EXPERIMENTAL STUDY OF THERMOCHEMICAL TREATMENT OF SPENT ION-EXCHANGE RESINS

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ABSTRACT

A thermochemical treatment technique was investigated for application to the volume reduction of spent ion-exchange resins of nuclear power plants. The thermochemical treatment technique uses powder metal fuel to incinerate the resins. Insignificant amounts of soluble species were found in the slag from the thermochemical treatment of H-type cation exchange resins. The slag could be solidified firmly with magnesium-potassium-phosphate ceramics. The volume ratio of initial resin to the final ceramics form was about 10. Leaching rates of radionuclides from the ceramics were low. Thus the thermochemical treatment technique was confirmed to applicable to the volume reduction of spent ion-exchange resins.

INTRODUCTION

Activation products in the cooling water of nuclear reactors are removed by ion-exchange resins in the purification system. These spent resins are stored on-site and will be disposed underground after a volume reduction treatment in the future.

The following items are necessary for their treatment. High volume reduction efficiency is necessary to minimize the waste generation. A system with simple components and low energy consumption is necessary to minimize the cost of waste treatment. The system should be suitable for remote operation and maintenance to minimize the exposure because dose rate of the spent resins is relatively high.

The authors have investigated the application of a thermochemical treatment technique for the volume reduction of spent resins. The thermochemical treatment technique uses powder metal fuel (PMF) composed of chemically reactive materials such as magnesium. When the PMF is mixed with the wet organic substance, it interacts with the water, generates heat and decomposes the organic substances.

SIA "Radon" has investigated the applicability of the thermochemical treatment technique for some ion-exchange resins[1]-[7]. Thermochemical treatment yields slag, which is a mixture of oxides or compounds of PMF and resin constituents. Under certain conditions, soluble compounds such as magnesium sulfate are formed in the slag. Considering disposal of the slag underground as waste, attention should be paid to the behavior of any soluble species. If groundwater comes into contact with the slag, the soluble species are released from the waste forms. The species dissolved in the groundwater may change the properties of engineering and natural barriers. Thus, the amount of soluble species in the slag should be minimized during the thermochemical treatment of spent ion-exchange resins.

In this study, the authors carried out the thermochemical treatment of ion-exchange resins using several kinds of PMFs. The compositions of the slag were analyzed and the formation of soluble species was investigated. The authors also investigated a solidification method of the slag from the thermochemical treatment of ion-exchange resins which used magnesium-potassium-phosphate ceramics.

PRELIMINARY THEORETICAL CALCULATIONS

The thermochemical reaction conditions were surveyed for various PMFs by thermodynamic calculations using the "TERRA" computer code [6]. The calculations were based on the entropy maximum principle, which is true, according to the second law of thermodynamics, for any equilibrium system. Details have been described previously [6].

The composition of slag depends on the amount of PMF added to the ion-exchange resin, reaction temperature, and the amount of air supplied to the PMF and resin mixture. The compositions of reaction products under various conditions were calculated using the TERRA code.

Optimum reaction conditions were determined by minimizing the design parameter Θ defined by Eq.1.

$$\Theta = 1/ \Sigma (Ci / MPCi) \qquad \text{(Eq.1)}$$

Here Ci is the calculated concentration of the i^{th} product in off-gas, and MPCi is its maximum permissible concentration.

Based on the thermodynamic calculations, experimental conditions were decided as follows.

1) Ratio of PMF: 10-30wt%
2) Reaction temperature: 600 – 800℃
3) Molar ratio of supplied oxygen to stoichiometrically required oxygen: > 2

EXPERIMENTAL

Reagents

In this study, the cation exchange resins listed in Table I were examined. The authors focused on cation exchange resins because soluble sulfate compounds such as $MgSO_4$ might be generated during their thermochemical treatment.

