(i) Contract Number

566/RB & 566/R1/RB

(ii) Title of Project

Utilization of Korean clays and minerals for radioactive liquid waste treatment and disposal

(iii) Institute where research is being carried out

Reactor Engineering Division, Atomic Energy Research Institute, Seoul, Korea

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1 October 1967 - 14 November 1969

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1. Introduction

This is the final report of the project contracted with IAEA from October 1, 1967 to December 14, 1969 for two years (Contract No. 566/RB & 566/R1/RB). The main objects of the project are to develop the utilization of Korean domestic clays and minerals, such as kaolinite, montmorillonite and vermiculite groups, in the treatment of radioactive liquid waste and their disposal.

It is well known that clay minerals have cation exchange capacities and there have been many studies on clay from the standpoint of low level radioactive liquid waste treatment. As the utilisation of radioisotopes is incrsased gradually at the Atomic Energy Research Institute, Seoul, Korea, the treatment and safe disposal of the waste to the environment become one of the major problems to be studied. Therefore, in 1964 a waste disposal plant was constructed on the site of this Institute and a three-stage liquid waste treatment facility, in which low level liquid waste (10^{-4} μc/ml-10^{-6} μc/ml) is absorbed by domestic clay, was designed and constructed in the Reactor Engineering Division.

The wastes are produced mainly by the Laboratories of isotope production, radioactive analysis and other isotope handling section. Most of nuclides are short live isotopes and their activities are low-level. At the present, 2 MW research reactor is under construction in our Institute and also power reactor is under construction by Korean Electric Company by 1975.

The objects of this contract enhance to develop of low level liquid waste treatment and their disposal by means of natural occouring ion exchange clay minerals. Mineralogical studies on chemical and physical properties of the representative domestic clays were experimentally evaluated by chemical analysis, particle distribution measurement, X-ray analysis and electrophoretic mobility. The ion exchange capacities and the sorption of a radionuclides Sr-90 and Cs-137 were also studied.

In order to make much of the effective utilization of the clay in the liquid waste treatment facilities, efforts were concentrated to the pretreatment of the clays which leads to more economic and simple methods. The Model test to optimise of the plant scal application using domestic clays was introduced as a preliminary study on this experiment.

2. Minieral Studies

2-1. Occurrence

The clay minerals in Korea are superier in quality as well as abundant in quantity. It was proved that excellent Korean pottery had been manufactured earlier than other countries. Most Korean kaolines are consisted of halloysite in the sedimental deposits formed by efflorescence. The distribution is spread all over the country from southwest to north and south of the peninsula. Depth of the deposits reaches opproximately 35 meters. Acid clays produced mainly from south-eastern part of Korean are consisted of montnorillonite group. Vermiculites distributed over central area of peninsula are belonged to the old period precambriam and are known as the efflorescence micaceous gneiss.

Representative samples of the above minerals were taken from the deposits located in following districts :

Kaolin : (1) Kaekak-Ri, Okjong-Myun, Hadong-Kun, Kyongnam.
(2) Naekok-Ri, Oou-Myun, San-Chong-Kun, Kyongnam.
Acid clay : Yakjon-Dong, Donghae-Myun, Yong-Il-Kun, Kyonbuk.
Vermiculite: Yangsa-Ri, Bibong-Myun, Chong-Yang-Kun, Chungnam.

2-2. Mineralogical Identification

Results of chemical analysis by ASTM C323-56 and characteristics of the representative sample clays are shown in Table (1) and Table (2). The particle size distribution of the sample clays was measured by Andreason pipette method such that about 1% clay aqeous suspension, to which sodium phosphate was added to give a good clay dispersion, was put into the pipette and the settling time as well as the settled particle weight was measured. The Stoke's equation for a spherical particle with the correction factor for a cubic body was applied in the calculation of the particle size distribution,

$$\text{i.e. } r = \sqrt{\frac{9 h \eta}{2(D_1-D_2)\, gt}}, \quad (K = 1.612\ r)$$

where r= radius of the spherical particle (cm)

η = viscosity of fluid (g/cm/sec)

h= height (cm)

D_1= specific gravity of the particle (gr/cm)

D_2= specific gravity of the fluid (gr/cm)

g= gravity acceleration (dyne/cm)

t= time (sec)

k= radius of Andreason pipette (cm)

The measured size distribution were shown in Table (2) and the specific gravities of the each samples were as follows :

	specific gravities at 13°C
Ha-Dong kaolin	2.52
San-Chong kaolin	2.44
Yong-Il acid clay	2.52
Chang-Yang vermiculite	2.36

As x-ray diffraction analysis of Chong-Yang vermiculite shows typical peak at 14A, which can be considered as consisting of two layers structure as indicated in Fig (1). In the analysis of Ha-Dong and San-Chong kaolin, the peaks of the hydrated halloysite were clear as shown in Fig. (1), thus it means good quality of kaolin. The peak of Yong-Il acid clay in Fig. (1) suggested that the minerals contain a lot of cristobalite and some other impurities. X-ray diffraction data of purified clays shows generally amorphous Fig (2).

The cation exchange capabilities of the clays were measured by Ca ion adsorption. The measured capacities are shown in Table (3). From this table it is obvious facts that Vermiculite has good exchange capacity than other clay samples.

3. Surface Characteristics of Suspended sample clays

Sedimentation velocity of fine particle is an expression of surface characteristics of the particle. It was found that, in general, maximum sedimentation velocity occurred at the iso-electric point of the particle surface. The aqeous clay suspension, made of under 100 mesh particle, was put into mess cylinder and the sedimentation velocity was measured. The kaolin type clay (Ha-Dong and San-Chang) showed a maximum sedimentation velocity in strong acidic region, but other two clays (Yong-il and Chong-Yang) showed the velocity increased as the acidity increased. The results of sedimentation velocity of sample clays for various pH were shown in Fig. (3).

For the efficient dispersion of the clay, the carbonate in the sample clay was removed by washing with a slightly acidic solution (NaAc buffer) and the removal of organic matter as well as free manganese oxide was accomplished by the treatment of the clay with hydrogen peroxide solution. It was also necessary to remove free iron oxides by treating with the solution of sodium acetate and sodium bi-carbonate for a effective segregation of the clay particle. The clay suspension added sodium carbonate solution was then warmed for about 20 minutes. The fine clay mineral(under 2 micron) was obtained by decantation and centrifugation of the clay suspension and used for the measurement of the electrophoretic mobility.

The electrokinetic properties of the sample clays were investigated by measuring the electrophoretic mobility of their aqeous suspension as a function of pH. A flat-type, vertical micro electrophoretic cell was used for the measurement. The results of measurements for purified fine clay and alumina for comparative purpose were shown in Fig. (4).

The elctrophoretic mobilities of Yong-Il acid clay and Chong-Yang vermiculite were negative regardless of pH, but kaolinite type clays (Ha-Dong and San-Chong) have positive values in strong acidic region. For alumina the mobility was null and the sedimentation velocity was maximum at around neutral region.

At this coincident point, so called iso-electric point, the particle would have minimum surface charge and the sedimentation velocity was maximum by the increase of the flocculation. It can be observed that the iso -electric point of the kaolinite is between 2.0 and 2.5 of pH and for the other, the mobilities approach to null when the acidity increases. These results agree well with the sedimentation measurement as shown in Fig. (3).

4. Sorption of radionuclides

The experiments of radionuclide adsorption phenomena by using Kaolinite, Montmorillonite and Vermiculite groups were carried out. Prior to this actual adsorption tests, pretreatments of sample clays were conducted to study the adsorption effect of Sr-90 and Cs-137. Comparing studies between raw clay minerals and pretreated clay minerals of adsorption characteristics were made. Sr-90 and Cs-137 consist in the from of Sr-90 NO_3 and Cs-137 Cl solution prespectively which were purchased from Amersham Radiochemical Centre in U.K.

Pretreatment of sample clays.

