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# Decontamination of Radioactive Contaminants Using Liquid and Supercritical CO<sub>2</sub>

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## 1. Introduction

Nuclear power plants have been used as one of major sources of energy all over the world [1]. Nuclear energy is intrinsically clean in environmental viewpoints since it is a highly-concentrated energy source generating much less amount of wastes compared to chemical energy sources such as coals and oils. However, nuclear energy produces inevitable dangerous radioactive wastes. Volume reduction of radioactive wastes is desirable, and additionally should be done in environmentally favorable ways. We introduce CO<sub>2</sub> as a cleaning solvent for the decontamination of radioactive contaminants. The subjects for decontamination are diverse – clothes, parts, equipments, tools, solid/liquid wastes, and soil. Main target elements are Co, Sr, Cs, Tc and actinides with chemical forms of metal spikes, oxides, hydroxides and metallic salts [2,3].

Decontamination technology should assist in minimizing waste volume by concentrating the radioactivity of the wastes. However, generation of secondary radioactive waste during decontamination processes produces another problem. If we apply carbon dioxide as a cleaning medium, the secondary waste can be minimized because of the ease of CO<sub>2</sub> recycle (simply depressurize and pressurize again). This is why CO<sub>2</sub> is gaining attention as an alternative solvent for decontamination of radioactive contaminants. However, CO<sub>2</sub> is non-polar, and allows very limited solubility of polar materials such as metallic ions. To make it possible to dissolve polar and ionic materials in CO<sub>2</sub>, we developed water-in-CO<sub>2</sub> micro- and macroemulsions. Water-in-CO<sub>2</sub> microemulsion can dissolve most of the polar and ionic substances as well as non-polar substances because aqueous and organic phases can be dispersed in CO<sub>2</sub> uniformly at the given sufficient stabilization of the interface.

This chapter shows the surface decontamination of radioactive specimens based on CO<sub>2</sub> micro- and macroemulsions. Since most radioactive contaminants contain a variety of metal oxides or metal salts, it is needed that acid solution instead of water be added to the emulsions. We briefly reviewed past works regarding the microemulsion of water in CO<sub>2</sub> and its applications. Then, the formation regions of microemulsions with small amounts of water (or acid solution) were mentioned. And, ultrasound effects on the stability of micro- and macroemulsions were explained. Then, we showed the applications of micro- and macroemulsions of acid in CO<sub>2</sub> in the dissolution test of Cu-coated parts (nuts) and real contaminated radioactive samples. And the applicability of this technique was discussed.

## 2. Reviews on the application of micro- and macroemulsions in CO<sub>2</sub>

In 1990s, much experimentation attempted to identify surfactants capable of forming water in liquid/supercritical CO<sub>2</sub> microemulsions. K. A. Consani and R. D. Smith [4] reported that the solubilities of over 130 surfactants were tested in supercritical CO<sub>2</sub> at 50°C and pressures of 100~500 bar. Consequently, most ionic surfactants (e.g., salts, acids, quaternary ammonium compounds and alkyl phosphate salts) were found to be relatively insoluble in CO<sub>2</sub>. This is mainly due to the fact that the majority of the amphiphiles evaluated were found to have minimal solubility in CO<sub>2</sub>. However, nonionic surfactants with suitable hydrocarbon chain length appeared to be able to exhibit reasonable solubility in liquid/supercritical CO<sub>2</sub> at moderate pressure.

On the other hand, owing to favorable solubility parameters, certain fluorocarbons and to a lesser extent silicon, a few surfactants dissolve in CO<sub>2</sub>. Based on the fact that fluorocarbons and CO<sub>2</sub> are compatible, Beckman's group designed the first effective fluoro-surfactants for CO<sub>2</sub> [5]. Next, the fluorinated surfactants variously synthesized by Johnston [6-10] and Desimone [10, 11] seem to have high solubility in supercritical CO<sub>2</sub>.

A micelle is an aggregation (or cluster) of surfactant molecules. The molecule must have a polar 'head' and a non-polar hydrocarbon chain 'tail'. When this type of molecule is added to water, the non-polar tails of the molecules clump into the center of a ball like structure called a micelle, because they are hydrophobic. In a reverse micelle, the polar groups of the surfactants are concentrated in the interior and the lipophilic groups extend towards and into the non-polar solvent (Fig. 1). At certain water-to-surfactant ratios (W), water will be incorporated into the core of the micelle, generating a nano-droplet of water in a CO<sub>2</sub> solution (i.e., microemulsion). These droplets are extremely small, ranging from 5 to 100 nm in diameter. The nano-sized water droplet is carried to surfaces by the supercritical CO<sub>2</sub>, allowing extraction of metals in a way not possible with liquid/ supercritical CO<sub>2</sub> only. Therefore, the reverse micelle may be used as an environmentally benign solvent in synthesis of nanometer-sized metal catalysts, cleaning of precision parts and extraction of polar species. Generally, microemulsions are clear, thermodynamically stable solutions.

The macroemulsions are a dispersion of droplets of one liquid in another with which it is incompletely miscible. As shown in Fig 2, macroemulsions of droplets of an organic liquid (a 'CO<sub>2</sub>' like oil) in an aqueous solution are indicated by the symbol CO<sub>2</sub>-in-water (C/W) and macroemulsions of aqueous droplets in an organic liquid as water-in-CO<sub>2</sub> (W/C). In macroemulsions the droplets exceed 0.1 μm [12]. The relative sizes are shown in detail in Fig. 3.

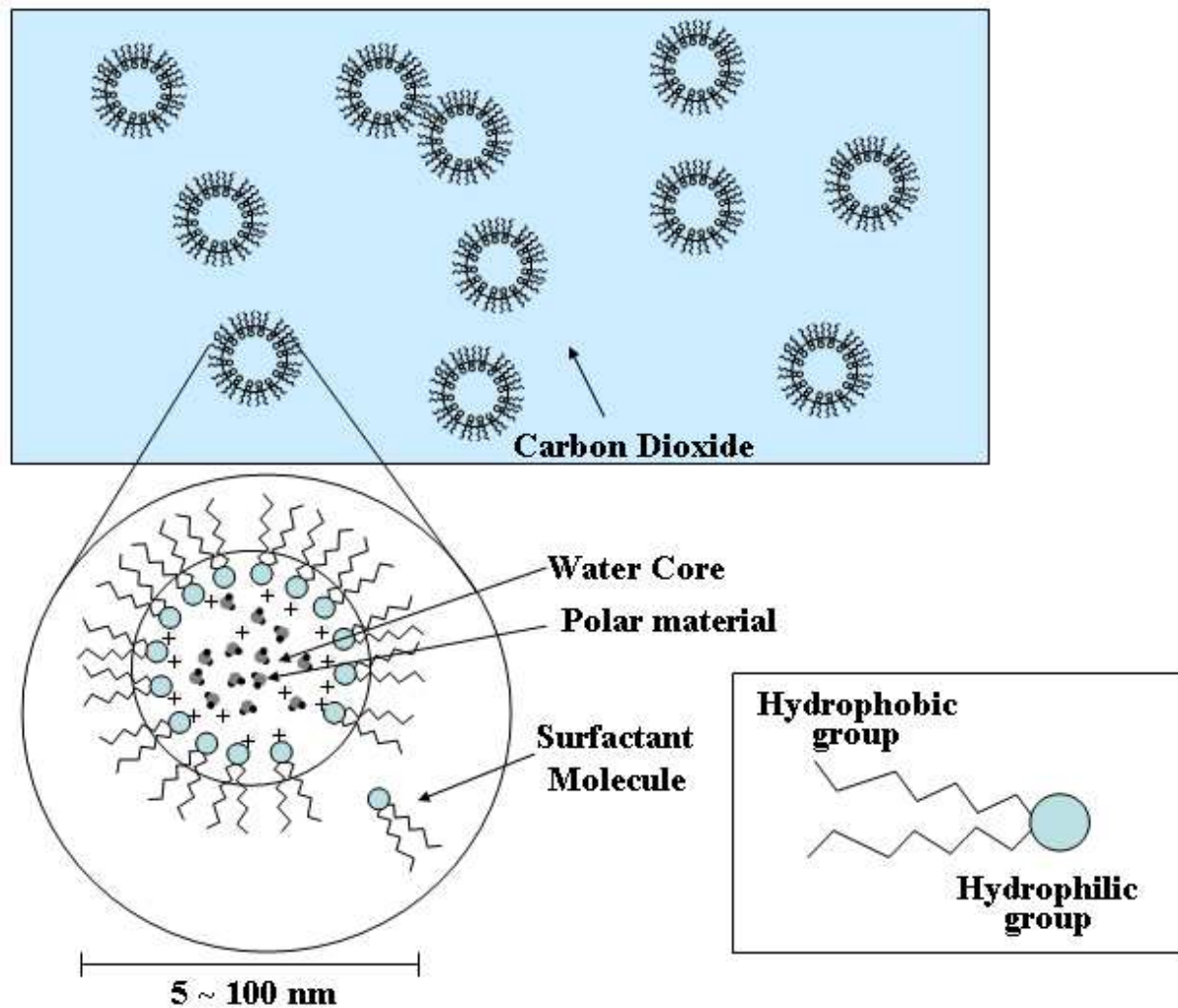


Fig. 1. Structure of reverse micelles and formation of microemulsions in CO<sub>2</sub>.

