



Original Article

Effective removal of non-radioactive and radioactive cesium from wastewater generated by washing treatment of contaminated steel ash



P. Sopapan^{*}, U. Lamdab, T. Akharawutchayanon, S. Issarapanacheewin, K. Yubonmhat, W. Silpradit, W. Katekaew, N. Prasertchiewchan

Radioactive Waste Management Center, Thailand Institute of Nuclear Technology (Public Organization), Ongkharak, Nakhon Nayok, 26120, Thailand

ARTICLE INFO

Article history:

Received 9 May 2022

Received in revised form

21 August 2022

Accepted 7 October 2022

Available online 13 October 2022

Keywords:

Ash-washing solution

Cesium removal

Co-precipitation

Iron-potassium ferrocyanide

Nickel-potassium ferrocyanide

ABSTRACT

The co-precipitation process plays a key role in the decontamination of radionuclides from low and intermediate levels of liquid waste. For that reason, the removal of Cs ions from waste solution by the co-precipitation method was carried out. A simulated liquid waste (^{137}Cs) was prepared from a 0.1 M CsCl solution, while wastewater generated by washing steel ash served as a representative of radioactive cesium solution (^{137}Cs). By co-precipitation, potassium ferrocyanide was applied for the adsorption of Cs ions, while nickel nitrate and iron sulfate were selected for supporting the precipitation. The amount of residual Cs ions in the CsCl solution after precipitation and filtration was determined by ICP-OES, while the radioactivity of ^{137}Cs was measured using a gamma-ray spectrometer. After cesium removal, the amount of cesium appearing in both XRD and SEM-EDS was analyzed. The removal efficiency of ^{137}Cs was 60.21% and 51.86% for nickel nitrate and iron sulfate, respectively. For the ash-washing solution, the removal efficiency of ^{137}Cs was revealed to be more than 99.91% by both chemical agents. This implied that the co-precipitation process is an excellent strategy for the effective removal of radioactive cesium in waste solution treatment.

© 2022 Korean Nuclear Society, Published by Elsevier Korea LLC. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

1. Introduction

In an era where nuclear technology is advancing rapidly, radioactive materials are being utilized in many sectors such as nuclear power plants, medical therapy, industrial factory, and agricultural application, resulting in large-scale contamination. One of the affected sectors is the metallurgical industry, particularly radioactive contamination in the steel industry [1,2]. Using the scrap steel recycling process, radioactive cesium (^{137}Cs) contaminated ashes have recently been found in many steel production factories around the world, leading to immediate and long-term concerns over possible radiation hazards [3,4]. One of the most serious consequences of these ashes was the leaching of water and the continuing risk of groundwater contamination [5]. As ^{137}Cs has a long half-life (~30 years) and high concentration, the disposal of the radioactively contaminated steel ashes is becoming a global environmental issue that must be managed urgently [6–8].

It is known that the cesium ion (Cs^+) is an alkali metal element similar to potassium ion (K^+) and sodium ion (Na^+), with very high solubility in an aqueous medium, which are harmful to human safety and environmentally impactful [9,10]. Therefore, the development of methods and techniques for removing cesium and various hazardous chemicals from radioactive liquid waste has become a research focus in the field of radioactive liquid waste [11–13]. Several methods have been used for removing cesium ions from radioactive liquid waste such as co-precipitation, solvent extraction, and adsorption [14–17]. Amongst the available approaches, the co-precipitation process is a simple and low-cost method [11,18]. The highly selective cesium precipitation would be a good potential process for removing radioactive liquid waste containing cesium ions and various hazardous chemicals because of its simplicity and efficiency in the treatment of liquid waste in large volumes [19,20]. Another advantage of chemical precipitation method is the volume reduction of the waste stream. By this method, the contamination amount is reduced and consequently the transportation and management are more economical and expedient. The radioactive waste generated from the sedimentation

^{*} Corresponding author.

E-mail address: poonaphob@tint.or.th (P. Sopapan).

process could be stored conveniently and safely or disposed of in a licensed low-level waste repository [21,22].

Potassium ferrocyanide is considered a promising approach for the treatment of cesium from radioactive liquid wastes due to its excellent cesium selectivity and adsorption capacity [23]. Transition metals have also been used as chemical agents for supporting the co-precipitation process. For example, Osmanlioglu used potassium ferrocyanide and nickel(II) nitrate for the removal of radioactive cesium. The results showed the excellent removal efficiency of radioactive cesium from radioactive liquid waste by the co-precipitation process [18]. However, nickel-potassium ferrocyanide (NiKFC) is known to be hazardous to both human health and the environment. Finding a chemical agent that has high efficiency for removing cesium while being safer is a challenging approach that researchers are focusing on. There have been relatively numerous reports of using iron sulfate to remove the various hazardous chemicals in wastewater. However, there is hardly evidence concerning its use to remove radionuclides in radioactive liquid waste [24,25]. Therefore, the use of iron-potassium ferrocyanide (FeKFC) as a precipitant is an interesting way to support cesium removal in aqueous solutions.

The purpose of this work is to decontaminate non-radioactive and radioactive cesium from aqueous waste solutions by co-precipitation using potassium ferrocyanide as a chemical agent, with nickel(II) nitrate and iron(II) sulfate chosen for supporting the precipitation. A gamma-ray spectrometer, ICP-OES, XRD, and SEM-EDS were used to characterize the solution and sludge samples after the cesium removal process. In order to assess the effects of use, both precipitating agents were also compared in terms of the removal efficacy of cesium and environmental toxicity.

2. Materials and methods

2.1. Chemicals and materials

For the experiment, cesium-simulated liquid waste was prepared from cesium chloride (CsCl, 99.90%, Sigma Aldrich, USA), while the radioactive waste solution was generated by washing ^{137}Cs contaminated steel ash. Potassium hexacyanoferrate(II) trihydrate ($\text{K}_4[\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}]$, 99%, Sigma Aldrich, USA), Nickel(II) nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 99.99%, Sigma Aldrich, USA), and Iron(II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 97%, Ajax Finechem) were used to purify the CsCl solution and the washing wastewater contaminated with ^{137}Cs . In addition, deionized water (DI) was used in all experiments.