Heat treatment

The particle size of 80 mesh Yong-11, Ha-Dong clays and 20 mesh Chong-Yang Vermiculite were calcined in the electric furnace at a temperature of 700°C for 1 hour and 650°C for 30 minutes, respectively

Acid treatment

Calcined Yong-11 and Ha-Dong clays were washed by distilled water and dried at a temperature 100°C. After then treated with 20% hydrochloric acid at the ratio 1 volume of dried clays to 2 volumes of hydrochloric acid at a temperature 100°C for 1 hour. In order to remove free acid from the acid treated samples, washing procedure was also employed. These samples might be changed into "hydrogen saturated" clays and removed impurities of possible lime stone.

Alkali treatment

Same procedures were acceptable in the alkali treatment of sample clays (Yong-11 and Ha-Dong) as mentioned above acid treatment except the treatment of alkali with 10% soduim hydroxide. Also these samples might be converted to "sodium saturated" clays and minimized lattice destruction.

Sodium treatment

It is well known 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 transformations of mica-vermiculite mixture to pure vemiculite in order to obtain and increase of their cation exchange capcities were carried out by the 1N sodium chloride and hydrogen peroxide treatment. These samples might be saturated with alkli metal and incresed cation exchange capacities.

4-2 Batch processes for determining the selectivity of Cs-137

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

The adsorption test for Cs-137 to yong-11 and Ha-Dong clays with pre-treatment, including acid and being calcined at 700°C was shown in Fig. (5). It shows that removal percent of Cs-137 are superior.

In practical operation of three-stage liquid waste treatment plant, in order to avoid complicated pre-treatments of clay samples and considering economical problems, simple method of pre-treatment of clay minerals was applied as follows. In acid treatment, very dilute hydrochloric acid

(36% HCl : 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 same samples without being calcined.

The adsorption data of the non-calcined clay samples can be observed in Fig (6). Comparing the two figures, removal percent of Cs-137 was generally decreased in the non-calcined samples than calcined ones. It is indicated that the removal percent of Cs-137 is found to be 95 percent in non-calcined Yong-il acid clay which was treated by dilute hydrochloric acid.

It means that the simplified pre-treatment method and Yong-il acid clay are available to employ in the treatment of liquid waste. 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 (7). Vermiculite is well known for its 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 kali-metal cations or amonia, the lattice spacing changes measurably and results in steric effects that improved the exchange properties for cesium.

Fig (7) shows that the adsorption of Cs-137 to calcined Vermiculite which was activated by 1 M sodium chloride was obtained a little higher value than non-calcined one. The Maximum adsorption point of heat treated vermiculite indicated on the curve was found to be 97.86% at the pH 7 and the maximum adsorption point of Cs-137 to raw one was 93.21%.

Generally speaking, affinity for radiocesium is remarkably superior regardless of pH range in the simulated waste solution.

4-3 Batch processes for determining the selectivity of Sr-90

Adsorption tests to strontium-90 were carried out similarly as the experiments of cesium-137. As we pointed out in the progress report, Fig (8) 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. The removal percent of strontium to raw Yong-il acid clays marked 96-99 percent between pH 6 and pH 9 (Fig 9), while the removal percent was over 99 percent between pH 6-7 when 1.500 mg of heated clays at 700°C were added into 50 ml of radiosolution.

The experiments of non-calcined 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.

Yong-Il acid clays treated by dilute hydrochloric acid were shown 99% removal of Sr-90 around the pH 6 as shown in Fig. (10) 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.

Yong-Il acid clay which consists of montmorillonite group, generally speaking, has a property of dispersion in water because of its swelling property, so the proper particle size can be made easily by heat treatment. For improving this fault, a new stable exchanger was prepared by the calcination of granular montmorillonite. The decrease of ion-exchange capacity due to the calcination can be improved by the treatment with hydrochloric acid or sodium hydroxide. It was found that the Na-form and H-form exchanger treated with sodium hydroxide and hydrochloric acid were excellent in exchange capacity and decontamination factor for radioactive ions than non-treated raw clay.

In the vermiculite tests for the Sr-90 adsorption affinity was much inferior than Cs-137 adsorption as shown in Fig. (10, 11) there is no use saying that adsorptions of Sr-90 to vermiculite in practical operation of the plant are economically inadequate at the present time.

5. Plant application

5-1. 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 labaratory has been operated. The low level liquid

...tes have been collected monthly through storage tank and transported ... waste disposal plant.

For model test, 5 mm acrylic cylinder in the volume of one-third of the three stage reaction tank including an agitator (200 r.p.m) and a ... meter was prepared as shown in Fig (12). The experimental work on adsorption of radionuclides by using the acrylic cylinder were carried out. ... strontium and cesium (approximately 10^{-3} μc/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 ... in practical operation. The Yong-il acid clays were activated by ... hydrochloric acid (36% HCl : water = 1 : 50), washed by water for removing free acid, dried at room temperature and crushed to 60 mesh.

... 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. (13) shows that the decontamination which was upgraded by increasing the clay dosage was its best when the flow rate was 0.5 liters per minute than one or two liters per minute. However the removal percent of Sr-90 is less than 85 percent in the presence of 0.5 liters per minute of flow control, while the removal percent reaches 97 percent without flow control for an hour reaction time.

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 minute 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 (...) in condition of 2 liters per minute of flow rate and 2 percent clay dosage as shown in Fig (13). It was also indicated that the removal percent of Cs-137 was found to be 90 percent (D.F=10) in 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.

5-2. Plant design :

5-2-1 Theoretical problem and decontamination factor

(a) The relation of equilibrium between clay and solution

The typical plot in equilibrium state between the concentration of clay, X and the concentration of radiosolution, Y is shown in Fig (14). The radioactivity concentration of the solid (clay) and the solution would be graphed as a diagonal line, and finally as unchanging constant curve beyond a certain value X. The change of the curve would depend upon the adsorption ability of clay, pH, temperature, and the concentration of the solution.

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 experiments was in a small range of radioactivities to 10^{-3}-10^{-6} $\mu c/ml$ level.

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

where k is a proportional constant which is similar to Henr'ys 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 before. 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

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

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

When the values of X and Y are put into above equation (1),

ks = for Sr-90 could be calculated as followes.

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

For Cs-137

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

$$2X = 100\,Y_o\left(1 - \frac{1}{10}\right)$$

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

(b) Calculation of stage and feed ratio

The flow diagram of three stage counter current system of the plant between clay and radiosolution is given in Fig. (15)

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

$$\left.\begin{aligned} L_o Y_o - L_1 Y_1 &= S_1 X_1 - S_2 X_2 \\ L_1 Y_1 - L_2 Y_2 &= S_2 X_2 - S_3 X_3 \\ L_2 Y_2 - L_3 Y_3 &= S_3 X_3 - S_o X_o \end{aligned}\right\} \quad \ldots\ldots\ldots (2)$$

The initial concentration of clay inlet, is taken $X_o = 0$

and $L_o = L_1 = L_2 = L_3 = L$

$S_o = S_1 = S_2 = S_3 = S$

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

$$kK' = K$$
$$= \frac{S}{L} \cdot \frac{X}{Y}$$
$$Xi = k\ Yi$$

Then equilibrium condition reaches from each stage of the system.

Equation (2) becomes

$$\left.\begin{aligned} (1+K)\,Y_1 - K\,Y_2 &= Y_o \\ -Y_1 + (1+K)\,Y_2 - KY_3 &= 0 \\ -Y_2 + (1+K)\,Y_3 &= 0 \end{aligned}\right\} \quad \ldots\ldots\ldots\ldots\ldots \quad (3)$$

In first stage

$$\frac{Y_1}{Yo} = \frac{1 + K + K^2}{(1+K^2)(1+K)} \quad \ldots\ldots\ldots\ldots\ldots \quad (4)$$

in Second stage

$$\frac{Y_2}{Yo} = \frac{1 + K}{(1+K^2)(1+K)} \quad \ldots\ldots\ldots\ldots\ldots \quad (5)$$

in final stage (third stage)

$$\frac{Y_3}{Yo} = \frac{1}{(1+K^2)(1+K)} \quad \ldots\ldots\ldots\ldots\ldots \quad (6)$$

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

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

$$K = kK'$$

For Sr-90

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

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

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

For Cs-137

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

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

D. F. Values calculated for Sr-90 are 4.3 in fist 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.

5-2-2. Treatment facilities

Principle design criteria of the treatment facilities was low level liquid waste treatment using local clay minerals which have natural occuring ion exchange capacities. The plant conists of three unit of sludge settling tanks and three reaction tanks as shown in Fig. (16,17). 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 plat.

