Determination Method for Maximum Calcium Releasing Potential from Steel Slags, Marine Sands Alternatives in Seawater

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Sea grass beds and tidal flats are facing imminent dangers of extinction. Steel slags are one of the promising alternative materials for marine sands to restore sea grass beds and tidal flats. On the other hand, significant pH increase and solidification attributed to dissolving calcium released from the slags are sometimes negative impact on ecosystems. To quantify the dissolved calcium, Japan Cement Association Standard method is conventionally used. However, our study leveled the method underestimate the dissolved calcium from the steel slags. The purpose of this study is to optimize the determination method for maximum calcium releasing potential from steel slags. Powdered sample (0.1 g) was stirred in 40 mL of 99.5% ethyleneglycol-100 mM tris buffer solution for 6 h at 80±5°C. Thereafter, the solution filter through 0.45 μm filter and the dissolved calcium was determined by ICP-AES. The optimized condition proposed in this study recovered the dissolved calcium from the slag in seawater perfectly.

KEY WORDS: alternative materials; free lime; hydrolysis; solidification; marine sand.

1. Introduction

Sea grass beds and tidal flats play important roles in marine primary production, providing habitat for fishes and facilitating natural seawater purification. They also contribute towards ecosystem services especially nutrients cycle and waste treatment.1) However, sea grass beds and tidal flats are facing imminent dangers of extinction.2) According to the global assessment, it is estimated that sea grasses have been disappearing at a rate of 110 km²/yr since 1980.3) The significant deterioration of sea grass beds and tidal flats were observed everywhere and is reaching a critical point beyond which sustainable aquaculture cannot be maintained. Therefore, restoration projects and studies for the recovery of sea grass beds and tidal flats have been conducted all over the world.4-6) In Japan, dredged sea sands were used conventionally to restore deteriorated sea grass beds and tidal flats. However, the dredging process has been blamed for environmental destruction of dredged areas. For instance, in the Seto Inland Sea which is the largest enclosed sea in Japan, the collection of sea sands was prohibited to prevent environment destruction starting in 1997. Considering the recent momentum towards promoting a recycling conscious society and environmental restoration, it is desirable to explore applications of slag as alternative materials for restoring sea grass beds and tidal flats.

Iron slags are by-products which are generated from iron and steel making processes. They are roughly classified into two types: blast furnace slag produced from the conversion of iron ore into pig iron, and steel slag generated through steel making processes which purify pig iron. In Japan, 24.4 and 14.5 Mt of blast furnace slag and steel slag were generated in 2010, respectively.7) Commonly, the slag has been utilized for roadbed construction material, as coarse aggregate for concrete and as raw material for cement.7,8) Recent studies have revealed that steel slag is one of the promising alternative materials of sea sands identified for restoring sea grass beds and tidal flats from the standpoint of their large volume. These materials had some advantageous applications for environmental remediation. For example, it has been reported that iron slag could suppress phosphate liberation from the sediment9) and decrease acid volatile sulfide in organically enriched sediments.10) Steel slag also can create reef-like habitat for fishes11) and promote growth of some marine phytoplankton.12) On the other hand, a large amount of calcium in the form of uncombined calcium called ‘free lime’13,14) can be dissolved into seawater or sediment from slag. However, with the application of slag to the marine environment, the free lime is easily transformed to calcium hydroxide through hydration reactions. Accordingly, hydrolysis of calcium hydroxide raises pH to 12.3-15,16) The significant pH increase largely depends on the amount of free calcium oxide. The calcium ion derived from the hydrolysis of calcium hydroxide also reacts with silicate and aluminate and accordingly forms lime-pozzolan.16,17) There-
fore, it can be said that the lime pozzolan formation which develops solidification is controlled by the calcium concentration therein.

The significant pH increase and solidification might have negative impact on biological activities. For example, it has been reported that diatoms show decreased growth rate at over pH 8.5.\(^{18-20}\) Hardness of intertidal flat sediment is one of the important factors in benthic habitats.\(^{21,22}\) Hence, it is very important to quantify the maximum amount of calcium dissolved from slag (Maximum calcium releasing potential: MCRP), which plays key roles in controlling pH and hardness in sediment, in the use of slag to construct or remediate artificial sea grass beds and tidal flats.

