Extraction of Co ions from ion-exchange resin by supercritical carbon dioxide

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1. Introduction

There are a number of liquid treatment processes for eliminating radioactive ionic contaminants in nuclear facilities. One of the most common treatment methods for aqueous streams is the use of ion exchange, which is a well-developed technique that has been employed for many years in the nuclear industry. More specifically speaking, systems that ion exchange method is applied to in nuclear power plants are liquid radioactive waste treatment system, chemical and volume control system, steam generator blowdown treatment system, and service water supply system. During the operation of nuclear power plants, radioactive contaminants such as Co-60, Mn-54, Fe-59 and Cs-137 are contained in liquid radioactive wastes. And the wastes containing small amount of uranium are generated in nuclear fuel cycle facilities.

To treat the liquid radioactive waste, we usually install ion exchangers rather than evaporators due to their simplicity and effectiveness, and this trend is increasing. However, the ion exchange process produces large volume of spent organic resin, and has some problems of radiation damage and thermal instability. And the reuse of the resin is limited due to the degradation of ion-exchanging ability. For this reason, we should consider a better method to expand the lifetime of the resin or to reduce the volume of radioactive resin wastes by extracting radioactive contaminants located in the resin.[1-5]

Supercritical fluid CO_2 has many good points as a process solvent that include low viscosity, negligible surface tension, and variable selectivity. And supercritical fluids have physical properties of both liquid and gas such as good penetration with a high dissolution capability. Supercritical fluids have been widely used in extraction, purification, and recovery processes. A number of workers applied supercritical CO_2 solvent for cleaning of precision devices and waste treatments [6-7]. Since supercritical CO_2 has its mild critical point at 31℃ and 73.8bar as well as low surface tension, it is potentially suitable for cleaning substance. The operational costs of CO_2 cleaning were estimated to be lower than other cleaning processes [8].

In this paper, we considered the possible use of supercritical CO_2 fluid in extracting radioactive contaminants from contaminated resin (simulated). We measured the extraction efficiency of Co-ions from the resin using supercritical carbon dioxide, and discussed the possible use in decontamination.

2. Experiment

2.1 Materials and Ligands

Carbon dioxide with a minimum purity of 99.98% was purchased from Air Tech, Korea. Cobalt chloride ($CoCl_2 \cdot 6H_2O$, 99.9995% purity) was purchased from Aldrich. Resin (NRW-100, cation exchange resin, nuclear grade) was obtained from Purolite, Korea. HFA (hexafluoroacetylacetone) was purchased from Fluka, Japan..

2.2 Experimental apparatus

We made a extracting device that consists of a syringe pump, a mixing cell and a extracting cell (see figure 1). The volume of the mixing cell (Hanwoul Engineering Co. Ltd) is 10ml and a tube containing contaminated resin was used as the extracting cell. CO_2 is supply from a liquid CO_2 cylinder through a syringe pump (ISCO, model 260D, Lincoln, NB). Both the mixing and the extracting cells are immersed under the water bath.
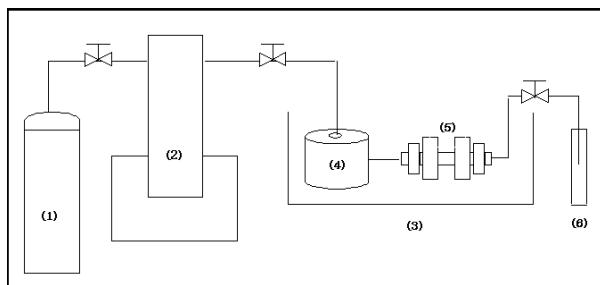

Figure 1. Experimental apparatus ; (1) CO_2 cylinder (2) Syringe pump (3) Water bath (4) Mixing cell (5) Tubing cell (6) Collector

2.3 Specimen preparation

The contaminated resin (simulated) were prepared by immersing fresh resin into $CoCl_2$ solution (1mM) for 24 hours. And we rinsed the resin with distilled water and dried it by air. We filled the resin (about 0.5g) into a glass tube and enclosed both ends with cotton. The glass tube was inserted into the extracting cell (i.e., tube) for extraction tests.

2.4 supercritical CO_2 extraction and Analysis

After the contaminated resin specimen in the extraction cell was ready, we started to extract Co ions from the resin using supercritical CO_2 containing

ligands. Solution of CO_2-soluble ligands and supercritical CO_2 was prepared in the mixing cell. We set the extraction condition, 60℃, and 200~250bar. The extraction was done by a static reaction (30min), followed by a dynamic extraction (1.5ml/min). The total CO_2 volume used was 40ml (liquid 20℃). After experiment, the specimen was taken out and immersed in nitric acid. And the original contaminated specimen (Co ions not extracted) was also immersed in nitric acid. We obtained the extraction efficiency by comparing the Co ion concentration in nitric acid containing the extracted resin specimen and that containing the originally contaminated resin. The Co ion concentration in nitric acid was obtained by ICP.

3. Results and Conclusion

Based on the ICP analyses, the extraction efficiency of Co ions from the resin was obtained. Table 1 shows the results, when we used HFA (hexafluoroacetylacetone) as the ligand. Table 2 is the results when cyanex-272 and DEA (diethylamine) were used together as ligands. Extraction efficiency was about 35 ~ 50%. Mixing ligands (cyanex-272 and DEA) seems to show the better results than single ligand.

Table 1. Extraction condition and Extraction efficient using supercritical carbon dioxide

Ligand[a]	Additive	Temp (℃)	Pressure (bar)	Efficient (%)
HFA 30$\mu\ell$	No	60	200	34.8
HFA 30$\mu\ell$	Water 50$\mu\ell$	60	200	39.4
HFA 300$\mu\ell$	Water 50$\mu\ell$	60	200	45.5

[a] HFA (hexafluoroacetlyacetone)

Table 2. Extraction condition and Extraction efficient using supercritical carbon dioxide

Ligand	Additive	Temp (℃)	Pressure (bar)	Efficient (%)
Cyanex-272 230$\mu\ell$ DEA[a] 16$\mu\ell$	Water 50$\mu\ell$	60	200	40.9
Cyanex-272 230$\mu\ell$ DEA[a] 16$\mu\ell$	HNO_3 50$\mu\ell$	60	200	49.9

[a] DEA(Diethylamine)

The extraction efficiency turned out to be not so high. The main reason may be from the cation exchange mechanism. In the ion-exchange resin, substitution reactions of resident cation to the ions in the fluid occur. HFA extracts Co ions in the resin, and leaves proton instead. This exchange reaction seems not very active. DEA usually enhances deprotonation of cyanex-272, which results in the better efficiency. Based on these results, we can conclude that the application of supercritical CO_2 in extraction of contaminate ions seems possible. However, the extraction efficiency has to be improved by putting more additives that can enhance the exchange reactions in the resin.

Acknowledgment

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