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A Study on Leaching Characteristics of Paraffin Waste Form Including Boric Acid

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Abstract

Preliminary experiment was performed to investigate the leaching characteristics of paraffin waste forms that had been recently generated in large quantities at domestic nuclear power plants. At first, waste simulants whose compositions were different in mixing ratio of paraffin to boric acid were prepared. Their compressive strengths were measured and ninety-day leaching test of specimen including cobalt was carried out according to ANSI/ANS-16.1 test procedure. Water immersion test was also conducted keeping pace with leaching test and the weight change and the compressive strength of specimen were observed after ninety days. The compressive strength of waste form exhibited 666 psi (4.53 MPa) in the case where mixing ratio of boric acid to paraffin was 78/22, which was adopted in concentrate waste drying system of domestic nuclear power plants. The leaching test resulted in about 50% of the cumulative fraction leached for boric acid and cobalt, respectively. The specific gravity of waste form was 0.87 [g/g] whose value was less than that of water because the weight loss of about 39% occurred after the water immersion test of ninety days. It was also observed that the waste form which had undergone ninety-day water immersion test exhibited the compressive strength of 203 psi (1.38 MPa).

Key Words : paraffin waste form, compressive strength test, leaching test, water immersion test, cumulative fraction leached, boric acid, cobalt

1. Introduction

Low- and intermediate-level radioactive wastes, arising from the operation of nuclear power plants, can be immobilized by various solidification techniques prior to disposal. Liquid radioactive wastes have been treated with filtration, ion exchange resin, evaporation, and so on. The remaining liquid concentrate wastes after the treatment of evaporator have been immobilized by making using of solidifying agents such as cement, asphalt, and plastic, and then they are filled and packaged in several kinds of containers. Because waste forms including radionuclides are immobilized with solidifying agents and finally disposed of, they can be safely stored in geological repository, isolated from a human being' s living environment for a long time. However, if many engineered barriers and natural barriers of radioactive waste repository would be functionally useless and the radioactive waste forms would be directly in contact with the groundwater, the releases of radioactive species from the waste forms may occur by leaching mechanism. Therefore, acceptance criteria of radioactive waste forms have been developed to guarantee long-term safety performance of radioactive waste repository. Waste form properties of particular significance regarding an evaluation of performance in the disposal environment include contents of free water, mechanical properties such as compressive strength, thermal stability, leachability, non-corrosiveness to the waste form container, biological properties related with gas generation, and radiation resistance.

Liquid borate wastes have been recently converted to paraffin waste forms by utilizing concentrate waste drying system in domestic nuclear power plants. But researches on leaching characteristics of paraffin waste forms are rarely made until now, and so preliminary experiment was performed to investigate the leaching characteristics of paraffin waste forms. Paraffin waste simulants whose compositions were different in mixing ratio of paraffin to boric acid were prepared. Their compressive strengths were measured to confirm the integrity of waste forms. The ninety-day leaching test of specimen including boric acid and cobalt was carried out according to ANSI/ANS-16.1 test procedure and the cumulative fraction leached of boric acid and cobalt was investigated. Also, water immersion test was conducted keeping pace with leaching test and the weight change of specimen and the compressive strength were observed after ninety days.

2. Experimental Procedures

2.1. Experimental Materials

Waste simulants were prepared by making use of paraffin wax and boric acid used at Yong-gwang Nuclear Units. This paraffin wax(Aristowax) is highly refined-wax which is manufactured in UNICAL of the United States. The specific gravity of paraffin wax is 0.933 [g/g] and its melting temperature is 72℃. It becomes a liquid of low viscosity in proportion to a rise in temperature. Paraffin wax is also insoluble in water and has thermoplastic properties. Paraffin is physically mixed with boric acid, not any chemical bonding with it and simply plays a binding role within waste form. Boric acid(H_3BO_3) has a specific gravity of 1.44 [g/g], so it makes a difference between boric acid and paraffin in specific gravity. But the phenomenon of stratification can be avoided during preparing waste form if mixing ratio of boric acid to paraffin is well adjusted. Melting temperature and boiling temperature of boric acid are 171℃ and 359℃, respectively.

