

The Decarbonization of Sea Water by LD Slag

Ki-Hyun Han, Hyung-Suek Kim, M.S. Oh, Tae-Bong Byeon

Materials Utilization & Recycling Research Team,
Research Institute of Industrial Science & Technology, Korea

LD slag, that is, a by-product of steel making process, has been mainly used as land construction materials. Recently, the seashore application of LD slag was tried in Japan and Korea but the reaction between LD slag and seawater was not studied yet. We tried to clarify the leaching reaction and/or mechanism of LD slag and the reaction between seawater and LD slag. We tried to apply these results to the decarbonization of seawater for seawater magnesia process.

The high pH solution(over 12) was injected into the sea water and the pH of mixed liquid was adjusted to 9.8. This mixed solution was aged for 8 hours and the 104ppm of CO_3^{-2} in the sea water was decreased to 23ppm with the negligible loss of Mg^{2+} ion. The slag particle was directly inserted into the seawater for practical application. The 0.5~1mm particles were suitable for decarbonization when 5 grade slags mentioned above were reacted with sea water. In this case, the content of CO_3^{-2} in the sea water was 53 ppm with the negligible loss of Mg^{2+} ion after 8 hours aging. The direct application of slag particle for the decarbonization of seawater takes more reaction time.

Keywords : LD slag, decarbonization, seawater

Introduction

LD slag, that is, a by-product of steel making process, has been used as road base material, iron source for cement preparation and earth works.

Recently, the seashore application of LD slag such as artificial reef and marine block was tried. ^{[1],[2],[3]} When LD slag was contacted with sea water, white precipitate was formed, but the reaction(mechanism) between LD slag and sea water was not studied thoroughly yet.

In order to identify the white particle, it was tried to separate this particle from reaction bath of LD slag and seawater. It was difficult to get pure

white particle because of intermixing of slag particle. White particle was settled down on the upper part of slag aggregate and bottom of reaction beaker. From this result, it was thought that the white particle was formed by the reaction between the effluent solution of slag and seawater.

The white particle was made by the reaction between the leached solution of slag and seawater. This white particle was analyzed by XRD and it was mainly calcium carbonate. Therefore, the decarbonization of seawater was tried by the leached solution of LD slag.

Experiment

The leached solution of slag was added into the seawater. In order to prevent the absorption of carbon dioxide from the air, the decarbonization reaction of seawater was carried out in the glove box. The pH of reaction bath was measured and the content of CO_3^{2-} , Mg^{+2} was analyzed by the ICP, AA, IC.

Results and Discussion

The leached solution of slag that had pH 12 was added into the seawater in order to clarify the behavior of decarbonization of sea water. The change of pH is shown in fig.1.

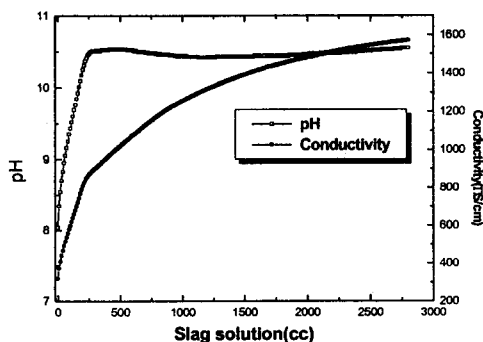


Fig.1 Conductivity and pH: slag solution was added continuously to seawater 500cc

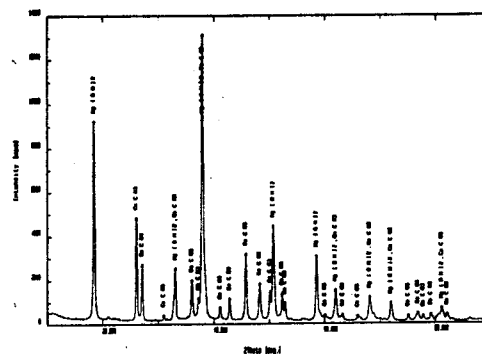


Fig.2 The XRD pattern of product

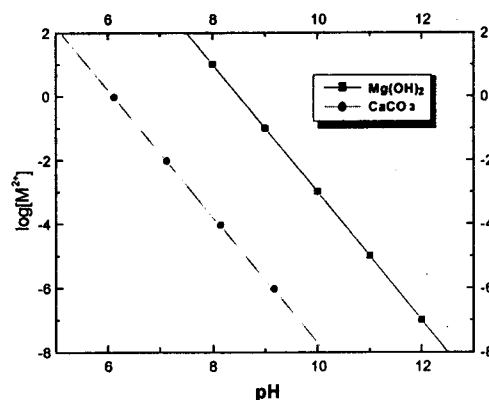
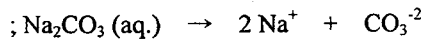