2.2. Preparation of waste solution by washing ^{137}Cs contaminated ash

The steel ash was collected from a scrap steel recycling factory in Thailand. The ash has been found to be contaminated with high levels of radionuclide cesium (^{137}Cs). The ^{137}Cs contaminated steel ash was washed using deionized water at a solid-liquid ratio of 1:2. About 200 g of ash and 400 mL of deionized water were added into a 1000 mL beaker, and then the mixed solution was kept at a stirring speed of 200 rpm for 3 h. After the specified time, the solid-liquid mixture was separated by centrifugation at 4000 rpm for 5 min. The previously washed ash was extracted repeatedly. The resulting ash was then oven-dried at 60 °C for 24 h. The element compositions of steel ash determined through WDXRF spectrometer (S8 Tiger, Bruker AXS GmbH, Germany) are mainly Zn (29.1947%), Fe (28.6355%), O (25.8369%), Ca (3.2948%), Mn (2.5449%), Pb (1.8624%), and others. The radioactivity of ^{137}Cs in the ash, before and after the washing process, was measured via gamma-ray spectrometer (GEM-C40, Ametek Ortec, USA) using

coaxial high-purity germanium (HPGe) detector with MCA to quantify the ^{137}Cs -removal efficiency. By washing with deionized water in two stages, it is possible to reduce around 80% of the radioactivity from ^{137}Cs contaminated ash. Due to its excellent water solubility, the ^{137}Cs and some elements in steel ash are released along with the aqueous solution. This resulting solution was applied as the initial wastewater for the precipitation process. The washing process of ^{137}Cs contaminated ash for preparing the initial waste solution is shown in Fig. 1.

2.3. Co-precipitation process

In order to eliminate the non-radioactive and radioactive cesium from the prepared solutions, the co-precipitation process was applied using potassium ferrocyanide ($\text{K}_4[\text{Fe}(\text{CN})_6]$), nickel nitrate ($\text{Ni}(\text{NO}_3)_2$), and iron sulfate (FeSO_4). Herein, $\text{K}_4[\text{Fe}(\text{CN})_6]$ concentration was fixed to be 0.05 M. The precipitation process was examined by observing the amount of change in the supporting precipitates $\text{Ni}(\text{NO}_3)_2$ and FeSO_4 without pH adjustment of the solution. Briefly, details of the co-precipitation process are as follows: 25 mL of 0.1 M CsCl solution was prepared for the non-radioactive precipitation process, while the radioactive waste solution was generated utilizing ash extraction with deionized water. Then, 0.05 M of $\text{K}_4[\text{Fe}(\text{CN})_6]$ was added to the CsCl solution and the wastewater in each studied condition. The mixed solution was obtained by stirring for 10 min. Different amounts of $\text{Ni}(\text{NO}_3)_2$ (4, 12, and 20 mg/mL) were added to the mixed solution, and the green precipitate was obtained. Amounts of FeSO_4 (4, 12, and 20 mg/mL) were added to the mixed solution to obtain the blue precipitate. For all experiments, the reaction solution was kept under regular stirring for 30 min for a complete dissolution of contents and then permitted to settle overnight. The suspension solutions were collected by filtering supernatants using filter paper (Whatman® qualitative filter paper, Grade 1). The precipitate was dried at 60 °C for 24 h. To study the removal efficiency, structure, and chemical composition, the obtained solution and sludge were characterized. Fig. 2 shows a schematic diagram of the entire process for the waste solution treatment using the co-precipitation method.

2.4. Characterization

After settling time, the solid sludge and aqueous solution were separated by using filter paper before testing. The crystal structure of the sludge samples was analyzed by XRD (D8 Advance, Bruker AXS GmbH, Germany) with LYNXEYE XE-T detector at 40 kV accelerated voltage and 40 mA current. The characteristics of morphology and elemental composition on the obtained sludge were successfully investigated by scanning electron-energy dispersive X-ray spectroscopy (SEM-EDS, SU5000, Hitachi, Japan). Cesium concentration in the obtained solution was measured by using inductively coupled plasma optical emission spectroscopy (ICP-OES, Spectroblue FMX36, SPECTRO Analytical Instruments Inc., USA), while the radioactivity of ^{137}Cs was measured by gamma-ray spectroscopy. The removal efficiency of stable and radioactive cesium was determined using the displayed equation [26,27]:

$$\% \text{ Removal Efficiency} = \frac{C_i - C_f}{C_i} \times 100\% \quad (1)$$

where C_i and C_f are the initial and final concentration of Cs ions and/or radioactivity of ^{137}Cs in the aqueous waste solution, respectively.

According to the radioactivity before the decontamination stage (A_i) and radioactivity after the decontamination stage (A_f) in the ash-washing solution, the decontamination factor (DF) for precipitation processes is usually defined as [18]:

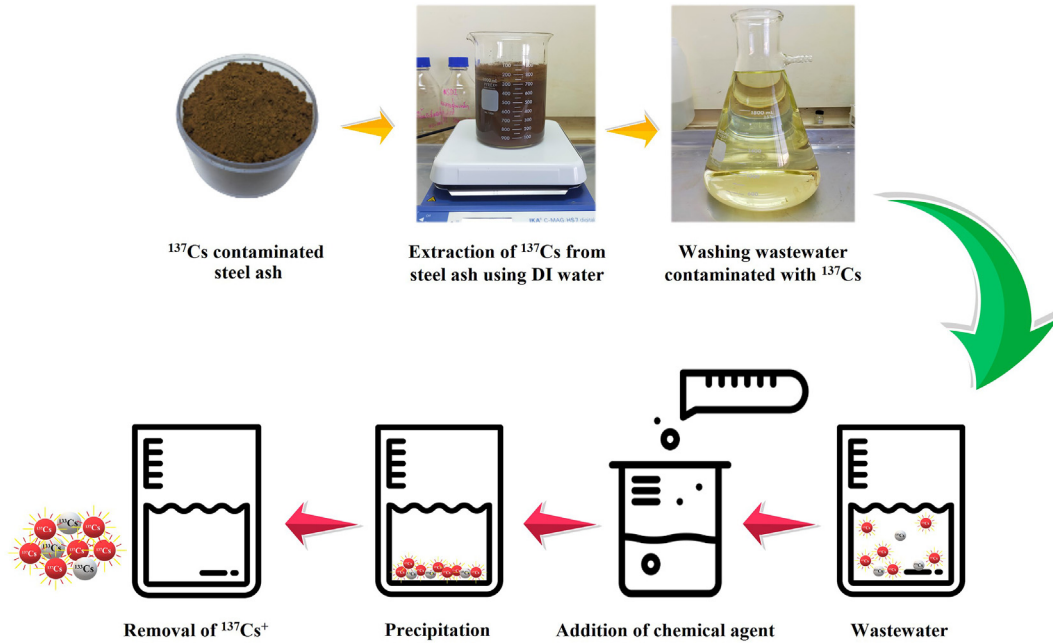


Fig. 1. Washing process for removal of ¹³⁷Cs from contaminated steel ash and wastewater treatment with co-precipitation method.

