Development of Decontamination Methods using Liquid/Supercritical CO2

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ABSTRACT

A major problem of nuclear energy is the production of radioactive wastes. Needs for more environmentally favorable method to decontaminate radioactive contaminants make the use of liquid/supercritical CO2 as a solvent medium. In removing radioactive metallic contaminants under CO2 solvent, two methods - use of chelating ligands and that of water in CO2 emulsion - are possible. In the chelating ligand method, a combination of ligands that can make synergistic effects seems important. We discuss about the properties of microemulsion formed by F-AOT. By adding acid in water core, decontamination of metallic parts, soils were possible.

1. INTRODUCTION

Radioactive wastes are essentially produced after nuclear fissions [1], the volume reduction of wastes is continuously needed. Conventional methods produce lots of secondary wastes during decontamination. Supercritical fluid extraction (SFE) using CO_2 process can be

considered as a future decontamination technique that resolves the secondary waste problem. CO_2 is environmentally benign, and also economical. CO_2 becomes liquid or supercritical fluid by pressurization, which can be used as a solvent for cleaning. By depressurization, CO_2 becomes a gas state that does not have any solubility for dissolved contaminants. There is no secondary waste production by applying this high- and low-density cycle in decontamination process. However, CO_2 cleaning process has a limitation in dissolving the polar or ionic contaminates owing to the inherent nonpolar property of CO_2 [2]. The problems of limited solubility can be solved by two methods – addition of chelating ligands and formation of water in CO_2 emulsion. This paper is aimed at explaining the development of SFE processes for decontamination of nuclear contaminants.

2. PROCESS USING CHELATING LIGANDS

Radioactive contaminants are quite diverse. The source of nuclides can be divided into fission products, corrosion products, and actinides. Chemical forms are metallic ions, metallic spikes, oxides, and hydroxides. Chelating ligands are necessary for dissolving metallic ions to organic solvents such as CO2. Theses ligands form complexes with metal ions that can be dissolved into CO2. There are lots of chelating ligands tested for the application to metal extraction into CO2 [3-9], after a frontier work of Wai [3]. The important variables for metal extraction into CO2 are the solubility of ligands, the solubility of metal complexes, the existence of water, temperature and pressure, the chemical form of metallic contaminants, and the matrix where the contaminants are located [7]. Figure-1 shows the metal elements that can be extracted by the chelating ligand method in CO2 so far [6-23]. The ligands were grouped into 5 groups that were used by Wai [7]. The numbers above the element symbol indicate the number of ligand group that can be used in metal extraction.