It should also pay attention not only to keep from the damage of radiation hazards but also the operation faults during treating radioactive materials. 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 as shown in Fig. (18,19).

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

5-3. 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 hydrochloric acid (36% HCl : water = 1:50) were used in this plant application experiments, because of its mainly montmorillonite group in mineralogical compontion, its low cost and its abundance in quantiti.

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. paddale type agitator. Waste solution used in this experiments contains Sr-90 ($Sr^{90}NO_3$), Cs - 137 ($Cs^{137}Cl$) separately. In the third reaction tank, the clays and waste solution are reacted initially, after then the slurry is pumped up to third settling tank in order to settle down in solid phase. The sludge settled are flowed into the second reaction tank where second stage reaction occured between clays and waste solution. Also three times reactions were accomplished in the every stages as similar fashion mentioned above.

The disc filter with a compressor and two vacuum pumps is connected with fist settler for separating clay sludge from slurry condition solution as shown in Fig. (20) 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 wastes and the effluent is pumped from disc filter to storage tank.

Secondarily, radiosolution is feeded 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 minuite and the clay dosage is 40 grams per minuite (2% by weight). Four sampling points were selected at feed tank and on the tops of each settling tanks. Samples were taken every hours after steady state was reached and counted in order to compare with the theoretical volues and experimental ones. We have had a plant operational experiments 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 counter current flow was reached approximately arond 25 hours after starting operation of the plant.

Fig. (21) shows that the decontamination factor of the plant was found to be approximately 100 in final stage when Sr-90 was used. These values abtained by the plant application test well agreeded with the theoretical ones in fist and final stages while slightly inferior value was shown than theoretial one in second atage. Fig (22) shows that D. F. was found to be approximately 800 in final stage when Cs-137 was used and the values of the test were well satisfied with theoretical ones in all stages.

6. Economic evaluation

The objects of the cost evaluation are to include the etements which should be necessary not only straight forward operational costs of waste management but also indirect costs. At the present time, expenditures of raw clays and pretreatment by using clay minerals to be included in this study will be defined.

It might be expected that the capacity of the plant would be 1440 liters per month when the plant runs 6 hour a day 6 days a week operation, and the flow rate of the plant is 2 liters per minuite. Assuming 2% (by weight) clay minerals are used, approximately 4 tons per year of raw clays will be necessary and required pre-treatment so as to improve D. F. Value. Costs of clay munerials including pre-treatment are as follows.

Yong-ill acid clay	Vermiculite
Acid treatment(dilute HCl)	Raw clay
$200/ton x 4	$260/ton x 4
= $800/year	= $1120/year

Alkali treatment

$300/ton x 4

=$1,200/year

It shows that the costs of alkali treatment of Yong-11 acid clay are higher 1.5 times than acid treatment. The costs of acid treamtent of Yong-11 acid clay will be within 10% of the overheads of managing low level liquid wastes in our Institute.

7. 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 prdouced mainly east and south coast in our contry.

Preliminary studies of this contract covered mineralogical studies and their sorption characteristics of long-lived nuclides such as Sr-90, and Cs-137.

Extensive works on plant appication and its economic problems were concentrated to find optimum operation conditions of the three stage liquid waste facilities through the fundamental adsoption studies, plant design criteria and Model test.

The conclusions summarised are as follows :

1. The representative clay samples such as Yong-Il acid clay, Ha-Dong clay and Chong-Yang Vermiculite have base exchange capacities of 56.1, 15.4 and 70.8 Meq/100 gr respectively. And their chemical compositions are SiO_2 for Yong-11 acid clay and Ha-Dong clay, and SiO_2 and MgO for Chong-Yang Vermiculite.

2. Maximum removal percent on 2% of Yong-11 acid clay treated by dilute hydrochrolic acid (less than 1%) was found to be 95%, while 93.2% of removal of Cs-137 on 2% raw Vermiculite and maximum 97.88% of removal on 2% Vermiculite treated by 1M NaCl were obtained at the wide range of pH.

3. 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-11 acid clay treated by HCl (less than 1%) was obtained around pH 6, while the removal percents of Sr-90 for 2% and 3% Yong-11 acid clay treated by 20% HCl were indicated to be 90-95% and over 99%. The affinity of Vermiculite on Sr-90 was inferior than Cs-137.

4. Considering the problems of disposal of the clay sludge and practical waste treatment, 2% dosage of clay and 2 liter per minuite of flow rate of feed solution would be appropriate in the Model test.

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

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Table (1) Chemical composition of collected clays

	SiO_2	Al_2O_2	Fe_2O_3	CaO	MgO	K20	Na_2O	Ig Loss
Ha-Dong Kaolin	42.34	40.23	0.37	1.87	0.63	Tr	Tr	13.41
Yong-Il acid clay	49.19	27.72	6.50	1.48	1.24	-	-	12.55
Chong-Yang Vermiculite2	39.75	15.89	8.62	3.52	21.37	2.70	0.32	27.64

Table (2) Characteristics Data of the sample clays

Sample No,	Commercial Name	Color	pH of the Aqueous suspension	Size distribution, % (<50 u
1.	Ye-San Clay	Light gray	5.12	66
2.	Ha-Dong "	white	7.42	78
3.	Dong-hae Diaspore	Light brown	5.15	14
4.	Shin-Ro-Won clay	Light gray	5.96	76
5.	Ye-Ri "	Light pino	6.10	57
6.	Po-Chun "	Light gray	8.46	–
7.	Yong-Il "	White	5.08	49
8.	Chu-An "	Gray	7.41	43
9.	Ui-Sung "	Light gray	8.45	35
10.	Chong-Yang Vermiculite	Yellowish brown	6.25	–

Table (3) Cation (Ca^{++}) Exchange Capacity

Sample	Cation Exchange Cap. (Meq/100g)
Ha-Dong Kaolin	15.4
Yong-IlAcid Clay	56.1
Chong-Yang	70.8