Microemulsions are thermodynamically stable, and typically consist of dispersed phase droplets of 5 to 100 nm in diameter. In contrast to microemulsions, macroemulsions are thermodynamically unstable, often requiring considerable energy input to induce their formation, and existence. Furthermore, macroemulsions may be formed with higher interfacial tensions between water and oil (or CO<sub>2</sub>) than in the case of microemulsions, and thus have lower values of surfactant adsorption at the interface. Therefore, emulsions may be formed for a wide range of surfactant concentrations [13].

There is increasing interest in using reverse micelle and microemulsions for many applications such as solutions for enhanced oil recovery, for the separation of proteins from aqueous solutions, as media for catalytic or enzymatic reactions, and as mobile phases in chromatographic separations.

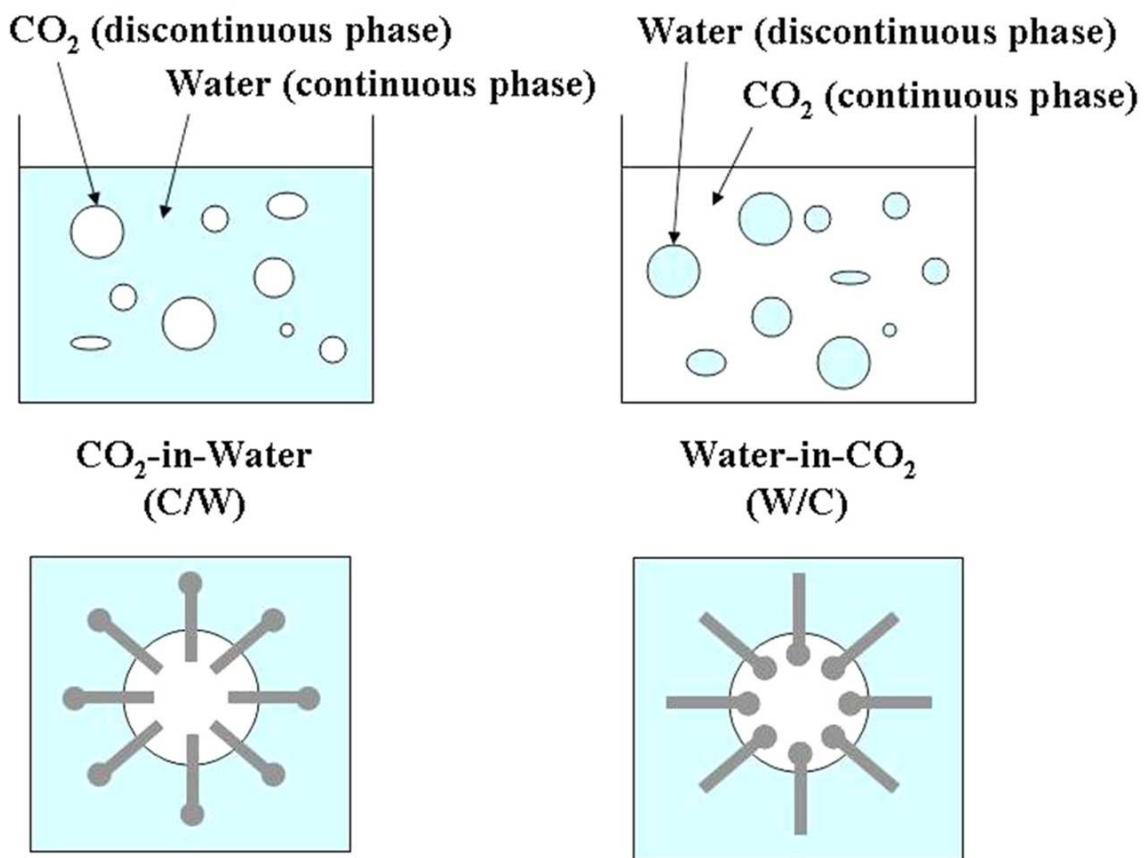


Fig. 2. Structures of C/W and W/C emulsions in CO<sub>2</sub>.

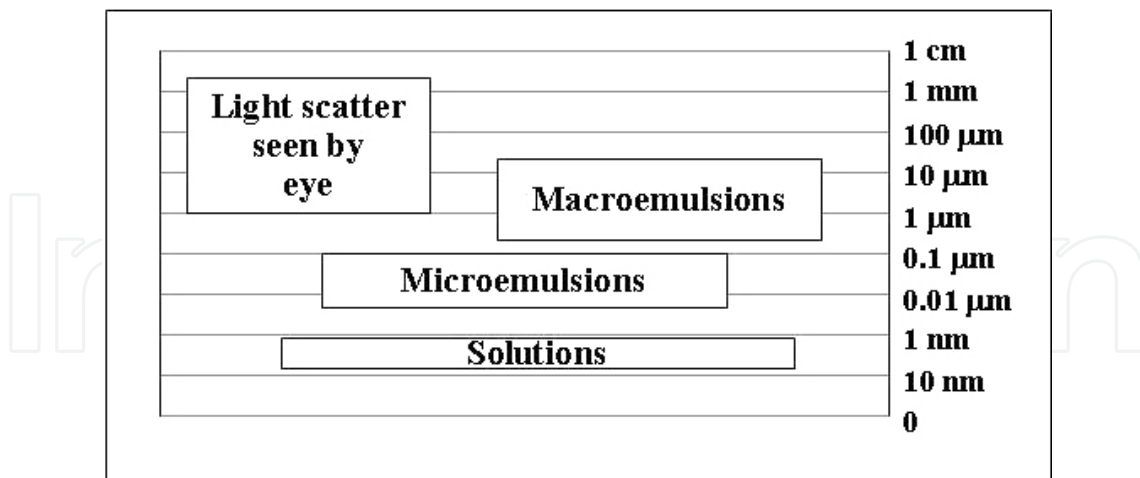


Fig. 3. Size ranges of micro- and macroemulsions [12].

In 1987, Fulton and co-workers reported the first observations of microemulsions in supercritical fluid [14]. The formation of reverse micelles and water-in-oil (W/O) microemulsions in supercritical fluids using the surfactant sodium bis(2-ethylhexyl) sulfosuccinate (AOT). Fluids that are supercritical at moderate temperatures and pressures include ethane ( $T_C=32.4^\circ\text{C}$ ,  $P_C=34.8\text{bar}$ ), propane ( $T_C=97^\circ\text{C}$ ,  $P_C=43.3\text{bar}$ ), and xenon



( $T_c=16.6\text{ }^\circ\text{C}$ ,  $P_c=58.4\text{ bar}$ ) [14-16]. Also, the properties of microemulsions such as structure, microemulsion size, and the solvent environment of AOT were measured by using dynamic light scattering, small angle X-ray scattering (SAXS) and view cell determinations of phase behavior [17,18].

Johnston and co-workers initially studied the phase behavior of hydrophilic substances such as proteins and amino acids and described this as microemulsions with AOT. They reported large effects on the droplet size and phase behavior of microemulsions in compressible liquids with changes in four principal variables such as pressure, temperature, salinity, and molecular volume of the alkane solvent [19-21]. Later, to favor bending of the interface around water, and to prevent liquid crystal formation, hybrid surfactant with a fluorocarbon and hydrocarbon tail,  $\text{C}_7\text{F}_{15}\text{CH}(\text{C}_7\text{H}_{15})\text{OSO}_3^-\text{Na}^+$ , was newly synthesized. The formation of microemulsions with a fluorocarbon-hydrocarbon hybrid surfactant must have been due primarily to the presence of the fluorocarbon tail, given the lack of success of many nonfluorinated surfactants [22]. In 1996, his group developed a new fluoroether surfactant, ammonium carboxylic perfluoropolyether (PFPE), to form stable reverse micelles in supercritical CO<sub>2</sub> [23]. The water cores within these microemulsions were probed by elegant techniques including X-band electron paramagnetic resonance (EPR), time-resolved fluorescence depolarization [24], UV-VIS spectroscopy, and FTIR [25].

Water-in-CO<sub>2</sub> macroemulsions may be substituted for toxic organic solvents in chemical processing. Macroemulsions have been used for phase-transfer reactions between CO<sub>2</sub>-soluble substrates and hydrophilic nucleophiles. Further studies of the mechanism of emulsion stabilization are needed for the rational design of surfactants for this newly emerging field. However, the formation of macroemulsions in CO<sub>2</sub> has been challenging due to its weak van der Waals forces, as reflected by its low polarizability per unit volume. To date, a majority of the investigation into the formation of macroemulsions in CO<sub>2</sub> has focused on the development of surfactants. Johnston found that water-in-supercritical CO<sub>2</sub> (W/C) emulsions were formed with a variety of surfactants such as fluorinated [26, 27], block copolymer [28-30], nonionic polymer [31], and hydrocarbon [32].