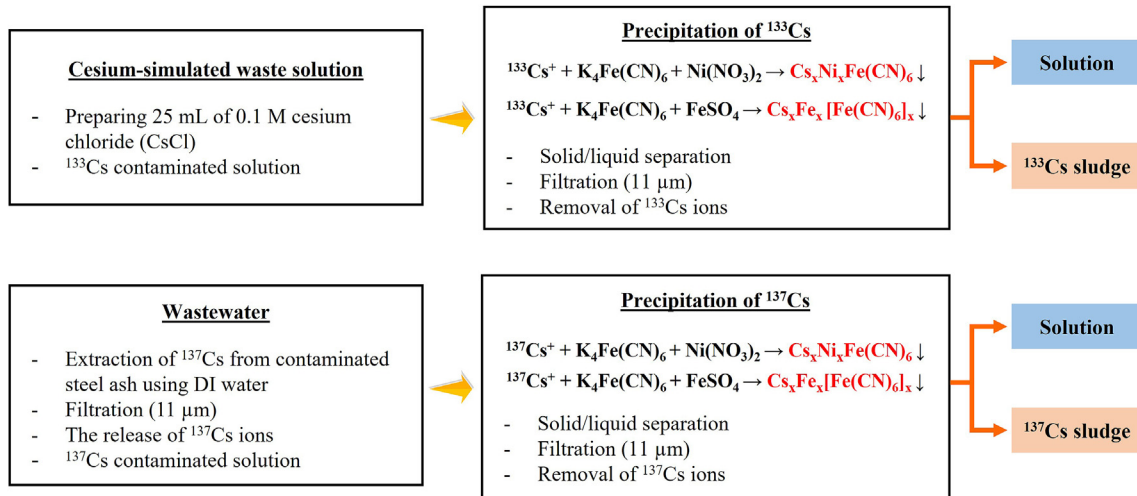


Fig. 2. Schematic diagram of aqueous waste treatment.

$$DF = \frac{A_i}{A_f} \quad (2)$$

3. Results and discussion

3.1. Removal efficiency of non-radioactive and radioactive cesium

The present study was undertaken to decontaminate stable and radioactive cesium. Using the co-precipitation process, the decontamination of cesium and other ions in waste solution can be carried out effectively. Table 1 shows the results of the cesium removal efficiency by co-precipitation using 0.05 M K₄[Fe(CN)₆] combined with Ni(NO₃)₂ and FeSO₄, which were analyzed by ICP-OES. It can be seen that cesium removal efficiency at 4, 12, and 20 mg/mL of Ni(NO₃)₂ was 19.53%, 60.21%, and 48.53%, respectively. In the case

of FeSO₄, the cesium removal efficiency was 16.34%, 51.86%, and 43.72%, respectively. From the obtained results, the total removal efficiency of cesium by Ni(NO₃)₂ was greater than that by FeSO₄ dosage. Moreover, the addition of Ni(NO₃)₂ and FeSO₄ significantly improved the cesium removal efficiency. As exhibited in Tables 1 and 12 mg/mL of Ni(NO₃)₂ and FeSO₄ (NiKFC–12 and FeKFC–12) showed the highest cesium removal efficiency in the CsCl solution.

Table 1

The removal efficiency of ¹³³Cs in simulated waste solution by co-precipitation with different amounts of NiKFC and FeKFC.

Samples	Initial Cs ions (mg/L)	Final Cs ions (mg/L)	Removal efficiency
NiKFC4	15.49 ± 1.00	12.46 ± 0.63	19.53%
NiKFC12	15.49 ± 1.00	6.16 ± 0.14	60.21%
NiKFC20	15.49 ± 1.00	7.97 ± 0.14	48.53%
FeKFC4	15.49 ± 1.00	12.96 ± 0.26	16.34%
FeKFC12	15.49 ± 1.00	7.45 ± 0.26	51.86%
FeKFC20	15.49 ± 1.00	8.72 ± 0.19	43.72%

However, the addition of Ni(NO₃)₂ and FeSO₄ reached 20 mg/mL (NiKFC–20 and FeKFC–20), and the removal efficiency decreased slightly. This could be controlled by limiting the competition effect from nickel (Ni), iron (Fe), and cesium (Cs), resulting in a decrease in the removal efficiency of cesium [28].

