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韓國產 粘土鑛物質을 利用한 放射性 液體癈棄物의 處理

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Use of Korean Clay Minerals in the Treatment of Radioactive Liquid Wastes

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요 약

점토광물이 양호한 양이온 교환능을 가졌다는 것은 주지의 사실이다. 점토광물질을 이용한 저방사성 액체 폐기물의 처리 연구는 선진국에서는 지금까지 많이 연구되어 왔다. 이의 주목적은 폐기물 처리를 위한 비용의 절감이며 우리나라에서도 점토 광물질을 이용한 삼단계 처리장치의 설계, 설치하여 실제사용하고 있는 실정이다. 여기서 처리되는 폐액의 방사성 준위는 우리나라 TRIGA MARK-II 원자로에서 나오는 폐액의 대부분을 차지하는 10^{-4}-$10^{-6}\mu c/ml$ 의 것이다. 한국산 점토질은 그 질이 양이온 교환능에서 우수할뿐 아니라 양적으로 풍부하여 그 이용도가 더 증가되어 가고 있다. 여기서 사용한 대표적인 점토광물질의 원강은 kaolinite, montmorillonite, vermiculite 족속에 해당된다. 이들 점토질의 화학적 물리적 성질은 이미 규정된 바 있으며 원광과 활성화된 점토질을 사용하여 핵종 Sr-90과 Cs-137의 흡착능도 조사하였다. 동시에 삼단계 처리장치에 적용하기 위해서 model test를 통해서 실제 이용의 가능성도 조사하고 끝으로 plant application의 최적 조건을 결정하였다. 여기서 우리는 한국 점토질을 이용한 저방사성 액체 폐기물의 처리가 경제적으로 저렴하고 만족스러운 제염개수를 얻을 수 있다는 것을 알았다.

Abstract

One of the most economical methods of treating the low-level radioactive liquid waste may be clay adsorption of radionuclides. In this study, Kaolinite, Montmorillonite and Vermiculite groups were selected as representative clay minerals.

The Atomic Energy Research Institute of Korea has operated three stage liquid waste treatment facilities which process the low-level liquid waste (10^{-4} $\mu c/ml$-$10^{-6}\mu c/ml$). This study dealt with not only fundamental sorption properties including uptake of Cr-137 Sr-90 and Model Test, but also determining optimum conditions of the three stage unit for the plant application.

The optimum operating conditions of the three stage unit were fixed up and decontaminations in the plant tests were well satisfied with the theoretical ones in all stages.

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1. Introduction

Clay minerals have cation exchange capacity and a great deal of investigations on clay mineral have been made in the field of radioactive liquid waste treatment. [1)2)] As the utilization of radioisotopes is gradually increased at the Atomic Energy Research Institute, Seoul, Korea, the treatment and safe disposal of the waste becomes one of the major problems to be studied. The waste disposal plant was constructed at the Institute in 1964 and three-stage liquid waste treatment facility, in which low level liquid waste ($10^{-4}\mu c/ml$-$10^{-6}\mu c/ml$) is treated by domestic clay, was designed and constructed in the Reactor Engineering Division.

The object of this study is to develop the method of low level liquid waste treatment and disposal by using naturally occouring ion exchange clay minerals. The sorptions of radionuclides, Sr-90 and Cs-137 were investgated. [3)4)] In order to make much of the effective utilization of the clay in the liquid waste treatment facility, efforts were concentrated to the pretreatment of the clay which leads to more economic and simplified method. The Model test to optimies the plant scale application using domestic clay was introduced as a preliminary study in this experiment.

2. Sorption of Radionuclides

The experiments of radionuclide adsoption phenomena by using Kaolinite, Montmorillonite and Vemiculite groups were carried out. Prior to this actual adsoption test, pretreatments of sample clay were conducted to study the adsoption effects of Sr-90 and Cs-137. Differences of adsorption characteristics between raw clay mineral and pretreated clay mineral were investigated. Sr-90 and Cs-137 consist in the form of Sr-90 NO_3 and Cs-137 Cl solution respectively which were purchased from Amersham Radiochemical Centre in U. K.

Heat Treatment.

The particle size of 80 mesh Yong-Il, Ha-Dong clays and 20mesh Chong-Yoang Vermiculite were calcined in the electric furance at temperature of 700°C for 1 hour and 650°C for 30 minutes, repectively. [5)6)]

Acid Treatment.