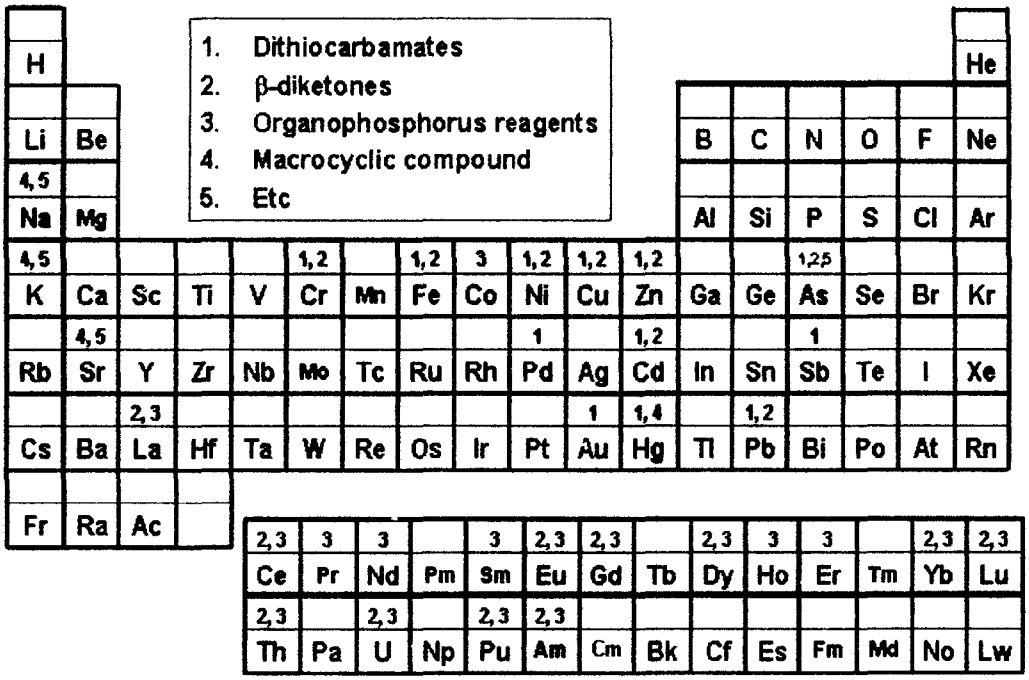

Figure 1. The metal elements that can be extracted by the chelating ligand method.

The number indicates the group in the table.

Important elements in nuclear industry are actinides, and fission products such as Cs, Sr, and lanthanides, and corrosion products such as Co, Zr, Nb. The actinide ions (U, Pu, Th) can be extracted by TBP, FOD, TTA, HFA. Especially, uranium oxides can be extracted directly into CO2, if TBP-HNO3 compound is mixed with CO2 [22,23]. And, a synergistic effect in metal extraction was observed when -diketone and TBP was used together. We also observed the synergistic effect in metal extraction when both NaDDC and cyanex-272 were used. Figure-2 shows the experimental results. The metallic ions (Cd, Co, Cu, Pb, and Zn) were spiked to the filter paper, and the extraction rate was obtained by comparison between the amounts of metallic ions in the filter paper before and after the CO2 flow with

chelating ligands (200atm, 60oC, 1 hour). The extraction rates from NaDDC were about 30-70%, and those from cyanex-272 were lower than 10%. However, if we used the two ligands together, the extraction rates increase up to 98%. This phenomenon can be explained by the role of armine that appears from the dissociation of NaDDC. If we use this synergistic effect correctly, more effective extraction of metallic ions is possible, and more work on the synergistic effects have to be examined closely.

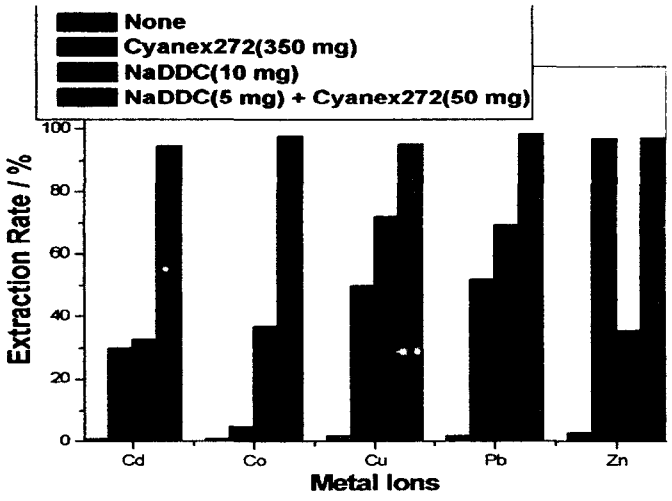

Figure 2. Extraction measurement of metallic ions using NaDDC and Cyanex-272.

3. PROCESS USING MICROEMULSION

Emulsions of water in CO_2 can be formed if adequate surfactants are added in the mixture of water and CO_2. Microemulsion also can form in CO_2 solution, and the size of the water cores in microemulsion is less than 100 nm when the microemulsion is transparent. Water cores in the emulsion can extract the ionic contaminants that are insoluble to CO_2. After extraction, we can destabilize the microemulsion by reducing the pressure, and the

water in emulsion splits from CO_2 solvent and can be collected separately while the surfactant is still dissolved in CO_2. Using this phenomenon of destabilization of emulsion, we can recycle both CO_2 and the surfactant. Figure-3 shows the concept of the recycle of both surfactants and CO_2.