Table I Composition of cation exchange resins

Name	Empirical Formula
KY-2-8	$C_{45.8}H_{51.4}S_{4.97}O_{14.9}$
KA-11	$C_{41.6}H_{42.2}S_{4.44}O_{13.3}Na_{4.44}$

The three kinds of PMFs listed in Table II were investigated. MTKD-45 and MTKSK were used for treatment of organic substances previously. The main reactive species of MTKD-45 and MTKSK were magnesium and a mixture of magnesium and calcium, respectively. B-14 was a newly prepared PMF aiming at fixing sulfate ion generated from cation exchange resin as insoluble $BaSO_4$. The composition of B-14 was determined from thermodynamic calculations.

Table II Composition of powder metal fuels

Name	Empirical Formula	Bulk Density (g/cm^3)
MTKD-45	$Al_{17.4}Mg_{19.4}K_{0.39}N_{0.39}O_{1.19}C_{1.41}H_{2.27}$	0.65
MTKSK	$Mg_{4.03}Ca_{1.47}Si_{9.08}Fe_{1.40}K_{0.58}N_{0.58}O_{1.77}C_{1.41}H_{2.27}$	0.88
B-14	$Al_{17.4}Mg_{19.4}Ba_{1.36}N_{0.39}O_{1.19}C_{1.41}H_{2.27}$	0.89

Thermochemical treatment

An outline of the experimental apparatus is shown in Fig.1. The apparatus was composed of an electric furnace, off-gas line, gas sampling port and off-gas treatment system. A cylindrical container made of stainless steel net was used for a reaction vessel. Its volume was about 190mL. For the test, the container was installed in the electric furnace according to the following.

- The ignition fuse was placed in the bottom part of the container
- A starting portion of PMF (about 15mL) was put on the bottom
- A separation net was placed on this starting portion
- The mixture of sample resin and PMF was placed on the separation net
- The ignition fuse was ignited
- The reaction container was loaded into the working volume of the electric furnace

The furnace was adjusted to 700℃ and the reaction was allowed to take place for about 20 min. Off-gas was collected periodically during the thermochemical reaction. After the furnace was turned off, the reaction container was removed. Mass and apparent volume of the slag that remained in the reaction container were determined and the slag and off-gas samples were analyzed.

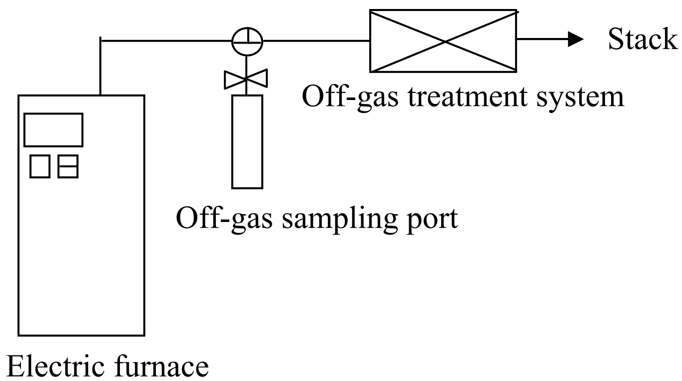


Fig.1. Outline of experimental apparatus

Immobilization of slag

All the slag formed in the thermochemical treatment contained MgO because the examined all PMFs contained magnesium as their reactive component. Thus an immobilization method which involved the formation of magnesium-potassium-phosphate ceramics was examined.

The magnesium-potassium-phosphate ceramics was formed according to the following reaction.

$$MgO + KH_2PO_4 + 5H_2O = KMgPO_4 + 6H_2O \quad \text{(Eq.2)}$$

Owing to its very poor solubility in water, this ceramics was expected to be a chemically stable matrix for radioactive wastes.

The slag-based magnesium-potassium-phosphate ceramics was obtained in the following sequence.

- Milling the slag obtained in the thermochemical treatment
- Mixing the milled slag and solid KH_2PO_4
- Tempering the mixture with water
- Molding the solution into a cubic pan

The solution hardened within several hours, and reached the maximal strength in some days.