Micro- and macroemulsions have been used to solubilize hydrophilic substances in CO<sub>2</sub> (e.g., salts, water soluble catalysts, metal nano-particles, electroplating, metal ions, electroactive probes, proteins, and enzymes). McCleskey [33, 34] demonstrated the extraction of metal ions from a variety of solid substrates using microemulsions in supercritical CO<sub>2</sub>. Microemulsions are especially advantageous for the extraction of metals, because the amount of water required is only proportional to the amount of metal to be extracted, not to the amount of waste to be cleaned. Liu [35] also used microemulsions with nonionic surfactant (X-100) to extract copper ions. More than 99% of the copper is extracted from filter paper surface, and 81% of the used surfactant was recovered and generated. Water-in-microemulsions were presented as a new strategy for promising method of metal ion extraction.

Sawada applied microemulsions for dyeing fiber in supercritical CO<sub>2</sub>. Pentanethylene glycol *n*-octyl ether and a co-surfactant were used for forming the microemulsions [36]. Co-surfactants generally make the chemical process complicated. Sawada also used one type of surfactant such as PFPE to make microemulsions in CO<sub>2</sub>[37].

Yonker [38] has demonstrated membrane separations with reverse micelles in near- and supercritical fluid solvents. Reverse micelles were formed and used for the separation of polar, water-soluble macromolecules in solvents. This technique directly extends the capabilities of membrane separations in supercritical fluids to include both non-polar and polar molecules.

Wai [39] reported that metal nano-particles were synthesized within the core of microemulsion droplets. Microemulsions containing  $\text{AgNO}_3$  were stabilized by a mixture of AOT and PFPE- $\text{PO}_4$ , acting as surfactant and co-surfactant, respectively. On addition of a reducing agent to the microemulsion system, silver particles were formed inside the emulsion droplets and the particle dimensions were controlled by the size of the water cores. The metal nano-particles formed in this way can be used as in situ catalysts for chemical reactions in the fluid phase, for example the hydrogenation of olefins [40]. Also, new nanomaterials such as CdS and ZnS [41] were obtained using the mixture of two microemulsions containing different metal ions in their micelle water cores.

Sone [42-44] found that electroplating using nickel could be performed in a macroemulsion of supercritical  $\text{CO}_2$  with nonionic or anionic surfactants. Generally, conventional wet plating methods produce lots of liquid toxic waste, which need expensive waste treatment systems. And the products usually have surface defects such as pinholes and cracks by hydrogenation. By comparison, better quality nickel films have been produced by electroplating in macroemulsion in supercritical  $\text{CO}_2$ . The electroplated film has a good and uniform with a smaller nano-grain size, and a significantly higher Vickers hardness.

Our group has also found that Ni electroplating could be carried out in the emulsion of supercritical  $\text{CO}_2$  formed by ultrasound. Emulsion of nickel plating solution in  $\text{CO}_2$  was formed by the agitation from an ultrasonic horn. Electroplating of Ni on the iron sheet was successfully made. The coated surface was very uniform without any pinholes or cracks due to hydrogenation. Only 5-10% of electroplating solution was needed for Ni plating compared to general wet plating. The used electroplating solution could be reused after a recovery process [45].

### 3. Experimental section

#### 3.1 Chemicals and specimens

We selected the two types of surfactants. One is sodium bis(2,2,3,3,4,4,5,5-octafluoro-1-pentyl)-2-sulfosuccinate (fluorinated-AOT), a fluorinated ionic surfactant synthesized by our group [41]. The other is the ethoxylated nonyl phenol series (NP-series), a non-ionic surfactant which is commercially available. NP-series was supplied by Nicca Korea Company in Korea. The surfactants were NP-2, 3, 4, 6, 8, 10, and 16. Nitric acid and organic solvents (HPLC grade) were obtained from Ducksan Pure Chemical Co. Ltd. Inorganic acids such as oxalic and citric acids were obtained from Aldrich Chemical Co.

Cu-coated parts (nuts) plated by electroplating were prepared. The conditions for electroplating were as follows; 2.5 mA/dm<sup>2</sup> for 7minutes on a nut (surface area: 4.4±0.5 cm<sup>2</sup>) under Cu electroplating solution. Real radioactive parts (bolts, nuts, connectors), contaminated by radioactive nuclides (such as Co-60, Cs-137, Mn-54, etc), were obtained from Unit 1 of the Wolsung and Unit 2 of the Kori Nuclear Power Plants during overhaul periods.

### 3.2 Apparatuses for measurements

A variable volume cell (from 4.2mL to 22.4mL, Hanwoul Eng.) was used to measure the solubility of a subject in a high pressure media. The known amounts of a surfactant was placed into the cell, and heated to a goal temperature. CO<sub>2</sub> was introduced by a syringe pump (260D, ISCO, USA). The solubility or cloud point could be determined by a direct visual observation through sapphire windows placed on both sides. The deviation of temperature was  $\pm 0.5^\circ\text{C}$  and that of pressure was  $\pm 1\text{bar}$ .

Two agitation methods were used to form a stable microemulsion – stirring by a magnetic bar and direct agitation by an ultrasonic horn. Stirring agitation was obtained by putting a magnetic bar into the reactor cell which was located on a magnetic rotator. We made a high-pressure cell containing an ultrasonic horn that was connected to a sonar vibrator outside (Fig. 4). The frequency of the horn was 20kHz. The amount of energy dissipation by the horn inside the cell is not clearly known, however, we guess approximately 10~20 W, which is the energy efficiency of 5~10 % of 200W of the total energy consumption of the sonar [46, 47].

The decontamination efficiency of actual radioactive contaminated parts was analyzed by the gamma-spectrum using a Ge-detector (HPGE P-type, EURISYS, France).

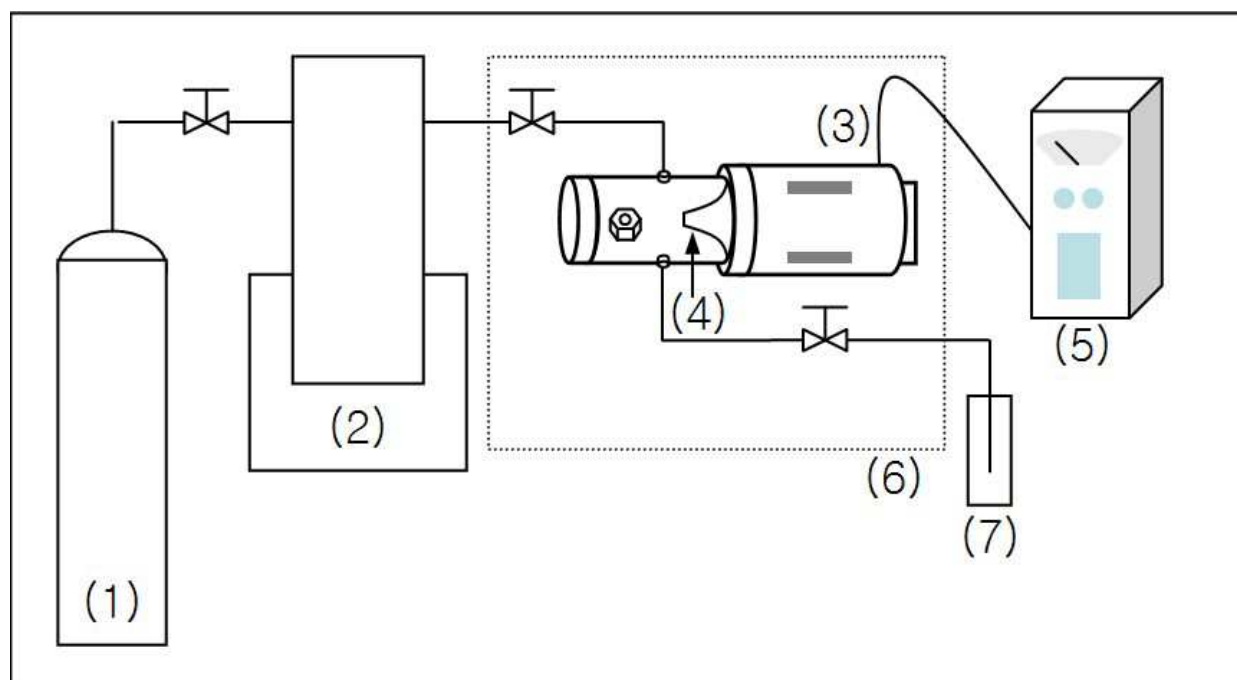


Fig. 4. Decontamination apparatus with ultrasound. (1)CO<sub>2</sub> cylinder, (2)syringe pump, (3)high pressure cell (87mL), (4)ultrasonic horn, (5)ultrasonic power supply, (6)oven, (7)collecting vial.

## 4. Results and discussion

### 4.1 Microemulsion formation in supercritical CO<sub>2</sub>

The basic structure of NP-series is shown in Fig. 5. It has both a hydrophilic and a CO<sub>2</sub>-philic group. The length of the hydrophilic functional group becomes longer as n value increases, and thereby polar solubility increases. The NP-series surfactants are commercially available



with economic price. Since it is electrically neutral, it is less sensitive to the presence of electrolyte, and less affected by pH value. Solubilities of NP-series surfactants in supercritical CO<sub>2</sub> were measured using the solubility apparatus, and the results are shown in Fig. 6. Due to the CO<sub>2</sub>-philic property of the alkyl chain, NP-series are quite soluble in CO<sub>2</sub>. The ethylene oxide chain is a hydrophilic functional group, and as its length increases, solubility within CO<sub>2</sub> becomes lower. For example,  $1.0 \times 10^{-3}$  mol fraction of NP-2 was clearly dissolved at (or above) 95 bar. On the contrary, 300 bar or higher pressure was needed to dissolve the same mol fraction of NP-16. From the solubility measurements of surfactants, we concluded that NP-series surfactants were soluble to CO<sub>2</sub> enough to form a microemulsion in CO<sub>2</sub>.