Calcined Yong-Il and Ha-Dong clays were washed with. distilled water and dried at a temperature 100°C. After then, treated with 20% hydrochloric acid at the ratio of 1 volume of dried clay to 2 volumes of hydrochloric acid at a temperature 100°C for 1 hour. In order to remove free acid from the acid treated sample, washing procedure was followed. These samples might be changed into "hydrogen saturated" clays and imprurities of possible lime stone might be removed.

Alkali Treatment.

Same procedure was acceptable in the alkali treatment of sample clays(Yong-Il and Ha-Dong) as mentioned above, acid treatment except the treatment of alkali with 10% sodium hydroxide. Also these samples might be converted to "sodium saturated" clays and minimized lattice destruction.

Sodium Treatment

It is well known fact that the mineral vermiculite exists in nature in association with its parent material mica and offers less cation exchange capacity than pure one. In our present study, the transformation of mica-vermiculite mixture to pure vermiculite in order to obtain and increase of their cation exchange capacities was carried out by 1 M sodium chloride and hydrogen peroxide treatment. This sample might be saturated with alkali metal and increased cation exchange capacity.

2-1. Batch Process for Determining the Selectivity of Cs-137

In this batch experiment to study the uptake of radionuclide, the simulated waste solution was made with distilled water spiked by radiocesium. In order to investigate duly adsoption properties for radiocesium as a function of *pH* variation of simulated waste solution to solected sample clays, 2% dosage of clay (by weight)was added into the solution. After the equilibrium, the effluent was centrifuged with 3,000 r. p. m. for 10min. and 2 ml sample was drawn to planchet for counting in well scintillation detector (Nuclear Chicago Corporation Model 202).

The adsorption tests for Cs-137 to Yong-Il and Ha-Dong clays pretreated with acid and calcined at 700°C were shown in Fig. (1). It shows that removal percent of Cs-137 to both of Yong-Il and Ha-Dong clays are generally superior without regard to *pH* value.

In prictical operation of three-stage liquid waste treatment plant, in order to avoid complicated pretreatments of clay samples and considering economical problems, simplified method of pretreatments in clay minerals was applied as follows. In acid treatment, very dilute hydrochloric acid (36% HCI:Water=1:50) was used to treat Yong-Il acid clay without being calcined. In alkali, treatment 10 percent of sodium hydroxide was used to the samples without being calcined.

The adsorption data of the non-calcined clay samples can be observed in Fig. (2). Comparing Fig. (1) with Fig(2), the removal percent of Cs-137 to the two samples treated with acid was generally decreased in the non-clacined samples than calcined ones, while the removal percent in constant without regard to pH value. It is indicated that maximum removal percent of Cs-137 is found to be about 95 percent at the pH of 5 in non-calcined Yong-Il acid clay which was treated with dilute hydrochloric acid.

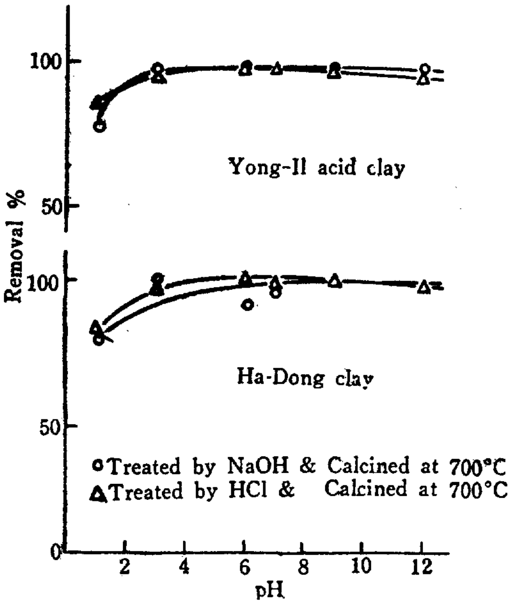

Fig. 1. Cs^{137} adsorption as a function of pH

It means that the simplified pretreatment method and Yong-Il acid clay are available to employ in the treatment of liquid waste. Yong-Il acid clay is available in Korea and its abundant quantity was found.

