

Chemical Treatment of Low-level Radioactive Liquid Waste (I)

Sang Hoon Lee, Jong In Choe and Yong Eak Kim

Radioactive Waste Management Division Korea Atomic Energy Research Institute
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Abstract

This experiment has been carried out for the removal of long-lived radioactive-nuclides (Sr-90, Ru-106, Cs-137 and Ce-144) contained in the low-level radioactive effluents from the spent fuel reprocessing plant and nuclear power plant, in order to determine the decontaminability of various chemical coagulants and domestic clay mineral (montmorillonite).

Phosphate process showed prominent efficiency for the removal of Ce-144, and lime-soda process did good removal efficiency for Sr-90. About Cs-137 copper-ferrocyanide process is much desirable. In phosphate or lime-soda process, most favorable removal efficiency was obtained at more than pH 11.

The montmorillonite treated with sodium chloride showed a considerable improvement in the removal of the radioactive-nuclides.

By a combined chemicals-montmorillonite process, the radioactive-nuclides could be more effectively removed than by the only chemicals process.

요 약

핵연료 재처리 과정이나 원자력발전소에서 대량으로 발생되는 비교적 반감기가 긴 핵종들(Sr-90, Ru-106, Cs-137, Ce-144)의 화학응집제와 국산점토 광물(montmorillonite)에 의한 제거 효율을 결정하기 위해 본 실험이 수행되었다.

Phosphate process는 Ce-144의 제거에 있어서 99.5% 이상의 극히 좋은 효율을 나타냈고, lime-soda process는 Sr-90에 대하여 93%의 높은 제거율을 보였으며, Cs-137에 대해서는 copper-ferrocyanide가 제거율 99%의 매우 적절한 화학 응집제임을 나타냈다. Phosphate나 lime-soda process에서 가장 좋은 제거효율은 pH 11 이상에서 얻어졌다.

그리고 NaCl로 처리된 montmorillonite가 방사성 핵종들은 제거하는데 있어서 natural montmorillonite보다 향상된 제거 효율을 보여주었다.

1. Introduction

It is very important to decontaminate the low-level radioactive effluents from the spent

fuel reprocessing plant and the nuclear power plant in order to operate the plants safely. Nowadays the methods of treatment about radioactive liquid wastes have been developed with respect to ion exchange, evaporation

and chemical treatment at various countries.

By Hunter-Ballon Diagram⁹⁾, distribution ratios of fission products contained in liquid waste show that 6 days after, strongest active-nuclides are ⁹⁹Mo and ¹³³Xe; and one year after, Nb-95, Ce-144 and Pr-144; after 10 years, other nuclides except Sr-90, Cs-137 and Pm-147 are almost distinguished.

So, as an effective treatment method of long-lived radioactive nuclides (Sr-90, Ru-106, Cs-137 and Ce-144), chemical treatments have been experimented.¹⁻⁶⁾

And many workers have reported that clay minerals have very significant use for the waste treatment, because of the high ionic selectivity, radiation stability and heat stability of these minerals.⁸⁻¹⁰⁾

In this chemical treatment, we used calcium-phosphate, lime-soda, copper-ferrocyanide as coagulants, and added the domestic clay mineral (montmorillonite at Kyeong-Nam, Yong Il).

Through Jar test, precipitation behaviors of radioactive-nuclides by coagulation and adsorption were observed, and in order to obtain optimum condition of this treatment, removal efficiency by change of pH, dosage was investigated.

2, Experiment

1) Sample preparation

a) Chemicals

The stock solutions of Na₃PO₄·12H₂O, NaCO₃, Ca(OH)₂, CuSO₄·5H₂O and K₄Fe(CN)₆·3H₂O were made by distilled water to become, respectively, 0.1% solution. Then these chemical solutions were added in the simulated waste.

b) Additives (Montmorillonite)

Montmorillonite was ground into small pi-

eces with ball mill, and was sieved to make sure that the grains were less than 170 μ in diameter, than dried in electric oven at 110° C. This will be called natural-montmorillonite (M₁).