In Japan, the calcium dissolved from materials is conventionally determined following the JCAS (Japan Cement Association Standard) method (I-01:1997).\(^{23}\) Determination methods for free lime in cement, clinker and steel slag were also proposed.\(^{13,14,24}\) However, these methods might underestimate the amount of calcium dissolved from the alternative materials since they were optimized to determine free lime ranging from a few to around 10%, much lower free lime content compared to those of the alternative materials. The MCRP (more than 20%) obtained by our proposed method was much higher than that measured by the JCAS method.

It is also well known that EPA method 1311 proposed by United States Environmental Protection Agency is applied to evaluate leaching potential for toxic substances.\(^{25}\) This method is not suitable for quantifying the MCRP of steel slag in seawater since this method is conducted under pH 4.93 or 2.88, whose value is much lower than that of seawater (pH 8.2).

The purpose of this study is to optimize the determination method for the maximum amount of dissolved calcium from marine sands alternatives with high calcium contents such as steel slags into seawater to restore sea grass beds and tidal flats.

2. Material and Method

2.1. Steel Slag Tested in This Study

Steel slag was selected in this study since steel slags contained large amount of calcium compared to other alternative materials for marine sands. Two kinds of steel slag, A (particle size: < 250 μm) and B (particle size: 75 to 160 μm) were tested and their chemical composition were shown in Table 1. The chemical composition except sulfur and sodium determined by a simultaneous multi element XRF (Simultix14, Rigaku) using the calibration curve method with glass beads. Sulfur and sodium were measured by the combustion method on the basis of JIS-M8217 and the atomic absorption spectrometry (AA-6800, Shimadzu) after wet decomposition using HCl, HF and HClO₄, respectively.

The slags A and B are one of steel slags which are generated through decarburization processes to produce steel from pig iron. In this paper, these slags are defined as decarburization slag. The calcium dissolving capacities of the decarburization slag were higher than any other steel slag. Therefore, the decarburization slag was selected in this study. The slag A was used to optimize the analytical condition since its MCRP was higher than that of B.

| Element (%) | Slag A | Slag B |
|-------------|--------|--------|
| T-CaO       | 41.0   | 55.4   |
| T-Fe        | 16.0   | 6.1    |
| SiO₂        | 11.8   | 8.6    |
| MgO         | 6.1    | 3.1    |
| Al₂O₃       | 2.9    | 2.0    |
| MnO         | 2.5    | 2.1    |
| P           | 0.9    | 0.3    |
| TiO₂        | 0.5    | 0.5    |
| V           | 0.1    | 0.2    |
| S           | 0.03   | 0.03   |
| Na₂O        | 0.03   | 0.02   |

2.2. JCAS Method

First of all, the free lime was determined following the JCAS method [23]. Briefly, 1.0 g of powdered sample was stirred in 40 mL of 99.5% ethyleneglycol solution for 5 min at 80±5°C. Thereafter, the amount of dissolved calcium from the sample was titrated by the ammonium acetate ethanol solution. The ammonium acetate ethanol solution was prepared by dissolving 16 g of ammonium acetate to 1.5 L of ethanol. The normality of the ammonium acetate solution was calibrated by titrating an appropriate amount of CaO standards (0.02 to 0.03 g). The CaO standard was prepared by calcining CaCO₃ at 900 to 1000°C for 1 d.

2.3. Determining the MCRP of the Decarburization Slag in Seawater

Two experiments were carried out to determine MCRP, namely continuous extraction and single batch extraction. The MCRP was defined as the weight percentage of dissolved calcium to total calcium contained in testing material.

In the continuous extraction, 10 g of powdered sample (< 250 μm) was stirred in 100 mL of 3% artificial seawater, which was prepared from 35 g of ‘sealife’ (Artificial seawater agent, Marinetech Co., Ltd.) added to 1 L of pure water, at 20°C. The seawater was replaced every 6 h. Thereafter, each fraction was filtered through 0.45 μm hydrophilic nitro cellulose filter (Millipore, HA) and the dissolved calcium was determined by ICP-AES (Varian, 720-ES).