Fig.(1). X-ray diffraction Data of Crude clays

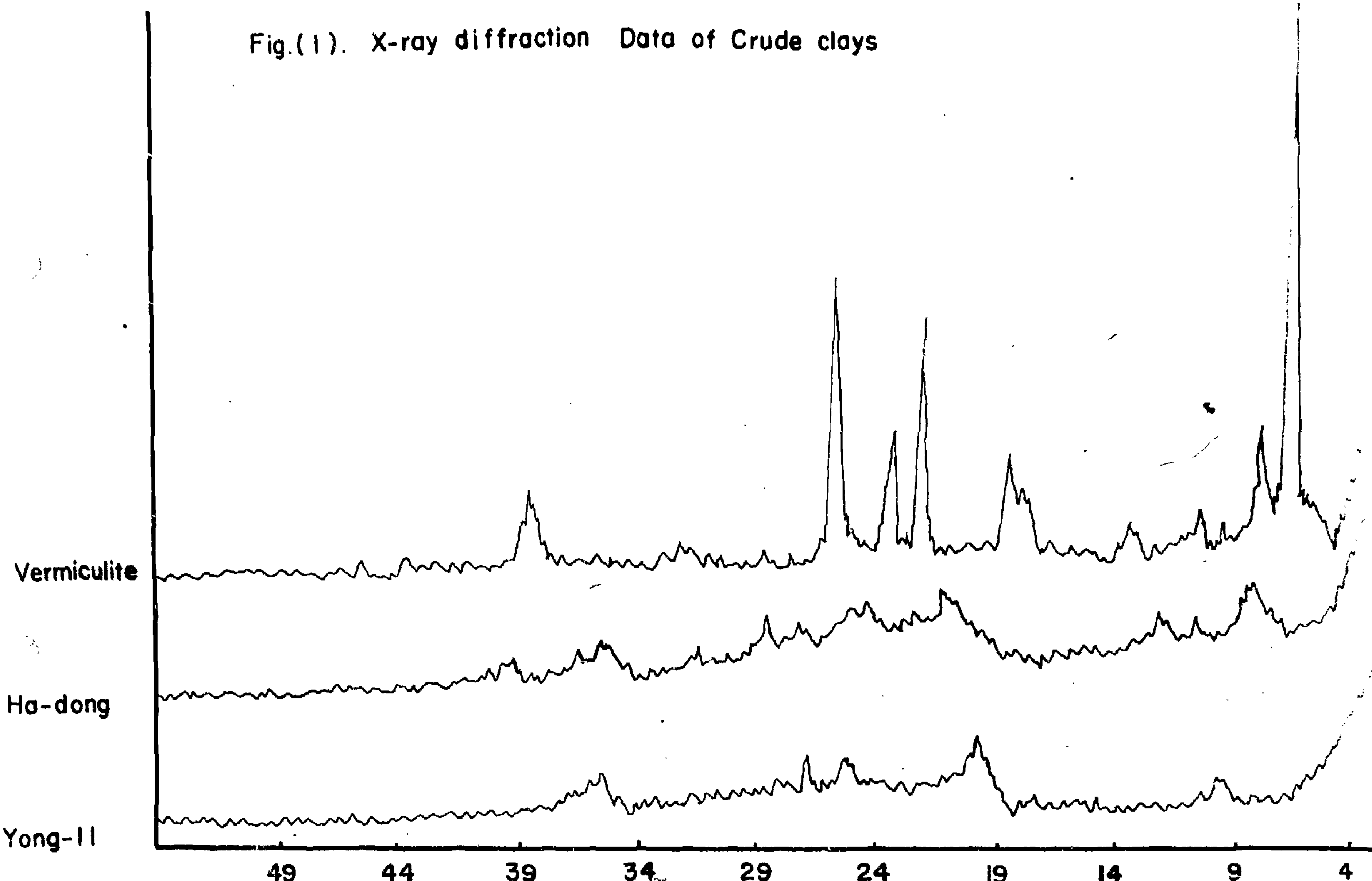
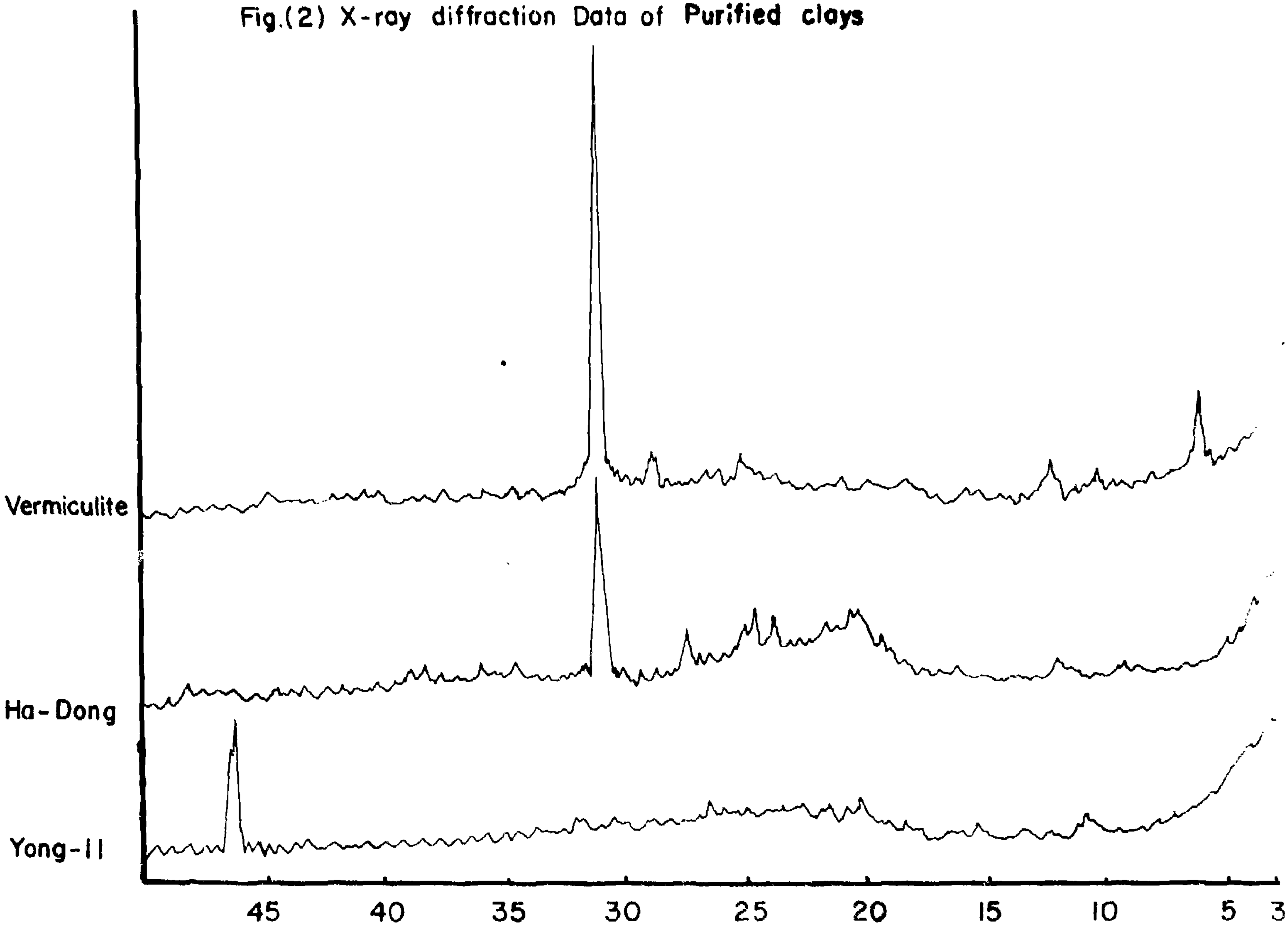


