

Decontamination of Radioactive Contaminants Using Reactive Microemulsion of Organic Acid in Supercritical Carbon Dioxide

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In order to decontaminate radioactive waste, citric or oxalic acids dispersed in SF-CO₂ in the form of a microemulsion by polyoxyethylene (2) nonylphenyl ether (NP-2) was applied to ferrites present on clothes and pipes at 323 or 353 K, 25 MPa. Citric acid in the core of the microemulsion was effective for the dissolution of ferrite on the pipes at 353 K. The addition of a reducing agent, Fe(II), effectively removed CoFe₂O₄ from clothes. Oxalic acid was also effective for the removal of CoFe₂O₄ from clothes.

INTRODUCTION

In the nuclear industries, the generation of radioactive wastes has become a serious problem. A large number of pipes and valves are used in the nuclear power plants for the water cooling system at high temperature. On the internal surface of these components, radioactive contaminants are accumulated and fixed. Typical constituents of the contaminants are identified as nickel-substituted ferrite (Ni_xFe_{3-x}O₄) and chromium and nickel-substituted ferrite (Ni_xFe_{3-x-y}Cr_yO₄) [1]. The contaminated pipes and valves are replaced with new ones during the maintenance period, and then discharged as nuclear waste. Some of the contaminants are transferred to clothes during the maintenance operation. The chemical dissolution of the ferrites could remove the radioactive contaminants from the surface of the contaminated materials. However, this treatment will result in the generation of secondary wastes. The generated volume amount of the secondary waste is usually greater than that of the original contaminants.

For the volume reduction of the wastes, we propose a new method to remove the radioactive contaminants from the materials using a reactive microemulsion of organic acids in supercritical carbon dioxide (SF-CO₂). Citric and oxalic acids, which have the ability to dissolve ferrites, were utilized in the form of a microemulsion in SF-CO₂. The organic acid solutions were dispersed into SF-CO₂ by polyoxyethylene (2) nonylphenyl ether (NP-2). The organic acid, citric and oxalic acids, and NP-2 consist of carbon, hydrogen and oxygen, and they do not contain any troublesome elements, such as fluorine. In this study, we used them to remove ferrites from clothes and pipes in order to examine their applicability for the

decontamination of waste materials.

I- EXPERIMENTAL

I-1) Organic Acids and Surfactants

Citric acid (Wako Pure Chemical Industries, Japan) and oxalic acid (Wako Pure Chemical Industries, Japan) were employed as the reactive organic acids. Polyoxyethylene (2) nonylphenyl ether, NP-2 (Wako Pure Chemical Industries, Japan) was used to disperse these acids in SF-CO₂ and form a microemulsion. It is well known that fluoric surfactants effectively form a microemulsion in SF-CO₂ [2, 3]. In this study, one of the fluoric surfactants, pentadecafluorooctanoic acid, PFOA (Tokyo Kasei Kogyo, Japan) was used as an acid as well as a surfactant. This chemical contains both fluoric and carboxyl groups, and was compared to the NP-2 and an organic acid.

I-2) Preparation of Simulated Contaminated Materials

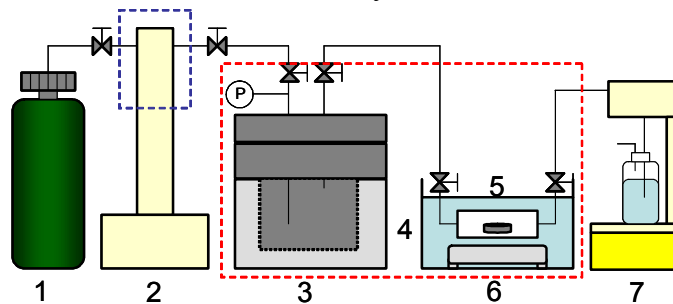
The contaminated pipe and clothes were simulated using iron pipes whose surface was covered with non-radioactive ferrite and white cotton clothes on which non-radioactive cobalt-substituted ferrite (CoFe₂O₄) was fixed, respectively. The ferrites were prepared as follows: a carbon steel pipe whose diameter and length were 10 mm and 5 mm, respectively, was heated with steam at 1273 K for 2 min. As for the cobalt-substituted ferrite, Co(NO₃)₂, FeSO₄ and NaOH solutions were mixed in a beaker, and the precipitants formed in the beaker was spotted on a piece of cloth, and dried at 378 K for 2 hr.