In the single batch extraction, 0.1 g of powdered sample (< 250 μm) was stirred in 100 mL of artificial seawater at 20°C for 24 h. Thereafter, the solution was filtered through 0.45 μm hydrophilic nitro cellulose filter (Millipore, HA) and the dissolved calcium was determined by ICP-AES (Varian, 720-ES).

2.4. Optimized Procedure for Determining MCRP

The JCAS method was modified appropriately. The contact time, L/S (liquid (volume)-solid (mass) phase ratio) and tris buffer concentration to keep pH value as close to normal seawater (pH 8.2) were optimized in the range of 5 min-120 h, 40–1000 and 0–200 mM, respectively.

The analytical procedure for MCRP was optimized by stirring powdered sample (0.1 g) into 40 mL of 99.5% eth-
tion in seawater and fresh water were set to 30‰, 11 mM. Under this condition, the effect of tris buffer solution on calcium determination using ICP-AES would be negligible.

Mineral calcium dissolved from the mineral standard was also investigated. The mineral standards were purchased from Nichica Inc., (Hedenbergite; CaFeSiΩO6, Xonotlite; Ca[(OH)2Si2O5], Wollastonite; CaSiO3, Gehlenite; Ca2Al(AlSi)2, Epidote; Ca2(Al,Fe3+)3(SiO)3(OH)) and powdered using a mortar and rinsed with pure water for 5 min (L/S=1 000) to remove calcium adsorbed on the surface of the minerals. Thereafter they were filtered through glass microfiber filters with 1.2 μm (GF/C, Whatman) to collect the mineral particles. Successively, the mineral particles were dried at 60°C for 1 d. Finally, the dissolved calcium from the mineral particles was determined followed by the optimized procedure.

The calcium solubility at each pH was calculated using the thermodynamic simulation software, Geochemist’s Workbench 9 (RockWare). In this calculation, HCO3– activity was set at 0.002 which was the actual HCO3– concentration considering CO2 gas pressure. The temperature was set at 25 or 80°C followed by Lund et al 2003.26) The activity in seawater was determined followed by the optimized procedure. The calcium solubility at each pH was calculated using the thermodynamic simulation software, Geochemist’s Workbench 9 (RockWare). In this calculation, HCO3– activity was set at 0.002 which was the actual HCO3– concentration considering CO2 gas pressure. The temperature was set at 25 or 80°C followed by Lund et al 2003.26) The activity in seawater was determined followed by the optimized procedure.

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3. Results and Discussion

3.1. MCRP of Decarburization Slag in Seawater

The MCRP obtained by the JCAS method and each extraction method are shown in Fig. 1. The MCRP was only 6.9% determined following the JCAS method, while under continuous extraction with 15 times replacement of seawater under L/S=10, the MCRP was approximately 21%. This value was consistent with the results obtained by using L/S=1 000 under a single batch method.

The recovery of MCRP obtained by the continuous extraction of the decarburization slag is shown in Fig. 2. The recovery was defined as the percentage of cumulative amount of dissolved calcium for MCRP. The calcium dissolution was observed up until 15 times replacement of the seawater. In this case, a contact volume of 150 mL was required to collect calcium dissolved totally from the slag. Therefore, the JCAS method conducted under the L/S=40 does not have enough solvent volume to quantify the MCRP of the materials with high calcium content such as the decarburization slag.

3.2. MCRP Determined by the Modified JCAS Method

First of all, the dissolved calcium from the decarburization slag was determined under L/S=40 following the JCAS method. In the JCAS method, ethyleneglycol was used as an extracting solvent to prevent calcium precipitation.23,28) On the basis of the JCAS method, the contact time is 5 min. However the dissolved calcium was 6.9%, which was much lower than MCRP obtained by continuous extraction or single batch method described above (Fig. 3). Therefore, after 5 min the dissolved calcium from the slag was monitored under ambient conditions till the calcium dissolution was not detectable. Significant calcium dissolution was observed even after 5 min and beyond indicating that the JCAS method might have underestimated the dissolved calcium (Fig. 3) since the contact time was too short to extract the dissolved calcium. Furthermore, the dissolved calcium did not reach the MCRP.