Fig.(2) X-ray diffraction Data of Purified clays



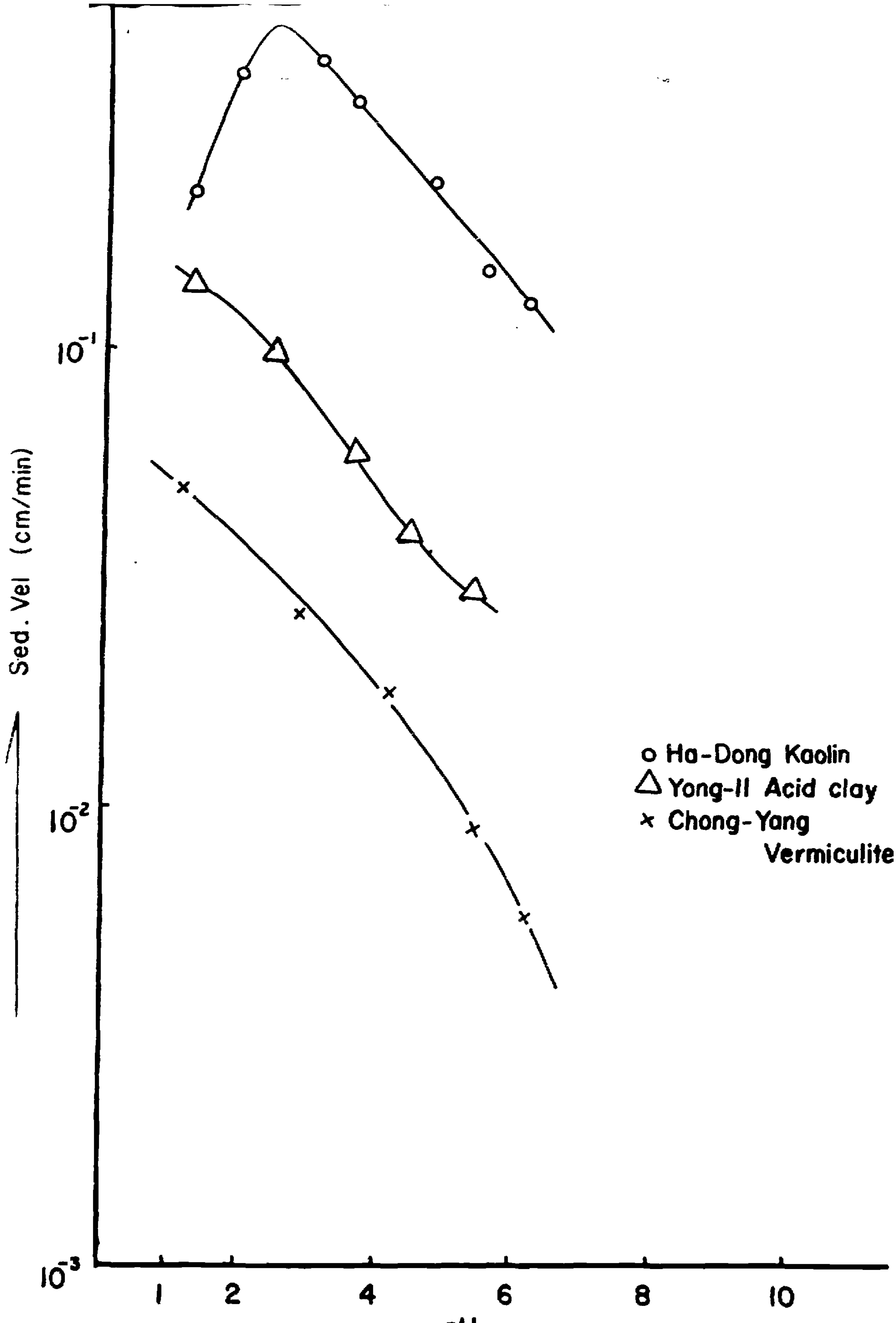


Fig. (3) Sedimentation Velocities

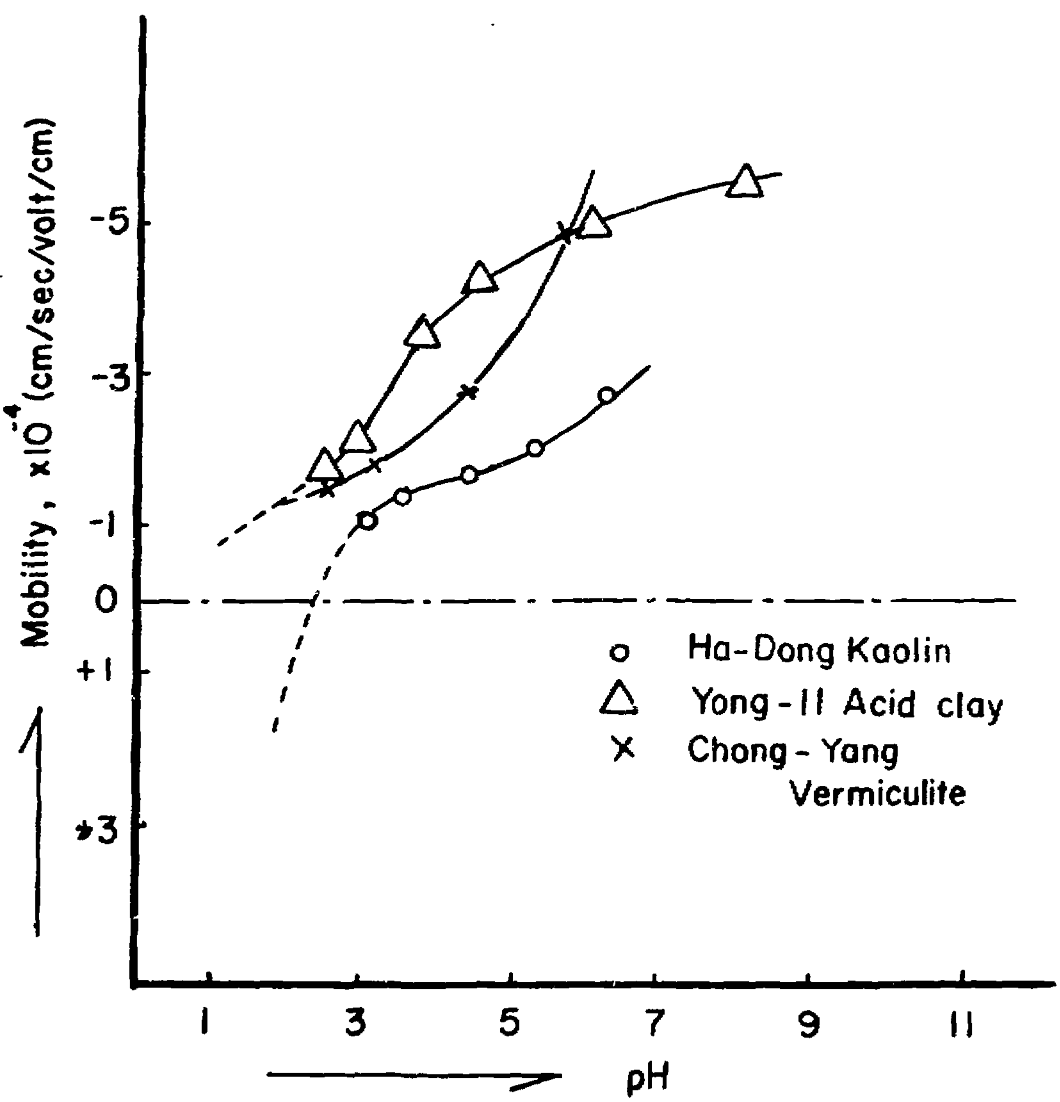


Fig.(4) Electrophoretic Mobility