In the same way as the precipitation in the simulated solution, equal amounts of K₄[Fe(CN)₆], Ni(NO₃)₂, and FeSO₄ were used in waste solution contaminated ¹³⁷Cs. After the sludge and solution were separated by the filtration method, the residual radioactivity in the liquid was calculated to determine the removal efficiency of ¹³⁷Cs. The results of ¹³⁷Cs radioactivity and removal efficiency of cesium in the wastewater are listed in Table 2. The initial solution obtained by washing steel ash had a radioactivity of 29,719 ± 624 Bq/L with a pH level of 9.5 ± 0.5. After precipitation, the successful treatment of the ¹³⁷Cs contaminated wastewater using NiKFC and FeKFC was confirmed by measuring the radioactive decay of the solution with a gamma-ray spectrometer. By using K₄[Fe(CN)₆], Ni(NO₃)₂, and FeSO₄, the expression of ¹³⁷Cs removal efficiency was greater than 99.91%. This proves that the precipitation method using NiKFC and FeKFC as precipitants is an excellent approach to treating ¹³⁷Cs contaminated wastewater. Besides determined removal efficiency as shown in Table 2, the decontamination factor achieved in each case was also calculated. Depending on the amount of precipitating agent, all the decontamination factors are higher than 1 × 10³. Since decontamination factor is dimensionless, the effluent concentration may be solubility controlled and, thus, the decontamination factor will vary with the initial concentration. Fig. 3 shows a comparison of the ¹³³Cs and ¹³⁷Cs removal efficiency in the prepared waste solutions. By using Ni(NO₃)₂ (Fig. 3(A)) and FeSO₄ (Fig. 3(B)) as precipitating agents, it was clear that the removal efficiency of ¹³⁷Cs was significantly higher than that of ¹³³Cs in all the concentrations. The optimum removal efficiency of ¹³⁷Cs for the ash waste solution was determined to be 99.99%, while the maximum removal efficiency of ¹³³Cs for the simulated liquid waste was revealed to be 60.21%. However, both the stating solutions are on a different basis such as initial pH and Cs-ion concentration. For this experiment, the CsCl solution with pH 6 and concentration of Cs ions as 15.49 mg/L was introduced, while the ¹³⁷Cs contaminated solution with pH 9 was obtained by washing the contaminated steel ash. Although the initial activity of ¹³⁷Cs in the wastewater obtained from the washing process was measured as 29,719 ± 624 Bq/L, the concentration of ¹³⁷Cs ions was found to be negligible. With appropriate pH and ion concentration, the obtained results thus led to the higher removal efficiency. Additionally, the use of Ni(NO₃)₂ and FeSO₄ as precipitating agents provides similar performance for decontamination of the washing wastewater.

Influence of pH levels was also considered to enhance the removal efficiency of radioactive cesium from wastewater. Fig. 4 presents the ¹³⁷Cs removal efficiency in the wastewater with pH level in ranged from 3 to 13 using nickel-potassium ferrocyanide (NiKFC) and iron-potassium ferrocyanide (FeKFC). The experimental results showed that removal of ¹³⁷Cs via co-precipitation using NiKFC and FeKFC had a widely suitable pH range from

acidic to alkaline environments. However, pH values between 9 and 11 showed superior removal efficiency. This result supported the removal of radioactive cesium from wastewater with an initial pH level of 9.

Table 3 shows the volume proportions of clean water and total sludge obtained from treatment of the wastewater. From the results listed in Table 3, the radioactive sludge depends on the initial dose of the chemical agent. The initial wastewater volume of 25 mL became the radioactive sludge to approximately 1–3 mL and the remaining volume is clean water, showing similar results by using NiKFC and FeKFC agents. As shown in Fig. 5, the amount of radioactive sludge became infinitesimal when compared to the initial volume of ¹³⁷Cs-wastewater. By this method, approximately 96% of the decontaminated water has been recovered. Additionally, the handling of sludge is more thrifty, uncomplicated and safer method than the management of starting wastewater. Hence, the results of this successful study can be applied on a larger scale to remove ¹³⁷Cs contaminated wastewater.

3.2. Characteristics of the sludge

Studies on the structure and chemical composition of the obtained sediment confirm the presence of cesium and also provide useful information on the subsequent management of this sludge. The crystal structure of the sludge samples after cesium removal was characterized by X-ray diffraction (XRD), as shown in Fig. 6. From Fig. 6(A), the XRD pattern of the ¹³³Cs contaminated sludge resulting from the NiKFC shows typical diffraction peaks at 2θ values 24.69°, 30.40°, 35.17°, 43.56°, 50.53°, 57.19°, and 68.55°, corresponding to (220), (320), (400), (422), (440), (620), and (642) planes, respectively. The crystal structure can be attributed to the cubic cesium-iron-nickel-cyanide (Cs₄Ni₄[Fe(CN)₆]₃), corresponding to the joint committee on powder diffraction standard (JCPDS) file no. 00-024-0286. The diffraction peaks at 2θ angles of 24.40°, 29.96°, 34.78°, 42.71°, 49.71°, 56.12°, and 67.98° can be indexed as characteristic of (220), (222), (400), (422), (440), (620), and (642) peaks, respectively, appearing in the solid sludge resulting from the FeKFC precipitating agent. The crystal structure can be attributed to the cubic crystal structure of cesium-iron-cyanide (Cs₁₆Fe₄[Fe(CN)₆]₇), corresponding to JCPDS file no. 00-024-0257 [29,30]. The strong diffraction peak in the lattice planes of (220), (400), and (422) is characteristic of cesium after the co-precipitation process. Therefore, the XRD patterns illustrated that the cesium structure agreed with the cesium removal by using K₄[Fe(CN)₆], Ni(NO₃)₂, and FeSO₄. Meanwhile, the XRD patterns of the ¹³⁷Cs contaminated sludge after precipitation with NiKFC and FeKFC in wastewater are presented in Fig. 6(B). The XRD pattern of all ¹³⁷Cs contaminated sludge samples was similar to that of ¹³³Cs contaminated sludge samples. However, an additional strong peak occurred at positions 17.40° (FeKFC) and 17.65° (NiKFC), which is the lattice plane of (200), indicating the presence of iron-cyanide (JCPDS file no. 01-073-0689) and iron-nickel-cyanide (JCPDS file no. 01-057-0049) in the sludge obtained by precipitation of the ash washing solution, respectively. In the present case, it was clear that the sludge

Table 2
The removal efficiency of ¹³⁷Cs and decontamination factor (DF) in ash-washing solution by co-precipitation with different amounts of NiKFC and FeKFC.