2.2. Specimen Preparation

Paraffin was mixed with boric acid after it had been completely melted in steel beaker over a heating apparatus. The operational temperature was maintained within the range of 120~140℃ and the speed of stirrer was 600 r.p.m. The mixture was poured into cylindrical PVC mold after 15 minutes and hardened at a room temperature for a week. Then the mold was removed and the cylindrical waste form with a diameter of 5 cm and a height of 10 cm was prepared. At this point, the mixing ratio of boric acid to paraffin was very important in order to make a homogeneous waste form. It was difficult to make a waste simulant due to a low fluidity if the paraffin content was small in quantity as compared with boric acid. While the phenomenon of stratification began to occur due to difference of specific gravity between boric acid to paraffin if the paraffin content exceeded a certain limit of mixing ratio. In this study, the mixing ratio of boric acid and paraffin was chosen as 85/15, 80/20, 79/21, 78/22, 77/23, 76/24, 75/25, and 70/30, respectively. In the case where the ratio of paraffin content was 15%, the mixture was put into mold with the help of spoon, and in the case where the ratio of paraffin content was more than 25%, the stratification began to occur from the upper part of specimen.

2.3. Compressive Strength Test

The compressive strength test whose purpose was to confirm the integrity of produced waste form was carried out after the hardening time of a week. The compressive strength test was applied to at least three specimens under each test condition of different mixing ratios between boric acid and paraffin. The test was performed according to ASTM C39-86[1] and the compressive strength was given as applied maximum load divided by a cross-sectional area of specimen. It is suitable that the specimen has a cylindrical shape with the height/diameter ratio of 2, because the restriction effect, that is, the increase effect of apparent strength by virtue of friction between loading plate and specimen, can be reduced at a minimum. It is recommended by the U.S. Nuclear Regulatory Commission(NRC) that the suggested standard of > 60 psi(408 kPa) and > 500 psi(3.4 MPa) for asphalt and cement waste form, respectively, should be satisfied before and after the water immersion test[2].

2.4. Leaching Test

The standard leaching test methods for the assessment of leaching characteristics of radioactive waste form include IAEA test[3], ISO-6961[4], ANSI/ANS-16.1[5], MCC-1P, MCC-2P, MCC-3S, MCC-4S, MCC-5S[6], and so forth. These leaching tests have been largely employed to provide comparisons of the leachability of different waste forms under a specific set of test conditions, and to predict long-term releases in the disposal environment. In this study, ANSI/ANS-16.1 leaching standard procedure was used to investigate the leaching characteristics of paraffin waste form. ANSI/ANS-16.1 test was developed by an American Nuclear Society(ANS) Standards Committee(Working Group 16.1) for the characterization of solidified low-level radioactive waste forms. This procedure uses demineralized water as the leachant and is conducted at a temperature of (22.5 ± 5)℃. Sufficient leachant is used to provide a ratio of leachant volume to specimen external geometric surface area of (10 ± 0.2)cm. The leachant is sampled and replaced at the following frequency:

(a) 2, 7, and 24 h from the initiation of the test
(b) then at 24 h intervals for the next 4 d
(c) then at 14, 28, and 43 d intervals to extend

