Effect of LiNO₃ on Corrosion Prevention of Aluminum Wastes after Their Land Disposal

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(Received March 18, 1996), (Revised June 21, 1996)

After their land disposal, LiNO₃ added to cement solidified miscellaneous wastes inhibits hydrogen gas generation due to alkaline corrosion of aluminum contained in the wastes. We considered the presence of an Li-Al preservation film prevents hydrogen gas generation, and then, we assumed a scenario in which the amount of LiNO₃ included in the waste packages is lowered by underground water penetration, resulting in dissolution of the Li-Al preservation film. This dissolution allows the alkaline underground water to reach and corrode the aluminum materials. The loss of Na₂O and K₂O in cement by underground water penetration lowers the pH, so that the aluminum corrosion in the waste packages with LiNO₃, expected when the Li-Al preservation film dissolves, is less than that without LiNO₃.

To test this scenario, we measured solubility of the Li-Al preservation film, Li⁺ ion concentration, pH variation by underground water penetration, and aluminum corrosion when the Li-Al preservation film had dissolved. The measured solubility of the Li-Al preservation film was 3×10⁻⁴ M at 298 K. At that time, pH was lowered from 12.9-13.0 to 12.2-12.3. As a result, with LiNO₃ addition the aluminum corrosion amount was reduced to 10% of that without LiNO₃ addition, because of the pH decrease.

KEYWORDS: lithium, lithium nitrates, cement solidification, dry active wastes, aluminum wastes, hydrogen, corrosion inhibitors, land disposal, long term effect, pH value, corrosion protection

I. Introduction

Treatment methods of dry active wastes generated from nuclear power plants must be developed with consideration about their applicability to waste land disposal. Such wastes include aluminum materials used as coverings for heat insulating materials, high efficiency particulate air (HEPA) filters, and so on. When conventional cement solidification is applied to wastes containing aluminum materials, alkaline corrosion of the aluminum occurs because of the high pH of cement paste, which is around 13.0. This corrosion of aluminum is accompanied by generation of hydrogen gas. Generally, dissolution of the Al₂O₃ surface layer formed on metallic aluminum is responsible for the hydrogen gas generation¹, and the concentration of OH⁻ ions is responsible for the dissolution⁵. A difference of one pH unit can lead to a 10 times larger volume of hydrogen gas generation¹.

In addition, the underground water would become alkaline as it penetrated through the waste forms and the engineered concrete (mixture of cement and stones) barrier of the waste repository. From the standpoint of land disposal of the waste packages, the alkaline underground water may reach the aluminum materials in the waste packages and cause aluminum corrosion.

We developed a method employing addition of a corrosion inhibitor, LiNO₃, to the cement, which successfully prevents aluminum corrosion and hydrogen gas generation during the cement solidification³. We examined the reaction mechanism of LiNO₃ and found there was formation of an insoluble, lithium aluminate double salt (LiH₂AlO₂·5H₂O, or Li-Al) preservation film on the metallic aluminum surfaces³(⁴). Because the long term effect of LiNO₃ after disposal has not been considered yet, we examined cases of hydrogen gas generation due to loss of the Li-Al preservation film after the land disposal.

II. Scenarios and Experimental Procedures

1. Selection of Cases for Hydrogen Gas Generation

Without LiNO₃ addition, the aluminum materials corrode just after the land disposal of the waste packages. With LiNO₃ addition, the aluminum materials corrode...
when the Li-Al preservation film is lost. There are three possible cases to describe the Li-Al preservation film loss after the land disposal, leading to hydrogen gas generation. The details are explained below.

(1) Scenario 1 (Fig. 1)
- When underground water penetrates the concrete wall of the waste repository and reaches the waste forms, LiNO$_3$ included there dissolves into the water because of its large solubility and moves away from them. Then, the Li$^+$ concentration is lowered in the waste forms.

