Decomposition for the analysis of radionuclides in solidified cement radioactive waste

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1. Introduction

Spent ion exchange resins make solid radioactive wastes when mixed with cement as solidifying material that was widely used in securing human environment from radionuclides for at least hundreds years [1]. The cumulative increase of low and medium level radioactive wastes results in capacity problem of temporary storage in some NPPs (Nuclear Power Plants) of Korea around 2008. Radioactive wastes are scheduled to be disposed in a permanent disposal facility in accordance with the Korean Radioactive Wastes Management Program. It is mandatory to identify kinds and concentration of radionuclides immobilized for transporting them from temporary storage in NPPs to disposal facility. Accordingly, the effective sample decomposition prior to radiochemical separation is prerequisite to obtain the analytical data about radionuclides in cement waste forms. The closed-vessel microwave digestion technology among several sample preparation methods is taken into account to decompose cement waste forms.

In this study, SRM 1880a (Portland cement) which is known for its certified values was used to optimize decomposition condition of cement waste forms containing nonradioactive ion exchange resins from NPP. With such variables as reagents, time, and power, the variation of the transparency and the color of the solution after closed-vessel microwave digestion can be examine. SRM 1880a is decomposed by suggested digestion procedure and the recoveries of constituents were investigated by ICP-AES and AAS.

2. Methods and Results

2.1 Decomposition of SRM 1880a

The manual for the MLS 1200 microwave digestion system recommends the addition of 2.5 ml of 65 % HNO_3, 2.5 ml of 32 % HCl, and 5 ml of 50 % HBF_4 for the digestion of 0.5 g cement [2]. However, this study shows that SRM 1880a is completely decomposed with the use of HNO_3 2 ml, HCl 8 ml, H_3PO_4 2 ml, and HF 0.5 ml for the digestion of SRM 1880a in closed-vessel microwave digestion system. The digestion program was performed in 4 steps: (1) 5 min at 250 watt, (2) 5 min at 400 watt, (3) 5 min at 500 watt, and (4) 5 min at 600 watt. The recoveries of constituents were investigated by ICP-AES and AAS, and the standard deviations presented were based on n = 4. The recoveries obtained form suggested digestion program is satisfactory for all elements with a range of 95 % obtained for Al, Ca,.. except K, Si and 100 % for the other elements (Table. 1).

Table 1. Recoveries (%) of metals obtained from 1880a (Portland cement).

Constituents	Certified Values*	Measured Values*	Recovery (%) ± STD
Al_2O_3	5.18	4.95 [a]	95.47 ± 1.06
CaO	63.83	62.29	97.59 ± 1.03
Cr_2O_3	0.007	0.011	154.82 ± 1.11
Fe_2O_3	2.81	3.04	108.35 ± 0.90
K_2O	0.92	0.74	80.68 ± 1.48
MgO	1.72	1.84	107.22 ± 1.06
Mn_2O_3	0.127	0.137	109.59 ± 0.92
Na_2O	0.19	0.18	95.73 ± 3.14
P_2O_5	0.22	-	-
SiO_2	21.3	19.58	91.93 ± 4.45
SrO	0.083	0.103	123.92 ± 1.38
TiO_2	0.25	0.27	106.37 ± 4.98

a : Average values, n = 4 * Unit : Mass fraction, %

Ce, Co, Cs, Fe, Ni, Re, and Sr (analytical elements in radioactive wastes) were added to the SRM 1880a, for the general application to radioactive cement waste forms from NPPs. The recoveries are presented in Table 2, each solution was analyzed with ICP-AES and AAS. The recovery yield for 5 different elements was over 99 %. It is indicated that proposed method is precise and accurate.

Table 2. Recoveries of 5 different elements added to SRM 1880a.

	Added (ppm)	Found (ppm)	Recovery (%) ± STD
Ce	8	8.13	101.63 ± 0.96
Co		8.00	100.03 ± 1.08
Cs		8.03	100.31 ± 2.57
Fe		8.08	101.00 ± 1.89
Ni		7.98	99.75 ± 1.65
Re		7.96	99.53 ± 1.68
Sr		7.97	99.66 ± 0.77

2.2 Decomposition of nonradioactive cement waste forms

The blank and mimic cement waste forms, nonradioactive materials were supplied by uljin nuclear power plant of Korea. The mimic cement waste forms were prepared with the use of portland cement and ion exchange resins with mixing ratio 68/32. Only portland cement is solidified and became blank cement waste forms.

The established microwave digestion program using SRM 1880a was applied to blank cement wastes forms. And 0.1 g of mimic cement waste forms were microwave digested with the use of HNO_3 8 ml, HCl 7 ml, H_3PO_4 2 ml, and HF 0.5 ml in closed-vessel. The solution obtained form acid digestion by the proposed microwave digestion method was colorless and transparent. Only the very constituents of SRM 1880a are sought after in the analysis of there two cement waste forms (Table 3.).

Table 3. The constituents of blank and mimic cement waste forms.

Constituent (wavelength)	Average (%) ± STD	
	Blank cement*	Mimic cement*
Al_2O_3	6.16 ± 2.15	3.25 ± 2.16
CaO	45.31 ± 2.31	42.91 ± 0.41
Cr_2O_3	0.01 ± 1.11	0.02 ± 9.82
Fe_2O_3	2.16 ± 1.19	2.04 ± 2.42
K_2O	0.84 ± 3.06	0.71 ± 7.34
MgO	3.08 ± 1.42	2.13 ± 2.30
Mn_2O_3	0.15 ± 1.47	0.14 ± 2.56
Na_2O	0.11 ± 1.26	0.05 ± 3.57
SiO_2	20.70 ± 2.29	13.03 ± 1.28
SrO	0.05 ± 7.40	0.03 ± 6.62
TiO_2	0.40 ± 0.93	0.19 ± 1.17

* Unit : Mass fraction, %

3. Conclusion

It was demonstrated here that SRM 1880a, blank and mimic cement waste forms can be efficiently acid-digested in a closed-vessel microwave system with the use of mixed acid. The established decomposition method using SRM 1880a could be widely used for cement waste forms from NPPs. The elemental analysis of nonradioactive blank and mimic cement waste forms by the proposed microwave acid digestion conditions is expected to be useful basic data for analysis of kinds and concentration of radionuclides immobilized.

REFERENCES

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