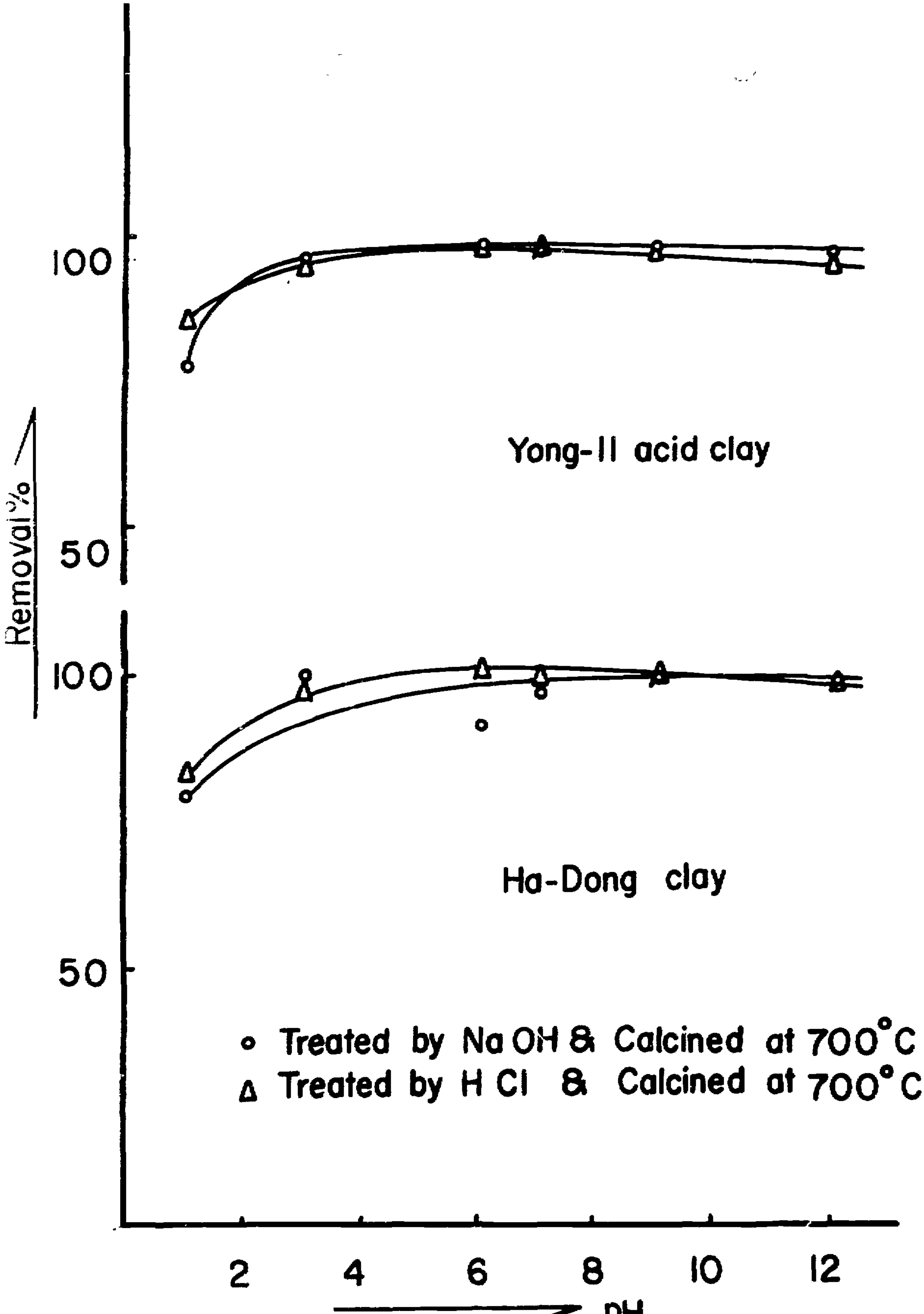


Fig (5) Cs^{137} adsorption as a function of pH

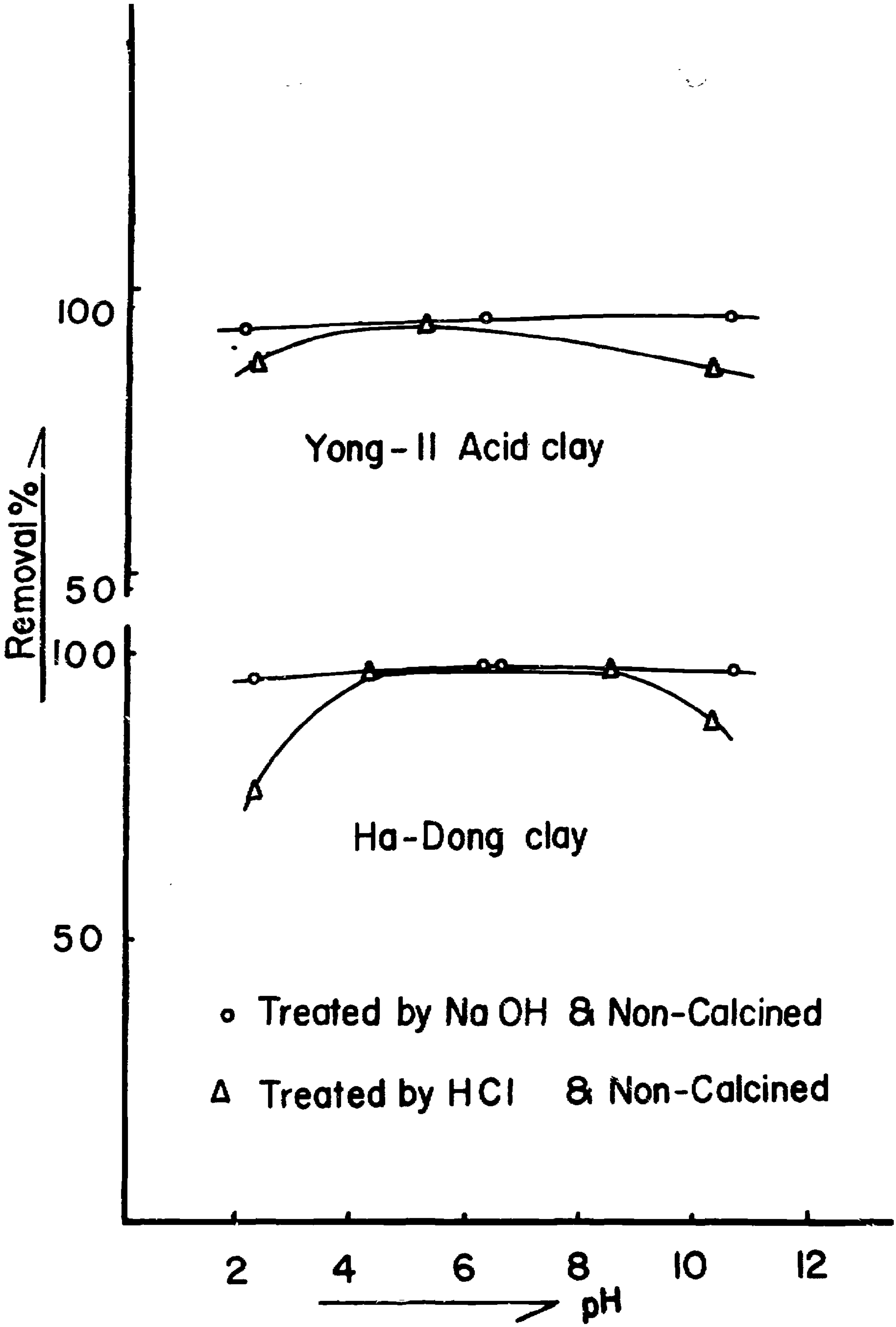


Fig (6) Cs^{137} adsorption as a function of pH

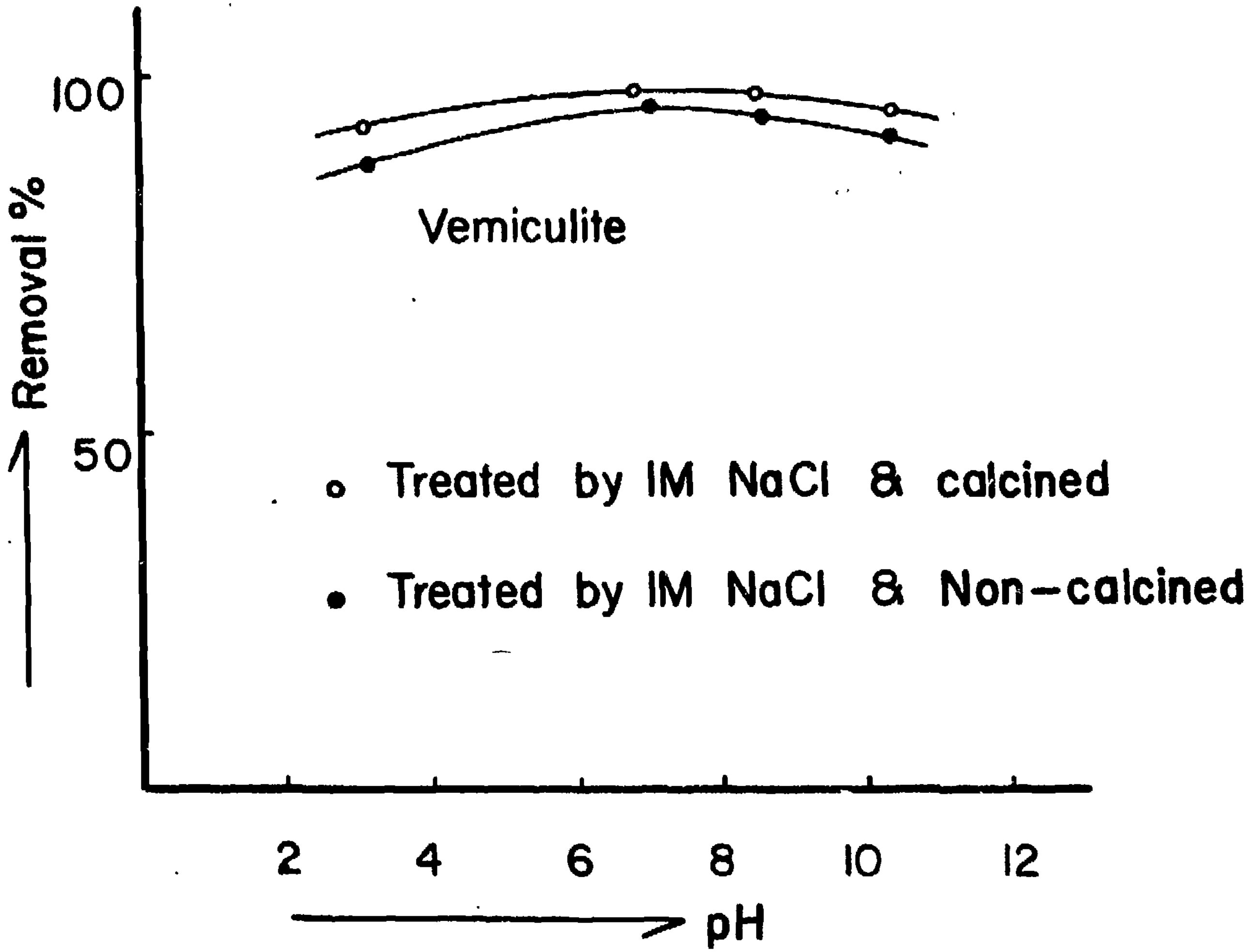