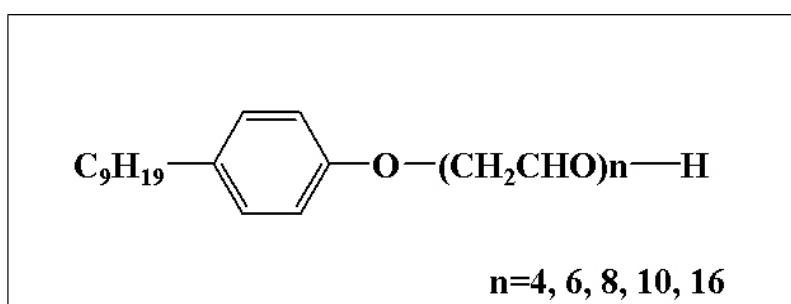


Fig. 5. Basic structure of the NP-series.

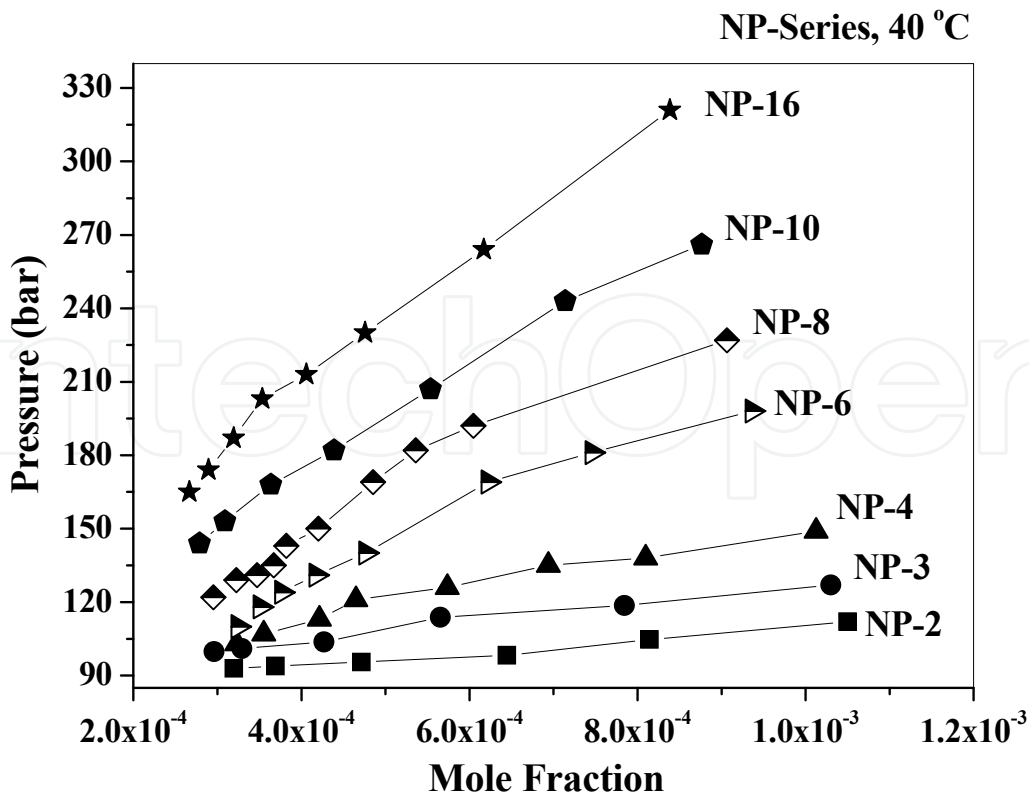


Fig. 6. Solubilities of the NP-series in supercritical CO<sub>2</sub>.

The formation pressures of microemulsions of water in supercritical CO<sub>2</sub> by NP-series surfactants are shown in Fig. 7. The W value for each surfactant was taken as 20, and temperature was maintained at 40 °C. The formation pressures were measured to be in the order of NP- 4 > 6 > 3 > 2 > 16 from the lowest. The stability of a microemulsion depends on the stability of interface between water and CO<sub>2</sub>. The stability of the interface depends on the types of surfactants. Microscopically speaking, the water cores are surrounded by the surfactants and the surfactants should make the water cores stable to be a reverse-micelle. Both hydrophilic and CO<sub>2</sub>-philic parts of the surfactant should be mechanically balanced to maintain stable water cores in CO<sub>2</sub> matrix. NP-4 seems to make mechanical equilibrium easily in the interface between the water droplets and the surrounding CO<sub>2</sub>. We chose NP-4 as an optimal surfactant for the microemulsion formation.

The formation pressures of a microemulsion with different W values were also measured using NP-4. The cloud points at different W values are shown in Fig. 8. In each case, a greater pressure is required to make a microemulsion as the concentration of surfactants (and water the amount of which was set by W value) increases in CO<sub>2</sub>. In other words, a greater pressure is required to dissolve a large amount of water at a given mole fraction of surfactants.

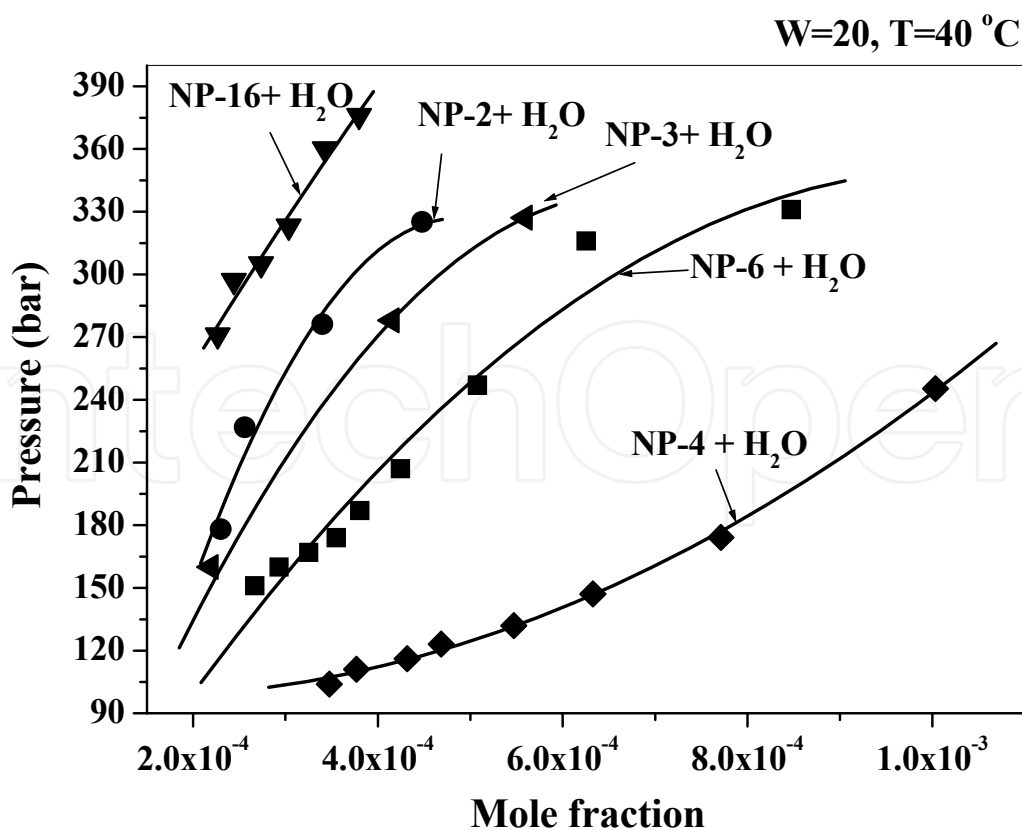


Fig. 7. Formation regions of water-in-CO<sub>2</sub> microemulsions with the NP-series.

