

Possibility of removing radionuclides in landfill leachate using advanced wastewater treatment processes

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Radionuclides released by the nuclear accident at the Fukushima Daiichi Nuclear Power Plant are being partly concentrated to sewage sludge ash and waste ash. These ashes, in which radiocesium concentration is lower than 8000 Bq/kg, are being disposed of in a controlled landfill site. The leachate from the landfill site is treated in a leachate treatment system combined with some treatment steps before it is discharged into receiving water. In this study, in place of radionuclides, stable element concentrations in the leachate and treated water at each treatment step were measured to estimate the possible extent of radionuclide removal from the leachate step-by-step. It was found that Cs was not removed in any treatment steps, while more than 85 % of the Sr, Co, Ni, and Mn present was removed in the alkaline earth element removal step.

Key Words: landfill leachate, stable isotopes, cesium, strontium

1. Introduction

The nuclear accident at the Fukushima Daiichi Nuclear Power Plant that occurred subsequent to the Great East Japan Earthquake on March 11, 2011, resulted in a significant release of radionuclides into the environment. With the passage of time, some amount of the radionuclides are being concentrated into sewage sludge ash¹⁾ and waste ash²⁾. The Japanese government has allowed ashes with a radiocesium concentration lower than 8000 Bq/kg to be disposed of at a controlled landfill site³⁾.

The leachate from the landfill site, possibly containing radionuclides dissolved from the ashes, is treated in a leachate treatment plant before it is discharged into receiving water. The leachate treatment system is a combination of several treatment steps that are used to

remove alkaline components, organic pollutants, suspended solids, heavy metals, and other substances. Some studies have been performed to evaluate the effectiveness of the removal of hazardous materials such as endocrine-disrupting chemicals⁴⁾ and metals⁵⁾ in leachate treatment systems. However, the extent of removal of any radionuclide present in the leachate in each step is not clear.

In the present study, the concentrations of certain stable elements were determined in the leachate and treated water at each treatment step, in place of radionuclide concentration, to indirectly estimate the extent of radionuclide removal from the leachate after each step. Leachate samples were collected in July and September, 2012, at a leachate treatment plant located at a controlled landfill site in Iwate Prefecture, where ash (e.g., sewage sludge ash and waste ash) known to contain

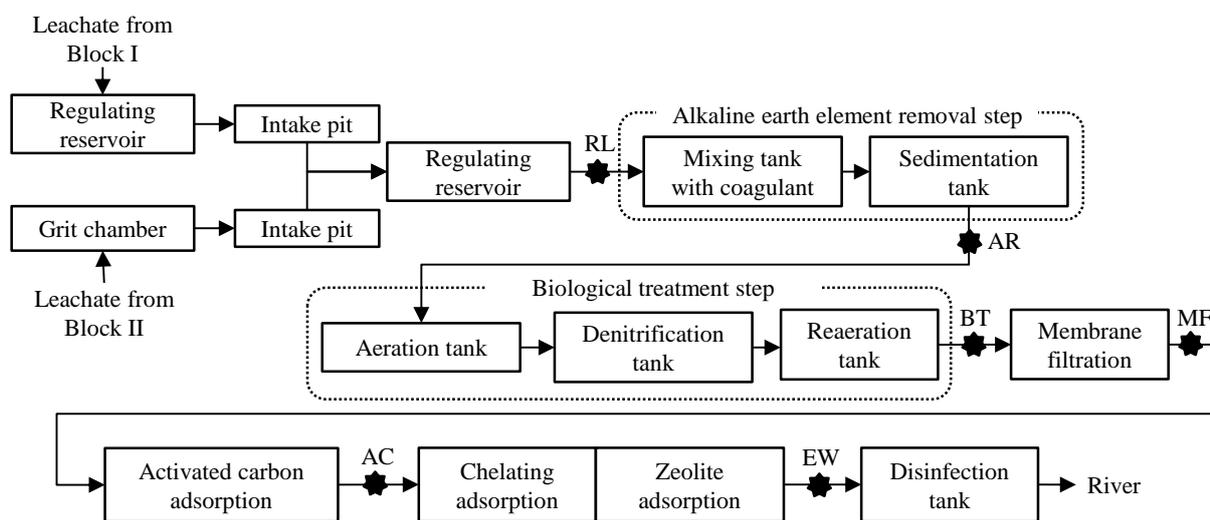


Fig.1 Leachate treatment system and sampling points (★)

radionuclides was being disposed of. Elements selected for the evaluation were Cs, Sr, Co, Ni, and Mn; they include radionuclides (^{134}Cs , ^{137}Cs , ^{90}Sr , ^{58}Co , ^{60}Co , ^{54}Mn , ^{59}Ni , and ^{63}Ni) that were detected or for which detection was attempted in environment samples after the nuclear accident⁶.

