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Leaching Behavior of LD Slag

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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.

At first, LD slag was milled and classified into 5 grades, that is, (i)45㎛ under, (ii)0.25～0.5mm, (iii)0.5～1mm, (iv)1～2mm, (v)2.36～3.35mm. These slags were leached in the distilled water. In case of 45㎛ under, the pH of the leached solution was over 12. The chemical analysis of leached solution showed that the Ca^{+2} was main component and the Si^{+4} was very low. On the other hand, the content of Si^{+4} in leached solution was decreased with the increase of pH of this solution. The nearly pure calcium solution was made and the ultra high purity MgO could be made with this calcium solution.

The leaching behavior of LD slag was different between the fine particle and coarse particle. The calcium was leached by bulk dissolution in the coarse particle and by surface controlled reaction in fine particle. The leaching rate was slow in coarse particle and fast in fine particle. Therefore, the high pH solution, that is, over 12, was obtained in fine particle.

Keywords : LD slag, leaching, dissolution

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 sea water. It was difficult to get pure white particle because of intermixing of slag particle. White particle was settle 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 sea water. Therefore, we tried to clarify the leaching reaction and/or mechanism of LD slag.

Experiment

LD slag was milled and classified into 5 grade, that is, (i) 45㎛ under, (ii) 0.25 α 0.5mm, (iii) 0.5 α 1mm, (iv) 1α 2mm, (v) 2.36 α 3.35mm . These were leached in the distilled water. The pH and the chemical composition of leached solution were measured by pH meter and ICP, AA, FT-IR and/or IC.

Results and Discussion

The final pHs of the leached solutions that 10g of each classified slag was reacted with distilled water for 24hrs are shown in Fig.1 and Fig.2.

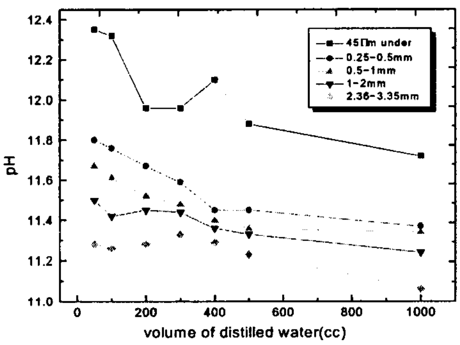
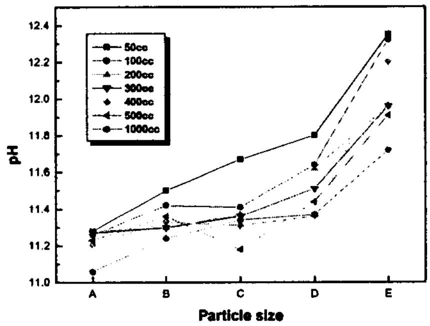


Fig.1 pH of slag solutions 24hours later, as a function of volume of distilled water in 5 species of slag size

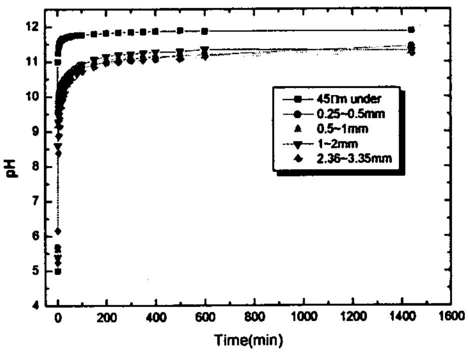
Fig.1 shows the degree of alkalinity that each grade of slag is reacted with distilled water. When 10g slag of 45㎛ and less was reacted with distilled water 100cc and below, the pH of leached solution was nearly the saturation pH of calcium hydroxide. When the distilled water was more than 100cc the pH of leached solution was decreased with the increase of the distilled water.



X -axis	Particle size	Specific surface area (mm^2/g)
A	2.36~3.35 mm	540
B	1~2 mm	1200
C	0.5~1 mm	3000
D	0.25~0.5mm	7600
E	45㎛ under	1080000

Fig.2 pH of slag solutions 24 hours later as a function of particle size in various ratios between slag and distilled water.