In the case of L/S=400, wherein the liquid phase volume was 10 times higher than that of the JCAS method, the dissolved calcium also did not reach the MCRP within 5 min (Fig. 3). The dissolved calcium was also monitored under ambient condition till the calcium dissolution was not detectable. When the contact time was extended to 72 h, the amount of dissolved calcium was totally recovered (Fig. 3).
3.3. Optimization of Tris Buffer Concentration

As shown in Fig. 3, the MCRP can be basically determined by titration using ammonium acetate ethanol solution until calcium dissolution is no longer detectable. The titration in Fig. 3 was conducted not only for determining the dissolved calcium but also for keeping the pH. Otherwise the pH increased up to around 11 due to the hydrolysis of calcium. In fact, the solution pH was 10.9 before the titration. Because the calcium dissolution is controlled by the pH, the calcium solubility at each pH was calculated using the thermodynamic simulation software, Geochemist’s Workbench 9 (RockWare) as shown in Fig. 4. The activity of calcium at pH 11 is much lower than that at pH 8.2 which is the normal seawater pH (Fig. 4), indicating that the MCRP determined at pH 11 was underestimated owing to formation of calcite precipitates. Therefore it is necessary to control pH so as to determine the MCRP of the slag in seawater.

However, it is time consuming and troublesome to maintain pH at normal seawater level by titration. Therefore, tris buffer concentration to maintain pH was investigated at the time when the dissolved calcium concentration reaches MCRP (Fig. 5). When the tris buffer solution concentration was less than 50 mM, the pH increased to over 10 due to the hydrolysis of calcium, whereas at concentration of more than 100 mM, the pH did not increase significantly. The tris buffering capacity was also investigated by adding CaO (Fig. 6). It was effective at less than 890 mg-Ca L\(^{-1}\) when calcium concentration corresponded to 36 wt%-Ca in the sample. (The amount of dissolved calcium from 100 mg of sample was 36 mg, which was calculated by the concentration of calcium in the solution (890 mg-Ca L\(^{-1}\)) and volume of the solution (40 mL), respectively.) Therefore, the maximum limit for determining MCRP should be set at 36 wt% of dissolved calcium in the sample when using this proposed method. The calcium content (weight percent of total Ca) in steel slag ranged between 21 to 40\% (29-31). Therefore, the MCRP of the steel slag may be considered to be less than the above range. Thus, this proposed method can be applied to determine the MCRP for almost all slag types. As will be described later, the MCRP of decarburization slag which is the one of the highest calcium content in slag at 24.6 wt\%, indicated that the proposed method is useful for determining the MCRP of decarburization slag.

3.4. Optimization of Contact Time

To optimize the contact time, the time course of dissolved
calcium from decarbonized slag was monitored under the L/S=400 in ethyleneglycol solution with 100 mM tris buffer (Fig. 7). The dissolved calcium percentage of both decarbonization slag A and B became constant after 6 h. Therefore, the contact time was set at 6 h. The dissolved calcium percentage of decarbonization slag A compared well with the MCRP obtained through continuous extraction.

It was reported that the minerals dissolved after 3 h had created positive errors. The percentages of dissolved calcium from some minerals determined by this proposed method are shown in Table 2. The mineral was selected on the basis of slag composition. As described above, the mineral was rinsed beforehand to only check mineral calcium dissolution. As shown in Table 2, the dissolution of calcium from minerals was less than 0.2 wt%. Therefore, mineral calcium dissolution could be negligible under the proposed method.

3.5. MCRP of Steel Slag Obtained by Optimized Method

The MCRP measured by the proposed method and dissolved fraction ratio of the slag are shown in Table 3. The MCRP of the decarbonized slag A was 24.6 wt%, indicating that 84% of calcium contained in the decarbonization slag A can be dissolved. While the MCRP of decarbonization slag B were 11.2 wt% and corresponds to 28%, respectively. This value is very close to 37% which was obtained from 12 times of elution test on an electric arc furnace oxidizing slag. The difference of MCRP might be attributed to difference of mineral composition of the slags.

3.6. Implication

3.6.1. MCRP of Slag in Natural Water

In this study MCRP from steel slags into seawater has been optimized. As previous mentioned, the solution pH was adjusted to normal seawater level (pH 8.2) by adding tris buffer solution to prevent from increasing pH since the solubility of calcium from the slags was dependent on solution pH.