Samples	Initial activity (Bq/L)	Final activity (Bq/L)	Removal efficiency	DF
NiKFC4	29,719 ± 624	19.78 ± 5.37	99.93%	1.50 × 10 ³
NiKFC12	29,719 ± 624	2.92 ± 0.58	99.99%	10.18 × 10 ³
NiKFC20	29,719 ± 624	2.58 ± 0.00	99.99%	11.52 × 10 ³
FeKFC4	29,719 ± 624	26.34 ± 5.49	99.91%	1.13 × 10 ³
FeKFC12	29,719 ± 624	3.25 ± 0.58	99.99%	9.14 × 10 ³
FeKFC20	29,719 ± 624	2.92 ± 0.58	99.99%	10.18 × 10 ³

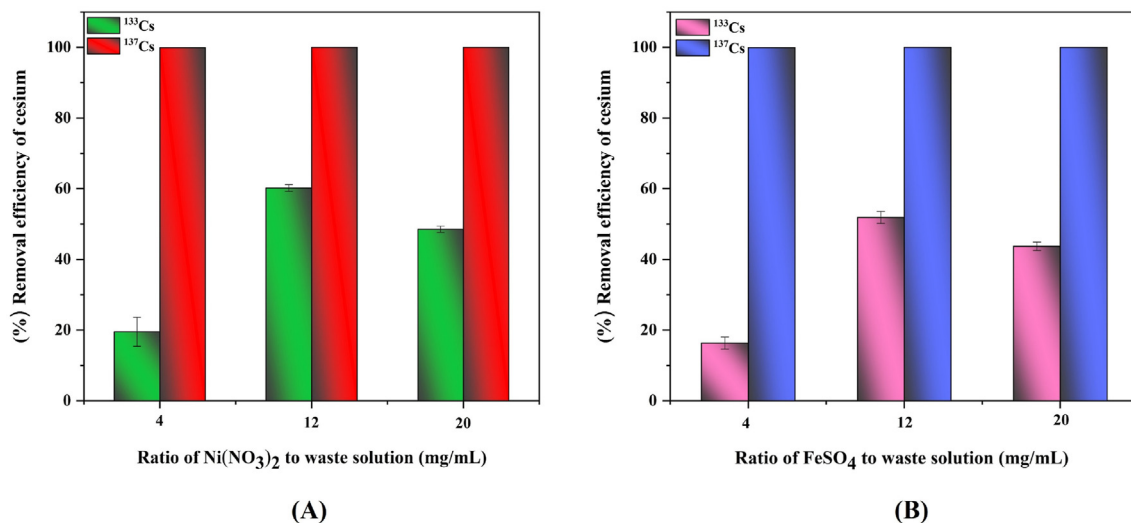


Fig. 3. The ¹³³Cs and ¹³⁷Cs removal from waste solution without pH adjustment by the co-precipitation process using (A) nickel-potassium ferrocyanide and (B) iron-potassium ferrocyanide.

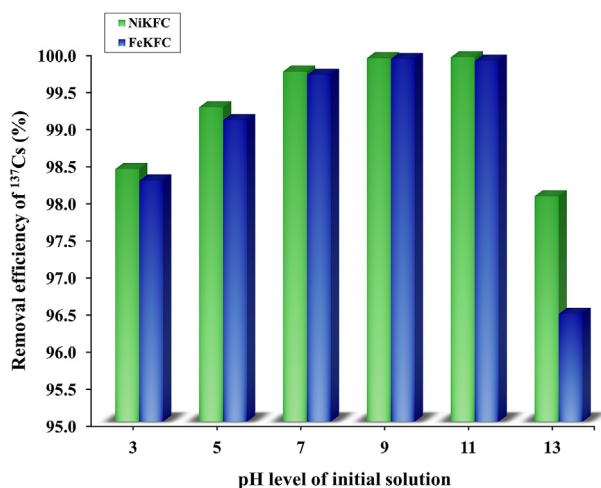


Fig. 4. The ¹³⁷Cs removal efficiency of wastewater with various pH values using nickel-potassium ferrocyanide (NiKFC) and iron-potassium ferrocyanide (FeKFC).

obtained after precipitation in the wastewater showed two overlapping phases of Cs₄Ni₄[Fe(CN)₆]₃ and Ni₂Fe(CN)₆ in NiKFC samples and Cs₁₆Fe₄[Fe(CN)₆]₇ and Fe₄[Fe(CN)₆]₃·(H₂O)₁₄ in FeKFC samples, respectively.

Scanning electron microscope (SEM) energy-dispersive X-ray spectroscopy (EDS) analysis can be used to describe the morphological characteristics and surface elemental composition of the sludge containing stable and radioactive cesium, as presented in Fig. 7. The corresponding SEM micrograph and EDS-elemental mapping of the sludge containing non-radioactive cesium are

Table 3

Volume of decontaminated water and total sludge obtained from treatment of the wastewater.

Treatment	Volume (mL)					
	NiKFC4	NiKFC12	NiKFC20	FeKFC4	FeKFC12	FeKFC20
Total wastewater	25.00	25.00	25.00	25.00	25.00	25.00
Decontaminated water	24.10	22.97	22.05	24.00	22.93	21.83
Total sludge	0.90	2.03	2.95	1.00	2.07	3.17

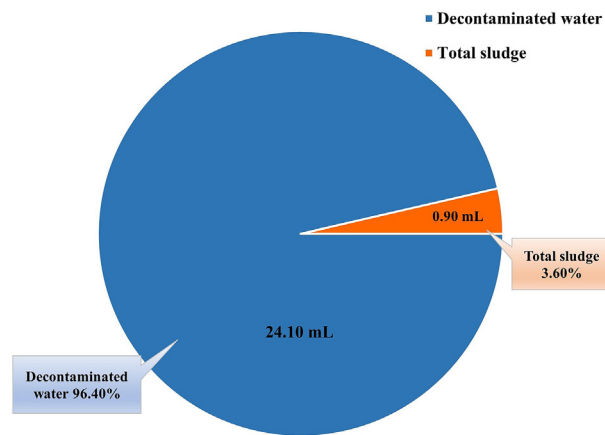


Fig. 5. Volumetric proportions of radioactive sludge and decontaminated water after treatment using chemical precipitation process.

shown in Fig. 7(A) and (B). According to the EDS results, it appears that the selected sludge samples consist mainly of Cs, C, N, Fe, Ni, O, K and Cl. When comparing the cesium content contained in the selected sediments, it was found that the NiKFC-12 sample had a higher cesium content than the FeKFC-12 sample. This can be explained by the existence of the cesium element indicating the removal efficiency of cesium by the co-precipitation process. The amount of cesium element in the sludge was related to the cesium removal efficiency and also supported the result of XRD. This result is consistent with the studies reported in the literature [31,32]. Meanwhile, the SEM-EDS results of the sludge sample after precipitation with NiKFC and FeKFC in wastewater are shown in