On the other hand, the pH of the leached solution of coarse slag was not nearly the saturation point. Fig.3 and 4 show the result of slag leaching with 500cc and 50cc distilled water. When the leaching behavior is compared with the particle size of slag. The slag of 45㎛ and less shows the highest value of pH and the rapid increase of pH, but the coarse particles show the low pH and slow increase of pH. The relation between the particle size of slag and final pH of leached solution is shown in Fig.2. The finer the size of slag particle was, the higher the final pH of solution became.



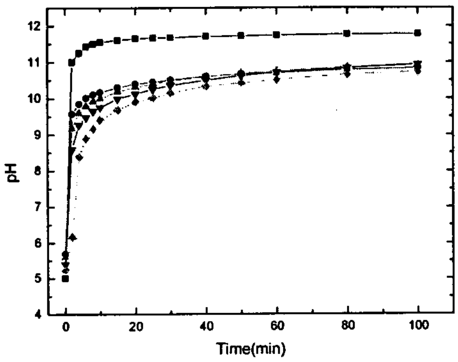
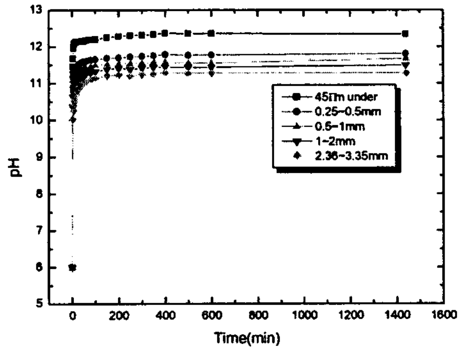


Fig.3 Effect of particle size on pH of solution as a function of time ; distilled water 500cc, slag10g

Table 1 shows the chemical composition of solution leached for 24 hours. The main component of pH increase was calcium ion. Fig.5 shows the relation between the pH of solution and the concentration of calcium ion.



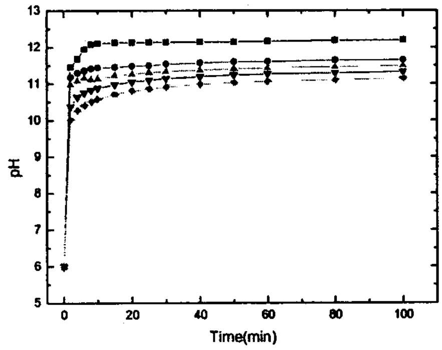


Fig.4 Effect of particle size on pH of solutions a function of time ; distilled water 50cc, slag 10g

Table 1. The contents of ions in slag solutions(ppm)

Sample No.	Ca	Si	Fe
1	212	6.5	0.03
2	79	16	0.03
3	51	19	0.03
4	66	21	0.03
5	60	21	0.03
6	214	8	0.03
7	73	17	0.03
8	76	21	0.03
9	67	21	0.03
10	62	22	0.03
11	292	7	0.03
12	99	18	0.04

13	84	21	0.03
14	73	22	0.03
15	69	23	0.03
16	352	4.2	0.03
17	129	19	0.03
18	98	18	0.03
19	90	20	0.03
20	68	20	0.03
21	526	3.5	0.05
22	146	14	0.03
23	95	17	0.03
24	87	19	0.03
25	79	20	0.03
26	711	3.5	0.05
27	189	8	0..03
28	108	23.5	0.03
29	96	20	0.03
30	69	21	0.03

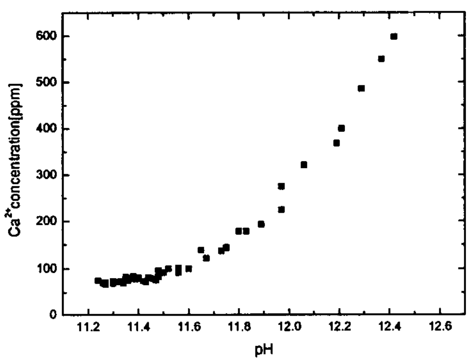


Fig.5 The relation between Ca^{2+} ion concentration and pH

From the above results of leaching reaction, the reaction mechanism was proposed. When the spherical particle of slag was inserted into the distilled water, the model figure of leaching reaction is shown in Fig.6. The used slag was composed with C_2S, C_2F and wüstite, but the main chemical composition of leached solution was calcium and silicon by the table 1. Therefore, the unreacted core of slag was assumed to be consisted of C_2S.