- When the concentration of Li$^+$ ions drops to a value below that due to the solubility of the lithium aluminate double salt which constitutes the Li-Al preservation film, the film is lost and the alkaline corrosion of aluminum begins.

At that time, the amount of the generated hydrogen gas is expected as described below.
- The high pH value ($\approx 13.0$) of water in cement is attributed to Na$_2$O and K$_2$O. They both have large solubilities and readily dissolve into water$^{(5\sim7)}$, as LiNO$_3$ does. Because Li$^+$, Na$^+$ and K$^+$ are alkali metal ions,
their concentrations also decrease as the underground water flows into the waste packages. The pH of the water in the waste forms is lowered by the loss of Na\(^+\) and K\(^+\) ions\(^{(1)(2)(8)}\). Then, as the concentration of Li\(^+\) ions decreases and reaches the very low value which is due to a low solubility of the Li-Al preservation film, the pH of the water in the waste forms also drops from 13.0 to at least below 12.5, the pH value of a saturated solution of Ca(OH)\(_2\) which is also included in cement.

Consequently, hydrogen gas generation occurs at a pH value below 12.5 when the Li-Al preservation film is dissolved, while hydrogen gas generation occurs at pH 13.0 without LiNO\(_3\) addition. So aluminum corrosion with LiNO\(_3\) addition can occur to a less extent than without LiNO\(_3\) addition because of the pH lowering.

(2) Scenario 2

With an intact Li-Al preservation film formed during the process of cement solidification, hydrogen gas generation does not occur. But, if wastes include components of complex shapes, it is possible that the Li-Al preservation film is not formed on some parts of the aluminum surface during the cement solidification. In this case, the scenario of hydrogen gas generation is described as follows.

- When the alkaline underground water reaches this bare aluminum surface, the hydrogen gas generation begins, accompanied by aluminum corrosion. However, the amount of the generated hydrogen gas is expected as described below.
- LiNO\(_3\) in the waste forms dissolves into the underground water, and forms the Li-Al preservation film on the bare aluminum surface at that time. Then, the hydrogen gas generation can be prevented.

(3) Scenario 3

While the Li-Al preservation film is stable, hydrogen gas is not generated. But, for some reason (e.g. earthquake shocks), just after the land disposal, the Li-Al preservation film on some part of the aluminum surface may be lost. In this case, the scenario of hydrogen gas generation is described as follows.

- When the alkaline underground water reaches this stripped aluminum surface, the hydrogen gas generation begins, accompanied by aluminum corrosion.
  At that time, the amount of the generated hydrogen gas is expected as described below.
- LiNO\(_3\) in the waste forms dissolves into the underground water, and restores the lost Li-Al preservation film on the stripped aluminum surface. Then, the further generation of hydrogen gas can be prevented.

2. Experimental Procedure

To examine the adequacy of scenario 1, the following experiments were carried out: (1) solubility measurements of the Li-Al preservation film (Sec.II-2(2)); (3) aluminum corrosion measurements in water with pH equal to that of the underground water penetrating the waste packages when the Li-Al preservation film is dissolved into it (Sec.II-2(3)). Then, for scenario 2, (4) aluminum corrosion measurements were made for cases without the Li-Al preservation film formation on an aluminum surface during cement solidification (Sec.II-2(4)). Finally, for scenario 3, (5) aluminum corrosion measurements were made for cases in which the Li-Al preservation film had been removed while the pH of the underground water penetrating the waste forms was still high (Sec.II-2(5)).

Substances used in these experiments were all purchased from Wako Pure Chemicals.