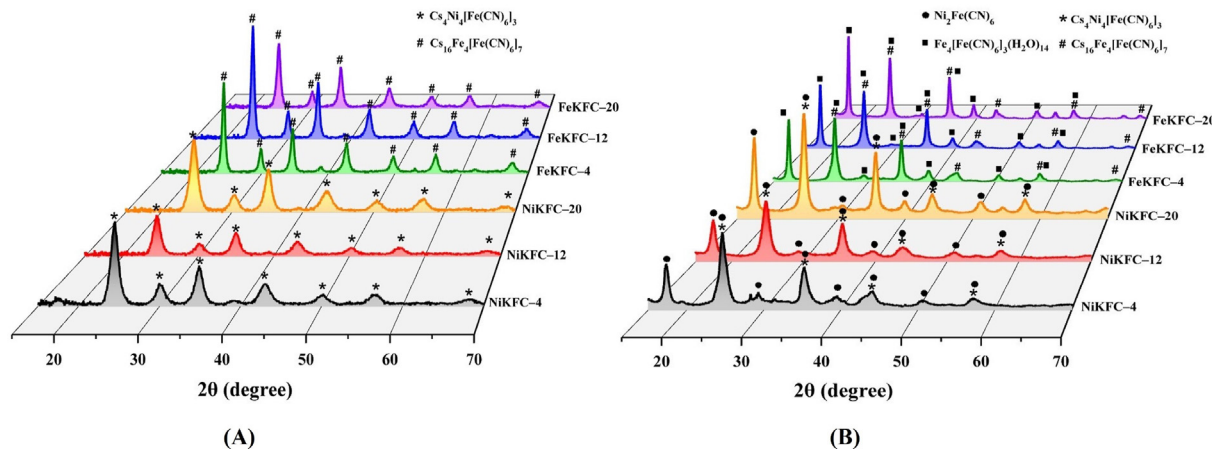


Fig. 6. Comparison of XRD patterns for all the solid samples after co-precipitation, including (A) ¹³³Cs contaminated sludge and (B) ¹³⁷Cs contaminated sludge.

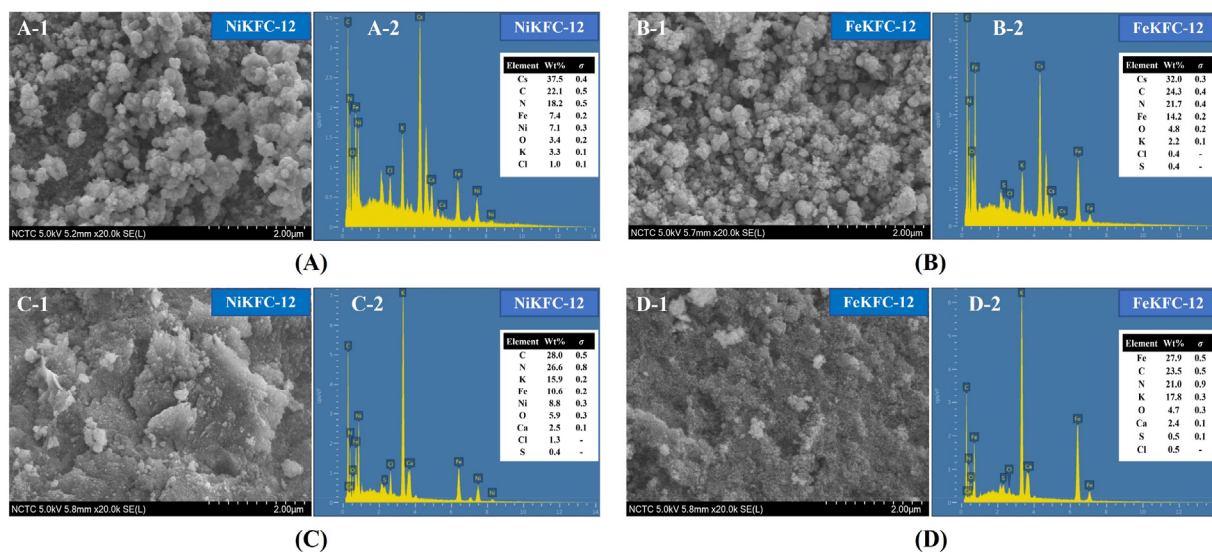


Fig. 7. SEM image and EDS mapping of the selected sludge samples after precipitation. (A) and (B) represent ¹³³Cs contaminated sludge, while (C) and (D) represent ¹³⁷Cs contaminated sludge.

Fig. 7(C) and (D), respectively. Although cesium was predominantly present in the sludge formed in the CsCl solution, it did not appear in the sludge resulting from the ash washing solution. The absence of cesium in the EDS spectrum may be due to instrument limitations. However, the ¹³⁷Cs radioactivity measured by a gamma spectrometer, as shown in Table 2, confirmed the existence of cesium doses. With all results, more than 99.91% of the cesium removal efficiency in the wastewater with low ¹³⁷Cs concentration indicates that the co-precipitation process using NiKFC and FeKFC is a suitable method for the removal of radioactivity from low-level waste [33].

All the obtained results show that the use of NiKFC and FeKFC provides a good basis for the removal of Cs ions in aqueous waste solutions. Although NiKFC exhibits a better removal efficiency than both ¹³³Cs and ¹³⁷Cs, FeKFC has multiple advantages in production cost and environmental friendliness. The impact of nickel and iron on the environment and human health has been discussed in several studies [34–36]. Therefore, the development of FeKFC as a precipitating agent is an interesting approach and could be a method used to eliminate the radioactive cesium from aqueous waste solutions in larger-scale treatment.

4. Conclusions

Successful lab-scale treatment with high-efficiency ¹³⁷Cs in the wastewater generated by washing treatment of radioactively contaminated steel ash is the major objective of this research. The resulting co-precipitation process using nickel and iron potassium ferrocyanide as chemical agents can be widely applied to efficiently remove cesium ions from radioactive liquid waste. The results of XRD and EDS confirmed the presence of cesium content in the sludge samples, and these results supported the removal of cesium ions from the prepared waste solution. The addition of Ni(NO₃)₂ and FeSO₄ at 12 g/L showed effective performance for the removal efficiency of stable cesium at 60.21% and 51.86%, respectively. Meanwhile, the excellent removal efficiency of ¹³⁷Cs in the wastewater was revealed to be over 99.91% under all conditions. The difference of removal efficiency between ¹³³Cs and ¹³⁷Cs depends on the concentration of cesium ions and the pH level of the initial solution. Moreover, by this method, it also reduced the volume of contamination by up to 96.04%. Due to the simple method, cost-effective, volume reduction of contamination, and high removal efficiency of ¹³⁷Cs from ash-washing solution, the co-precipitation

process using nickel and iron potassium ferrocyanide is a highly promising candidate. To enhance the applicability of removing radionuclides from liquid waste, additional concept research and scale-up approaches should be considered in the future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors would like to acknowledge the support provided by the Nuclear Technology Research and Development Center, Thailand Institute of Nuclear Technology (Public Organization) for the analysis of ICP-OES and XRD. This work was financially supported by Thailand Science Research and Innovation (TSRI).