After a 28-day solidification, cubic monolithic samples of the magnesium-potassium-phosphate ceramics were taken for their geometric surface. Samples were also used for leaching test. The specific content of ^{137}Cs and ^{90}Sr in the samples was about 10^6 Bq/kg. The leaching rates of these radionuclides were measured by a standard method.

RESULTS AND DISCUSSION

Thermochemical treatment of ion-exchange resin

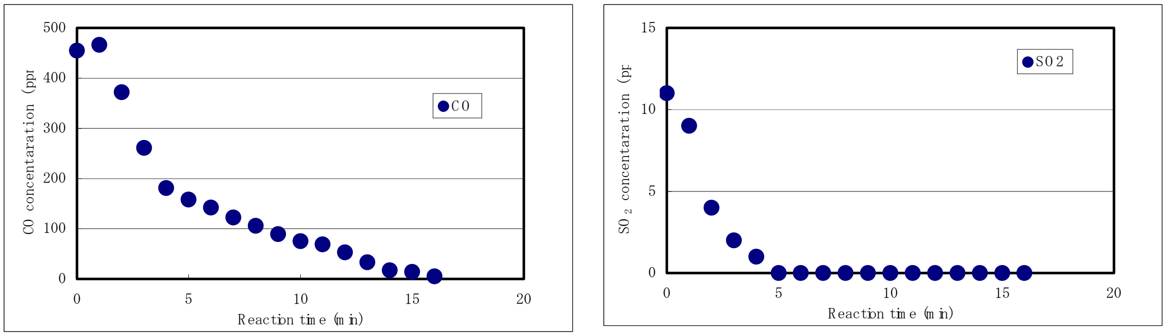
Table III summarizes the results of thermochemical treatment of cation exchange resin. A stable thermochemical reaction occurred for PMF ratio above 20%. Mass reduction factor (MRF) was defined as the ratio of initial resin weight to the slag weight. Generally, increasing the PMF ratio resulted in a decreased MRF since the PMF contained involatile materials. The MRF for H-type resin (KY-2-8) was higher than that for Na-type resin (KA-11) since sodium compounds remained in the slag of KA-11.

Table III Results of thermochemical treatment experiments

Experimental Conditions				Results of Thermochemical Treatment				
Resin	PMF	Moisture content (wt%)	PMF (wt%)	Result[a]	MRF	Slag density	SO_2 (ppm[b])	CO (ppm[b])
KA-11	MTKD-45	30	10	B	4.9	--	2	313
			20	A	2.6	0.37	1	209
			30	A	1.7	0.34	1	121
		50	10	A	3.7	0.35	1	350
			20	A	2.4	0.36	5	375
			30	A	1.6	0.33	8	306
	MTKSK	30	10	C	--	--	--	--
			20	A	2.6	0.35	8	77
			30	A	2.4	0.34	N.D.[c]	31
		50	10	C	--	--	--	--
			20	A	1.9	1.04	N.D.	213
			30	A	1.5	1.65	N.D.	108
	B-14	30	10	C	--	--	--	--
			20	A	2.5	0.30	2	57
			30	A	2.2	0.37	3	33
		50	10	C	--	--	--	--
			20	A	2.0	0.36	1	107
			30	A	1.3	0.38	2	42
KY2-8	MTKD-45	50	10	C	--	--	--	--
			20	A	8.9	0.24	2	154
			30	A	3.5	0.25	10	124
	MTKSK	50	10	C	--	--	--	--
			20	A	7.5	--	1	57
			30	A	2.7	0.37	N.D.	33
	B-14	50	20	C	--	--	--	--
			30	A	1.6	0.38	3	48

a) A: combustible, B: incomplete, C: non combustible
b) Averaged concentration in off-gas during reaction
c) Not detected

Average concentrations of SO_2 and CO in off-gas are also indicated in Table III. Typical CO and SO_2 concentration trends are shown in Fig.2. The SO_2 concentration was low, but the CO concentration was relatively high. This might be ascribed to insufficient oxygen supply into the center of the reaction container. Thus the combustion reaction was incomplete. Oxygen supply can be improved by changing the design of reaction container. Increasing PMF ratio seemed to enhance the reaction temperature, then the SO_2 concentration increased and the CO concentration decreased.