(1) Solubility Measurements of the Li-Al Preservation Film

The solubility of the Li-Al preservation film was measured using the following procedure. At first, the lithium aluminate double salt was synthesized. For synthesis of lithium aluminate double salt, 5 g of aluminum foil (1 mm thick, 99.99% purity) were soaked in 500 ml of 5 M LiOH solution at room temperature. After the formation reaction of lithium aluminate double salt was finished, the solution was filtered and the product was collected. Then, the synthesized product was identified by X-ray diffraction. Figure 2 is the X-ray diffraction pattern of the product. Formation of lithium aluminate double salt was confirmed. The synthesized lithium aluminate double salt was soaked in alkaline solutions to measure its solubility. The prepared alkaline solutions were KOH solutions of five different concentrations: \(1.25 \times 10^{-2}\), \(2.14 \times 10^{-2}\), \(3.40 \times 10^{-2}\), \(5.00 \times 10^{-2}\) and \(1.00 \times 10^{-1}\) M. Then, 0.20 g of the synthesized lithium aluminate double salt were soaked in 50 ml of each solution for one week at 283 K. After that, the solutions were filtered. The concentrations of dissolved Li\(^+\) and A\(^{3+}\) ions from the lithium aluminate double salt in the filtrates were measured with the Hitachi ICP P-5200.

![Fig. 2 X-ray diffraction pattern of the synthesized Li-Al preservation film](image)

\[\text{Intensity (kcounts)} \]

\[\begin{array}{c|cccc}
\hline
\text{Diffraction Angle (rad)} & \pi/18 & \pi/9 & \pi/6 & \pi/3 \\
\hline
0.5 & O & \text{Li H (AlOn)} & : 5H_2O \\
2.5 & \text{O} & \text{Li H (AlOn)} & : 5H_2O \\
7.5 & \text{O} & \text{Li H (AlOn)} & : 5H_2O \\
\hline
\end{array} \]
APPENDIX 1 describes how an aluminum specimen with the Li-Al preservation film would corrode when the concentration of Li\(^+\) ions was below the solubility of lithium aluminate double salt.

(2) Ion Concentrations and pH Variation Accompanied by Penetration of Underground Water

As mentioned in Sec.II-1, the concentration of Li\(^+\) ions decreases, and the pH of the pore water in the waste forms drops as the underground water flows into the waste packages after the land disposal. Then, ion concentrations and pH included in the pore water were measured for the condition that the underground water penetration into the waste packages was accelerated. The steps of this experiment were as follows.

The mortar (mixture of cement and sand) forms, including LiNO\(_3\), were molded at first. Contents of the forms are given in Table 1. The cement we used in this experiment was Portland blast-furnace slag cement (slag cement) type C, which is a mixture of ordinary Portland cement (OPC) with blast-furnace slag at the ratio of OPC:slag=35:65. After a one-month cure the mortar forms were powdered to below 12 mesh size. This powdering process promotes early realization of equilibrium in the solution in which the mortar was soaked.

Next, the powdered mortar forms were soaked in ion-exchanged water at the solid to liquid ratio of 1/2 for 3 d at 283K, so that Li\(^+\) and other metal ions contained in the mortar dissolved into it. While the powdered mortar forms were being soaked, the solutions were continuously stirred at 500 rpm. Figure 3 shows an example plot of pH variation during soaking and stirring. The water pH value equilibrated after 3 d.

The powdered mortar forms were filtered and soaked in a new sample of ion-exchanged water. Soaking and filtering were alternately repeated and the water filtrates were collected. The repetition of soaking and filtration was substituted for the slow and continuous penetration of underground water into the waste packages in order to accelerate the variations of ion concentrations and pH in the pore water. When specific gravity and porosity rate of the mortar are respectively about 2 and 1/3, doing this step once is equivalent to making 12 exchanges of the underground water filling the pores of the waste form. After that, pH and concentrations of Li\(^+\), Na\(^+\), K\(^+\) and Ca\(^{2+}\) ions were measured in each filtered water sample. The pH was measured by an acid-base titration using 0.1 m HCl solution, and an ethyl alcohol solution of phenolphthalein was used as an indicator. The ion concentration was measured by ICP analysis.

