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Development of Modified Product Consistency Test

Kwansik Choi, Jiawei Sheng, Sung-Jun Maeng, and Myung-Jae Song
Korea Electric Power Research Institute
103-16 Moonji-dong, Yusung-ku,
Taejon, Korea

ABSTRACT

Modified Product Consistency Test (M-PCT) has been developed as an alternative to other existing methods in determining the leachability of glass. M-PCT, the leaching method, is a hybrid of MCC-1 and PCT, but can provide quicker sample preparation. Larger diameter glass sample (1.0-2.0 mm) than in the PCT method can be used so that the glass beads are more easily produced and cleaned. From the M-PCT, the total mass loss (ML) of glass, the normalized elemental release rate (NLi), pH value of leachate have been obtained. For some selected glasses in which leaching rates have been known, their chemical durability have been tested using the M-PCT method. The results are compared to the literature data for the glasses. It is found that M-PCT method is reasonable and suitable in determining the leachability of Low and Intermediate Level Radioactive Waste glass form, such as the pH, elemental loss and total mass loss.

INTRODUCTION

Glass has been recognized by a number of countries as a promising medium for immobilization of high level radioactive waste (HLW) because of the commonly perceived durability of silicate glasses and the capacity of the glass to incorporate many different elements. Vitrification technology is applicable not only to HLW, but also to low level radioactive waste, hazardous wastes and mixed wastes.

The objective of waste immobilization is to limit the release of radioactive elements to the environment over the course of some large number of half-lives. However, when a glass is in contact with ground water or water vapor, the glass is altered physically or chemically, and glass components are released into the water. Leachability is a measure of the easiness of the glass components' release

into the environment. Major interest is on radioactive elements while the standard leaching test focuses on Si, B, Na or Li. Since vast effort is involved in identifying durable waste glasses and developing experimental methods to reliably measure their durabilities, there is a need to reduce the effort. A new leaching procedure has been developed by simplifying Product Consistency Test (PCT)[1], an existing leaching test, as a screening purpose. Until candidate glass formulas are selected from a large number of compositions, the Modified PCT could be applied to the glass candidates.

EXPERIMENTAL SET-UP

Glass Manufacture

For the purpose of simulating the waste glass formular, a designed composition of glass is balanced and mixed in oxide form and then melted in platinum crucible which is electrically heated under low voltage and high currunt. Some oxides are sometimes replaced by their carbonates. The melting temperature is maintained at 1150 ℃ for more than 1 hour. The crucible is tilted to pour the molten glass into a graphite mold which is preheated at 550 ℃. Then the glass is annealed at the temperature for 1 hour.

M-PCT Leaching Test Procedure

1. Sample preparation:
   (1) The block glass is washed with deionized water and dried at 110 °C for 1 hour;
   (2) The block glass is broken down by a grinder;
   (3) The glass particles between 1-mm and 2-mm are collected by sieving;
   (4) The powder is washed with deionized water 2 times for 15 seconds each, and then with anhydrous alcohol 2 times for 15 seconds each;
   (5) The glass powder is dried at 110 °C for 1 hour, and then cooled to room temperature;
   (6) The specific surface area of glass powder can be measured by BET or calculated. It is about 1.56 m^2/g.
2. Container cleaning:
   (1) Container material is PETT, and its volume is 30 ml;
   (2) The container is immersed in HNO_3 solution (6M) at 50 °C for 4 hours;
   (3) The container is rinsed with deionized water 3 times;
   (4) The container is immersed in fresh deionized water (80 °C) for 6 - 8 hours;
   (5) The container is boiled in fresh deionized water for 30 minutes;
   (6) The container is rinsed with deionized water until the pH value change does not exceed 0.5 between consecutive rinses.
3. Leaching procedures:

(1) Deionized water is used as the leachant;

(2) About 0.7g of powder sample is added into the container, and then deionized water is added so that the ratio of glass surface area to leachant volume (SA/V) is 50 m^{-1};

(4) The container is covered tightly with a lid to prevent leakage, and then put into the oven at 70 °C;

(5) After 24 hours, the container is covered tightly with a lid again;

(6) Every test should be carried out in triplicate with one blank;

(7) After 7 days, the oven is turned off and the container is cooled to room temperature.

4. Analysis and calculation:

(1) The upper clear solution (about 15 ml) is carefully poured into a clean polyethylene(PE) bottle; an aliquot of the solution is used to measure its pH, the other part of the solution is acidified with HNO_3 to a pH<2 (usually 1% of HNO_3), and then sent for analysis of its glass components (Na, Si, B, Al, et al.) by using ICP;

(2) The powder is washed with deionized water 2 times, and then dried at 110 °C for 2 hours. After cooled to room temperature, its mass is measured.

(3) The total mass loss is estimated as following:

$$ML = (m_0 - m_1) / (SA)$$

where ML is the total mass loss, ($g.m^{-2}.d^{-1}$); m_0 is the unleached glass sample mass, (g); m_1 is the leached glass sample mass, (g); and SA is the sample surface area, (m^2).