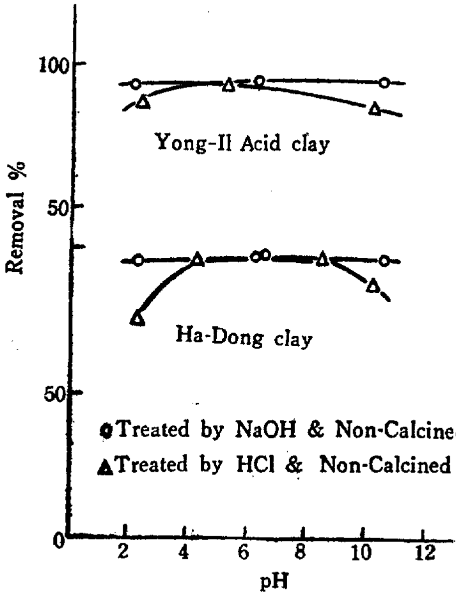

Fig. 2. Cs^{137} adsorption as a function of pH

In adsorption of Cs-137 to vermiculite, there was no difference, between raw clays and pretreated ones by 1 M sodium chloride, and no variation was observed regardless of the range of *pH* as indicated in Fig. (3). It is well known fact that Vermiculite has a high affinity of radiocesium. The use of vermiculite system for the removal of cesium is of interest for two reasons. Vermiculite is one of the few clay minerals with a sufficiently large particle size to be of practical use in waste decontamination, and when Vermiculite is treated with one of the alkali-metal cations or ammonia, the lattice space changes measurably to improve the exchange properity for cesium.

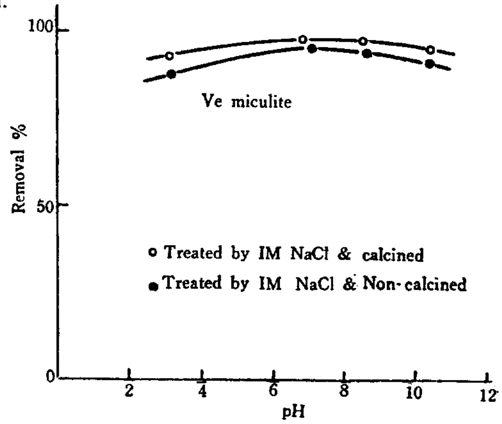

Fig. 3. $C.^{137}$ adsorption as function of pH

Fig. (3)shows that a little higher value, in the adsoption of Cs-137 to calcined vermiculite which was activated with 1 M sodium chloride, was obtained than non-calcined one. The maximum adsorption point of heat treated vermiculite indicated on the curve was found to be 97.88% at the *pH* 7 and the maximum adsorption point of Cs-137 to raw one was 93.2%.

Generally speaking, affinities of radiocesium to the represent clay minerals are remarkably superior regardless of pH range in the simulated solution.

2-2 Batch Process for Determining the Selectivity of Sr-90

Adsorption tests to strontium-90 were carried out similarly as the experiments of cesium-137. Fig. (4) shows that the removal percent of Sr-90 to the acid treated sample clays was better than alkali treated ones at the *pH* range of 6-9 approximately. The removal percent of strontium to raw Yong-Il acid clay marked 90 percent between pH 6 and pH 9 (Fig. 5), while the removal percent was over 95 percent between *pH* 7-9 when 1.500 mg of heated clays at 700°C were added into 50 ml of radiosolution (Fig. 4).

The experiments of non-clacined sample clays treated by dilute hydrochloric acid (less than 1%) were also observed. The removal percent of these sample clays was gradually decreased than that of calcined ones.