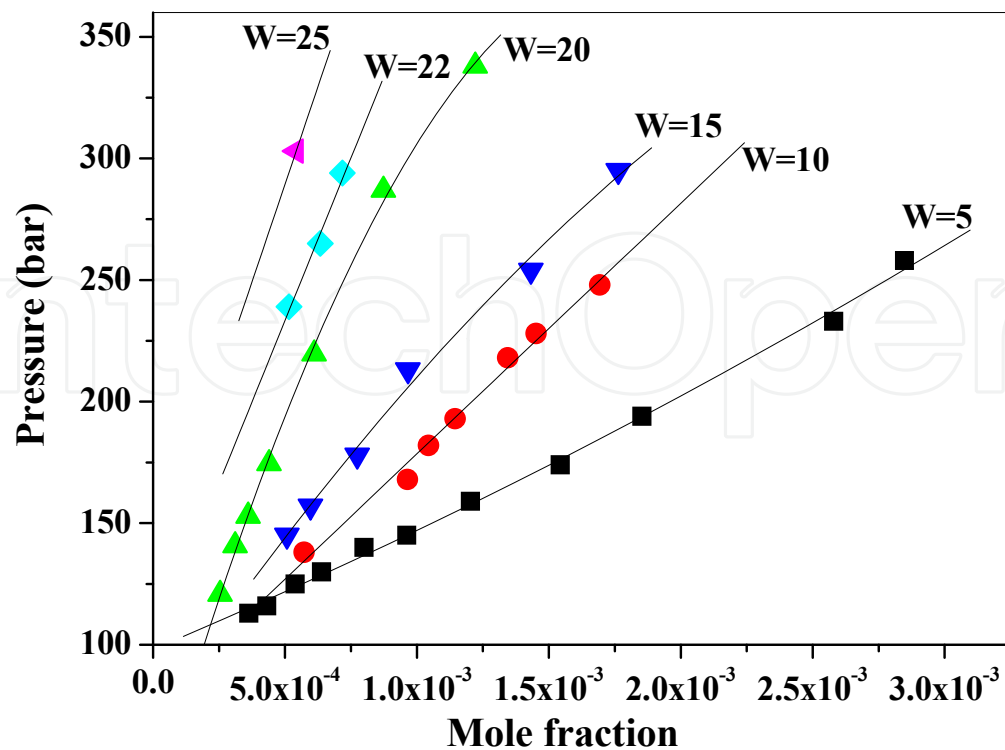


Fig. 8. Formation regions of water in supercritical CO<sub>2</sub> microemulsions with the NP-4 mole fraction in CO<sub>2</sub>. NP-4:20mM, temperature:40 °C.

Acid microemulsions in supercritical CO<sub>2</sub> were made and their formation pressures were measured using ionic (F-AOT) and non-ionic (NP-4) surfactants. The results are shown in Fig.9 and Fig.10, respectively. The formation pressure of a microemulsion by F-AOT was higher than its solubility pressure line (Fig.9). The formation pressure of the microemulsion of water in CO<sub>2</sub> by F-AOT increased continuously as the mol fraction of surfactant (and also that of water) increased. It seemed that higher pressure should be applied to stabilize the increased amount of aqueous droplets in CO<sub>2</sub> matrix. However, in the case of the microemulsion of acid, we could not obtain a microemulsion state when the mol fraction of surfactants exceeded a certain critical value ( $\sim 10^{-2}$  of mol fraction in the case of 3M nitric acid). The acid cores in a microemulsion seemed unstable above this critical mol fraction. The exchange reaction of Na in the hydrophilic head with protons in the acid cores might be a reason for the destabilization.

On the contrary, the NP-4 maintained the stability of microemulsions of acid cores with the increase of mol fraction of surfactant and acid (Fig.10). The formation pressure of acid microemulsion in CO<sub>2</sub> was measured to be higher than that of water in CO<sub>2</sub>. It is believed that the non-ionic surfactant, NP-4 forms a stable microemulsion of acidic solution in CO<sub>2</sub> enough to be used in decontamination.

Organic acids are more commonly used in surface treatment of metals. The formation pressures of the microemulsion containing oxalic and citric acids by NP-4 were measured respectively. As shown in Fig. 11, stable microemulsions of organic acid were possible with non-ionic surfactant, NP-4. The formation pressure of a microemulsion containing citric acid in the core turned out to be lower than that of oxalic acid. When the two acids were mixed together, the formation pressure increased. Organic acids needed higher pressure to form microemulsions in CO<sub>2</sub> than inorganic acid.

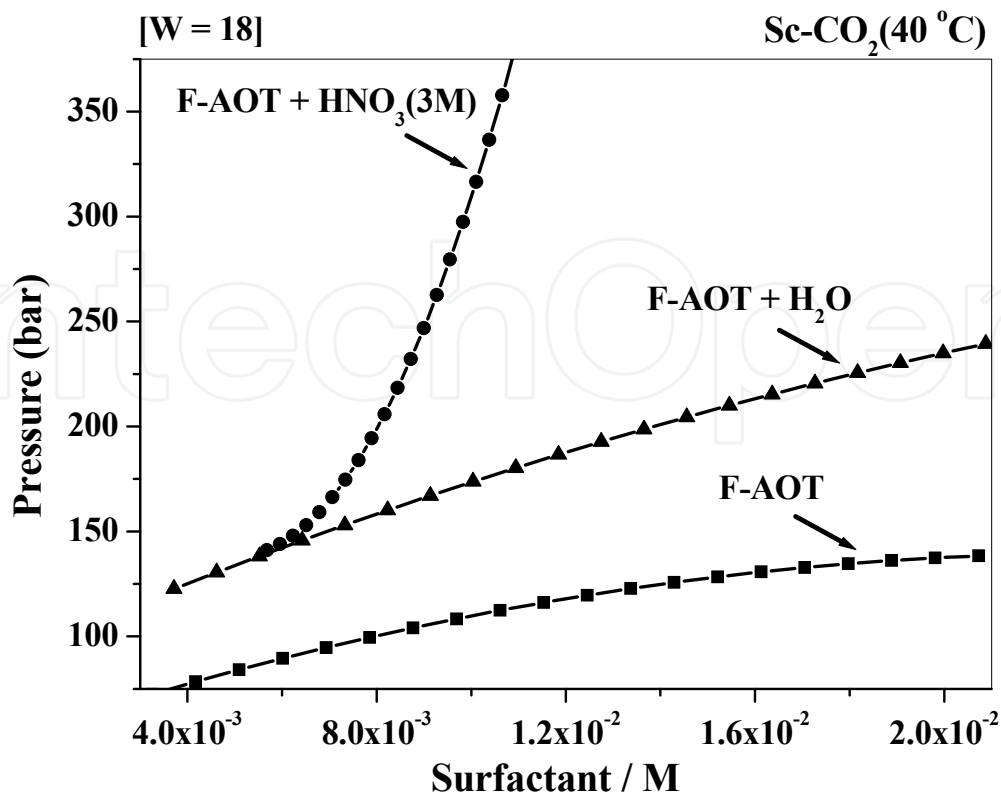


Fig. 9. Formation regions of microemulsions with F-AOT as acidity increases.

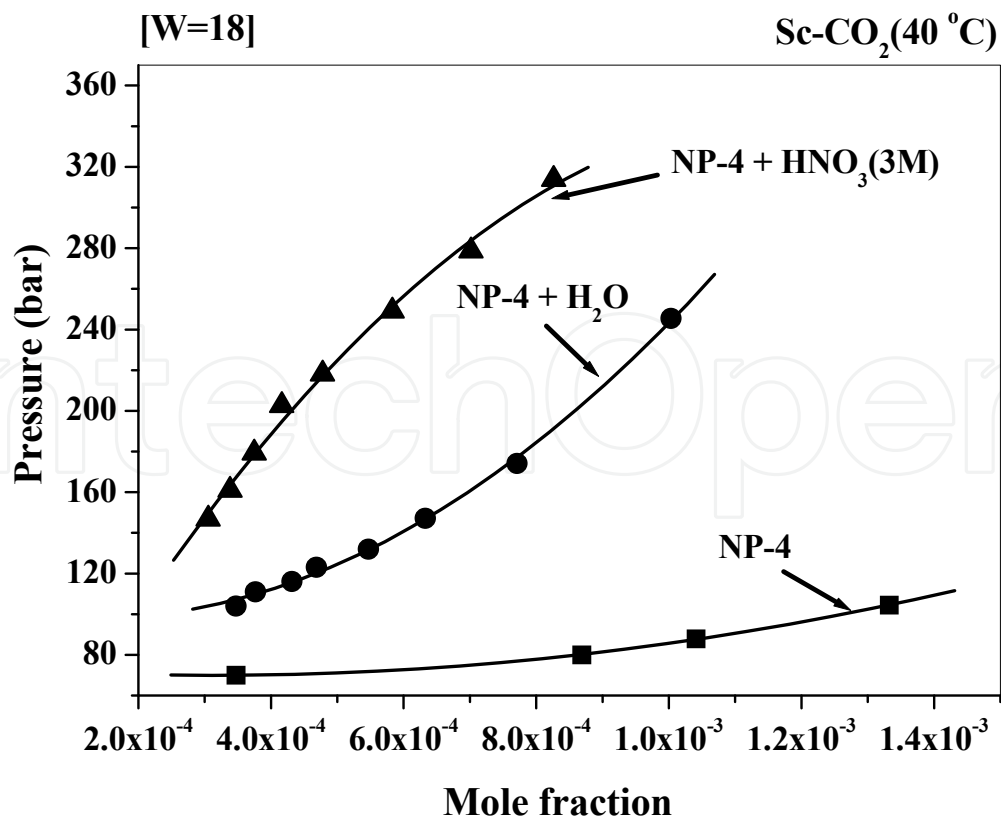


Fig. 10. Formation regions of microemulsions of acid cores and those of water cores with NP-4.