(4) The normalized element mass loss is calculated as following:

$$NL_i = C_i \times V / (SA \times f_i)$$

where NL_i is the normalized element i mass loss, ($g.m^{-2}.d^{-1}$); C_i is concentration of element i in the leachate, (g/m^3); V is the volume of leachant, (m^3); f_i is the mass fraction of element i in the unleached glass.

Selection of Glass Compositions to Prove the Feasiblity of M-PCT

For the purpose of testing the feasibility of M-PCT as our screening tool of optimal glass compositions, glasses have been selected with wide range of leachability. Table 1 show their compositions and the normalized silicon losses using the MCC-1 leaching method [2].

EXPERIMENTAL RESULTS AND DISCUSSIONS

Fig. 1 compares total mass loss from M-PCT and normalized elemental release rate from MCC-1. The total mass loss from the glass samples SK-1 thru SK-6 was measured between 1.35 and 61.68 g/m^2 in 7 days. Meanwhile, *A.J.G. Ellison* [3] cited the element mass loss of Si as 4.0 -198.9 g/m^2 in 28 days using MCC-1 for the samples SK-1 thru SK-6. Our data shows the element mass loss of Si as 0.10-34.23 g/m^2 in 7 days using M-PCT for the samples SK-1 thru SK-6. The trends of leaching rate resemble

each other.

Fig. 2 also compares our values of pH of leachate for the samples SK-1 thru SK-6 after 7 days using M-PCT with the pH values of Allison[3] after 28 days using MCC-1. The tendency is similar in these two test conditions. The pH is assumed to be strongly affected by the mass of sodium contained in its original glass sample. In Table 3, the contents of sodium tend to increase from SK-1 thru SK-6. However, SK-3 and SK-6 are comparatively low in the sodium content. This is the reason that the samples SK-3 and SK-6 show oddly lower pH values than expected. Also, after comparing the sodium levels between SK-4 and SK-5 in Table 1, the pH is expected to show almost no difference. In this respect, MCC-1 data would represent the glass samples better with pH than M-PCT data. Fig. 3 shows the relationship between elemental loss in mg/L from M-PCT and Si loss from MCC-1. It is found that the trends of leaching rate of M-PCT resembles MCC-1. Since the total mass loss, ML, is quickly and easily measured. ML can be used to monitor the glass durability in future tests.

CONCLUSIONS

It is found that M-PCT method provides an alternative in determining the leachability of Low and Intermediate Level Radioactive Waste glass form such as the pH, and elemental loss and total mass loss. The M-PCT also speeds up the screening process for the selection of glass composition which yields high chemical durability and provides high waste loading.

REFERENCES

[1] C.M. Jantzen, N.E. Bibler, D.C. Beam, W.G. Ramsey and B.J. Waters, Nuclear Waste Glass Product Consistency Test (PCT) Method- Version 5.0(U), Westinghouse Savannah River Company Report WSRC-TR-90-539, Rev. 2 (1992)

[2] Nuclear Waste Materials Handbook, DOE/TIC-11400(1982)

[3] A.J.G. Ellison, J.J. Mazer, and W.L. Ebert, Effect of Glass Composition on Waste Form Durability: A Critical Review, ANL-94/28, Argonne National Lab.(1994)

Table 1: Composition of some typical waste glass forms

	SK-1	SK-2	SK-3	SK-4	SK-5	SK-6
SiO_2	59.92	47.17	36.59	35.59	35.17	58.87
B_2O_3	11.59	9.55	23.57	19.85	19.80	19.49
Na_2O	15.57	20.71	11.68	28.81	30.91	20.95
Al_2O_3	12.50	5.07	8.48	8.28	4.52	0.44
Fe_2O_3		9.75	19.44		9.35	
CaO	0.42	7.76	0.24	7.47	0.25	0.25
Si loss* g/m^2 in 28 days	4	11.6	20.9	56	122.6	198.9

* [3]