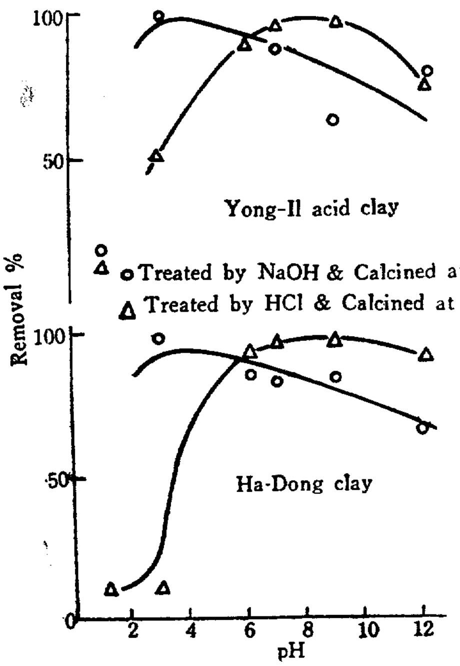

Fig. 4. Sr^{90} adsorption as a function of pH

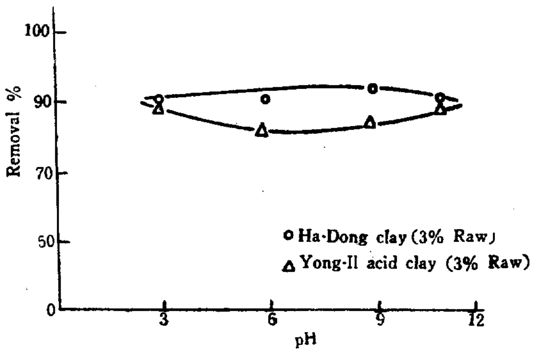

Fig. 5. Sr^{90} adsorption as a function of pH

Yong-Il acid clays treated by dilute hydrochloric acid were shown 93% removal of Sr-90 around the *pH* 6 as shown in Fig. (6). Considering economic point of view of heating and concentrated hydrochloric acid (20%) treatment, the complicated activations of clays with HCl could be simplified when the liquid waste plant is operated in a large scale.

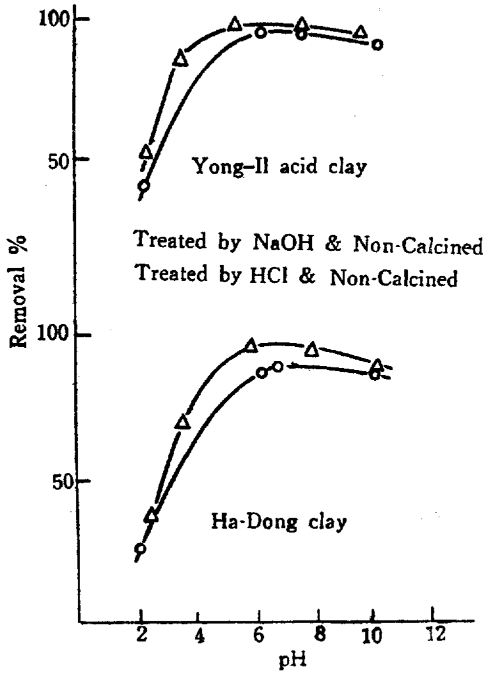

Fig. 6. Sr^{90} adsorption as a function of pH

It was found that the Na-form and H-form exchanger treated with sodium hydroxide and hydrochloric

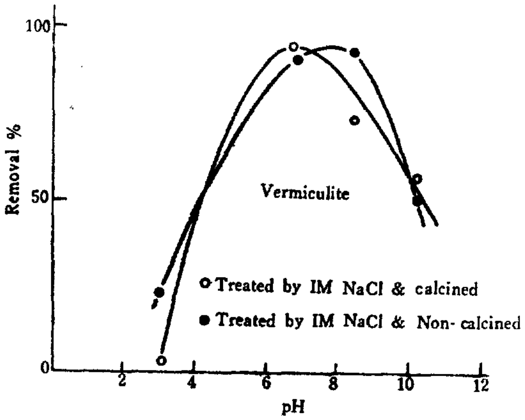

Fig. 7. Sr^{90} adsorption as function of pH

acid were excellent in comparison with non-treated raw clay in exchange capacity and decontamination factor for radioactive ions. In the vermiculite tests adsorption affinity of Sr-90 was much inferior to Cs-137 adsorption at wide pH range except pH 6-9. as shown in Fig(3, 7).

3. Plant Application

3-1. Model Test

A three-stage liquid waste treatment facility which processes the low level liquid wastes producing mainly from radioisotope production building and activation analysis laboratory has been operated. The low level liquid wasten have been collected monthly through storage tank and transported to the waste disposal plant.

For Model test, 5mm acrylic cylinder in the volume of one-third of the three stage reaction tank including an agitator (200 r. p. m.) and a flow meter was prepared as shown in Fig (8). The experimental work on adsorption of radionuclides by using the acrylic cylinder was carried out. Radiostrontium and cesium (appr. 10^{-3} $\mu c/ml$ level) were used in this model test. The model test would be helpful very much in operating the three stage plant and observing the adsorption phenomena between clays and radiosolution.