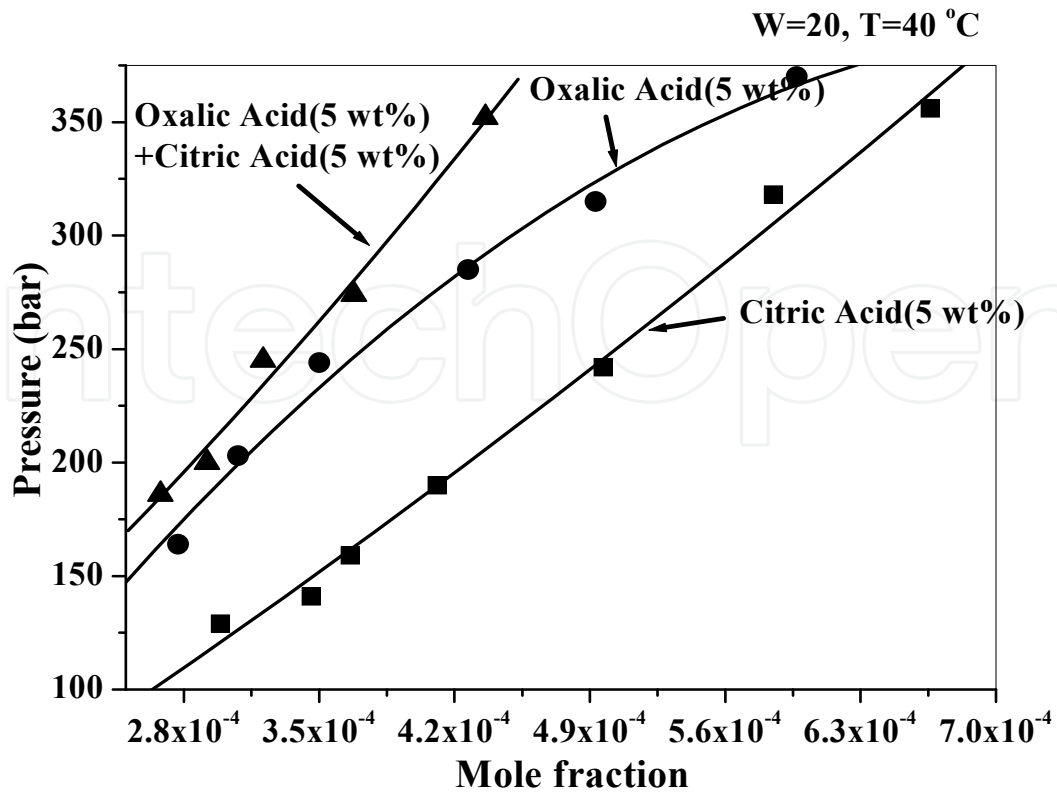


Fig. 11. Formation regions of microemulsions with organic acids (citric acid, oxalic acid).

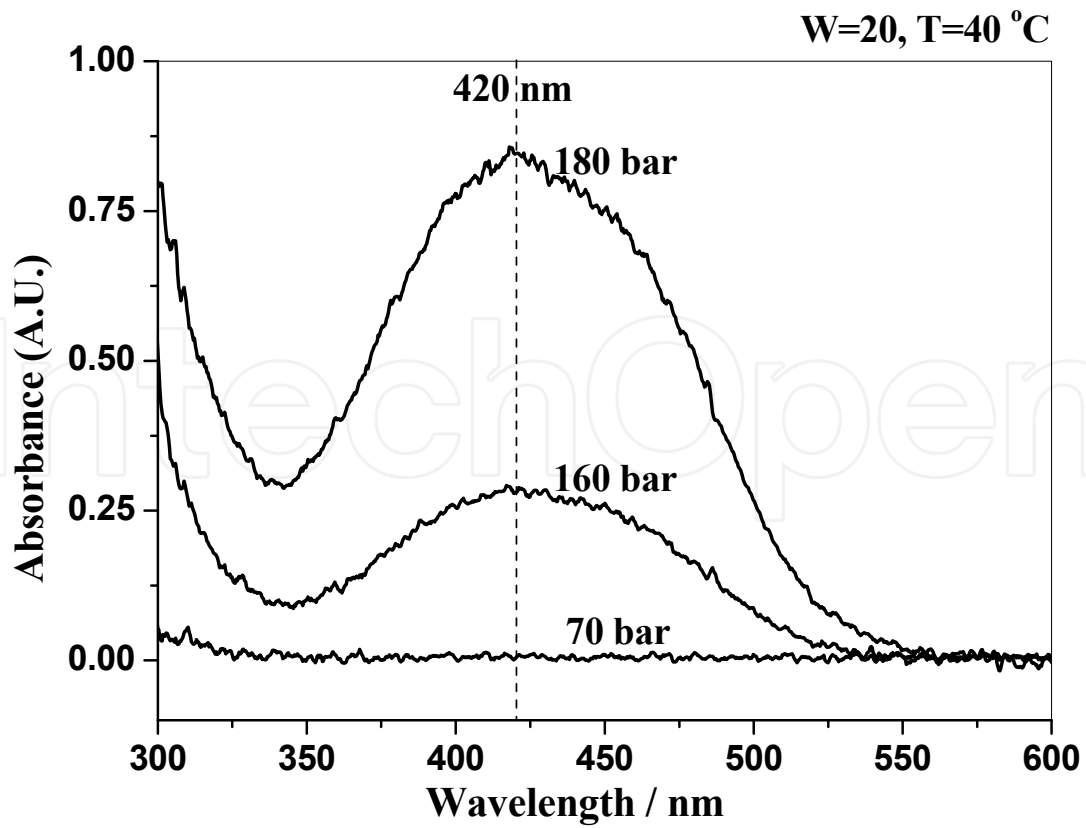


Fig. 12. UV-VIS spectrum of methyl orange in supercritical  $\text{CO}_2$  microemulsions with NP-4.



The formation of a microemulsion can be checked by the absorption spectrum of a UV-VIS spectrometer. For a clear observation, methyl orange was injected into the cell. We measured the variation of the UV-VIS spectrum with the increase of CO<sub>2</sub> pressure (Fig.12). A clear peak (420nm) of methyl orange appeared at the pressure of 160bar at 40 °C. And, the fact of the peak growth with applied CO<sub>2</sub> pressure indicated that more stabilized microemulsion was formed under the higher pressure.

#### 4.2 Enhanced stabilization of micro- and macroemulsions by ultrasound

Two types of agitating methods - a stirrer and an ultrasound horn- were used for comparing the stability of microemulsions. In the stirrer system, it takes about 20 minutes to form a stable microemulsion. The dispersed behavior of inner contents (nitric acid, surfactant and CO<sub>2</sub>) and a magnetic bar were observed through a view cell. We photographed the formation process with time, as shown in Fig.13.

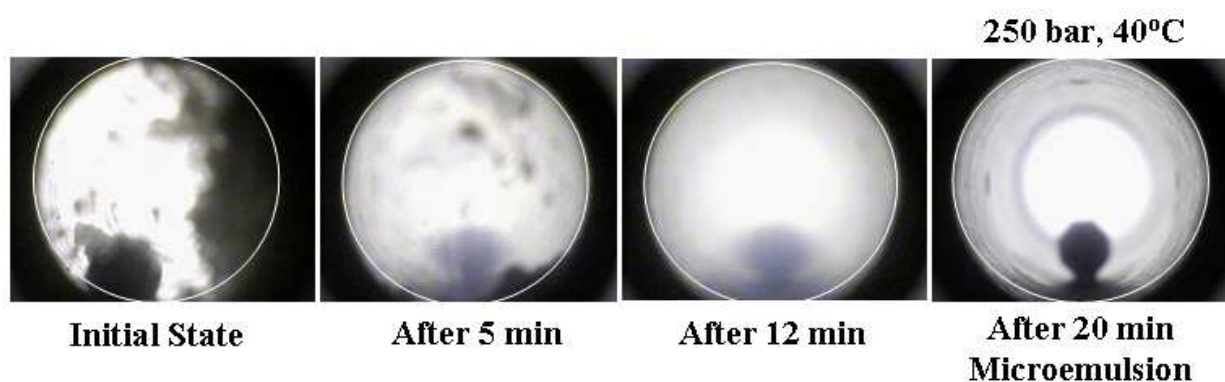


Fig. 13. Microemulsions formation using a stirrer (400rpm) with time at 250bar and 40 °C (to form the microemulsions, nitric acid (1M, 24.5 L) and surfactant (NP-4, 24.8 L) were used inside the pressure cell (10mL)).