References

- J.O. Lubenau, J.G. Yusko, Radioactive materials in recycled metals, *Health Phys.* 68 (1995) 440–451, <https://doi.org/10.1097/00004032-199504000-00001>.
- T. Hrnčir, M. Panik, F. Ondra, V. Necas, The impact of radioactive steel recycling on the public and professionals, *J. Hazard Mater.* (2013) 254–255, <https://doi.org/10.1016/j.jhazmat.2013.03.038>.
- J.M. Arnal, M. Sancho, B. García-Fayos, Treatment of ^{137}Cs contaminated water by selective adsorption, *Desalination* 321 (2013) 22–27, <https://doi.org/10.1016/j.desal.2013.04.019>.
- K. Yubonmhat, T. Akharawutchayanon, P. Nuanjan, S. Issarapanacheewin, W. Katekaew, N. Prasertchiewchan, Progress and challenges of radioactive waste management in Thailand, *J. Hazard. Toxic Radioact. Waste.* 26 (2022), 04022009, [https://doi.org/10.1061/\(ASCE\)HZ.2153-5515.0000693](https://doi.org/10.1061/(ASCE)HZ.2153-5515.0000693).
- Q.T.N. Le, K. Cho, Caesium adsorption on a zeolitic imidazolate framework (ZIF-8) functionalized by ferrocyanide, *J. Colloid Interface Sci.* 581 (2021) 741–750, <https://doi.org/10.1016/j.jcis.2020.08.017>.
- B. Sun, X.G. Hao, Z.D. Wang, G.Q. Guan, Z.L. Zhang, Y.B. Li, S.B. Liu, Separation of low concentration of cesium ion from wastewater by electrochemically switched ion exchange method: experimental adsorption kinetics analysis, *J. Hazard Mater.* (2012) 233–234, <https://doi.org/10.1016/j.jhazmat.2012.07.010>.
- X.H. Fang, F. Fang, C.H. Lu, L. Zheng, Removal of Cs^+ , Sr^{2+} , and Co^{2+} ions from the mixture of organics and suspended solids aqueous solutions by zeolites, *Nucl. Eng. Technol.* 49 (2017) 556–561, <https://doi.org/10.1016/j.net.2016.11.008>.
- B.M. Jun, M. Jang, C.M. Park, J. Han, Y. Yoon, Selective adsorption of Cs^+ by MXene ($\text{Ti}_3\text{C}_2\text{Tx}$) from model low-level radioactive wastewater, *Nuclear Engineering and Technology, Nucl. Eng. Technol.* 52 (2020) 1201–1207, <https://doi.org/10.1016/j.net.2019.11.020>.
- H. Thorring, L. Skuterud, E. Steinnes, Influence of chemical composition of precipitation on migration of radioactive caesium in natural soils, *J. Environ. Radioact.* 134 (2014) 114–119, <https://doi.org/10.1016/j.jenvrad.2014.03.006>.
- J. Kim, K. Lee, B.K. Seo, J.H. Hyun, Effective removal of radioactive cesium from contaminated water by synthesized composite adsorbent and its thermal treatment for enhanced storage stability, *Environ. Res.* 191 (2020), 110099, <https://doi.org/10.1016/j.envres.2020.110099>.
- H. Rogers, J. Bowers, D.G. Anderson, An isotope dilution–precipitation process for removing radioactive cesium from wastewater, *J. Hazard Mater.* 243 (2012) 124–129, <https://doi.org/10.1016/j.jhazmat.2012.10.006>.
- J. Wang, S. Zhuang, Cesium separation from radioactive waste by extraction and adsorption based on crown ethers and calixarenes, *Nucl. Eng. Technol.* 52 (2020) 328–336, <https://doi.org/10.1016/j.net.2019.08.001>.
- X. Yang, L. Jiang, S. Peng, L. Zhang, G. Huang, Removal of cesium from liquid radioactive waste by in situ electrochemical synthesis of cesium zinc ferrocyanide, *Colloids Surf. A Physicochem. Eng. Asp.* 626 (2021), 127050, <https://doi.org/10.1016/j.colsurfa.2021.127050>.
- G.M. Rashad, M.R. Mahmoud, M.A. Soliman, Combination of coprecipitation and foam separation processes for rapid recovery and preconcentration of cesium radionuclides from water systems, *Process Saf. Environ.* 130 (2019) 163–173, <https://doi.org/10.1016/j.psep.2019.08.007>.
- X. Zhang, X. Tan, C. Li, Y. Yi, W. Liu, L. Zhang, Energy-efficient and simultaneous extraction of lithium, rubidium and cesium from lepidolite concentrate via sulfuric acid baking and water leaching, *Hydrometallurgy* 185 (2019) 244–249, <https://doi.org/10.1016/j.hydromet.2019.02.011>.
- M.M.A. Dawoud, M.M. Hegazi, H.M. Saleh, W.K. El-Helew, Removal of stable and radio isotopes from wastewater by using modified microcrystalline cellulose based on Taguchi L16, *Int. J. Environ. Sci. Technol.* (2022) 1–12, <https://doi.org/10.1007/s13762-022-04073-3>.
- H.M. Saleh, H.R. Moussa, F.A. El-Saied, M. Dawoud, E.A. Nouh, R.S. A Wahed, Adsorption of cesium and cobalt onto dried Myriophyllum spicatum L. from radio-contaminated water: experimental and theoretical study, *Prog. Nucl. Energy* 125 (2020), 103393, <https://doi.org/10.1016/j.pnucene.2020.103393>.
- A.E. Osmanlioglu, Decontamination of radioactive wastewater by two-staged chemical precipitation, *Nucl. Eng. Technol.* 50 (2018) 886–889, <https://doi.org/10.1016/j.net.2018.04.009>.