Fig (7) Cs^{137} adsorption as function of pH

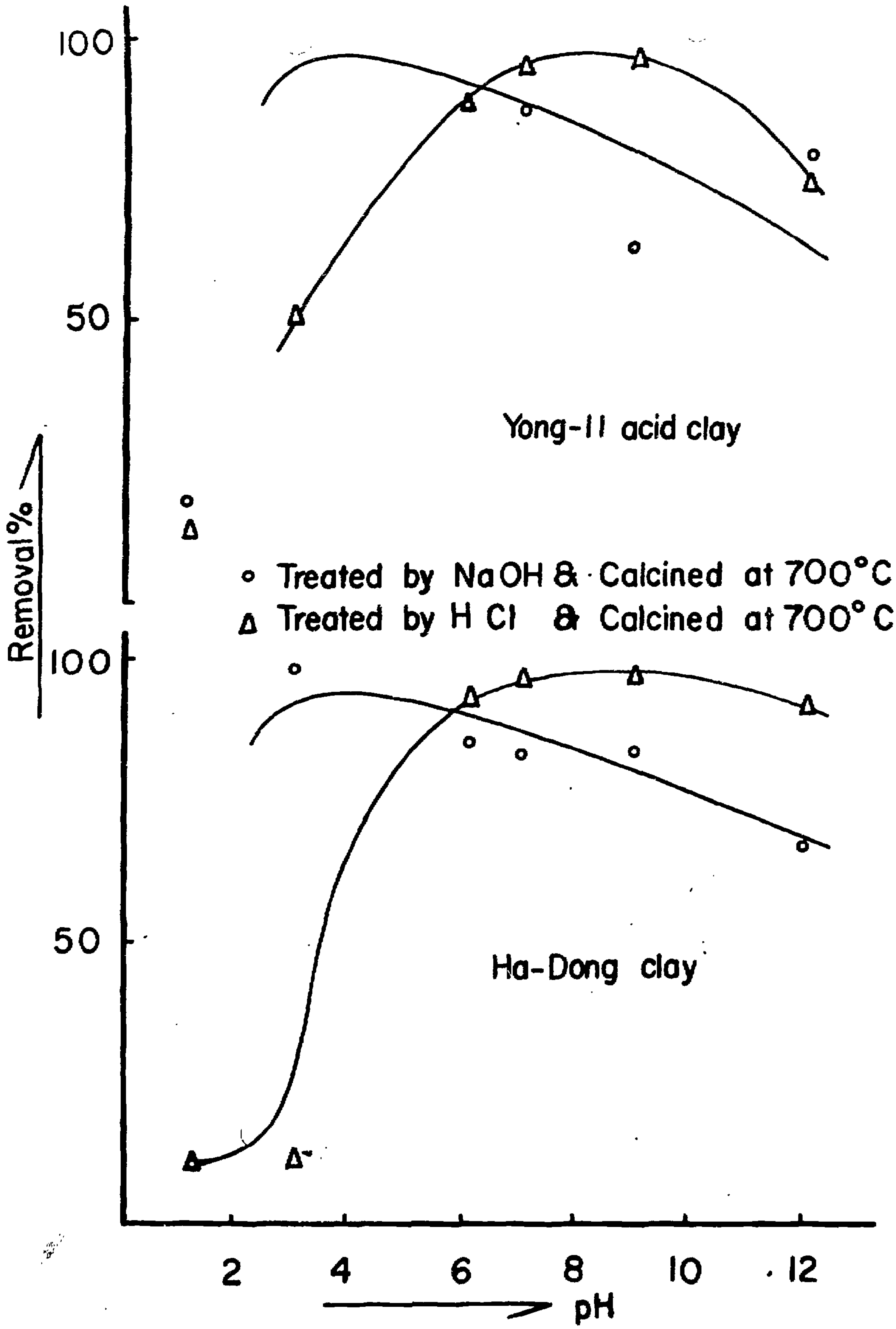


Fig (8) Sr^{90} adsorption as a function of pH

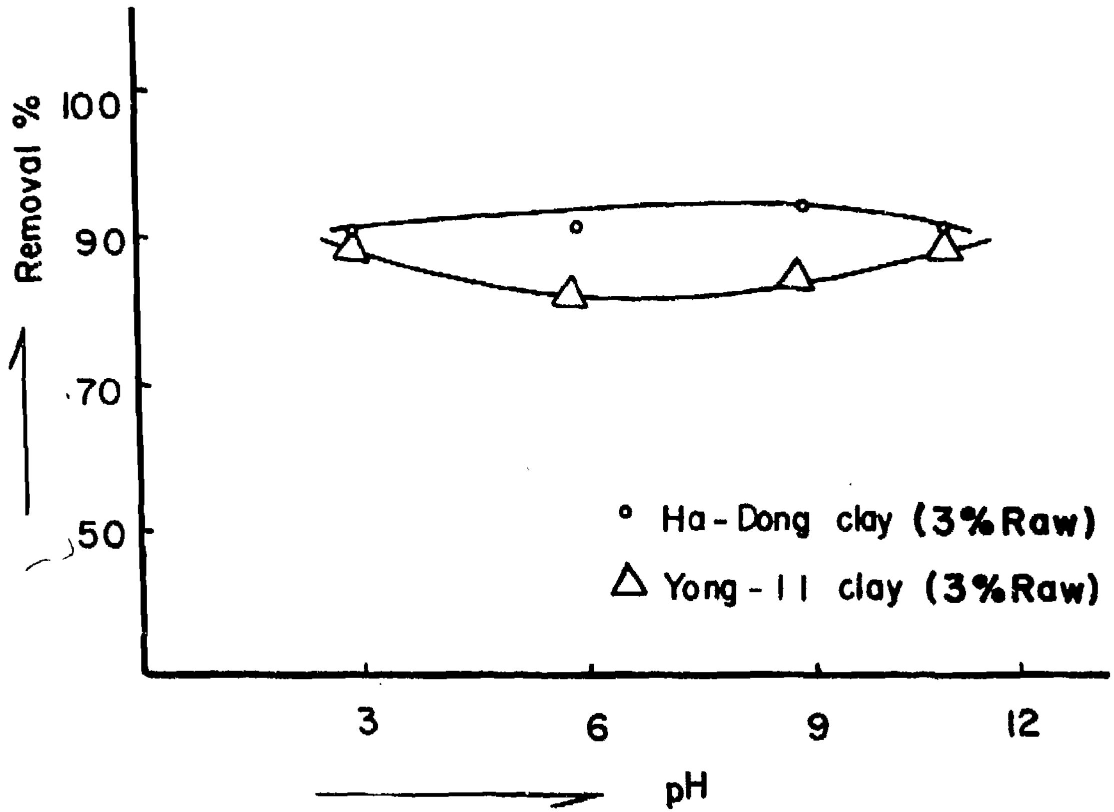