Yong-Il acid clays were selected for this test because of its cheap prices in practical operation. The Yong-Il acid clays were activated with dilute hydrochoric acid (36% HCl: Water=1:50), washed with water for removing free acid, dried at room temperature and crushed to 80 mesh.

3-2. Experiments of Model Test with Flow Control

We investigated the decontamination effect of Yong-Il acid clay with variable clay dosage and controlling the flow rate of the radiosolution in acrylic model reaction tank. Fig. (9) shows that the decontaminations which was upgraded by increasing the clay dosage was its best when the flow rate was 0.5 liters per minuite than one or two liters per minuite. However the removal percent of Sr-90 is less than 89 Percent in the presence of 0.5 liters per minuite of flow control, while the removal percent reaches to 97 percent without flow control for one hour reaction time.

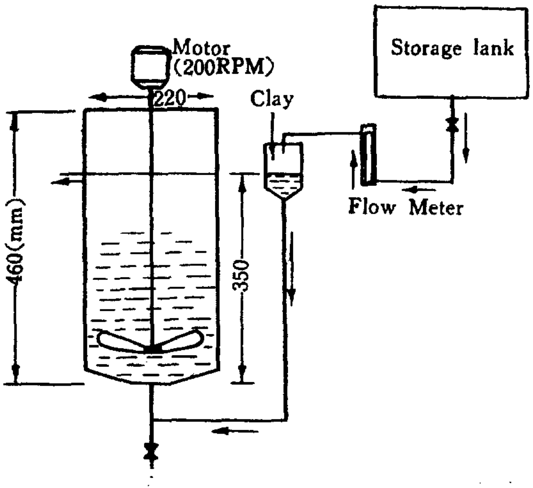

Fig. 8. Flow diagram on of Model Test

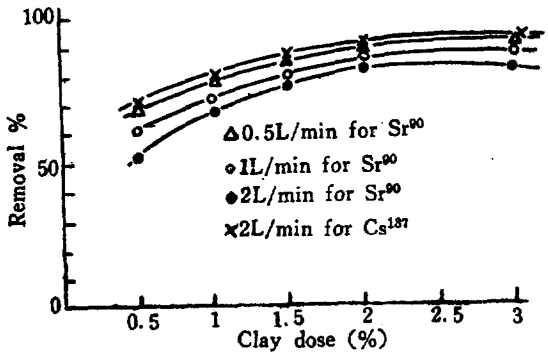

Fig. 9. Model Test with flow control

Two percent of clay dosage will be proper, considering the treatment of clay sludge which is concerned with the problem of solid waste disposal and the flow rate of 2 liters per minuite will be appropriate than 0.5 or 1 liter per minute in order to handle a large volume of low level liquid wastes. It was indicated that the removal percent of Sr-90 at single acrylic column was found to be 81 percent(D. F=5.3) in condition of 2 liters per minuite of flow rate and 2 percent clay dosage as shown in Fig. (9). It was also indicated that the removal percent of Cs-137 was found to be 90 percent (D.F=10) as same condition as Sr-90. These D.F. values for Sr-90, Cs-137 in this model test will be applied in the following plant operation test.

3-3 Plant Design

3-3-1 Theoreticalproblem and decontamination factor

(a) The Relation of Equilibrium between Clay and Solution

The typical plot in equilibrium state between the concentration of clay, Y and the concentration of radiosolution, Y is shown in Fig. (10). The radioactivity concentration of the solid (clay) and the solution would be graphed as a diagonal line, and would finally be unchanging constant curve beyond a certain value X. The curve would depend upon the adsorption ability of clay, pH, temperature, and the concentration of the solution.