(a) Concentration of CO (b) Concentration of SO_2

Fig.2. Typical concentration trends of CO and SO_2 during thermochemical reaction
Cation exchange resin: KY-2-8, PMF: MTKD-45, Moisture content: 50%, PMF ratio: 20%

The slag from treatment of both resin types was light gray or grayish black in color, which indicated a part of carbon remained in the slag. An example of the slag particle size distribution is indicated in Fig.3. In some cases, the slag included big granules, but it was so porous that it could be pulverized easily.

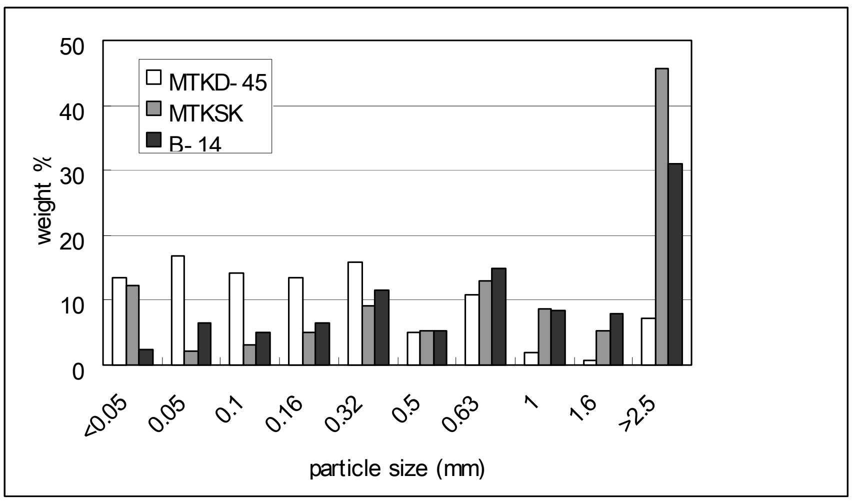


Fig.3. Example of granulometric composition of the slag
Cation exchange resin: KY-2-8, Moisture content: 50%, PMF ratio: 20%

Representative chemical compositions of slag are given in Table IV. The quantity of sulfate was higher in the slag of Na-type resin than H-type resin. The sulfate was considered to exist in the form of Na_2SO_4 in the slag of Na-type resin. The amount of sulfates in the slag decreased with increasing PMF ratio. This tendency was associated with the reaction temperature. The higher the PMF fraction, the higher the reaction temperature, so more the sulfur was carried away in the off-gas.

Table IV Chemical Compositions of slag from thermochemical treatment

Experimental Conditions				Chemical Composition of Slag				
Resin	PMF	Moisture content (wt%)	PMF (wt%)	MgO	Al_2O_3	Na_2O	K_2O	SO_4^{2-}
KA-11	MTKD -45	30	20	21.7	15.7	12.8	0.8	20.6
			30	34.9	16.1	17.4	0.7	13.7
		50	20	24.3	26.4	16.9	1.0	14.9
			30	19.5	27.0	7.7	0.9	5.7
KY2-8	MTKD -45	50	20	28.6	24.2	-	1.0	4.3

The results of X-ray diffraction analysis of slag are summarized in Table V. Na_2SO_4 was found in the slag of Na type resin (KA-11), but no significant amount of soluble species was found in the slag of H-type resin (KY-2-8).