2. Materials and methods

(1) Sample collection

Samples were collected from the controlled landfill site described above. The site is separated into block I (landfill capacity: 50300 m³) and block II (landfill capacity: 75000 m³). Block I is now closed, while more than half of the landfill capacity of block II remains available.

A flow sheet of the leachate treatment system and sampling points is presented in Fig.1. Leachates from blocks I and II were mixed in the regulating reservoir. Samples were collected from the following points: after the regulating reservoir (raw leachate: RL), after the alkaline earth element removal step using sodium carbonate (AR), after the biological treatment step (BT), after the membrane filtration step (MF), after the activated carbon adsorption step (AC), and after the chelating and zeolite adsorption step (effluent water: EW). With the exception of AC, which was only sampled in September, the samples were collected in July and September, 2012, from all locations. Zeolite (mordenite) adsorption for radiocesium adsorption was added to the process from May 2012. A pH regulating tank is used after each step.

(2) Analysis

The chemical characteristics of the samples were determined. The pH was measured with a pH meter (TOADKK, HM-25R). The amounts of suspended solids (SS) were determined using the standard method⁷. The total organic carbon content (TOC) was determined using a TOC analyzer (Shimadzu, TOC-V).

Concentration analyses of the target elements (Cs, Sr, Co, Ni, and Mn) and related elements were performed based on standard methods used for the examination of wastewater⁷. A total of 100 mL of the sample was digested with 1 mL of concentrated HNO₃ and 0.5 mL of concentrated HCl. This mixture was evaporated on a hot plate at around 120 °C. Then, deionized water was added to the sample to achieve a solution volume of 100 mL. The sample solution was filtered through a 0.45-μm membrane filter. Element concentrations in the filtrate were measured using an ICP mass spectrometer (Thermo, iCAP Qs) and ICP atomic emission spectrometer (Shimadzu, ICPE-9000). Standard solutions were purchased from Merck Chemicals (CertiPUR series). No contamination was found in the processed blank.

3. Results and Discussion

(1) Characteristics of samples

Table 1 lists the pH and the concentrations of SS and TOC in each sample. The level of SS in the leachate in September was substantially higher than that in July. Sediments in one of the two intake pits were moved to another pit during maintenance of the pit; and therefore, the turbidity in the pit in September was higher than that

Table 1 pH, SS and TOC in samples

	pH		SS [mg/L]				TOC [mg/L]			
	July	Sep.	July	±	Sep.	±	July	±	Sep.	±
RL	7.44	7.36	77.0	7.8	280.5	3.7	15.4	0.5	23.4	0.4
AR	9.95	9.30	12.0	2.8	15.1	1.7	9.6	0.8	23.5	0.6
BT	7.70	7.57	5.0	0.7	2.8	0.5	12.3	0.2	30.2	0.5
MF	7.14	6.96	1.3	0.2	1.1	0.2	8.2	0.0	1.8	0.0
AC	-	6.94	-	-	1.2	0.5	-	-	2.3	0.1
EW	7.07	6.95	2.2	0.2	0.9	0.1	5.1	0.0	4.0	0.1

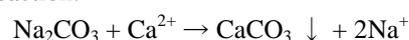
in July. More than 60% of the SS in the leachate was removed in the alkaline earth element removal step, and after the biological step, more than 90% of the SS was removed from the leachate. On the other hand, TOC was reduced after the membrane filtration step.

(2) Element removal at each treatment step

Table 2 lists the concentrations of target elements in each sample. Cs concentration in the leachate was not changed after any of the treatment steps, which implied that none of the treatment steps was effective for the removal of Cs in the leachate from the landfill site. It was noted that even the zeolite adsorption step (between AC and EW) was ineffective for removing the Cs present in the leachate. This result could be attributed to the presence of K and Rb in the leachate, which are elements in the same group of the Periodic Table as Cs. Since these same group elements have similar adsorption characteristics to zeolite and other minerals^{8,9)}, K and Rb

ions, which were present in substantially greater amounts (Table 3), were removed first. In particular, the K concentration was more than 100000 times higher than the Cs concentration in the samples. In addition, Na existed at high concentration may inhibit Cs adsorption by zeolite¹⁰⁾. Therefore, it was probably necessary to use other sorbents such as insoluble ferrocyanide sorbents¹¹⁾, which have a high selectivity for Cs adsorption.