M₁ was treated with the saturated NaCl solution for 72 hours at room temperature. Excessive electrolytes were decanted and rinsed with deionized water, followed by absolute ethanol until free of chloride and then dried in oven at 110°C. The treated sample will be called Na-montmorillonite (M₂).

And the heated samples which were obtained by heating M₁ with electric furnace to 300°C, 500°C, 700°C and 900°C for 30 minutes, will be called calcinated montmorillonite (respectively, M₃, M₄, M₅ and M₆).

c) Simulated Wastes

Simulated radioactive wastes which were made of ¹³⁷CsCl, ⁹⁰Sr(NO₃)₂, ¹⁴⁴Ce(NO₃)₃ were diluted with distilled water to have the activities of 2×10⁻² μ Ci/ml approximately.

2) Experimental procedure

100 ml of simulated waste of separate nuclide was poured into a 250 ml beaker, and added chemicals and/or additives according to the kind of process. The pH of the waste was adjusted with NaOH or HCl to the desired values. With Jar tester equipped with 2.5cm×4.3cm rectangular stainless-steel impellers, stirring was operated to flash mixing (150 rpm, for 5 minutes), and then gentle agitation (40 rpm, for 15 minutes). Then 30 ml portion of the stirred waste was taken out and centrifuged for 30 minutes at 2,000 rpm. Now 2 ml of the clear supernatant solution was transferred to a planchet, and dried with infra-red lamp, then the activity of decontaminated waste was counted in a well type G.M. Counter (Aloka TDC-6W).

This radioactivity was compared with the activity of nontreated waste.

Removal Efficiency

$$= \left(1 - \frac{\text{counts after treatment}}{\text{counts before treatment}}\right) \times 100$$

And X-ray diffraction of montmorillonite was carried out with a Shimadzu Research X-ray Goniometer (Type VD-1).

3. Results and Discussion

1) Phosphate coagulation

The decision to investigate the use of a calcium phosphate floc was based on a comparison of the insolubility of the phosphate and hydroxide, which showed that the number of highly insoluble phosphate compounds exceeded the number of insoluble hydroxides. This was considered desirable from standpoint of Hahn's adsorption and coprecipitation rule, which states that the adsorption and or coprecipitation of an ion by a precipitant depends on the surface charge of the adsorbing precipitate, and on the degree of insolubility of the adsorbed compounds in the solvent involed.

In Fig. 1 are shown data obtained by maintaining the ratio of sodium phosphate to calcium hydroxide of each sample with the value of 20ppm to 10ppm, and varying the pH of the waste. The action of pH is believed to be due both to its effect on the solubility of calcium phosphate and on the magnitude of the charge existing on the inner layer of the colloidal particle. As pH increased the solubility of calcium phosphate decreased and greater quantities of floc could be formed. With this pH change the quantities of HPO_4^{2-} , PO_4^{3-} , and OH^- in solution increased, increasing the Nernst potential of the colloidal particle. All of these reactions would tend to

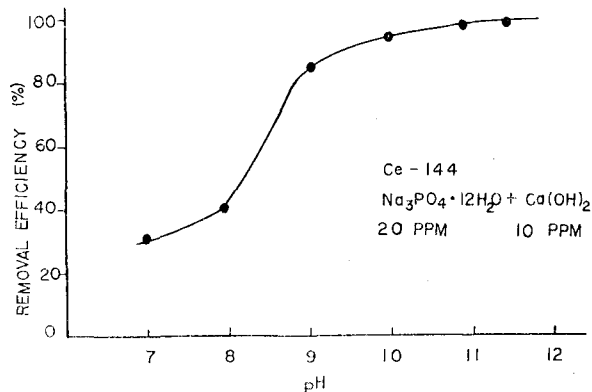


Fig. 1. Effect of pH in Calcium phosphate process

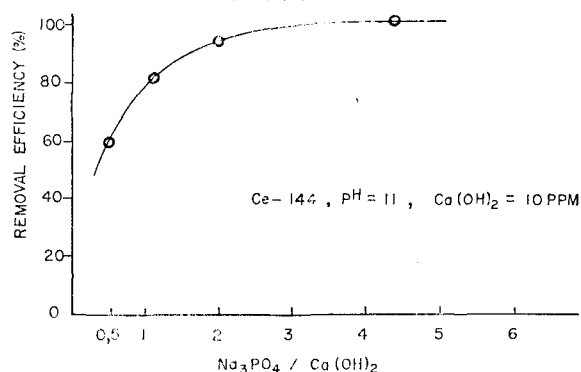


Fig. 2. Cerium Removed as Function of Ratio of Sodium Phosphate to Calcium Hydroxide

