Decontamination of Heavy Metal in Soil by Using Supercritical Carbon Dioxide

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1. Introduction

Due to an increase of the nuclear power plant, radioactive waste is also increasing trend and due to the large amount of radioactive waste disposal costs also increase. Decontamination of soil contamination is depending on the soil characteristics and environmental factor, so single decontamination method is difficult for effective decontamination. We need innovative method to decontamination, because existing methods of decontamination make many secondary waste and processing costs. Carbon dioxide in a supercritical state is very excellent permeability to penetrate into the contaminants so, it can be easily decontamination the narrow gap.
Also after extract contaminated material dissolved in supercritical carbon dioxide, it will be extracted again lowering the pressure of the contaminant. Because of that we can reduce secondary waste, so the cost of the process is significantly expected to be reduced. Because extracted dioxide can be reused, it is economically and ecofriendly decontamination method.

2. Experiment & Analysis Method

In this section some of the techniques used to decontaminate soil are described. Experiment and analysis include simulated sample, experiment apparatus and process, preprocessing and ICP-MS analysis.

2.1 Simulated sample

Selected soil for contamination of this experiment is sea sand (JUNSEL, chemical pure) which have large particle and small pore space. Considering contaminated soil from the accident of nuclear power plant, chosen heavy metal are Li, Na, Cs, Sr. Because supercritical carbon dioxide doesn't have solubility to metal, Crown Ether is added for extractive substance. When the soil is contaminated by heavy metals, it is contaminated in aqueous solution. Because of this phenomenon, nitric acid is used for adsorption of heavy metals in soils similar to the actual sample to make simulated sample. According to these features, to make the simulated sample, 20g of sea sand is mixed with 10ml of nitric acid and each 5ml of standard solution (Li, Na, Cs, Sr). After mixing each material by ultrasonic cleaner, mixed with an aqueous solution of nitric acid was evaporated from the soil in order to dry the metal ion by oven to dryness for 20hours.

2.2 Experiment apparatus & method

Figure 1 show the schematic diagram of experiment apparatus. This experiment apparatus are composed of carbon dioxide tank(1) and thermostat to make liquid carbon dioxide(2), syringe pump for pressure control(3), stirring vessel & heater for reacting with carbon dioxide and extractive substance(4), specimen container containing contaminated soil and thermostat(5), bubbler for discharging supercritical carbon dioxide in the shape of gas.

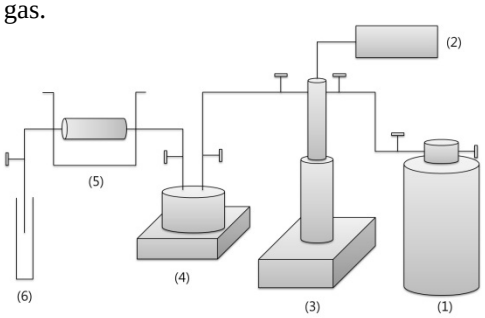

Figure 1. The schematic diagram of experimental apparatus

Firstly, connect each devices with using pipes then put Crown Ether into the stirring vessel (4) and connect specimen container(5) with pipe. Secondly, using a thermostat(2) make carbon dioxide into the syringe pump liquid state at 10℃, CO_2 become supercritical carbon dioxide at 40℃, 200bar.
Therefore, stirring vessel(4) and specimen container(5) are maintained at 10℃ by using thermostat(5) and heater(4). Also carbon dioxide into specimen container(5) is maintained at 200bar by the syringe pump. The inside of Experimental device that fills extractive substance dissolved in supercritical carbon dioxide. And then it decontaminate pollute soil from reaction with simulated soil.
After contaminated soil is fully reacted with supercritical carbon dioxide for 1hour, and then open the valve of bubbler to emit carbon dioxide like gas state.

2.3 Preprocessing

Quantitative analysis is method to analyze sort and quantity of every element constituting the sample, in the present study, the ICP-MS is used for quantitative analysis. Also, purpose of this quantitative analysis is to calculate total quantity from chemically or physically different type of elements in the sample. Especially, remaining organic of the soil should be decontaminate

for analyzing heavy metal in the soil.
Although organic of the soil`s amount is 5%, it has complex mechanism in case of absorbing heavy metal. There are various method of preprocessing commonly used in the preprocessing method of heavy metal. These are nitric acid method, nitric acid-hydrochloric acid, nitric acid-sulfuric acid, and micro wave method etc. In this study, the easiest and most common method of preprocessing, nitric acid is used. Nitric acid method is very simple and commonly used method, also it is easy to control amount of sample or acid and it is cheap process.
But depending on the sample, it may take a long response, and it may take the explosion responding with acid. Therefore, precise understanding of sample should be needed beforehand.