I-3) Observation of Phase Behavior

The phase behaviors of these mixed systems containing SC-CO₂ + NP-2 or SC-CO₂ + PFOA were studied using a view-cell whose internal volume was 60 cm³ (Taiatsu Glass Industries, Japan) in a similar manner as described in the literature [4, 5].

I-4) Decontamination Procedures

Figure 1 illustrates the apparatus used for the decontamination experiment. In the vessel whose volume was 100 cm³, the surfactant and one of the organic acids were well-mixed with SF-CO₂ in order to produce the homogeneous fluid at 25 MPa, 323 or 353 K. The simulated pipe sample was set in the column whose volume was 7.7 cm³, and then the valve between the vessel and the column was opened to bring the sample into contact with the supercritical fluids. The decontamination was carried out by ultrasonic irradiation (Honda Electronics Co.,



1: CO₂ cylinder, 2: Syringe pump, 3: Vessel (100 cm³), 4: Water bath, 5: Column (7.7 cm³), 6: Sonoreactor, 7: High pressure regulator

Figure 1 Apparatus for decontamination experiment

Ltd., WS-600) at 0.31 W cm^{-2} for 4 hr; *i.e.* a static decontamination for 1 hr and a dynamic decontamination for 3 hr. For the clothes, we set the sample in the vessel, whose internal volume was 100 cm^3 , with the surfactant and organic acid, and carried out a static decontamination for 1 hr and a dynamic decontamination for 2 hr without ultrasonic irradiation. The experimental conditions are summarized in Table 1.

For the evaluation, the weight of the ferrite fixed on the surface of the pipe was measured after dissolving all iron base of pipe by HNO_3 of 3 mol dm^{-3} . As for the cotton specimen, the amount of cobalt on the surface was determined by an ICP-AES (Shimadzu, ICPS-7000) analysis.

Table 1 Condition for decontamination

System	Surfactant	Core Materials	Pressure [MPa]	Temperature [K]
	[g]	[cm ³]		
NP-2/C.A.	NP-2	1 M Citric acid	25	323 or 353
	0.330	0.165		
NP-2/C.A.+Fe(II)	NP-2	1 M Citric acid 0.2 M FeSO ₄	25	323 or 353
	0.330	0.165		
NP-2/O.A.	NP-2	1 M Oxalic acid	25	323 or 353
	0.330	0.165		
PFOA/H ₂ O	PFOA	Water	25	323 or 353
	0.768	0.165		
Neat CO ₂	-	-	25	323 or 353

II- RESULTS AND DISCUSSION

II-1) Phase Behavior

In order to determine the experimental conditions, we observed the phase behaviors of SF-CO₂, the surfactants and the aqueous solutes. Figures 2 (a) and (b) show the phase behaviors of SF-CO₂, (a) NP-2 and citric acid, and (b) PFOA and water. The abscissa represents the molecular ratio of water to that of PFOA, *i.e.*, w . According to these figures, the pressure required for a single phase formation increased with an increase in the temperature. The density of the solvent, CO₂, seemed to effect this phenomenon. On the other hand, the

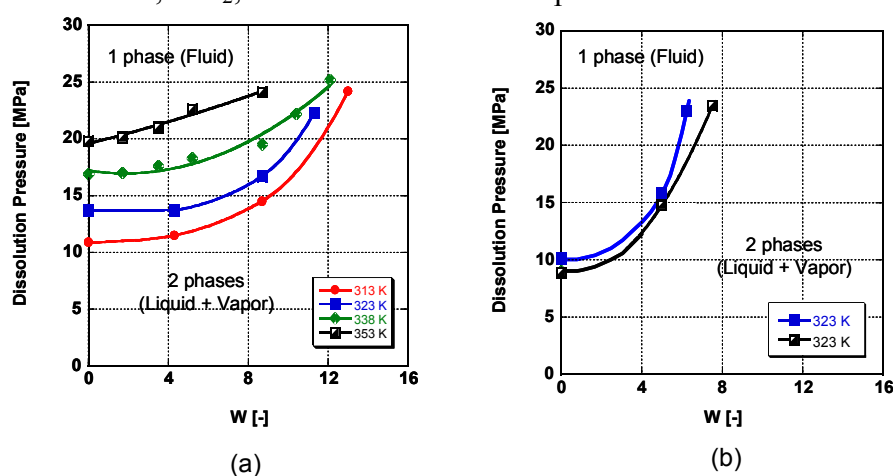


Figure 2 Phase behavior
(a) NP-2 and citric acid, (b) PFOA and water

dissolution pressure increased as w increases; higher pressures were necessary to dissolve larger amounts of the aqueous materials into the SF-CO₂.