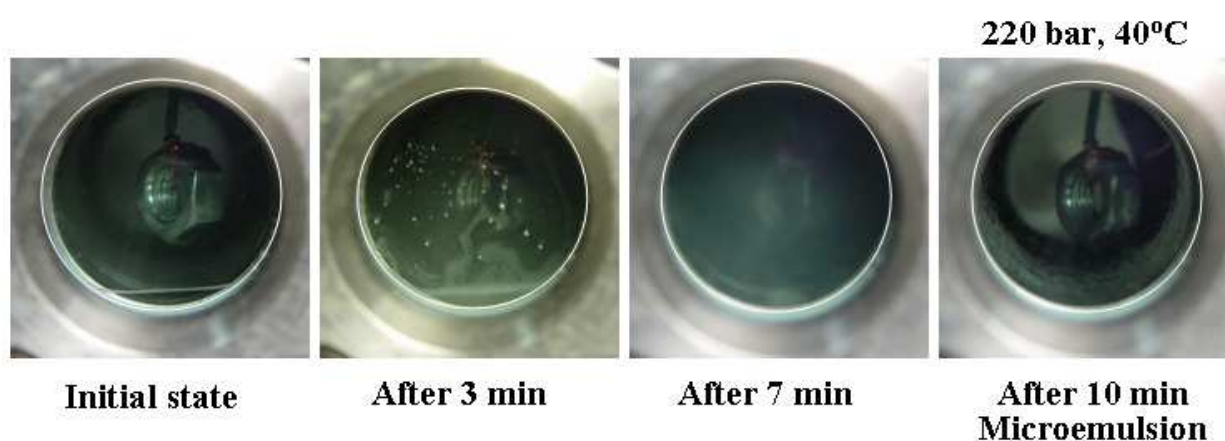


Fig. 14. Microemulsions formation using the ultrasound over time at 220bar and 40 °C. (to form the microemulsions, nitric acid (1M, 214 L) and surfactant (NP-4, 216 L) were used inside a pressure cell (87mL)).

In the ultrasound system, a microemulsion was formed in about 10 minutes as shown in Fig. 14. As seen in the photos, nitric acid was partially dissolved at 3 min. and a cloud state was seen at 7 min. And finally a clear microemulsion appeared after 10 min. Microemulsions are thermodynamically stable and their dispersed phase is at the nano-scale level. The ultrasound horn applied intense dispersing, stirring and emulsifying effects to the fluid [48], which provide additional power to mix water (or acid) with  $\text{CO}_2$ . All of these effects from the ultrasound horn enhance the stabilization of emulsion.

We conducted experiments about the formation of macroemulsions using an ultrasonic horn. The formation of macroemulsion can be observed visually through the sapphire windows of the high pressure vessel. After inserting the aqueous solution (10% of vessel volume, 5mL) and the surfactant (6v/o of the aqueous solution, 900 L) into the vessel (50mL), it was heated to 55 °C and pressurized to 120bar by  $\text{CO}_2$ . These mixtures existed in a completely separated state initially (Fig.15(a)). Then localized macroemulsions were formed after 10 seconds after agitation (Fig.15(b)), and the macroemulsion was uniformly formed in total in less than 30 seconds (Fig.15(c)). The macroemulsion existed as long as the ultrasound horn agitated the fluid in the cell. After the shut-down of power, the macroemulsion returned back to the initial state, i.e., separated mixtures.

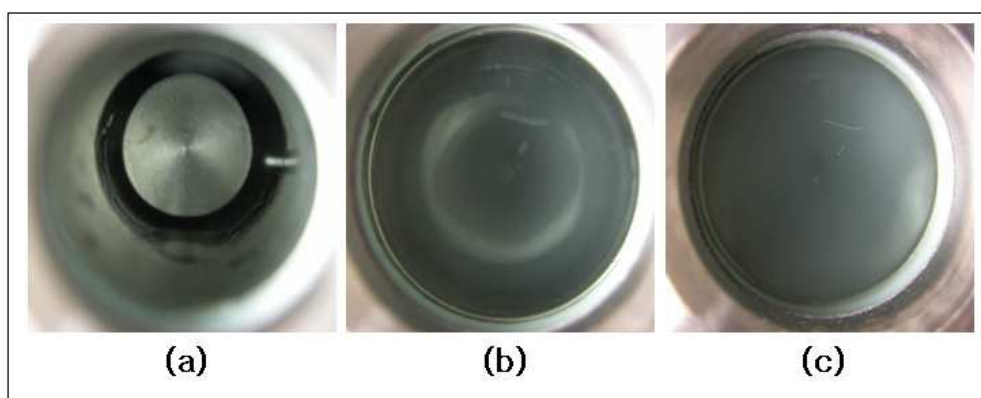


Fig. 15. Photos of emulsion forming processes by ultrasound. (a)state not subjected to ultrasound, (b)state in which an emulsion was partially formed after agitation for 10 seconds, (c)state in which an emulsion was uniformly formed after generation of ultrasound for 30 seconds.

### 4.3 Decontamination using Micro- and Macroemulsions in $\text{CO}_2$

#### 4.3.1 Dissolution test of Cu from Cu-coated substitute

As a mock-up test for surface decontamination of radioactive components, Cu-coated nuts were prepared. We put a Cu-coated nut into the reactor cell and let the nut contacted the acid-containing microemulsion. The Cu coating was removed under the microemulsions of acids (1M or 6M- $\text{HNO}_3$ ) in  $\text{CO}_2$ . After one hour of the removal process, most of the Cu-coating was removed and dissolved into the microemulsions. Fig. 16 shows the specimen before and after the experiments. Surface damages of the specimens (corrosion) were observed. We examined the removed surface via an optical microscope to see the surface damage by concentrated nitric acid (Fig. 17). 1M of  $\text{HNO}_3$  removed almost all of the Cu-

coating with small surface damage. However, 6M of HNO<sub>3</sub> not only removed the Cu-coating but also damaged heavily some portions of the surface. Anyway, with a very small amount of acid in the microemulsion, we could dissolve and remove the Cu-coating of the specimens very effectively.

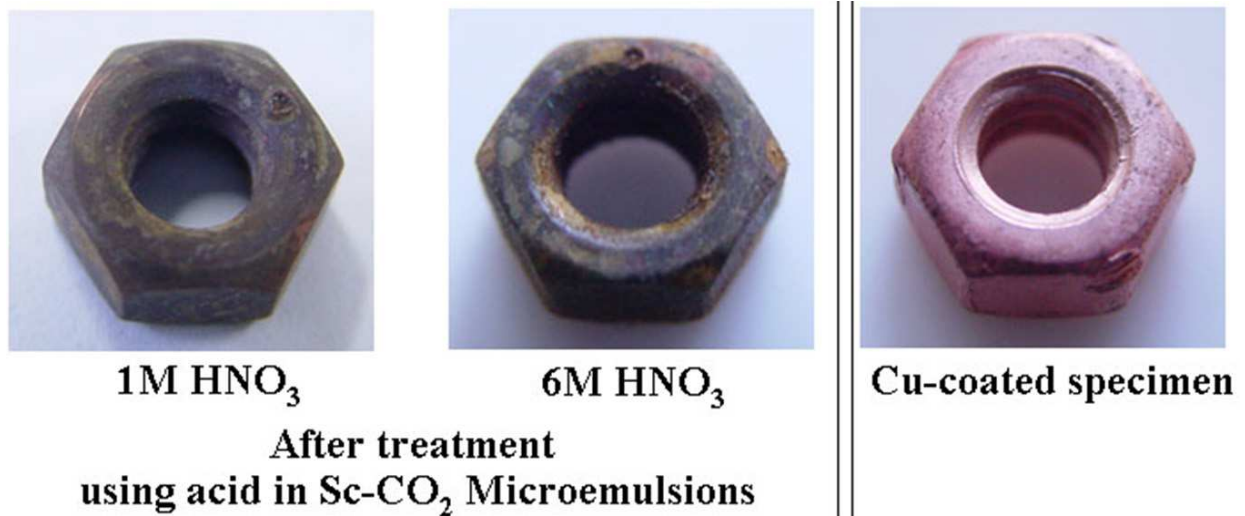


Fig. 16. The photos of specimen before and after acid in Supercritical CO<sub>2</sub> microemulsion treatment.