Table V X-ray Diffraction analysis results of slag from thermochemical treatment

Experimental Conditions				Results of Analysis	
Resin	PMF	Moisture content (wt%)	PMF (wt%)	Major Components	Minor Components
KA-11	MTKD-45	30	20	MgO, $MgAl_2O_4$, Na_2SO_4	$Na_6Mg(SO_4)_4$
			30	MgO, $MgAl_2O_4$, Na_2SO_4	$Na_6Mg(SO_4)_4$
		50	10	MgO, $MgAl_2O_4$, Na_2SO_4	$Na_6Mg(SO_4)_4$
			20	MgO, $MgAl_2O_4$, Na_2SO_4	$Na_6Mg(SO_4)_4$, K_2CO_3
			30	MgO, $MgAl_2O_4$	Na_2SO_4
	MTKSK	30	20	Na_2SO_4, $MgAl_2O_4$, MgO, $Na_2Si_2O_5$	Fe_3O_4
			30	$MgAl_2O_4$, Na_2SO_4, MgO, $Na_2Si_2O_5$	Fe_3O_4
		50	20	$Na_2SO_4 \cdot 10H_2O$, $MgAl_2O_4$, MgO, Na_2SO_4, $Na_2Si_2O_5$	Fe_3O_4
			30	MgO, $MgAl_2O_4$	Na_2SO_4, $Na_2Si_2O_5$, Fe_3O_4
	B-14	30	20	$MgAl_2O_4$, Na_2SO_4, MgO, $BaSO_4$, $BaAl_{12}O_{19}$	MgAlO
			30	$MgAl_2O_4$, Na_2SO_4, MgO, $BaSO_4$, $BaAl_{12}O_{19}$	MgAlO
		50	20	$MgAl_2O_4$, $Na_2SO_4 \cdot 10H_2O$, Na_2SO_4, MgO, $BaSO_4$	$BaAl_{12}O_{19}$
			30	$MgAl_2O_4$, MgO, Na_2SO_4, $BaSO_4$	$BaAl_{12}O_{19}$, MgAlO
KY2-8	MTKD-45	50	20	MgO, Al, $MgAl_2O_4$	MgAlO
			30	MgO, $MgAl_2O_4$, Al	MgAlO
	B-14	50	30	Al, MgO, $MgAl_2O_4$	$BaSO_4$, BaS, $BaAl_2O_4$, Al_2O_3, MgAlO

Immobilization of slag

Table VI shows the strength of the magnesium-potassium-phosphate ceramics form with the inclusion of slag. Sufficient strength could be obtained under appropriate conditions.

Table VI Compressive Strength of ceramics including slag

Slag content (wt%)	Compressive Strength (MPa)
50	4.6
65	4.9
70	8.5
75	2.4

The volume ratio of initial resin to final ceramics form, namely volume reduction factor, was about 10.

Table VII summarizes the leaching rates of cesium and strontium from magnesium-potassium-phosphate ceramics. The radionuclide leaching rates were.

Table VII Leaching rates of radionuclides from magnesium-potassium-phosphate ceramics

Thermochemical Treatment Conditions				Ceramics Form Preparation Conditions		Results of Leaching Test	
Resin	PMF	Moisture content (wt%)	PMF (wt%)	MgO content in slag (wt%)	Slag content in sample (wt%)	Leaching Rate of Cs (g/cm^2 day)	Leaching Rate of Sr (g/cm^2 day)
KA-11	MTKD	30	20	22	70	$5x10^{-4}$	$7x10^{-4}$
			30	35	60	$3x10^{-4}$	$2x10^{-4}$
		50	20	24	70	$6x10^{-4}$	$6x10^{-4}$
			30	24	70	$8x10^{-4}$	$6x10^{-4}$

CONCLUSION

The thermochemical treatment technique was applied for the volume reduction of cation exchange resin. The most important results were as follows:

(1) Na_2SO_4 was generated in the slag from the thermochemical treatment of Na-type cation exchange resin. On the other hand, an insignificant amount of soluble species was found in the slag from H-type resin.
(2) The slag could be solidified firmly with magnesium-potassium-phosphate ceramics. The volume reduction factor of cation exchange resin by the thermochemical treatment and ceramics solidification was about 10.
(3) Leaching rates of radionuclides from the immobilizing ceramic form were low. Hence the thermochemical treatment technique was concluded applicable to the volume reduction of spent ion-exchange resins of nuclear power plants.

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