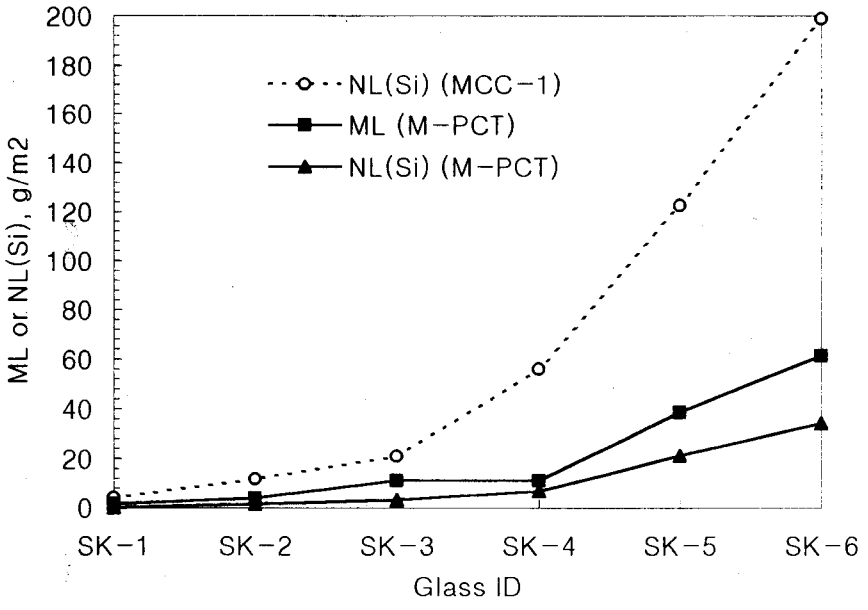

Fig. 1 Si Elemental Loss from the leaching tests MCC-1 and M-PCT and total Mass Loss from M-PCT

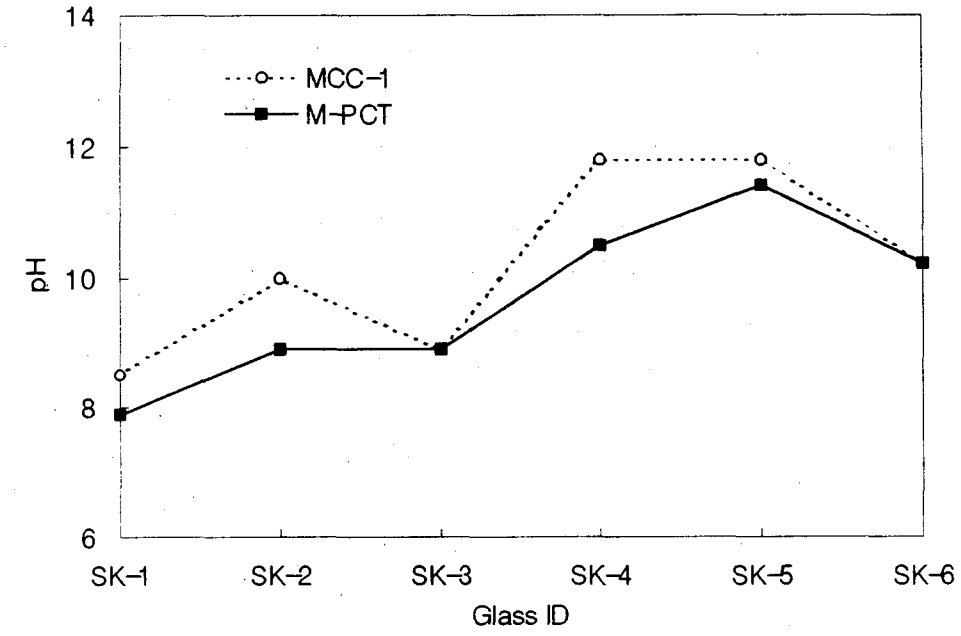

Fig. 2: pH values from the leaching tests MCC-1 and M-PCT

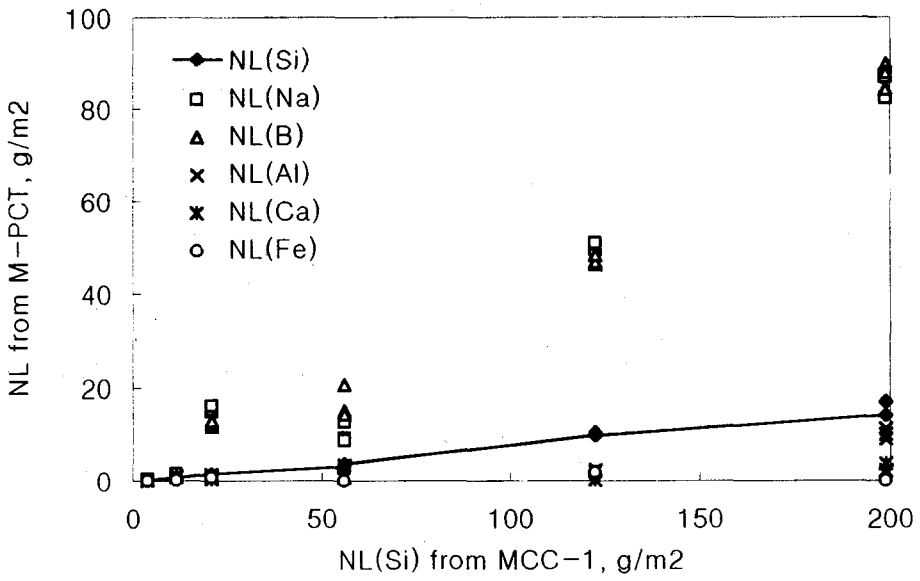

Fig. 3 Relationship between Normalized Elemental Losses from the tests MCC-1(SA/V=10m^{-1}) and M-PCT (SA/V=50m^{-1})