The measured pH and ion concentrations in each filtered water sample as a function of the number of soakings were considered to be equivalent to the actual variation of pH and ion concentrations caused by the underground water penetration. In this experiment, pH in the underground water when the Li-Al preservation film was dissolved could be estimated from the variation of Li\(^+\) ion concentration and the solubility of the Li-Al preservation film, obtained in Sec.II-2. APPENDIX 2 discusses how the variations of ion concentrations and pH in the pore water depend on the cement type used.

(3) Aluminum Corrosion after Loss of the Li-Al Preservation Film

From the first two experiments, we could estimate the pH value of pore water in the waste form when the Li-Al preservation film is dissolved. This value could be lower than the initial pore water pH. Then, aluminum corrosion measurements were performed using the mortar-soaked water, to estimate the effect of lowering pH. At first, the mortar-soaked water was produced using mortar form without LiNO\(_3\) addition (Table 1). The steps to get the mortar-soaked water were the same as described in Sec.II-2(2) (the mortar form was powdered, soaked in ion-exchanged water, and filtered). The pH of the mortar-soaked water was measured by an acid-base titration. The other mortar-soaked water sample with pH obtained just after the land disposal (estimated in the previous section) was produced in the same way.

Then, an aluminum specimen was immersed in the mortar-soaked water and the volume of hydrogen gas generated from aluminum corrosion was measured at 283 K. Ten grams of filtered mortar powder (i.e. mortar used for making the mortar-soaked water) and an aluminum specimen (1 mm thick, 1×8 cm, 99.99% purity) were placed in 40 ml of the mortar-soaked water. The volume of the hydrogen gas generation was plotted against time. Aluminum corrosion d (mm) is related to the volume of hydrogen gas generation V (ml) by the equation:

<table>
<thead>
<tr>
<th>Table 1 Composition of mortar</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cement</strong></td>
</tr>
<tr>
<td>55 wt%</td>
</tr>
</tbody>
</table>

1 In cases with LiNO\(_3\) addition

\[ V = d \cdot 10^3 \]
where $H_2$ gas generation per 1 mol of Al corrosion = $2/3$ (mol), atomic weight of Al = 27, density of Al = 2.703 (g/cm$^3$), and Al surface = 16 (cm$^2$).

(4) Aluminum Corrosion Measurements without the Li-Al Preservation Film Formation

If aluminum wastes have complex shapes, mortar paste may fail to reach some part of the aluminum surface during the cement solidification process. Therefore, there is a possibility that the Li-Al preservation film is not formed on this part of the aluminum surface (scenario 2). Then, the effect of the dissolved LiNO$_3$ on aluminum corrosion prevention was examined.

At first, two kinds of powdered mortar forms were soaked in ion-exchanged water at the weight ratio of powder/water = 1/2, for three days. The first mortar form included LiNO$_3$ and the second one did not. After filtration, the mortar-soaked water was obtained in each case.

Then, aluminum specimens were immersed in these two kinds of mortar-soaked water and the time profile of the hydrogen gas generation was measured at 283 K. The conditions were: 10 g of powdered mortar left on a filter paper; aluminum specimen (1 mm thick, 1 x 8 cm, and 99.99% purity); 40 ml of mortar-soaked water. Aluminum corrosion was estimated from the volume of the hydrogen gas generation. After this experiment, the surfaces of the aluminum specimens were examined by X-ray diffraction to see if the Li-Al preservation film was formed.

(5) Aluminum Corrosion Measurements after the Removal of the Li-Al Preservation Film

Aluminum corrosion was studied when the Li-Al preservation film was already dissolved while pH of the underground water penetrating the waste form was still high (scenario 3).