The RL samples contained 2.4–6.0 mg/L of Sr. More than 90% of Sr in the RL was removed in the alkaline earth element removal step. For this step, alkaline earth elements (mainly Ca) in the leachate were precipitated with sodium carbonate according to the following reaction:



Na concentration was 1.8–2.0 g/L in the RL, and it was increased after the alkaline earth element removal step to 2.4–3.2 g/L. These results supported the behavior that would be expected from the above chemical reaction. Sr is an alkali earth metal similar to Ca and Mg; therefore, Sr is expected to precipitate in the same manner as Ca. The sediment produced in the alkaline earth element removal step is expected to be SrCO₃ for Sr, and the sediment expected to be buried at the landfill site. The solubility of SrCO₃ is low (0.011 g/L at 18 °C in water); hence, dissolution from the sediment to a leachate is unlikely.

More than 85% of the Co, Ni, and Mn was also removed in the alkaline earth element removal step. As

Table 2 Target element concentrations at each step

	Cs [μg/L]				Sr [μg/L]				Co [μg/L]				Ni [μg/L]				Mn [μg/L]			
	July	±	Sep.	±	July	±	Sep.	±	July	±	Sep.	±	July	±	Sep.	±	July	±	Sep.	±
RL	2.77	0.03	2.22	0.02	5973	122	2407	22	20.3	1.5	11.5	0.1	76	6.3	84	0.8	2069	0.1	3280	99.6
AR	2.56	0.04	2.02	0.01	74	6.9	69	1.4	1.7	0.06	1.3	0.05	11	2.6	3.9	0.2	4.4	0.9	16	2.2
BT	2.66	0.03	2.09	0.01	343	2.8	95	0.9	2.4	0.08	1.1	0.04	14	2.8	6.6	0.3	8.4	0.4	0.3	0.1
MF	2.85	0.06	2.14	0.00	403	9.6	98	1.3	1.8	0.02	1.1	0.01	10	0.8	6.3	0.7	0.6	0.1	6.6	0.2
AC	-	-	2.14	0.02	-	-	101	0.7	-	-	1.5	0.10	-	-	9.5	0.4	-	-	1.7	0.1
EW	2.74	0.01	2.35	0.43	518	6.8	101	1.5	1.6	0.05	1.1	0.02	11	1.7	5.8	0.0	7.8	0.5	1.3	0.2

Table 3 Other element concentrations at each step

	K [mg/L]				Rb [μg/L]				Ca [mg/L]				Mg [mg/L]				Na [g/L]			
	July	±	Sep.	±	July	±	Sep.	±	July	±	Sep.	±	July	±	Sep.	±	July	±	Sep.	±
RL	617	17.7	362	1.4	478	1.5	301	3.2	163	1.1	657	0.0	39.1	1.2	31.2	0.3	2.0	0.2	1.8	0.1
AR	547	78.6	358	9.1	437	4.1	288	9.9	1.0	0.0	17.3	0.4	19.7	0.6	25.0	0.3	3.2	0.4	2.4	0.1
BT	553	27.9	378	4.3	421	6.1	293	7.5	3.3	0.0	22.0	0.1	18.4	0.2	25.9	0.2	3.1	0.2	2.4	0.1
MF	560	6.5	388	4.7	421	4.1	303	2.9	3.7	0.1	22.5	0.5	18.8	0.4	26.2	0.0	3.2	0.0	2.4	0.0
AC	-	-	393	5.7	-	-	306	6.9	-	-	24.0	0.6	-	-	26.3	0.1	-	-	2.5	0.1
EW	557	30.7	391	6.7	419	5.5	305	5.7	4.7	0.0	23.8	0.4	18.2	0.4	26.0	0.4	3.1	0.2	2.3	0.3

described above, the sediment produced in the alkaline earth element removal step is buried at the landfill site. To estimate the dissolution of these elements from the sediment, it is necessary to know the chemical form of each element in the sediment. On the other hand, the chelate sorbent and zeolite may be somewhat effective in removing these elements. However, almost all the sorption sites in these sorbents would probably be occupied by the more abundantly present alkali and alkaline earth elements (K, Mg, Ca, and Na) because their concentrations are substantially higher than Co, Ni, and Mn in the AC.

4. Conclusions

The following results were obtained in the present study.

- Cs could not be removed with any of the treatment steps in the existing treatment system. The use of an adsorbent such as zeolite was not effective because the ions from the same group as Cs, such as K and Rb, were present in substantially larger amounts; therefore, it was necessary to adopt other treatment steps for Cs removal.
- More than 85% of the Sr, Co, Ni, and Mn present could be removed in the alkaline earth element removal step. This result indicated that the existing treatment system would be effective for the removal of radionuclides present in leachate.

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