Taking into account these observations, we selected the following conditions for the decontamination experiments as shown in Table 1: $w = 8.7$ for NP-2, and $w = 5$ for PFOA.

II-2) Decontamination of Pipes

The results of the decontamination experiments for the pipes are shown in Table 2. There was no change in the appearance of the sample pipe after the decontamination treatments with both systems of NP-2/citric acid and PFOA/H₂O at 323 K. By increasing the temperature, the removal amounts of ferrite increased; 56 and 92 % for NP-2/citric acid and PFOA/H₂O at 353 K, respectively. It was found that citric acid in the water core of the microemulsion and PFOA effectively dissolved the ferrite. The removal ratio by the treatment with the NP-2/citric acid system was lower than that of the PFOA/H₂O. However, the NP-2/citric acid system was considered to be suitable for the decontamination. The amount of NP-2 in the system was lower than that of PFOA as shown in Table 1. It was considered that the removal ratio would be further improved by increasing the concentration of the citric acid or repeating the treatment.

Photos of one of the samples are shown in Figure 3. The surface of the pipe was covered by black ferrite before the decontamination treatment (Figure 3 (a)). After the treatment, the gray iron surface appeared obviously (Figure 3 (b)). The contaminants on the surface were removed without any significant damage to the base materials. The microemulsion seemed to permeate the ferrite layer, and react with the surface iron layer of

Table 2 Removal of ferrite from the surface of pipe

System	Temperature [K]	Ferrite [mg]		Removal [%]
		Before decontamination	After decontamination	
NP-2/C.A.	323 K	15.7 ± 3.1	15.6	1
	353 K	15.0 ± 3.0	6.6	56
PFOA/H ₂ O	323 K	16.0 ± 3.1	19.4	0
	353 K	15.6 ± 3.1	1.2	92
Neat CO ₂	323 K	17.4 ± 3.5	16.9	3
	353 K	16.3 ± 3.3	21.6	0



(a)



(b)

Figure 3 Pipe sample
(a) Before, and (b) after decontamination

the pipe. This point was considered to be one of the differences in the common treatment involving as aqueous acid dissolution. The reduction of the secondary waste might be achieved using the reactive microemulsion in SF-CO₂.

II-3) Decontamination of Cotton

Table 3 shows the results of the decontamination experiments for cotton. Although the removal ratio with the PFOA/H₂O system was 35 %, that with the NP-2/citric acid was only 4 %. When ferrite was removed from the pipe with the NP-2/ citric acid, the oxidation of the base iron with citric acid might cause a reduction of the ferrite thus resulting in the dissolution. In order to add the reducing agent, Fe(II) was added to the NP-2/ citric acid system. The removal ratio was improved up to 36 %. On the other hand, when oxalic acid, which has a stronger reducing power, was used in stead of the citric acid, the removal ratio increased to 73 %. Oxalic acid also seemed to be effective for the decontamination, especially for the materials which had no oxidized substances.

Table 3 Removal of ferrite from the surface of clothes

System	T [K]	Amount of Cobalt [mg]		Removal [%]
		Before decontamination	After decontamination	
NP-2/ C.A.	353	36.3±0.2	34.7	4
NP-2/C.A.+Fe(II)	353	36.3±0.2	23.3	36
NP-2/O.A.	353	36.3±0.2	9.7	73
PFOA/H ₂ O	353	36.3±0.2	23.6	35
Neat CO ₂	353	36.3±0.2	35.1	3

CONCLUSION

Citric and oxalic acids dispersed in SF-CO₂ in the form of a microemulsion by polyoxyethylene nonylphenyl ether (NP-2) were applied to ferrites on clothes and pipes at 323 or 353 K and 25 MPa. Citric acid in the core of the microemulsion was effective for the dissolution of ferrite on the pipe at 353 K. The microemulsion seemed to permeate the ferrite layer, then oxidize the surface iron layer of the pipe thus resulting in the dissolution of the ferrite. The addition of the reducing agent, like Fe(II) effectively removed CoFe₂O₄ from clothes. Not only citric acid, but also oxalic acid was effective for the removal of CoFe₂O₄ from clothes.

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