By using the mortar-soaked water listed in Table 2, the time profile of hydrogen gas generation was measured in the way as described in Sec.II-2(4). Aluminum corrosion was estimated from the volume of the hydrogen gas generation. In Table 2, years from just after the land disposal until when the Li-Al preservation film dissolved, are divided into 4 groups: sample 1 is the time when the pH of the underground water penetrating the waste form is as high as just after the land disposal. Samples 2 and 3 are the times during which pH is lowered, but higher than when the Li-Al preservation film dissolved. Sample 4 is the time just before the Li-Al preservation film dissolves. Before the experiment, the aluminum specimens were soaked for one week in 100 ml of 0.1 M KOH solution with 6 g of dissolved LiNO$_3$, to form the Li-Al preservation film on their surface. Then, the specimens were soaked in a large amount of ion-exchanged water to dissolve the Li-Al preservation film, i.e. until it could no longer be detected in the X-ray diffraction pattern. After the experiment, surfaces of aluminum specimens were examined by X-ray diffraction to make sure that the Li-Al preservation film reformed.

III. RESULTS

1. Solubility of the Li-Al Preservation Film

Figure 4 shows the concentrations of Li$^+$ and Al(OH)$_4^-$ ions dissolved from the Li-Al preservation film into KOH solution at 283 K, plotted against the concentration of OH$^-$ ion in the solution. The concentrations of Li$^+$ and Al(OH)$_4^-$ ions become lower as the concentration of OH$^-$ ion decreases. On the other hand, the lithium aluminate double salt, which composes the Li-Al preservation film, dissolves into solutions by the reaction:

$$\text{Li}^+ + 2\text{Al(OH)}_4^- + 2\text{H}_2\text{O} \rightarrow \text{LiH}_2\text{AlO}_2\cdot 5\text{H}_2\text{O} + \text{OH}^-.$$  (2)

![Fig. 4 Amount of ions dissolved from the Li-Al preservation film plotted against OH$^-$ ion concentration](image)
Then, the equilibrium constant of lithium aluminate double salt at 283 K can be described by

\[ K = \frac{[\text{OH}^-]}{[\text{Li}^+][\text{Al(OH)}_4^-]^2} \]  

(3)

In Fig. 5, the equilibrium constant was obtained as a function of \( \text{OH}^- \) concentration.

2. pH and Ion Concentrations in Penetrated Underground Water

In Fig. 6, pH and \( \text{Li}^+ \) ion concentration of pore water in the waste forms are plotted as a function of the volume of the penetrating underground water. The solubility of the Li-Al preservation film obtained from Fig. 5 is also plotted in Fig. 6. Both pH and \( \text{Li}^+ \) ion concentration decrease rapidly as the volume of underground water penetration grows. When the underground water penetration volume is 30 times as large as the waste form volume (exchange of underground water in the waste forms=90 times), the \( \text{Li}^+ \) ion concentration value is equivalent to the solubility of the Li-Al preservation film, \( 3 \times 10^{-4} \text{ M} \). At that time, pH is lowered from 12.9 - 13.0, which is obtained just after the land disposal, to 12.2 - 12.3, i.e. about 0.7 pH units. In Fig. 7, concentrations of \( \text{Li}^+ \), \( \text{Na}^+ \), \( \text{K}^+ \) and \( \text{Ca}^{2+} \) ions are plotted as a function of the volume of the penetrating underground water in the waste repository. Just after the land disposal, the concentrations of \( \text{Na}^+ \) and \( \text{K}^+ \) ions are much larger than concentration of \( \text{Ca}^{2+} \) ions. From Figs. 6 and 7, we see that the high pH obtained just after the land disposal contributes to the high concentrations of \( \text{Na}^+ \) and \( \text{K}^+ \) ions, and pH drops as the concentrations of \( \text{Na}^+ \) and \( \text{K}^+ \) ions decrease.

As a result, we recognized that the pH was in between 12.2 and 12.3 when the Li-Al preservation film dissolved, and that it was about 0.7 pH units smaller than just after the land disposal, being between 12.9 and 13.0.