The major calcium crystal phases of steel slags are calcium phosphate, calcium silicate and calcium oxide. Calcium phosphate is thermodynamically stable under natural water condition (pH 6–7). According to the stability diagram of silicate, calcium silicate (2CaO·SiO₂) can be dissolved by natural water and seawater. Hydrolysis of calcium oxide proceeds lower than pH ca.11. Therefore, these calcium compounds can be dissolved by both fresh and seawater. On the other hand, 3CaO·2SiO₂ is not dissolved by seawater because silicon concentration in seawater is exceeding the solubility equilibrated with these calcium silicates. However, in case with pH 7 or less, 3CaO·2SiO₂ can be dissolved.

The calcium carbonate can be also formed on the surface of steel slags through their aging processes. The activity diagram of between calcium and calcite is shown in Fig. 8. Calcite solubility is relatively low at pH 7. However, the solubility of calcite increase with the decrease of pH, and calcite can be dissolved around pH 6.5.

Therefore, in case with calcite enriched slag, carbonated slags and slag which contains 3CaO·2SiO₂, their MCRPs in fresh water around pH 7 or less might be higher than obtained by this proposed method.

![Fig. 7. Time course of the dissolved calcium dissolved from the decarbonization slags. The decarbonization slags (0.1 g) were added to 40 mL of ethaneglycol –100 mM Tris buffer solution and stirred at 80°C.](image)

![Table 2. Mineral calcium dissolved from the mineral standards under the optimized procedure.](image)

| Minerals      | Formula                                      | Dissolved mineral Ca(wt%) |
|---------------|----------------------------------------------|---------------------------|
| Hedenbergite  | CaFeSi₂O₆                                    | 0                         |
| Xonotlite     | Ca₆[(OH)₂|Si₆O₁₇]                                    | 0.19                      |
| Wollastonite  | CaSiO₂                                       | 0.064                     |
| Gehlenite     | Ca₂Al(AlSi)₉                                 | 0.024                     |
| Epidote       | Ca₂(AlFe³⁺)(SiO)₃(OH)                         | 0                         |

![Table 3. The MCRP of the steel slag tested in this study.](image)

|                  | Slag A | Slag B |
|------------------|--------|--------|
| Av. of MCRP (%)  | 24.6   | 11.2   |
| SD               | 2.5    | 0.3    |
| Total Ca (%)     | 29.3   | 39.6   |
| Dissolved Ca/ Total Ca(%) | 84 | 28 |

![Fig. 8. Activity diagram for calcite at 25°C. White and gray colored conditions were major dissolved species and mineral phase, respectively.](image)
3.6.2. Simplified Determination Method for MCRP using an EDTA Titrimetric Method

It is well known that calcium can be determined using the EDTA titrimetric method. However, calcium-ethylene glycol complexes are too stable to be titrated by EDTA. In order to weaken stability of the complexes, 99.5% ethylene glycol-100 mM tris buffer solution was diluted 10 times by adding ultrapure water. The calcium concentration in 10 times diluted ethylene glycol-tris buffer solution was determined by 0.01 M EDTA using 2-hydroxy-1-(2-hydroxy-4-sulfo-1-naphthylazo)-3-naphthoic acid as an indicator. The spiked calcium concentration vs the calcium concentration obtained by the EDTA titrimetric method are shown in Fig. 9. The calcium concentration in the ethylene glycol-tris buffer solution quantified by the proposed EDTA titrimetric method were nearly close to the spiked concentration. Therefore, the EDTA titrimetric method also can be applied to quantify MCRP instead of ICP-AES.

4. Conclusion

The MCRP of steel slag in seawater can be determined a modified JCAS method. The conditions of the proposed method are summarized as follows. Powdered sample (0.1 g) was stirred in 40 mL of 99.5% ethylene glycol-100 mM tris buffer solution for 6 h at 80±5°C. Thereafter, the solution was filtered through a 0.45 μm hydrophilic nitro cellulose filter and the dissolved calcium was determined by ICP-AES. The proposed method is more effective in determining MCRP from steel slag compared to the JCAS method.

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