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Decontamination of radioactive waste oil using a membrane and ion exchange resin assisted by supercritical carbon dioxide

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1. Introduction

Nuclear power is an intrinsically clean energy source due to its high energy density and low generation of waste. However, as the nuclear industry has grown, a variety of radioactive wastes have gradually increased. Pollutants in radioactive waste oil are generally heavy as are radioactive metals, metal oxides or ions in impure water. These radioactive waste oils are highly viscous fluids that are similar to used motor oil. Reducing radioactive waste is important from both economical and environmental viewpoints. Several processes have been developed for the regeneration of used motor oil, such as acid-clay treatment, chemical addition, vacuum distillation, thermal cracking and hydrofinishing. However, these technologies are difficult to apply to the separation of nuclides from radioactive waste oils. In recent years, a few laboratories have tried to use membrane for the regeneration of used motor oil. The membrane filtration of viscous fluids, however, demands high temperatures to increase the permeate-flow rate. Generally, the viscosity of fluids decreased with increased process temperatures of fluids up to 350℃ [1]. Consequently, the membrane filtration of viscous fluids is difficult in commercial operation because of high energy consumption. Hence, a new method of separation of used oils which overcomes these disadvantages is urgently needed. Also we need environmentally-friendly and efficient processes for the separation of waste oils. The present work has used supercritical CO_2 ($scCO_2$) as a viscosity-reducing agent at lower process temperatures in order to improve the membrane permeability and to decrease the energy consumption in the filtration process [2, 3]. $scCO_2$ is considered an alternative process medium since it is non-toxic, non-flammable, inexpensive and easy to handle [4]. Additionally, the tunable properties of carbon dioxide manipulation of pressure and temperature control are versatile for use in extracting many organic materials [5].

Filtration using a membrane can remove the particles in radioactive waste oil. However, the contaminants in radioactive ions are contained in impure water in the oil. Therefore, we tried to remove the ions in impure water. Hence, we introduced the membrane-based ion exchange resin (NRW-100).

2. Methods and Results

2.1 Apparatus

The experimental apparatus contains a pressurized cross-flow filtration loop to separate the filtrate and the retentate. The design pressure and temperature range up to 200bar and 200℃ (Fig 1). The ceramic membrane is a single tube (inner area =55 ㎠) of Al_2O_3. The membrane pore sizes are 0.02 ㎛, 0.1 ㎛ and 0.5 ㎛. These membranes are manufactured by CERACOMB CO., LTD. The high-pressurized filter housing is fabricated by HANWOUL ENGINEERING CO. The operating temperature was controlled by a PID controller. A high pressure preheater/mixer apparatus was used in order to ensure constant operating temperature and to increase the $scCO_2$ solubility of the radioactive waste oils. This was made of a 1/16 inch rolled tube. The radioactive waste oils were obtained from a nuclear power plant (Wolsong Nuclear Power Division).

The contaminated oil penetrates the ion exchange resin apparatus; then the ions in impure water are removed. Next, the membrane separates pure oil and particle waste in the oil. The contaminated materials are concentrated in the retentate oil, which contains metal oxides or radioactive metals. For this reason, we need the 'concentration run' process.

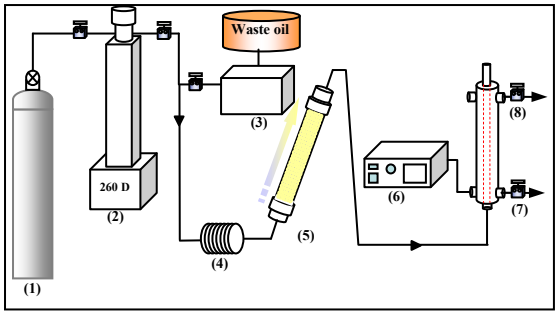

Figure 1. (1) CO_2 Tank (2) Syringe pump
(3) Liquid pump (4) Preheater / Mixer
(5) Ion exchange resin (6) Thermo-controller
(7) Filter out (8) Retentate

2.2 Experimental condition

Radioactive waste oil is supplied to the ion exchange resin apparatus by an HPLC liquid pump and the CO_2 is supplied by a syringe pump at constant operating pressure. After this, the radioactive waste oil penetrates the ion exchange resin apparatus through out the membrane cell. The density of the radioactive waste oil is nearly 0.84g/㎖. During the operation, the transmembrane pressure is maintained ($\Delta P = P_{CO2}$-

$P_{Filtrate}$) at less than 5bar, because the ceramic membrane is brittle. A transmembrane pressure of over 10bar could break the ceramic membrane.