3. Aluminum Corrosion after the Dissolution of the Li-Al Preservation Film

Figure 8 shows aluminum corrosion in the mortar-soaked water as a function of time at various pH obtained just after the land disposal (■: pH 12.9, □: pH 13.0), and when the Li-Al preservation film dissolves (▲: pH 12.2, △: pH 12.3). The aluminum corrosion obtained when the Li-Al preservation film dissolves is one fourth to one fifth that obtained just after the land disposal because of the difference of their pH. Figure 8 also gives a time dependence of corrosion of an aluminum specimen, on which the Li-Al preservation film was dissolved into water, at pH 12.2 - 12.3 (○: pH 12.2, ◦: pH 12.3). This amount of aluminum corrosion is one half to one third of that of the bare aluminum specimens placed in water at the same pH. From the X-ray diffraction pattern of the aluminum specimen surface obtained after the Li-Al preservation film dissolves (Fig. 9), we found...
that a layer of Al₂O₃·3H₂O was formed on the surface.
From the above results, we concluded that the total effect of the LiNO₃ addition after the land disposal of the waste packages is the reduction of aluminum corrosion prevention by 90% of that without LiNO₃ addition.

4. Aluminum Corrosion Measurements without the Li-Al Preservation Film Formation on Aluminum Surface

Figure 10 plots time profiles of aluminum corrosion amount in mortar-soaked water with and without LiNO₃ addition. Aluminum corrosion amount when LiNO₃ was added is 10% of that without LiNO₃ addition.

After the above experiment, the surface of the aluminum specimen soaked in the mortar-soaked water with LiNO₃ addition, was examined by X-ray diffraction, and the Li-Al preservation film was identified on its surface.
We considered that the LiNO$_3$ which dissolved from the mortar into the water on soaking reacted with aluminum to form the Li-Al preservation film, and that it prevented aluminum corrosion. The concentration of Li$^+$ ions is $7 \times 10^{-2}$ M in the mortar-soaked water when LiNO$_3$ was contained in the mortar.

From the above results, if mortar paste does not reach a part of the aluminum surface in the wastes and the Li-Al preservation film is not formed on it during the solidification process, LiNO$_3$ dissolves from the waste forms into the penetrating underground water to form the Li-Al preservation film on it after the land disposal, and aluminum corrosion is prevented.

5. Aluminum Corrosion Measurements after the Removal of the Li-Al Preservation Film at High pH

Figure 12 shows time profiles of the aluminum corrosion amount under the conditions listed in Table 2, with that of bare specimen at pH 12.9 (plotted in Fig. 8) as a reference. The pH and Li$^+$ ion concentrations in Table 2 are based on the results of the underground water penetration experiments (Fig. 6). In Fig. 12, all solutions give aluminum corrosion amounts of less than 10% of the reference curve which corresponds to the corrosive condition just after the land disposal when LiNO$_3$ was not added to the waste forms. Aluminum corrosion of this kind is expected to be just partial, not wide-spread over the aluminum surface. Then, the total amount of aluminum corrosion on the surface with the Li-Al preservation film partially removed is negligible compared with the aluminum corrosion obtained when LiNO$_3$ is not added.

Then, to find the reason why aluminum corrosion was prevented on its surface when the Li-Al preservation film was removed, the surface of the aluminum specimen was examined by X-ray diffraction after the corrosion amount measurements. Figure 13 is the X-ray diffraction pattern of the aluminum specimen for sample 1,
listed in Table 2. The Li-Al preservation film, which was removed once, was restored after the aluminum corrosion measurements. This restoration occurred because the concentration of Li+ ions was large when pH was high in the mortar-soaked water. Therefore, we thought that the aluminum corrosion was prevented by the restored Li-Al preservation film. On the other hand, sample 4 had few Li+ ions, but, pH has decreased to 12.3, as high as is obtained when the Li-Al preservation film dissolves, to prevent the aluminum corrosion. Then, it seems that the aluminum corrosion is prevented in samples 2 and 3 which are between samples 1 and 4, because a small fraction of Li+ ions was preserved in the waste forms, and pH was lower than case 1.

From the above results, aluminum corrosion on the surface where the Li-Al preservation film is removed for some reason, was less than 10% of that obtained when LiNO3 was not added.