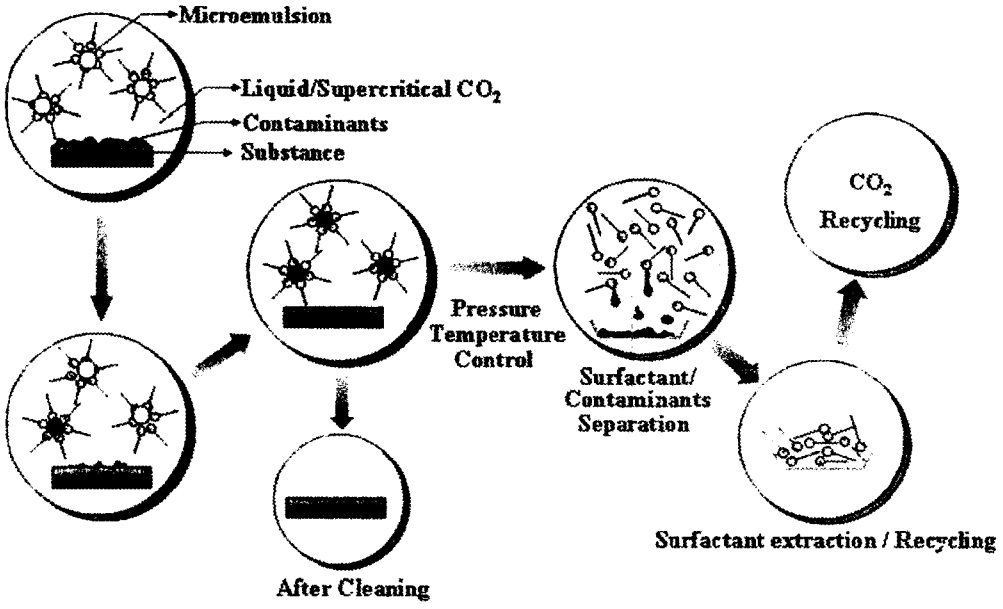

Figure 3. A conceptual diagram of the recycle of surfactants and CO2.

Aerosol-OT (AOT) is a good surfactant to form emulsions in aqueous solution. To increase the solubility of AOT in CO_2, we synthesized fluorinated AOT (F-AOT). The solubility of F-AOT was measured to be high enough to be used as a surfactant in CO_2 medium. Microemulsion was also formed with water in CO_2. The water in central cores in microemulsion could be replaced by nitric acid. A microemulsion containing 0.17% (volume %) of 1-M nitric acid in CO_2 was made and used to eliminate the surface film. We used copper coated nuts to test the surface layer removal by a microemulsion containing nitric

acid. Figure-4 shows the photos of the specimen before and after the etching test using microemulsion. The copper coating on the surface was totally removed after 1 hour operation.

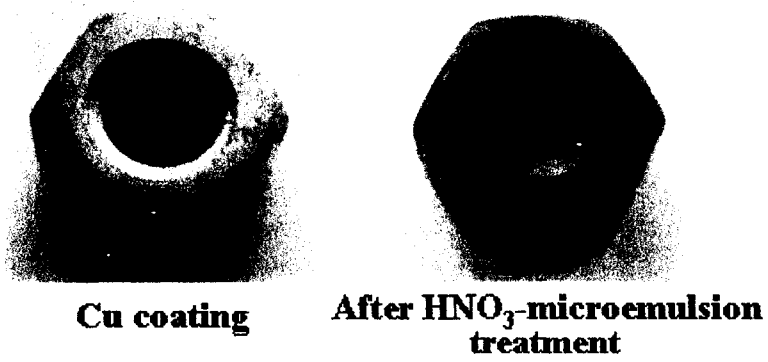

Figure 4. Cu-coated specimen before and after the etching using microemulsion.

The dissolution rate in a microemulsion containing 3-M HNO3 is about 2 times faster than in the case of 1-M HNO3. However, the dissolution rate did not increase as the amount of nitric acid in CO2 solution increases. This shows the characteristics of supercritical fluid that has high solubility with high penetrability.

4. CONCLUSION

Two methods – a technique using chelating ligands and that using microemulsion - have been developed for decontamination. In the chelating ligand method, synergistic effects of ligands seem important in developing an efficient decontamination solution. Armine from the dissociation of NaDDC can enhance the extracting ability of cyanex-272, which seems a reason for the synergistic effect. We can recycle both surfactants and CO_2 in the case of the

microemulsion method. By inserting nitric acid in the water core in microemulsion, we obtained a decontamination emulsion. The surface coating was easily eliminated by the decontamination microemulsion.

5. ACKNOWLEGEMENT

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