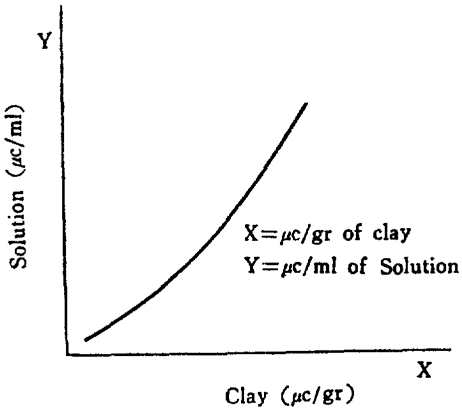

Fig. 10. Equilibrium state between dilute solution and clay

It is supposed that X and Y can be expressed as a linear equation concerned as the following manner, because the concentration of radiosolution, Y with which was dealt in the plant application experiment was in a small range of radioactivities to 10^{-3} -10^{-6} μc/ml level.

$$X=kY\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where k is a proportional constant which is similar to Henry's constant in the relationship of liquid and solid state.

It can be assumed that above equation (1) is available in the equilibrium condition of dilute solution.

The decontamination factor was found to be 5.3 for Sr-90 and 10 for Cs-137 in the model test as mentioned above. In the model test proper dosage of clay is 2% by weight of solution. If we take the initial concentration of radiosolution Yo, k values can be theoretically calculated for Sr-90 and Cs-137 respectively.

i.e. for Sr-90

$$Y=\frac{Yo}{5.3}\quad \mu c/ml$$

$$2X=100Yo\left(1-\frac{1}{5.3}\right)$$

When the values of X and Y are put in to above equation (1), k_s for Sr-90 could be calculated as follows.

$$k_s=\frac{X}{Y}=214\left(\frac{\mu c/gr \text{ of solid}}{\mu c/ml \text{ of solution}}\right)$$

for Cs-137

$$Y=\frac{Yo}{10}$$

$$2X=100Yo\left(1-\frac{1}{10}\right]$$

$$Kc=\frac{X}{Y}=450$$

(b) Calculation of stage and feed ratio between clay and radiosolution is given in Fig. (11)

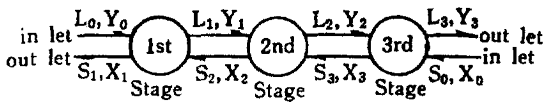

Fig. 11. Flow diagram of 3-stage counter current

Where L=flow rate of solution, ml/min.

S=flow rate of solid, gr/min.

Y=concentration of solution, μc/ml

X=concentration of solid, μc/gr

Taking material balance in each stage

$$\left.\begin{aligned} L_0Y_0-L_1Y_1=S_1X_1-S_2X_2 \\ L_1Y_1-L_2Y_2=S_2X_2-S_3X_3 \\ L_2Y_2-L_3Y_3=S_3X_3-S_0X_0 \end{aligned}\right\}\cdots\cdots\cdots\cdots\cdots\cdots(2)$$

The initial concentration of clay inlet, is taken

$X_0=0$

and $L_0=L_1=L_2=L_3=L$

$S_0=S_1=S_2=S_2=S$

Supossing $\frac{S}{L}$ is equal to K' and kK' is equal to K,

$$kK'=K$$

$$=\frac{S}{L}\cdot\frac{X}{Y}$$

$$Xi=kYi$$

When equilibrium condition reaches at each stage of the system.

Equation (2) becomes

$$\left.\begin{aligned} (1+K)Y_1-KY_2=Y_0 \\ -Y_1+(1+K)Y_2-KY_3=0 \\ -Y_2+(1+K)Y_3=0 \end{aligned}\right\}\cdots\cdots\cdots\cdots\cdots\cdots(3)$$

In first stage

$$\frac{Y_1}{Y_0}=\frac{1+K+K^2}{(1+K^2)(1+K)}\cdots\cdots\cdots\cdots\cdots\cdots(4)$$

in second stage

$$\frac{Y_2}{Y_0}=\frac{1+K}{(1+K^2)(1+K)}\cdots\cdots\cdots\cdots\cdots\cdots(5)$$

in final stage (third stage)

$$\frac{Y_3}{Y_0}=\frac{1}{(1+K^2)(1+K)}\cdots\cdots\cdots\cdots\cdots\cdots(6)$$

When 2% by weight of clay is added into radio-solution, the decontamination factor can be calculated as follows.

$$\frac{S}{L}=\frac{2}{100}=K'$$

$$K=kK'$$

For Sr-90

$$K=K_sK'=214\times\frac{2}{100}=4.3$$

D. F. values of each stage can be worked out when K value it put into equation (4), (5) and (6).

$$\frac{Y_1}{Y_0}=\frac{1}{4.3},\ \frac{Y_2}{Y_0}=\frac{1}{20.3},\ \frac{Y_3}{Y_0}=\frac{1}{103}$$