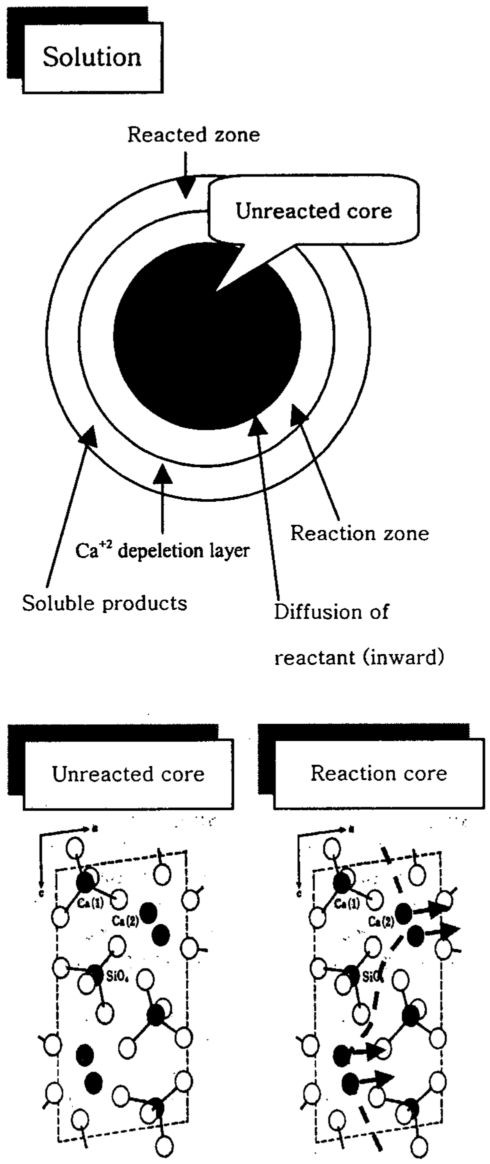


Fig. 6. Leaching mechanism of LD slag.

When the C_2S in slag was contacted with distilled water, Ca^{+2} ion was leached at first. When the calcium of surface layer of slag is depleted, reaction zone is moved into the inner part of slag and the calcium of inner part is dissolved. The silicon ion of leached solution means the dissolution of SiO_4^{-4} of C_2S. The SiO_4^{-4} of C_2S is network former. The dissolution of Si means the leaching of frame structure of C_2S, that is, bulk dissolution.

Slag is dissolved by

(1) Dissolution of calcium located in surface and surface layer (Surface reaction)

(2) Bulk dissolution

There are three elementary steps of the leaching reaction of slag. That is, (i) the interface reaction of slag and water (ii) the diffusion of Ca^{+2} ion in water, (iii) the diffusion of Ca^{+2} ion into reaction interface. The diffusion of Ca^{+2} ion into reaction interface is nearly impossible at room temperature. The leachability of Ca^{+2} ion in slag can be improved by the disintergration of slag that is similar to the acceleration of diffusion. Therefore, the inner Ca^{+2} ions of slag could be converted to be located on the surface of slag by the disintergration of slag.

The fine and the coarse particle of slag showed the different behavior of leaching. It was postulated that the reaction equation of each particle was as follows.