IV. DISCUSSION

In Fig. 8, because of the pH difference, the aluminum corrosion obtained when the Li-Al preservation film dissolves is one fourth to one fifth that obtained just after the land disposal. The decrease of pH by 0.7 units is identified with OH- ion concentration being 10^-0.7 (≈ 0.2) times. The concentration of aluminate ions is proportional to that of OH^- ions, as Al(OH)4^- = 10^-0.6·[OH^-]^{(9)}. Therefore, when the concentration of OH^- ions is lowered by 80%, the concentration of aluminate ions is also lowered by 80%. Assuming that the amount of aluminate ions is equivalent to the aluminum corrosion, the aluminum corrosion is proportional to the concentration of OH^-.

Consequently, the aluminum corrosion obtained when the Li-Al preservation film dissolves should be one fifth of that obtained just after the land disposal because the ratio of OH^- ion concentration between these two mortar-soaked water samples is 0.2. And this result agrees with that of the above aluminum corrosion measurements.

Figure 8 also shows that the amount of aluminum corrosion for the aluminum specimen on which the Li-Al preservation film was dissolved into water, at pH 12.2-12.3. The amount of aluminum corrosion is one half to one third of that when the bare aluminum specimens were placed in water at the same pH. And we found that a layer of Al2O3·3H2O was formed on the aluminum specimen surface, which was obtained after the Li-Al preservation film dissolved. We think that this Al2O3·3H2O layer emerged after the Li-Al preservation film dissolved, because it has already been reported that a Al2O3·3H2O layer was formed on the metallic aluminum surface and the lithium aluminate double salt layer was formed on this^{(3)}. We considered that the Al2O3·3H2O layer acted as a very weak barrier against aluminum corrosion, and that the additional aluminum corrosion reduction was attributed to it.

From the above results, we concluded that the LiNO3 addition during the cement solidification process has an effect on aluminum corrosion prevention after the land disposal of the waste packages, cutting it by 90% of that without LiNO3 addition, and that the effect is composed of a pH lowering effect and an Al2O3·3H2O layer inhibiting effect.

V. CONCLUSIONS

After the land disposal of waste packages including aluminum materials generated at nuclear power plants, the aluminum may corrode, generating hydrogen gas if underground water penetrates the concrete waste repository and reaches the aluminum in the waste forms. This paper examined the long term effect of LiNO3 addition to cement in the solidification process on aluminum corrosion prevention after the land disposal of the waste packages. The conclusions were as follows.

(1) The effect of LiNO3 on aluminum corrosion prevention was attributed to the formation of the Li-Al preservation film on the aluminum surface during the solidification process. When the Li-Al preservation film was present, hydrogen gas was not generated. Therefore, we considered hydrogen gas generation after the land disposal if the Li-Al preservation film was lost. We assumed three scenarios for the start of hydrogen gas generation, to evaluate the long term effect of LiNO3.

(2) When the underground water continuously penetrates into the waste package after the land disposal, LiNO3 concentration in the waste forms could decrease by dissolving into the water. If the concentration of Li+ ions is smaller than the solubility of the Li-Al preservation film (3×10^-4 M), this film will dissolve and hydrogen gas will be generated from the aluminum wastes. But, at that time, Na2O and K2O in cement will also dissolve. Then, the pH of pore water in the waste forms will be lowered from...
12.9-13.0 (obtained just after the land disposal) to 12.2-12.3 (obtained when the Li-Al preservation film dissolves) through 90 water exchanges in the waste forms. With LiNO₃ addition the aluminum corrosion amount was reduced to 10% of that without LiNO₃ addition, where the aluminum materials in the wastes corroded just after the land disposal (pH 12.9 -13.0).

(3) In the wastes with complex shapes, there may be bare aluminum surfaces having only a partial Li-Al preservation film, where hydrogen gas can be generated when the underground water reaches them. However, LiNO₃ included in the waste forms dissolves into the water at that time, and it reacts with aluminum to form the Li-Al preservation film. If for some reason, a part of the Li-Al preservation film is removed, LiNO₃ included in the waste forms also restores this removed part. Then, as a result, hydrogen gas generation is prevented.