Fig.3 Precipitation diagram of $\text{Mg}(\text{OH})_2$ and CaCO_3

The white precipitate was formed about pH 10.5. These white particles were CaCO_3 and $\text{Mg}(\text{OH})_2$ as shown in fig.2. According to fig.3, it was thought that CaCO_3 was formed prior to $\text{Mg}(\text{OH})_2$, but CaCO_3 and $\text{Mg}(\text{OH})_2$ were precipitated simultaneously. This means that reaction rate of CaCO_3 formation is slow compared with that of $\text{Mg}(\text{OH})_2$ formation. Therefore, the 1 M solution of Na_2CO_3 was added into seawater in order to confirm the rate determining step of decarbonization reaction.

Na_2CO_3 solution is dissociated into Na^+ ion and CO_3^{2-} ion. This CO_3^{2-} ion reacts with Ca^{+2} ion in sea water and precipitates the calcium carbonate.

Dissociation of Na_2CO_3



Formation of CaCO_3

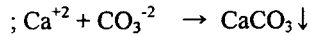


Fig.4 shows the change of pH with the lapse of time. On inserting Na_2CO_3 solution into sea water, the formation and redissolution of white particle was occurred.

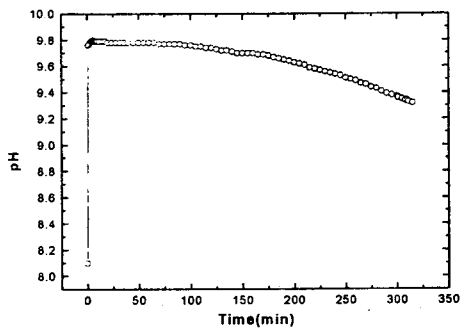
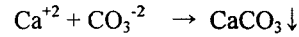


Fig.4 pH vs Time : Na_2CO_3 solution (1M) was added once to sea water 500cc and aging was done.

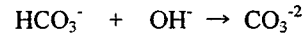
The white precipitate was stabilized at about pH 9.76(1st formation). After 1st formation, the precipitated solution was aged without the injection of Na_2CO_3 solution. It was observed that the white color became thick after 2hours of aging (2nd formation). This 2nd formation of white particle was made by the reaction between Ca^{+2} in seawater and CO_3^{-2} converted from HCO_3^- in seawater.

● 1st formation



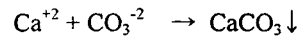
(Ca^{+2} :sea water, CO_3^{-2} : from Na_2CO_3)

● Reaction between 1st and 2nd formation



(HCO_3^- :sea water, OH^- : formed by Na^+)

● 2nd formation



(Ca^{+2} :sea water, CO_3^{-2} :converted from HCO_3^-)

The leached solution of slag was injected into the seawater and the pH of reaction solution was adjusted to 9.8. This solution was aged in order to compare the injection of Na_2CO_3 solution. The result of this experiment is shown in fig.5.

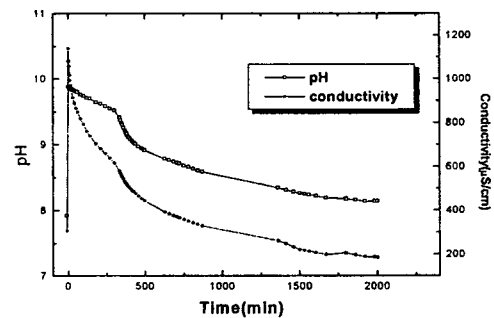
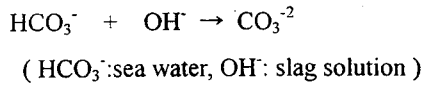


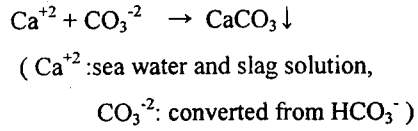
Fig.5 pH , Conductivity vs Time : after slag solution was added once to seawater 500cc and aging was done

In the case of injection of slag solution, the white precipitate was formed after 5 hours. The first formation of white particle which was formed in the addition of Na_2CO_3 solution was not observed. It is thought that the reaction equation of CaCO_3 precipitate with slag solution was as follows :

● Before precipitation



● Formation of white particle



It was proved that the conversion step of HCO_3^- to CO_3^{2-} was the rate determining step of precipitation reaction of CaCO_3 by comparing two experiment.

When the slag solution was injected into seawater, it took quite long time for the formation of CaCO_3 because of rate controlling step. When the concentration of CO_3^{2-} was increased and reached over the solubility product of CaCO_3 , CaCO_3 precipitated. The excess OH^- in this reaction solution makes the coprecipitation of $\text{Mg}(\text{OH})_2$ with CaCO_3 .