[Particle for -45㎛]

A. $3CaO{\cdot}SiO_2 + H_2O \leftrightarrow 3Ca^{+2} + SiO_4^{-4} + 2OH^-$

B. $2CaO{\cdot}SiO_2 + H_2O \leftrightarrow 2Ca^{+2} + SiO_3^{-2} + 2OH^-$

C. $2CaO{\cdot}SiO_2 + H_2O \leftrightarrow 2Ca^{+2} + 2OH^-$

(dissolution of Ca^{+2} ion)

[Coarse particle]

A. $3CaO{\cdot}SiO_2 + H_2O \leftrightarrow 3Ca^{+2} + SiO_4^{-4} + 2OH^-$

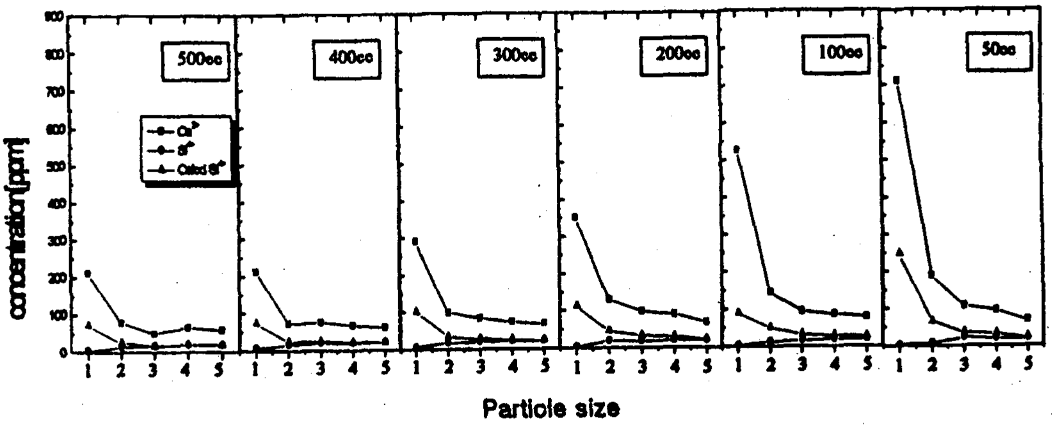
B. $2CaO{\cdot}SiO_2 + H_2O \leftrightarrow 2Ca^{+2} + SiO_3^{-2} + 2OH^-$

The Ca^{+2} ion of coarse particle was leached by the bulk dissolution because the small surface area of coarse particle makes the dissolution of the surface Ca^{+2} ion of slag difficult. The leaching rate was slow and the amount of leached Ca^{+2} ion was little in coarse particle.

The Ca^{+2} ion of fine particle was leached by the surface reaction because the large surface area of fine particle made the dissolution of surface Ca^{+2} ion of slag very easy.

The fig.7 shows this kind of interpretation. The analyzed and calculated values of Si^{+4} ion are shown in fig.7. In the case of calculated value, it was assumed that the Si^{+4} ion in slag was leached by the bulk dissolution of C_2S.

The analyzed and the calculated values of Si^{+4} ion were nearly the same in the coarse particle, but the analyzed value of Si^{+4} ion in the case of fine particle was lower than the calculated values of that. This means that the dissolution of fine particle was not bulk dissolution.



[X-axis definitions.]

• 1 : 45㎛ under • 2 : 0.25~0.5mm • 3 : 0.5~1mm • 4 : 1~2mm • 5 : 2.36~3.35mm

Fig.7 Leaching elements and quantity in slag solution.

Conclusion

We tried to clarify the leaching reaction and/or mechanism of LD slag and the reaction between seawater and LD slag for the seashore application of LD slag.

At first, LD slag was milled and classified into 5 grades, that is, , (i) 45㎛ under, (ii) 0.25 α 0.5㎜, (iii) 0.5 α 1㎜, (iv) 1α 2㎜, (v) 2.36 α 3.35㎜. These were leached in the distilled water. In case of 45㎛ under, the pH of the leached solution was over 12. The chemical analysis of leached solution showed that the Ca^{+2} ion was main component and the Si^{+4} ion was very low. On the other hand, the content of Si^{+4} in leached solution was decreased with the increase of pH of this solution. The leaching behavior of LD slag was different between the fine and coarse particles. The calcium was leached by bulk dissolution in the coarse particle and by surface reaction in fine particle. The leaching rate was slow in coarse particle and fast in fine particle.

Therefore, the high pH solution of over 12 was obtained in fine particle.

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