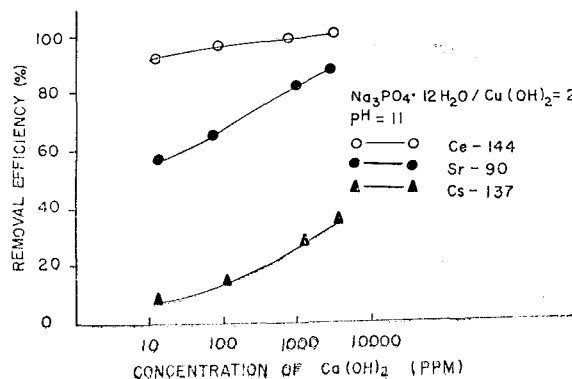


Fig. 3. Effect of Dosage in Calcium Phosphate Process

bring about an increase in cerium removals. ⁽¹³⁾

In Fig. 2 are shown data obtained by maintaining the pH of each sample above 11, and varying the ratio of trisodium phosphate

to calcium hydroxide between the value of 0.5:1 and 4:1. The percent of cerium removed increased rapidly as the ratio of phosphate of calcium was increased. A sharp break occurred at a ratio of 2.0 to 1. Above the ratio of 2.0 to 1 only a slight increase in the removal of cerium was noted.

In Fig. 3 are shown data obtained by varying the dosage of $\text{Ca}(\text{OH})_2$ from 10 ppm to 1000 ppm. About Ce-144 only 10 ppm of calcium phosphate showed prominent removal efficiency of 95%, and about Sr-90 more than 500 ppm of calcium phosphate obtained 80 percent removal, but about Cs-137 calcium phosphate process couldn't be good removal method.

2) Lime-soda process

Precipitation of radionuclide with calcium is known as coprecipitation or carrier precipitation. The formation of calcium carbonate precipitate in water provides a practical means of concentrating extremely dilute solutions of hazardous radioactive elements as foreign ions within the crystals of calcium carbonate. Among the ways in which coprecipitation may be accomplished are:

The formation of mixed crystals where foreign ions are incorporated homogeneously in the crystal lattice;

The acclusion of impurities as imperfections scattered at random through-out the crystal;

Surface adsorption of foreign ions by the precipitate after it has already been formed;¹⁰⁾

In Fig. 4 are shown data obtained by maintaining the ratio of sodium carbonate to calcium hydroxide with the value of 200 ppm to 100 ppm, and varying the pH of waste. Above pH 10, good removal efficiency of 93 percent was obtained. This was felt that as

pH increased the solubility of calcium carbonate decreased and greater quantity of floc could be formed.

In Fig. 5 are shown data obtained by varying the dosage of $\text{Ca}(\text{OH})_2$ from 10 ppm. It was founded that about Sr-90 and Ce-144 more than 100 ppm of calcium carbonate showed good removal efficiency of 90%, but that the removal of Cs-137 by lime-soda precipitation was not effective.