For Cs-137

$$K=k_cK'=450\times\frac{2}{100}=9$$

$$\frac{Y_1}{Y_0}=\frac{1}{9},\ \frac{Y_2}{Y_0}=\frac{1}{82},\ \frac{Y_3}{Y_0}=\frac{1}{820}$$

D. F. Values calculated for Sr-90 are 4.3 in first stage, 20.3 in second stage, and 103 in final stage respectively, and D. F. Values calculated for Cs-137 are 9, 82, and 820 respectively.

3-4. Treatment Facility of Radioactive Liquid Waste

Princippe design criteria of the treatment facility were applied to low level liquid waste treatment using local clay minerals which have natural occuring ion exchange capacities. The plant consists of three unit of sludge settling tanks and three reaction tanks as shown in Fig. (12)

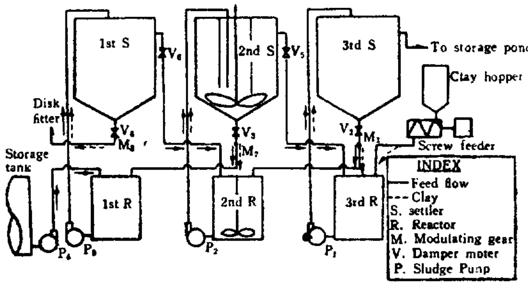

Fig. 12. Block diagram of waste plant

Feeding waste solution to first reaction tank and clay minerals to third reaction tank, count current flow system of waste solution and clay minerals has been employed in this plant.

It should also pay attention not only to keep from the damage of radiation hazards but also the operation faults during treating radioactive materals. Considering this point of view, a semi-automatic control system has been installed in this plant to prevent overflows of waste solution from settling and reaction tanks.

If the flows between settling tank and reaction tank are unbalanced, micro switches, magent switches, damper motors and others can be cut off automatically.

3-5. Operation Experiences and Results

In order to determine the decontaminable capacities of three stage plant the plant application test on radiostrontium, cesium, were carried out. Representative clay minerals such as Yong-Il acid clays pretreated by dilute hydrochoric acid (36% HCI: water

=1:50) were used in this plant application experiments, because of its mainly montmorillonite group in mineralogical composition, its low cost and its abundance in quantities.

The clays are supplied with 2% dosage (by weight of feed waste solution) by clay hopper apparatus into third reaction tank where has been installed a 200 r. p. m. paddle type agitator. Waste solution used in this experiments contains Sr-90 ($Sr^{90}NO_3$), Cs-137 ($Cs^{137}Cl$) respectively. In the third reaction tank, the clays and waste solution are reacted initially, after then the slury is pumped up to third settling tank in order to settle down in solid phase. The sludge settled are flown into the second reaction tank where second stage reaction occurs between calys and waste solution. Also three times reactions are accomplished in the every stages as similar fashion mentioned above.

The disc filter with a compressor and two vacuum pumps is connected with first settler for separating clay sludge from slurry condition solution. The clay sludge and effluent are well separated from the slurry during disc filter operation and extremely satisfactory result in volume reduction of the slurry was obtained. The separated sludge are handled as solid waste and the effluent is pumped from disc filter to storage tank.