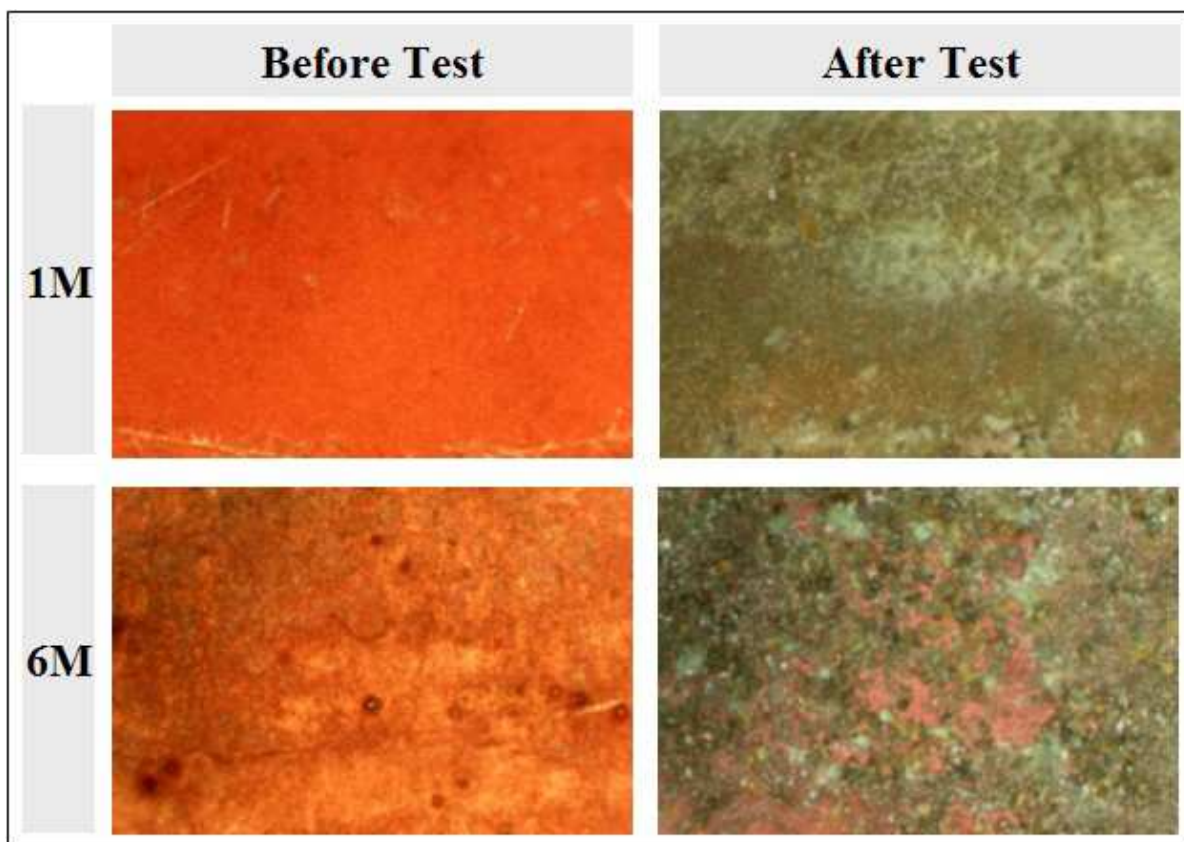


Fig. 17. Microscopic images of a Cu-plated nut using the acid-in-CO<sub>2</sub> microemulsions.



### 4.3.2 Decontamination of radioactive components

We obtained radioactive components (bolts, nuts, small pieces of pipes) from nuclear power plants (Wolsung and Kori) in Korea. The radioactivity of the obtained radioactive components were measured by a Ge detector, and classified. We selected radioactive specimens based on the level of contamination that should be mild enough to handle in the laboratory, and high enough to measure the decontamination efficiency. The selected specimens are shown in Fig.18.

For the purpose of comparison, three different decontamination methods were tried – cleaning by a conventional acid solution, microemulsion, and macroemulsion. In the conventional acid cleaning, the specimens were placed into a nitric acid (250mL, 0.1M) at 50°C for an hour with stirring by a magnetic bar. And additional experiments of decontamination by acid solution were done under ultrasonic agitation. In the case of microemulsion cleaning, the radioactive samples were decontaminated for about an hour in the microemulsions with a very small amount (~30 L) of nitric acid (1M, 6M) in supercritical CO<sub>2</sub> at 60 °C. Agitations by magnetic-bar stirring and by ultrasonic-horn vibration were done separately for comparison purposes.

A macroemulsion was made by ultrasonic horn agitation. In the reactor cell, 10% of total volume was filled by acid (0.1M or 5% oxalic acid) and the rest volume was by pressurized CO<sub>2</sub>. The reactor was maintained at the temperature of 50°C and pressure of 120bar during the cleaning process. The cleaning process lasted for an hour.

We measured the radioactivity of the specimen before and after the experiment, respectively; then the cleaning efficiency was calculated by the comparison of the activities of these two. A few of gamma radiation peaks (Co-60, Sb-125, Mn-54, Zr-95) were observed by a Ge-detector from the specimens we used. The strongest peaks were from Co-60, and we set the decontamination efficiency by the comparison of Co-60 activities. The uncertainty of gamma radiation detection using the Ge-detector was about 5%. Based on this uncertainty, we assume that 10% be the uncertainly limit in the value of decontamination efficiency.

The results of decontamination experiments using radioactive specimens are shown in Table 1. The conventional cleaning using 0.1M nitric acid with a stirrer gave the value of about 50% of decontamination efficiency. When ultrasonic agitation was applied, the efficiency increased up to 78%. Additional cleaning (2<sup>nd</sup> time) barely increased the efficiency (up to 84%). This might be the limit of cleaning efficiency when we used 0.1M nitric acid as a cleaning solution.

The microemulsion with nitric acid clearly worked well in decontamination of radioactive metal components. The volume fraction of acid used in the microemulsion cleaning was only 0.25%, and the size of the reactor cell was about 1/20 compared to the container used in the conventional acid cleaning. The decontamination efficiency was about 63% if 0.1M nitric acid was used. When strong nitric acids were used, the decontamination efficiency increased up to 100%.

A macroemulsion containing acid was also effective in decontamination of radioactive specimens. Due to strong agitation by an ultrasonic horn, the decontamination efficiency went to up to 89% when 0.1M nitric acid was used. Interestingly, oxalic acid (5%) was very effective in decontamination of metallic parts (100% elimination).

The cleaning methods using microemulsion and macroemulsion seemed very effective in decontamination of metallic parts contaminated on the surface. The amounts of acid used in these cleaning methods were very small (0.25%~10% in volume). Because it contains the removed radioactive contaminants, the aqueous acid used in cleaning becomes a secondary

waste. We can reduce the amount of the secondary waste revolutionarily if micro- or macroemulsion of acid in CO<sub>2</sub> is used in decontamination.



Fig. 18. Radioactive contaminants supplied from Unit 1 of the Wolsung and Unit 2 of the Kori Nuclear Power Plants during overhaul periods.

Decontamination methods	Acid types	Agitation methods	Acid in vol %	Efficiency / %	
				1 <sup>st</sup>	2 <sup>nd</sup>
Conventional acid cleaning	0.1M HNO <sub>3</sub>	Stirrer	100%	50±10	-
		Ultrasound		78±10	84±10
Supercritical CO <sub>2</sub> microemulsions	0.1M HNO <sub>3</sub>	Stirrer	0.25%	63±5	-
	1M HNO <sub>3</sub>	Ultrasound		87±10	-
	6M HNO <sub>3</sub>			100 ±10	-
Supercritical CO <sub>2</sub> macroemulsions	0.1M HNO <sub>3</sub>	Ultrasound	10%	89±10	-
	Oxalic Acid (5%)	Ultrasound		100±10	-

Table 1. The decontamination efficiencies of radioactive components (nut, bolt, etc) with respect to different cleaning methods.

## 5. Conclusion

New surface decontamination techniques using acid-CO<sub>2</sub> micro- and macroemulsions were developed to decontaminate radioactive components. NP-series, commercially available surfactants, were applied to form the micro- and macroemulsions in supercritical CO<sub>2</sub>. We found that micro- and macroemulsion could be formed if nonionic surfactants (NP-series) were used. And the formation points were measured with respect to the concentrations of surfactants in CO<sub>2</sub>. The results showed that the solubility of surfactant increased gradually as the hydrophilic group became shorter. In the formation of the microemulsion with water, it was confirmed that the NP-4 surfactant formed the most stable microemulsion, because



the hydrophilic and the CO<sub>2</sub>-philic parts of the surfactant were mechanically well balanced to maintain stable water cores in CO<sub>2</sub> matrix.

An ultrasonic horn was used to enhance the formation of micro- and macroemulsions. The agitation by an ultrasound horn was superior to that by a stirrer in obtaining a stable microemulsion. When the ultrasound was used, the microemulsion was formed quickly even at the milder condition.

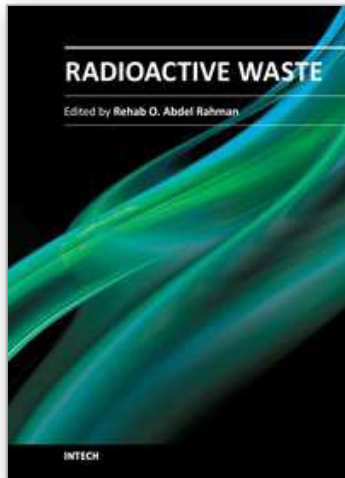
We tested Cu-coated parts to see whether the microemulsion containing nitric acid could remove the surface metal layer. Almost all of the Cu-coating was removed under the microemulsion of 1M HNO<sub>3</sub> in CO<sub>2</sub>. Both microemulsion and macroemulsion containing nitric acid clearly worked well in decontamination of radioactive metallic parts. The decontamination efficiency increased as the acidity of nitric acid increased. And oxalic acid in macroemulsion was very effective in the surface decontamination of metallic parts. The cleaning methods of micro- and macroemulsion seemed better in decontamination of metallic parts than conventional cleaning. Moreover, these methods produce very small amount of secondary wastes.

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The safe management of nuclear and radioactive wastes is a subject that has recently received considerable recognition due to the huge volume of accumulative wastes and the increased public awareness of the hazards of these wastes. This book aims to cover the practice and research efforts that are currently conducted to deal with the technical difficulties in different radioactive waste management activities and to introduce to the non-technical factors that can affect the management practice. The collective contribution of esteemed international experts has covered the science and technology of different management activities. The authors have introduced to the management system, illustrate how old management practices and radioactive accident can affect the environment and summarize the knowledge gained from current management practice and results of research efforts for using some innovative technologies in both pre-disposal and disposal activities.

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