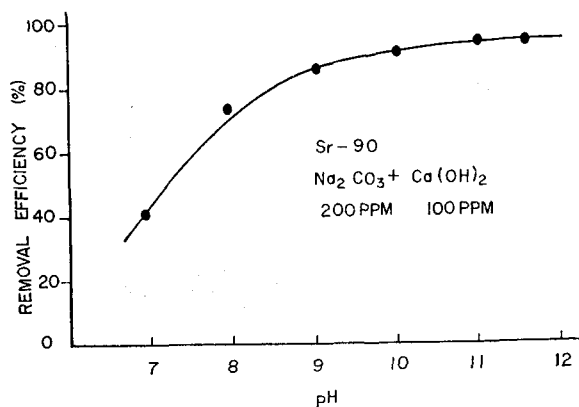


Fig. 4. Effect of pH in Lime-Soda Process

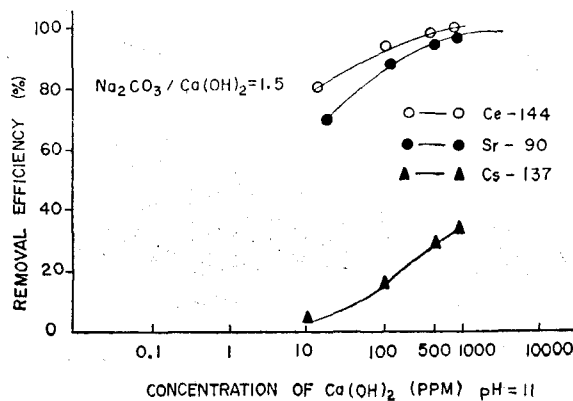


Fig. 5. Effect of Dosage in Lime-Soda Process

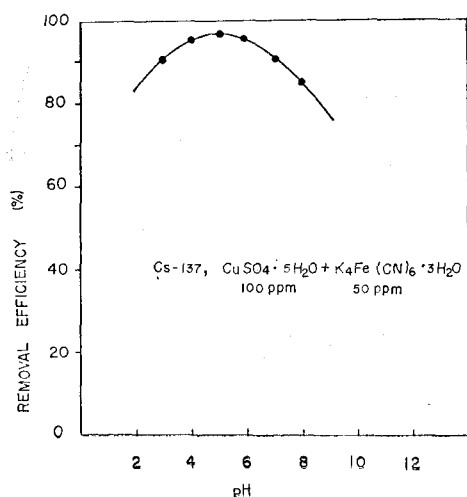
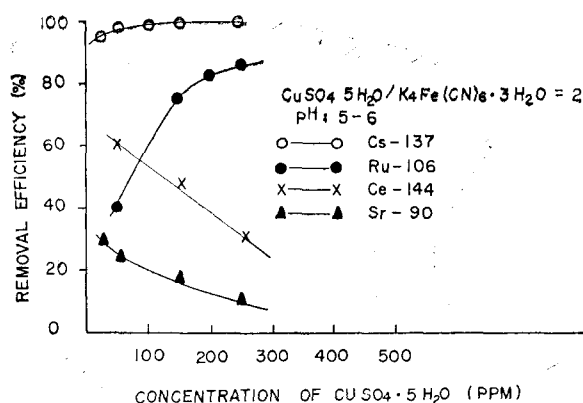
3) Copper-ferrocyanide process

This process is being performed by forming $\text{Cu}_2\text{Fe}(\text{CN})_6$ precipitate obtained between $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{Cu}(\text{SO}_4)$.

In Fig. 6 are shown data obtained by maintaining the ratio of $\text{K}_4\text{Fe}(\text{CN})_6$ to CuSO_4 with the value of 100 ppm to 50 ppm, and varying

Table 1. Adsorbability of radionuclides by montmorillonite

Reference clay 1000ppm	Removal Efficiency (%)			
	Sr-90	Ru-106	Cs-137	Ce-144
M ₁	48.4	29.6	50.4	66.9
M ₂	69.5	40.4	65.1	84.7
M ₃	65.9	32.5	57.6	76.7
M ₄	67.2	36.7	60.4	84.3
M ₅	68.6	44.5	63.4	85.2
M ₆	54.7	22.1	52.2	64.5

**Fig. 6. Effect of pH on Removal in Copper-Ferrocyanide Process****Fig. 7. Effect of Dosage in Copper Ferrocyanide Process**

the pH of waste(Cs-137). This indicated that between pH 4--6, good removal efficiency was obtained, among which pH 5 was most favorable.