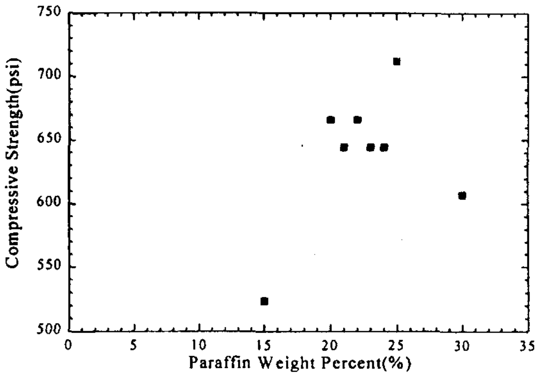

Fig. 1. Compressive Strength of Waste Form with the Change of Paraffin Content

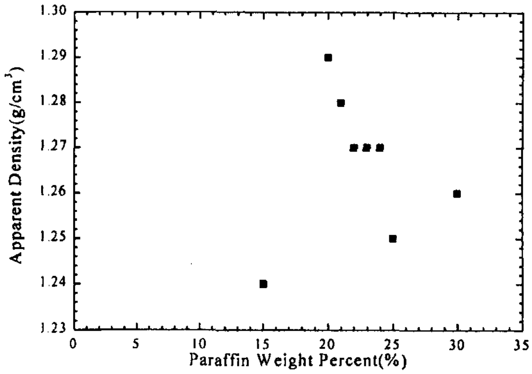

Fig. 2. Apparent Density of Waste Form with the Change of Paraffin Content

the entire test to 90 d

Non-radioactive species cobalt(II) chloride hexahydrate($CoCl_2 \cdot 6H_2O$) of 1g was added to paraffin waste form whose mixing ratio of boric acid to paraffin was 78/22, which was adopted in concentrate waste drying system of domestic nuclear power plants. An amount of cobalt(II) chloride hexahydrate corresponds to 0.48% of boric acid by weight, and its value was determined in consideration of detectable measuring range for the analysis of concentration. The concentration of cobalt included in leachate was measured by means of colorimetry, and that of boric acid within leachate was analyzed by titration. The concentration of boric acid cannot be directly determined by titration using strong alkali of sodium hydroxide because boric acid is weak acid with ionization constant of 5×10^{-10}. Accordingly, the mannitol of multivalent alcohol was appended to boric acid before it is titrated with sodium hydroxide standard solution(0.1N).

2.5. Water Immersion Test

Water immersion test for low-level radioactive waste form is mainly kept pace with leaching test of ninety days[2]. After leaching test of ninety days was completed, the surface of specimen stained with leachant was wholly dried out at a room temperature prior to measuring the weight change and compressive strength of waste form. An attention is paid to water immersion test so that evaporation of leachant might not occur during the whole testing period.

3. Results and Discussion

Fig. 1 and 2 show the compressive strength and apparent density of paraffin waste form with the change of mixing ratio between boric acid and paraffin. In case of waste form whose paraffin weight percent was 15%, the compressive strength and apparent density were 3.56 MPa (523 psi) and 1.24 g/cm³, respectively, which were relatively low values as compared with those of other waste forms with different mixing ratios. This was because that the mixture was such a low fluidity that it was put into mold with the help of spoon. The mixtures whose paraffin contents were within the range of 20~24% were easily poured into mold owing to good workability, and the compressive strength tests resulted in similar values of 644~666 psi (4.38~4.53 MPa) as shown in Fig. 1. But, in the case where the ratio of paraffin content was more than 25%, the stratification began to occur

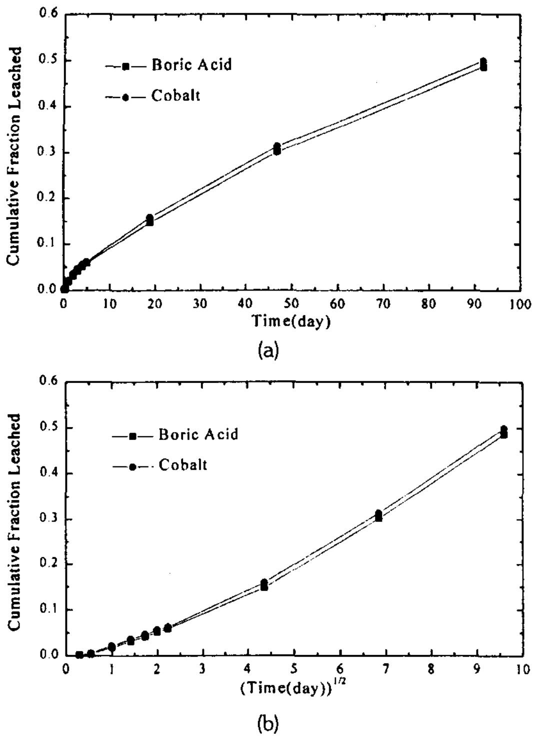

Fig. 3. Cumulative Fraction Leached of Boric Acid and Cobalt Plotted as a Function of Time(a) and Square Root of Time(b) in the Case Where Mixing Ratio of Boric Acid to Paraffin is 78/22

from the upper part of waste form and it was difficult to make a homogeneous waste simulant. Therefore, it comes to the conclusion that it is desirable to keep a paraffin weight ratio within the range of 20~24% in order to prepare a homogeneous waste form as the matters of fluidity and stratification are solved at a time. As shown in Fig. 2, the apparent densities of waste forms grew down as the higher content of paraffin except that paraffin weight percents were 15% and 30%.

