO₂(71.1%), and the lowest for Mg(OH)₂(48.9%).

Phosphorus on the sediment surfaces which binds to multivalent metal ions tends to release since the metal ion-phosphorus bond becomes broken[9] as the sediment goes anaerobic (lower ORP). With input of metal oxides the following two reactions (7) and (8) occur: i.e., phosphates

such as PO₄⁻³ and H₃PO₄ bind to Ca²⁺ and Ca(OH)₂, respectively to eventually form insoluble precipitates. Also dissolved phosphorus is even adsorbed on Mg(OH)₂ film formed by the reaction (1).

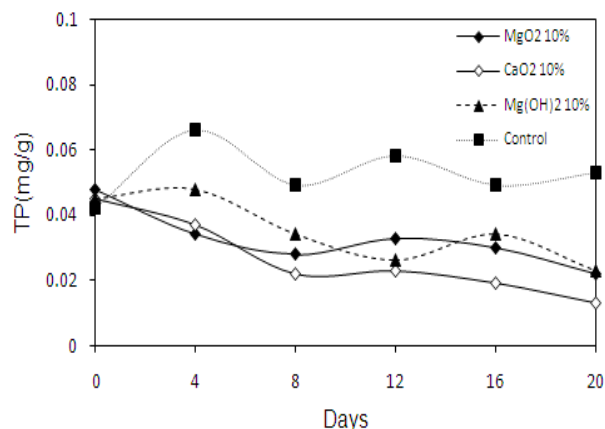
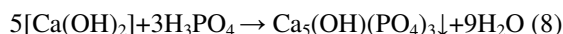
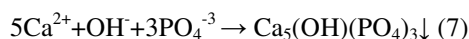


Fig. 5. Changes in TP for 20 days at inputs of 10% MgO₂, CaO₂, Mg(OH)₂.

5. CONCLUSIONS

For efficient bioremediation of marine sediment some ORC treatments were tested and the environmental indices were analyzed accordingly. Our findings are:

CaO₂ treatment was the most efficient for removing organic matter and nutrient salts but total nitrogen. For COD it was found to be 27.5%, which were much higher than the other two treatments. Better oxygen producer, CaO₂ could facilitate decomposition of organics via aerobic microbial activity. Similarly, the highly oxidic condition consumed AVS in the sediment rapidly. In particular CaO₂ treatment completely removed all AVS (initially 1.4 μg/g.dry) in 8 days. It happens because the treatments raised pH to the alkaline level and deactivated SRB by covering the sediment surfaces with hydroxide film. TP reduction for CaO₂ treatment was 71.1% (highest). TP removal seemed to be more complicated with possible three mechanisms; adsorption on the sediment surfaces, formation of precipitates via chemical reactions in the bulk water, and microbial ingestion of phosphorus. On the other hand, TN reduction was trivial for CaO₂ or MgO₂ treatment because ammonia release could not be blocked efficiently and a certain unbalance between nitrification and denitrification.

ACKNOWLEDGEMENT

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