If the excess slag solution were injected in sea water, two reactions could occur simultaneously. The loss of Mg^{+2} was increased by excess slag solution.

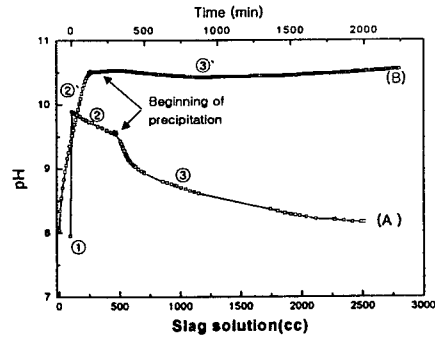
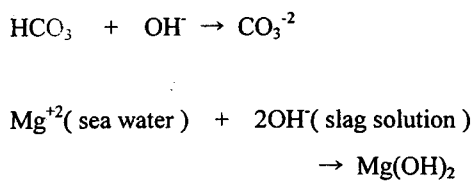


Fig.6 Decarbonization Model :

(A) Aging ; (B) adding continuously

When the reaction solution of seawater and slag solution was aged at about pH 9.8, the precipitated particle was only CaCO_3 as shown in fig.2. Fig.6 shows the comparison result of (a) aging of reaction solution started from pH 9.8(fig.1) (b)continuous injection of slag solution (fig.5).

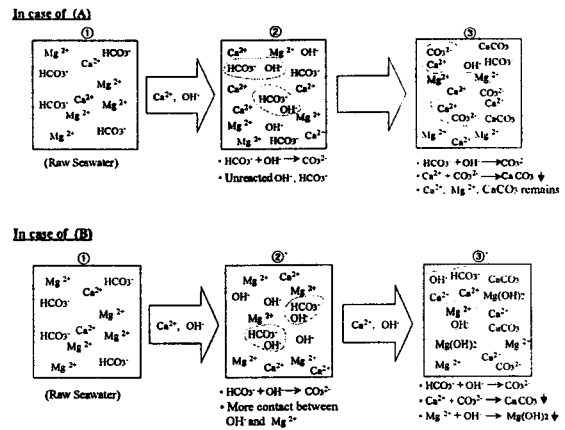


Fig.7 Illustration of decarbonization model.

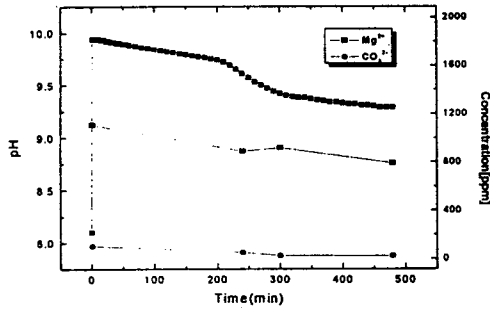


Fig.8 pH vs. Time, concentrations ;
Sea water 50cc + slag solution(pH=12)
,aging in glove box

In the case of (b), the CaCO_3 and $\text{Mg}(\text{OH})_2$ was precipitated simultaneously because the continuous injection of slag solution gave reaction solution two kinds of OH^- that were necessary for the conversion of HCO_3^- to CO_3^{2-} and for $\text{Mg}(\text{OH})_2$ formation.

On the other hand, in the case of (a), the CaCO_3 was precipitated because the OH^- was consumed by the conversion reaction of HCO_3^- to CO_3^{2-} (region ②), that is, the decrease of pH of reaction solution and the concentration of CO_3^{2-} was increased with lapse of time. The reaction model of two cases was shown in fig.7.

After 5 hours of reaction, the concentration of Mg^{+2} and CO_3^{-2} ion is shown in fig.8. The result of Mg^{+2} and CO_3^{-2} was 792 ppm and 23 ppm. This value was nearly the similar result to the present decarbonization process of seawater.

Conclusion

The high pH solution(over 12) was injected into the sea water and the pH of mixed liquid was adjusted to 9.8. This mixed solution was aged for 8 hours and 104 ppm of CO_3^{-2} in the sea water was decreased to 23 ppm with negligible loss of Mg^{+2} ion.

References

- [1] Hisahiro Matsunaga, 2001, "Studies on various properties of slag block made out of steel-making slag with a note on its merits as marine block", CAMP-ISIJ, vol.14, 144
- [2] Tatsuhiro Takahashi, 1999, "Production of large steelmaking slag block using a new carbonation process", CAMP-ISIJ, vol.12,141
- [3] Tsuneo Isoo, 1999, "New carbonation process for producing large steelmaking slag block", CAMP-ISIJ, vol.12,142