As shown in Fig. 7, it was found that about Sr-90 and Ce-144, copper-ferrocyanide couldn't be good coagulants, and that about Ru-106 more than 500 ppm of $\text{Cu}_2\text{Fe}(\text{CN})_6$ obtained 85% of removal efficiency, but that about Cs-137, only 100ppm of copper-ferrocyanide showed prominent removal efficiency of 99%. This results from that $\text{Cu}_2\text{Fe}(\text{CN})_6$ makes complexes with Cs^+ ion to become $\text{Cs}_2\text{CuFe}(\text{CN})_6$ or $\text{Cs}_2\text{Cu}_3[\text{Fe}(\text{CN})_6]_2$.¹⁵⁾

4) Montmorillonite process

Generally clay minerals show cation exchange and adsorption properties from the negative charge of the framework. Especially in montmorillonite, the unbalance of electrostatic charge is resulted from the substitution of Si^{+4} by Al^{+3} in tetrahedral structure, or Fe^{+3} by Mg^{+2} and Ca^{+2} in octahedral structure. This negative charge of montmorillonite is balanced by positive ions in the cavities, and these can be replaced by other ions, giving rise to the permutite type of ion exchange.¹⁶⁾

In Fig. 8, the structure of montmorillonite as domestic clay is denoted by X-ray patterns. And the X-ray patterns of Na-montmorillonite (M_2) and calcinate montmorillonite at 700°C(M_5) are also showed. In the change of (002) reflection, natural montmorillonite (M_1) shows 15.7 Å; M_2 does 12.6Å; M_5 does 9.82Å. These indicate that M_1 has double-layers of H_2O , and that M_2 has mono-layer of H_2O , and that M_5 is completely dehydrated¹⁶⁾.

As shown in Table 1, by montmorillonite Ce-144 is favorably removed, Sr-90 and Cs-137 is removed by 60-70%, but Ru-106 is not

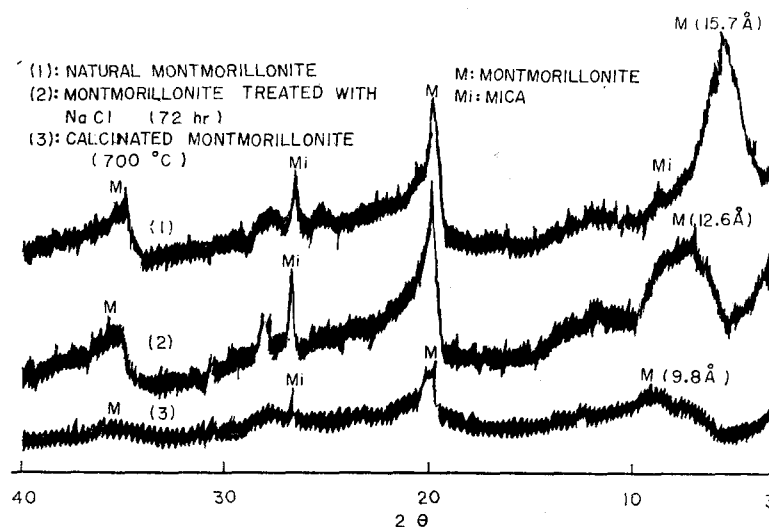


Fig. 8. X-ray Diffraction Patterns of Montmorillonite

Table 2. Effect of concentration of clay minerals on the adsorbability
 Removal Efficiency (%)

Concentration (ppm)	Montmorillonite			
	Sr-90	Ru-106	Cs-137	Ce-144
100	49.8	7.5	42.6	54.6
300	59.4	26.1	55.9	71.8
500	65.3	30.2	62.2	80.5
800	67.7	38.4	64.6	80.9
1000	69.5	40.4	65.1	84.7
2000	71.8	46.7	66.7	90.1
5000	76.8	49.3	72.8	93.8

fairly removed. This results from the greater affinity of Ce^{+3} because of larger electrostatic charge than Sr^{+2} , Cs^+ , Ru^+ . And radioactive nuclides were more removed by treated montmorillonite (e.g. M_2 , M_3) than by natural montmorillonite (M). It was felt that heating montmorillonites to temperatures that would result in irreversible collapse of the lattice to 10\AA would influence favorably radioactive nuclide sorption. Although it is known that high temperatures reduce the ion-exchange capacity of clays, earlier studies with synthetic micas

and vermiculite had shown that selectivity was of more importance than ion-exchange capacity in controlling the partial sorption capacity. Below 600°C the sorbed amount is not affected by heating, implying that rehydration of the lattice occurred even after heating to 600°C for 3 hr. Samples heated to 700°C sorb more radioactive nuclides than samples heated to any temperature, provided sufficient solution clay contact time is allowed. Samples heated to 900°C showed decreased sorption which may indicate that at this temperature the layer lattice structure has been destroyed and new phases introduced.⁹⁾