2.3 Result

We carried out the experiment that using a mock-up specimen. The mock-up specimen was prepared to accept insertion of metal ions (Co, Sr) in gear-oil. This has the advantages of being easy to analyze and safe for radiation. The metal ion has similar characteristics through the "isotope". The experiment used a membrane pore size of 0.02 ㎛, and the operating temperature and pressure were equal to those of the previous experimental conditions. After the experiment, the mock-up specimen was dissolved and extracted in HNO_3 for analysis by ICP-AES (LeeMan ABS CO. USA). As expected, the solubility of $scCO_2$ in gear-oil increased when the pressure was increased by increments and the viscosity of the mixture of gear-oil and agent ($scCO_2$) decreased. The operating temperatures were 40℃, 80℃ and 120℃. The operating pressures were 90bar, 120bar and 150bar. Membrane pore sizes of 0.02 ㎛, 0.1 ㎛ and 0.5 ㎛ were used. The gamma ray activities of the waste oil were measured by an HPGe γ-ray spectroscopy system (CANBERRA GC-2520, Suwon radioactivity survey laboratory) before and after the filtration. The specimen exhibited about 50 ㎖. The detection time was 80,000 seconds, which is the basis of environmental radioactivity detection. The efficiency of filtration is affected by membrane pore size, temperature and pressure.

We carried out the experiment to determine the optimum efficiency of many experimental conditions (pressure/temperature), using mock-up specimens as well as real radioactive waste oil. When we used only filtration, the filtration efficiency was as great as 75% at 120℃ (fig 2). The increment of temperature was most important for reducing the viscosity of the waste oil. Pressure increased filtration efficiency by increments of solubility, as the solubility depended on the density of the carbon dioxide. We found that small pore sizes also increased filtration efficiency. That is, filtration efficiency was as great as 65% at 120℃, 120bar (fig 3). A mock-up specimen was prepared using gear-oil to verify the efficiency of the filtration. After the mock-up test, the purity of the radioactive waste oil was tested using a membrane-based ion exchange resin. In the experiment, we observed a high removal efficiency, approximately 97%. Furthermore, we performed purification of real radioactive waste oil using a membrane added ion exchange resin apparatus with the same experimental conditions. As a result, we also observed a high removal efficiency (Cs-137:~97%, Co-60:~74%).

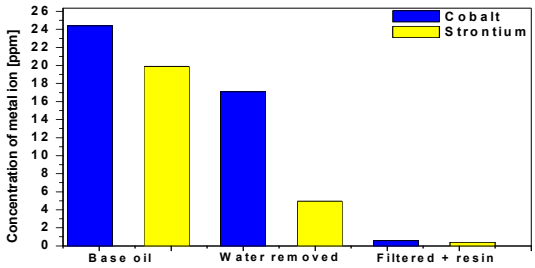

Figure 2. Removal efficiency (membrane-based ion exchange resin: mock-up test)

Table 1. Removal efficiency (membrane-based ion exchange resin: real radioactive waste oil)

	Cs-137	Co-60	
	661.7 keV	1173.2 keV	1332.5 keV
Water removed	66.5 [%]	47.2 [%]	47.8 [%]
Filtered + resin	97.4 [%]	74.5 [%]	74.2 [%]

3. Conclusion

Membrane filtration of radioactive waste oil from nuclear power plants, as well as a mock-up specimen, was tested. We observed the possibility of separating nuclides and metal ions from both oils. The membrane-based ion exchange resin worked as a filter and purifier for the contaminated material in the oil. The highest efficiency of decontamination was observed at ~97% in the mock-up test. We also observed a high removal efficiency (Cs-137:~97%, Co-60:~74%) in real radioactive waste oil.

Acknowledgment

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