Fig. 3 shows the results of short-term leaching test for paraffin waste form whose mixing ratio of boric acid to paraffin is 78/22. In Fig. 3(a), the vertical axis depicts cumulative fraction

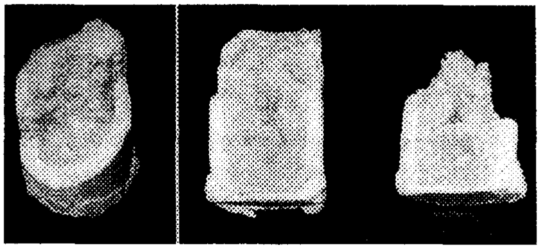

Fig. 4. Interior Section of Paraffin Waste Form After Leaching Test of 90 days and Compressive Strength Test

leached during the testing period and it was obtained that about 50% of boric acid and cobalt, respectively, were released after the lapse of ninety days. The values of cumulative fraction leached for boric acid and cobalt have no linear relation to square root of time as shown in Fig. 3(b). It seems that the leaching mechanism of paraffin waste form is controlled by dissolution. This is because that boric acid which occupies a large portion of paraffin waste form is easily dissolved from the surface of waste form by leachant. It is understood that cobalt immobilized within paraffin waste form follows the same path as boric acid and is leached in accompany with boric acid. Accordingly, the leaching of cobalt is thought to be mainly dependent on the dissolution of boric acid. This fact is supported by the photograph of Fig. 4 that are showing the interior section of paraffin waste form after the leaching test of ninety days and the compressive strength test. In this photograph, the white outside of paraffin waste form indicates the portion of only paraffin left over, and all the contents of boric acid and cobalt within this region were leached out. In particular, it was observed that this portion had the thickness of about 0.6 cm along the all surfaces, i.e., top/bottom and lateral sides, of the cylindrical waste form. In Fig. 4, the reason why the thickness of bottom side appears to be smaller than that of lateral side is that this photograph was taken after the compressive strength test. The fractional volume of this portion exactly corresponds with the cumulative fraction leached of boric acid (~50%) as shown in Fig. 3(a). It was also observed in Fig. 4 that the surface of waste form including boric acid and cobalt, that is to say, dissolution front, was continuously shrinking during the leaching test of ninety days, even if the external shape of paraffin waste form was maintained as intact form. Therefore, it is thought that the moving boundary model such as shrinking model is able to be applied to the analysis of leaching mechanism of paraffin waste form.

The weight change of waste form which had the mixing ratio of 78/22 between boric acid and paraffin was measured after the water immersion test of ninety days. The weight loss of about 39% occurred and the specific gravity of waste form was changed from 1.27 to 0.87 whose value is lower than that of water. The paraffin waste form which had suffered ninety-day water immersion test exhibited the compressive strength of 203 psi (1.38 MPa). The waste form appeared to be somewhat swollen and some fissures were observed after the water immersion test was completed, but the overall framework of paraffin waste form was maintained as intact form. This fact indicates that boric acid and paraffin are homogeneously distributed within waste form and the paraffin capturing boric acid is closely entangled.

4. Conclusions

Preliminary experiment was performed to investigate the leaching characteristics of paraffin waste forms that had been recently generated in domestic nuclear power plants. The compressive strengths were measured for various waste forms whose mixing ratios of boric acid and paraffin were different with one another. In the case where the weight ratio of paraffin was 20~24%, the compressive strength tests resulted in the values of 644~666 psi (4.38~4.53 MPa). The ninety-day leaching test was carried out according to ANSI/ANS-16.1 test procedure. The paraffin waste form with the mixing ratio of 78/22 between boric acid and paraffin, which was adopted in concentrate waste drying system of domestic nuclear power plants, was chosen for the object of leaching test. It was observed that about 50% of boric acid and cobalt, respectively, were released after the lapse of ninety days. As a result of water immersion test during ninety days, the weight loss of about 39% occurred and the waste form exhibited the compressive strength of 203 psi (1.38 MPa). It is concluded that the leaching mechanism of paraffin waste form is controlled by surface dissolution with the shrinking dissolution front.

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