2.4 ICP-MS analysis

ICP-MS is composed with ICP(Inductively Coupled Plasma) to ionize sample and MS(Mass Spectrometer) to distinguish from created ions, and Interface for connecting ICP with MS. ICP-MS is possible to analyze minimum quantity of the element from many other element expeditiously. And it becomes gradually increase because, it can analyze high precision with high sensitivity and accuracy. Therefore Quantitative analysis is performed by ICP-MS

3. Result & Discussion

3.1 Result by ICP-MS analysis

Figure 2 is the result of analysis using ICP-MS about decontamination with Crown Ether and supercritical carbon dioxide for one hour. Sea sand1 and 2 show result of analysis before and after decontamination experiment using supercritical carbon dioxide.

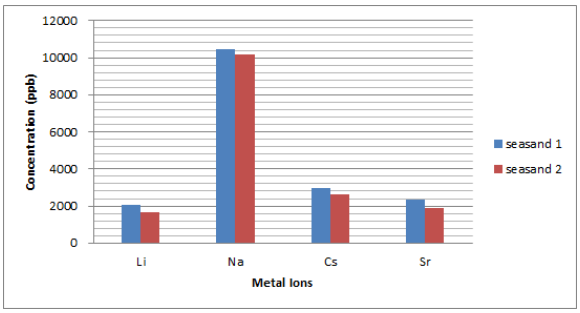

Figure 2. Result of decontamination by supercritical carbon dioxide

Looking at the results, using supercritical carbon dioxide to go through the decontamination process after decontamination is less than the previous sample about the number of heavy metal ions. Decrease in the number of heavy metal ions is supposed that heavy metal of the soil is extracted by decontamination process due to supercritical carbon dioxide and Crown Ether. However, through this experiment, decontamination effect is not large. Extraction rate is obtained to compare correct extraction of decontamination about heavy metal ions before and after. Next figure3 shows extraction rate after decontamination of sample.

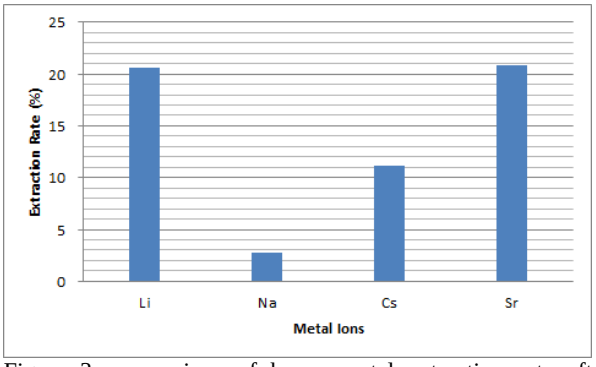

Figure 3. comparison of heavy metal extraction rate after decontamination

Looking at the extraction rate of heavy metal ions before and after decontamination, In the case of sodium showed about 3% the lowest extraction rate, cesium showed about 11%, lithium and strontium showed about 21% the highest extraction rate. At least about 3% up to about 20% of the metal ions is extracted. Therefore depending on the type of metal ion can be seen that extraction rate is different.

3.2 Discussion

Experimental results were shown in the results is relatively low extraction rate. It is because, supercritical carbon dioxide is not polar solvent but no-polar solvent. Therefore, if the contaminants are polar substance, it does not have an effect on decontamination, for that reason it is difficult to accurately analyze. Therefore, other substance should be added in addition to used extraction in this experiment to complement weakness.
By using effective extraction of strontium and lead known as the Net4-PFOSA(Perfluoro-1-octanesulfosic acid), non-polar solvent that supercritical carbon dioxide can be compensated to interaction with Net4-PFOSA in shape of a surfactant . Also preprocessing is different depending on sample and analytical equipment and component of analysis. Due to this mechanism, optimized preprocessing method should be used.
This alternative is to use microwave accelerated reaction system. It is used to burn solvent by microwave.
This method can be used for preprocessing more rapid and accurate than nitric acid method. After this experiment, using the microwave accelerated reaction system, a little more clear and reliable results can be obtained

4. Conclusions

Nuclear power generation doesn`t generate greenhouse

gas as a green energy, it is growing worldwide scale. Due to an increase of the nuclear power plant, radioactive waste is also increasing trend and due to the large amount of radioactive waste disposal costs also increase. Therefore, I research supercritical carbon dioxide instead of existing decontamination method to decontaminate soil, also it has very high permeability. In this study, the soil particle is large and small surface pore size are selected as sea sand for sample. And Li, Na, Cs, Sr of heavy metal were selected for polluted substance. Because supercritical carbon dioxide doesn't have solubility to metal, Crown Ether is added for extractive substance. After the quantitative analysis using ICP-MS, results using supercritical carbon dioxide can be checked that heavy metal ions in the decontamination are less. At least about 3% up to about 20% of the metal ions is extracted, but experimental results were shown in the results is relatively low extraction rate. It is because, supercritical carbon dioxide is not polar solvent but no-polar solvent. Therefore, other extractive substance should be added in the next study. Also preprocessing is different depending on sample and analytical equipment and component of analysis. Due to this mechanism, optimized preprocessing method should be used instead of nitric acid method using in this experiment.

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