A desirable physical change was noted in the montmorillonite heated to 700°C (M_5). The highly dispersing characteristic of montmorillonite was almost completely eliminated, and a well aggregated solid was maintained when the clay was suspended in water. And Na-montmorillonite (M_2) showed highly better removal efficiency than natural montmorillonite (M_1). The aggregation of the montmorillonite and the increased affinity by treating with NaCl and heating are desirable

Table 3. Removal efficiency of radionuclides by clays added to chemicals

Removal Efficiency (%)			
Chemicals (ppm)	Na ₂ CO ₃ :150 Ca(OH) ₂ :100	Na ₃ PO ₄ ·12H ₂ O:200 Ca(OH) ₂ :100	CuSO ₄ ·5H ₂ O:100 K ₄ Fe(CN) ₆ ·3H ₂ O:50
Clay (500ppm)	M ₂	M ₂	M ₂
Sr-90	85.5	90.1	
Ru-106	68.3	77.0	*79.8
Cs-137	74.9		98.3
Ce-144	96.5	98.3	

*: CuSO₄·5H₂O: 600ppm. K₄Fe(CN)₆:300 ppm

features encountered during this place of study.

In Table 2 are shown data obtained by varying the dosages of montmorillonites. It was found that as dosage increased, the removal efficiency increased.

5) Combined process

To decontaminate radioactive liquid wastes safely only one process is not adequate. So combined processes between chemicals and clay are now desirable.

In Table 3 are shown data obtained by combined treatment of chemicals and montmorillonite(M₂). It was found that about Sr-

Table 4. Removal efficiency of radionuclides by serial treatment of chemicals and clays

Removal Efficiency (%)			
Chemicals (ppm)	Na ₂ CO ₃ :150 Ca(OH) ₂ :100	Na ₃ PO ₄ ·12H ₂ O:200 Ca(OH) ₂ :100	CuSO ₄ ·5H ₂ O:100 K ₄ Fe(CN) ₆ ·3H ₂ O:50
Clay (500ppm)	M ₂	M ₂	M ₂
Sr-90	91.7	95.0	
Ru-106	72.0	81.9	*82.2
Cs-137	79.6		99.8
Ce-144	98.8	99.9	

*CuSO₄·5H₂O: 600 ppm, K₄Fe(CN)₆·3H₂O: 300 ppm

90 phosphate process with M₂ showed highly better removal efficiency of 90.1% than single processes(e.g. phosphate: 83% at 100 ppm, montmorillonite(M₂):69.5% at 500ppm)

As shown in Table 4, serial treatment, which is the method that first we add chemicals, and mix, then again add montmorillonite to the supernatant of the waste treated with chemicals, noted a little improvement comparing with combined process. So serial treatment will not be recommendable.

4. Conclusion

1. Phosphate process showed prominent efficiency for the removal of Ce-144, and lime-soda process did good removal efficiency for Sr-90. And about Cs-137 copper-ferrocyanide process is much desirable.

2. In phosphate or lime-soda process, most favorable removal efficiency was obtained at more than pH 11; and in copper-ferrocyanide process, at pH 5.

3. Domestic clay mineral(montmorillonite) shows the characteristic property which can be applied as additive about the chemical treatment of low-level radioactive liquid waste. For the removal of Sr-90, combined process (phosphate with M₂) showed good efficiency.

4. Montmorillonite had relatively high affinity for Ce-144 and Sr-90 than Ru-106 and Cs-137. And the montmorillonite treated with NaCl showed a considerable improvement than natural montmorillonite in the removal of the radioactive-nuclides.

5. References

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