---REFERENCES---

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[^APPENDIX]

1. The Dependence of Li⁺ Ion Concentration on Hydrogen Gas Generation

Hydrogen gas generation measurements were carried out under the condition that the concentration of Li⁺ ions was around the solubility of lithium aluminate double salt as obtained in Fig. 5. These measurements were to make sure that, when the concentration of Li⁺ ions was below the solubility of lithium aluminate double salt, an aluminum specimen with the Li-Al preservation film would corrode. At first, the Li-Al preservation film was formed on aluminum specimens (1×8 cm, 1 mm thick) by soaking them for one week in 100 ml of 0.1 m KOH solution with 6 g of LiNO₃. Then, aluminum specimens with the Li-Al preservation film were soaked in four different alkaline solutions listed in Table A1, to measure the volume of the generated hydrogen gas.

<table>
<thead>
<tr>
<th>Contents (mol/l)</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNO₃</td>
<td>5×10⁻⁵</td>
</tr>
<tr>
<td>KOH</td>
<td>2.0×10⁻²</td>
</tr>
<tr>
<td>Al(OH)₃</td>
<td>5×10⁻⁴</td>
</tr>
</tbody>
</table>

Solubility of the Li-Al film

Figure A1 shows the time profiles of the volume of hydrogen gas generation, and their dependence on the amount of LiNO₃ addition. When the amount of LiNO₃ addition leads to a larger concentration of Li⁺ ions than the one which is equivalent to the solubility of the Li-Al preservation film, the hydrogen gas is not generated. But when the amount of LiNO₃ addition results in a smaller concentration of Li⁺ ions than the solubility of the Li-Al preservation film, the hydrogen gas is gradually generated.

From these results, it was confirmed that when the concentration of Li⁺ ions was smaller than the solubility of the Li-Al preservation film, the hydrogen gas was slowly generated.

2. Dependence of Variations of Ion Concentrations and pH in the Pore Water on the Used Cement Type

In slag cement, the amount of calcium increases as the mixture ratio of OPC to blast-furnace slag is larger. We expected that this leads to a delay in the pH drop below 12.5 in Fig. 8. The same experiments as described in Sec.II-3 were carried out using slag cement type B (mixture ratio of OPC to blast-furnace slag at the ratio of OPC : slag=45 : 55, See Table A2) to examine the dependence of cement type used in the experiments on pH variation.

In Fig. 7, the concentration of Ca²⁺ ions is not so high just after the land disposal because the solubility of Ca(OH)₂ is smaller than that of NaOH or KOH so that the high pH caused by the high concentrations of

---Fig. A1 Dependence of hydrogen gas generation on Li⁺ ion concentration---
Na⁺ and K⁺ ions makes the concentration of Ca²⁺ ions much smaller. Reduction of Na⁺ and K⁺ ion concentrations accompanying the underground water penetration leads to a large concentration of Ca²⁺ ions; it is largest at pH 12.5 which is obtained in saturated solutions of Ca(OH)₂. Then, further underground water penetration lowers the concentration of Ca²⁺ ions gradually, accompanied by dropping of pH from 12.5. However, as seen in Fig. A2, there is little difference in pH lowering between slag cement type B and type C, which are conventional cement types used for waste solidification or construction purposes. Then, the difference of calcium content does not influence pH lowering between these kinds of cement.

<table>
<thead>
<tr>
<th>Cement</th>
<th>Ordinary portland cement (%)</th>
<th>Blast-furnace slag (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type B</td>
<td>45</td>
<td>55</td>
</tr>
<tr>
<td>Type C</td>
<td>35</td>
<td>65</td>
</tr>
</tbody>
</table>

**Table A2** Contents of portland blast-furnace slag cement

**Fig. A2** Dependence of pH variation in waste repository on mortar content accompanied by underground water penetration.