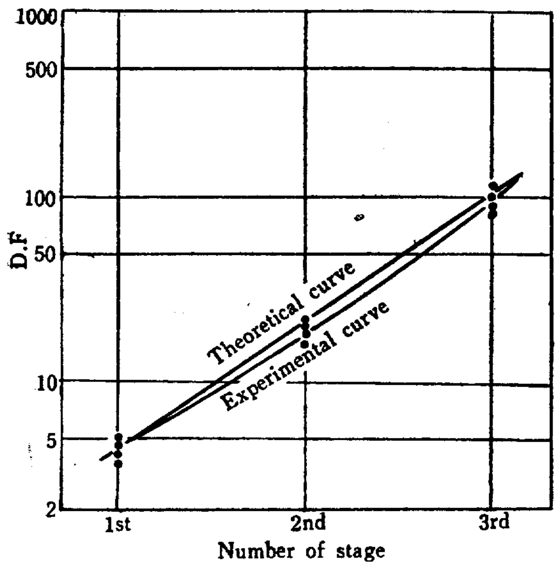

Fig. 13. D.F. value of Sr^{90} in each stage

Secondarily, radisolution is fed to the first reaction tank and reacted with clays. The solution decontaminated is discharged to concrete storage pond, monitored and finally released to environment. The flow rate of the feed solution is 2 liters per minute and the clay dosage is 40 grams per minute (2% by weight). Four sampling points were selected at feed tank and on the tops of each settling tank. Samples were taken every hour after steady state was reached and counted in order to compare with the theoretical values and experimental ones.

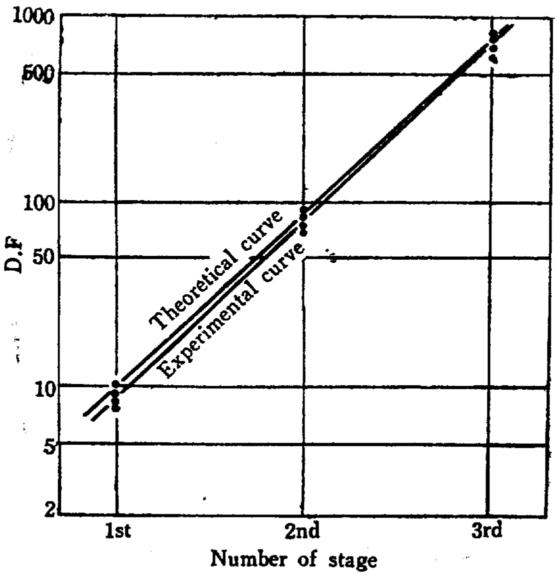

Fig. 14. D.F. value of Cs^{137} in each stage

We have had plant operational experiment using S-35 ($H_2S^{35}O_4$) and Cr-51 ($Na_2Cr^{51}O_4$) which are being produced by our reactor. In that experiment, It was known that the steady state in continuous conter current flow was reached approximately for 25 hours after starting operation of plant. [7]

Fig. (13) shows that the decontamination facter of the plant was found to be approximately 100 in final stage when Sr-90 was used. These values obtained by the plant application test are well agreed with the theoretical ones in first and final stages, while slightly inferior value was shown to theoretical one in second stage. Fig. (14) shows that D. F. was found to be approximately 800 in the final stage when Cs-137 was used and the values of the test were well satisfied with theoretical ones in all stages.

4. Conclusions.

The representative domestic clay minerals such as Yong-Il acid clay, Ha- Dong clay and Chong-Yang vermiculite were selected as groups of montmorillonite, kaoline and vermiculite from the ten samples which are produced mainly east and south coast in our country.

Preliminary study of this experiment covered mineralogical study of clay minerals and their sorption characteristics of long-lived nuclides such as Sr-90, and Cs-137.

Extensive work on plant application problem was concentrated to find optimum operation conditions of the three stage liquid waste facility through the fundamental adsoption study, plant design criteria and Model test.

The conclusions summrized are as follows:

1) Maximum removal percent for Cs-137 on 2% of Yong-Il acid treated clay with dilute hydrochrolic acid (less than 1%) and non-calcined was found to be 95%. Yong-Il acid clay could be used in our three stage unit as naturally occuring ion exchange clay minerals because of their abundant quantities and good quality.

2) For the removal of Sr-90, generally, acid treated clays are better than alkali treated ones. 93% of removal of Sr-90 on 2% Yong-Il acid clay treated with HCl (less than 1%) was obtained around pH 6, while the removal percents of Sr-90 for 2% and 3% Yong-Il acid clay treated by 20% HCl were indciated to be 90 and more than 95%. The affinity of vermiculite to Sr-90 was inferior than that to Cs-137.

3) Considering the problem of disposal of the clay sludge and practical waste treatment, 2% dosage of clay and 2 liter per minute of flow rate of feed solution would be appropriate.

4) Optimum operating conditions of three stage liquid plant were fixed up as 2 liters per minute of flow rate of feed solution and 2% dosage of clay treated with very dilute hydrochloric acid (less than 1%) to the feed solution and decontamination of the plant tests were well satisfied withthe theoretical ones in all stages

Acknowledgments

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