- Z. Li, T. Pranolo, Z. Zhu, C.Y. Cheng, Solvent extraction of cesium and rubidium from brine solutions using 4-tert-butyl-2-(α -methylbenzyl)-phenol, *Hydrometallurgy* 171 (2017) 1–7, <https://doi.org/10.1016/j.hydromet.2017.03.007>.
- N. Goyal, P. Gao, Z. Wang, S. Cheng, Y.S. Ok, G. Li, L. Liu, Nanostructured chitosan/molecular sieve-4A an emergent material for the synergistic adsorption of radioactive major pollutants cesium and strontium, *J. Hazard Mater.* 392 (2020), 122494, <https://doi.org/10.1016/j.jhazmat.2020.122494>.
- H.M. Saleh, H.R. Moussa, F.A. El-Saied, M. Dawoud, T.A. Bayoumi, R.S.A. Wahed, Mechanical and physicochemical evaluation of solidified dried submerged plants subjected to extreme climatic conditions to achieve an optimum waste containment, *Prog. Nucl. Energy* 122 (2020), 103285, <https://doi.org/10.1016/j.pnucene.2020.103285>.
- H.M. Saleh, R.F. Aglan, H.H. Mahmoud, Qualification of corroborated real phytoremediated radioactive wastes under leaching and other weathering parameters, *Prog. Nucl. Energy* 119 (2020), 103178, <https://doi.org/10.1016/j.pnucene.2019.103178>.
- C. Dong, X. Deng, X. Guo, B. Wang, X. Ye, J. Fan, C. Zhu, F. Fan, B. Qing, Synthesis of potassium metal ferrocyanide/Al-MCM-41 with fast and selective adsorption of cesium, *Colloids Surf. A Physicochem. Eng. Asp.* 613 (2021), 126107, <https://doi.org/10.1016/j.colsurfa.2020.126107>.
- P. Su, J. Zhang, Y. Li, Chemical fixation of toxic metals in stainless steel pickling residue by $\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$, $\text{FeSO}_4\cdot 6\text{H}_2\text{O}$ and phosphoric acid for beneficial uses, *J. Environ. Sci.* 90 (2020) 364–374, <https://doi.org/10.1016/j.jes.2019.12.016>.
- T. Zhang, Y. Zhao, H. Bai, W. Wang, Q. Zhang, Enhanced arsenic removal from water and easy handling of the precipitate sludge by using FeSO_4 with CaCO_3 to $\text{Ca}(\text{OH})_2$, *Chemosphere* 231 (2019) 134–139, <https://doi.org/10.1016/j.chemosphere.2019.05.117>.
- O.A.A. Moamen, I.M. Ismail, N. Abdelmonem, R.O. Abdel Rahmana, Factorial design analysis for optimizing the removal of cesium and strontium ions on synthetic nanosized zeolite, *J. Taiwan Inst. Chem. Eng.* 55 (2015) 133–144, <https://doi.org/10.1016/j.jtice.2015.04.007>.
- M. Li, J. Zhao, Y. Li, M. Li, Y. Wu, C. Wang, H. Jiao, P. Na, Enhanced adsorption of cesium ions by electrochemically switched ion exchange method: based on surface-synthetic $\text{Na}_2\text{Ti}_2\text{O}_7$ nanotubes, *Colloids Surf., A* 579 (2019), 123712, <https://doi.org/10.1016/j.colsurfa.2019.123712>.
- M.N. Nguyen, M. Yaqub, S. Kim, W. Lee, Optimization of cesium adsorption by Prussian blue using experiments and gene expression modeling, *J. Water Proc. Eng.* 41 (2021), 102084, <https://doi.org/10.1016/j.jwpe.2021.102084>.
- J. Li, Y. Zan, Z. Zhang, M. Dou, F. Wang, Prussian blue nanocubes decorated on nitrogen-doped hierarchically porous carbon network for efficient sorption of radioactive cesium, *J. Hazard Mater.* 385 (2020), 121568, <https://doi.org/10.1016/j.jhazmat.2019.121568>.
- S. Zhuang, J. Wang, Removal of cesium ions using nickel hexacyanoferrate-loaded bacterial cellulose membrane as an effective adsorbent, *J. Mol. Liq.* 294 (2019), 111682, <https://doi.org/10.1016/j.molliq.2019.111682>.
- H. Hayashi, Y. Sato, S. Aoki, M. Takaishi, In situ XRF analysis of Cs adsorption by the precipitation bands of Prussian blue analogues formed in agarose gels, *J. Anal. At. Spectrom.* 34 (2019) 979–985, <https://doi.org/10.1039/C9JA00025A>.
- S. Kang, J. Lee, S.M. Park, D.S. Alessi, K. Baek, Adsorption characteristics of cesium onto calcium-silicate-hydrate in concrete powder and block, *Chemosphere* 259 (2020), <https://doi.org/10.1016/j.chemosphere.2020.127494>.
- IAEA (International Atomic Energy Agency), Technical reports series No. 236, in: *Treatment of Low- and Intermediate-Level Liquid Radioactive Wastes*, IAEA, Vienna, 1984.
- K. McKinley, I. McLellan, F. Gagné, B. Quinn, The toxicity of potentially toxic elements (Cu, Fe, Mn, Zn and Ni) to the cnidarian *Hydra attenuata* at environmentally relevant concentrations, *Sci. Total Environ.* 665 (2019) 848–854, <https://doi.org/10.1016/j.scitotenv.2019.02.193>.
- G. Genchi, A. Carocci, G. Lauria, M.S. Sinicropi, A. Catalano, Nickel: human health and environmental toxicology, *Int. J. Environ. Res. Publ. Health* 17 (2020) 679, <https://doi.org/10.3390/ijerph17030679>.
- N.R. Jyothi, Heavy metal sources and their effects on human health, in: M.K. Nazal, H. Zhao (Eds.), *Heavy Metals-Their Environmental Impacts and Mitigation*, IntechOpen, London, 2020, pp. 21–32, <https://doi.org/10.5772/intechopen.91574>.