Fig. (9) Sr^{90} adsorption as a function of pH

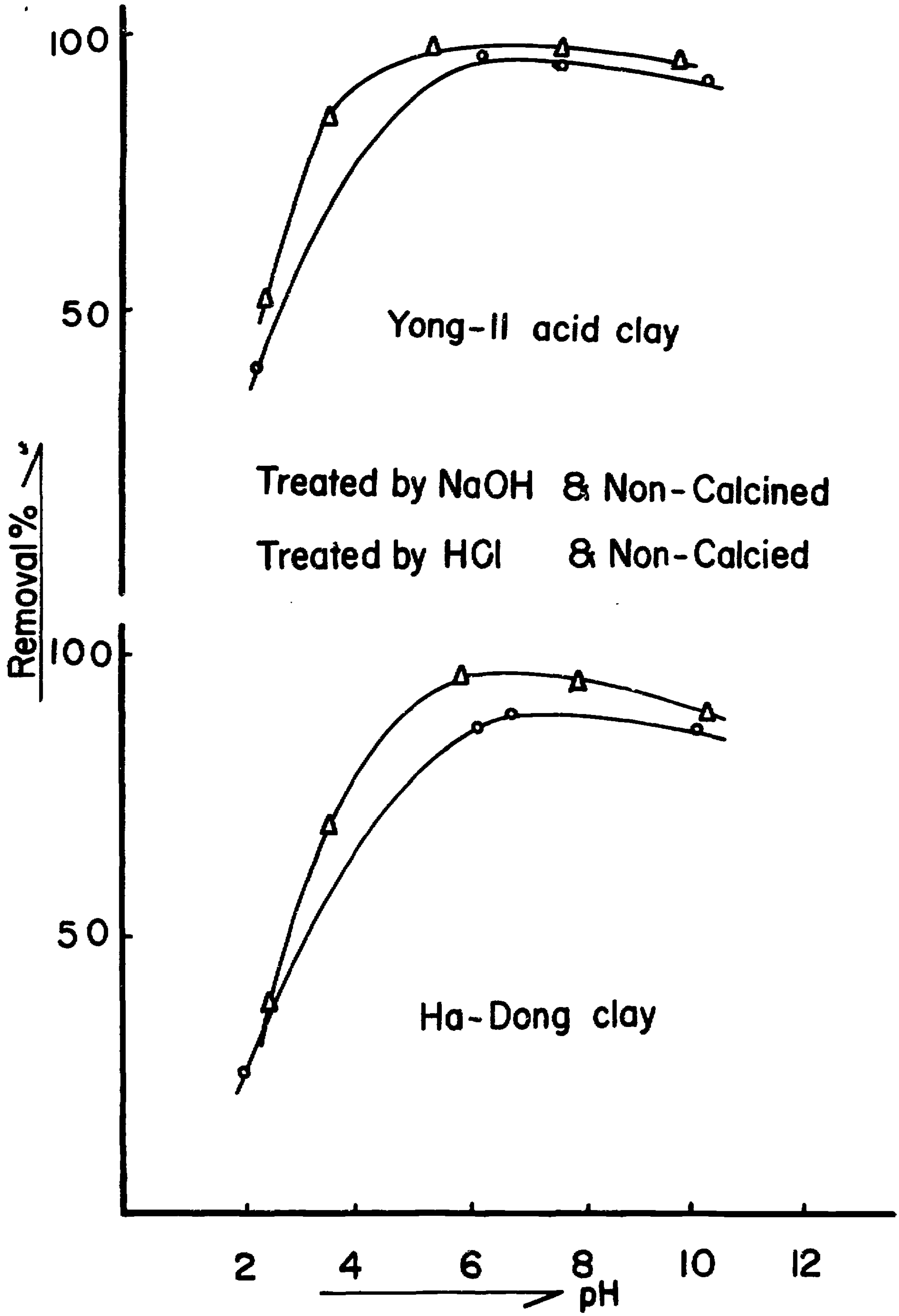


Fig (10) Sr^{90} adsorption as a function of pH

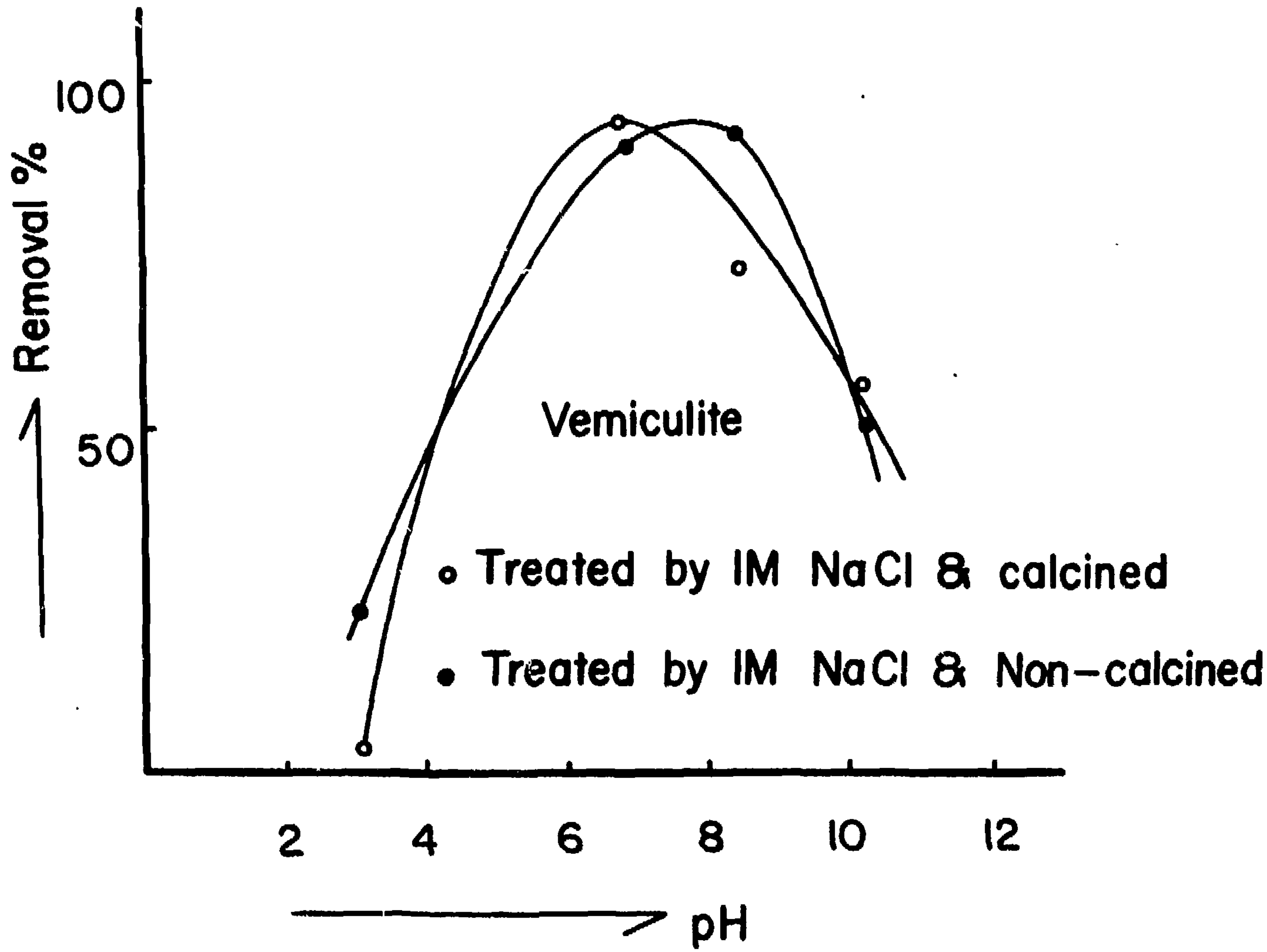


Fig (11) Sr^{90} adsorption as function of pH

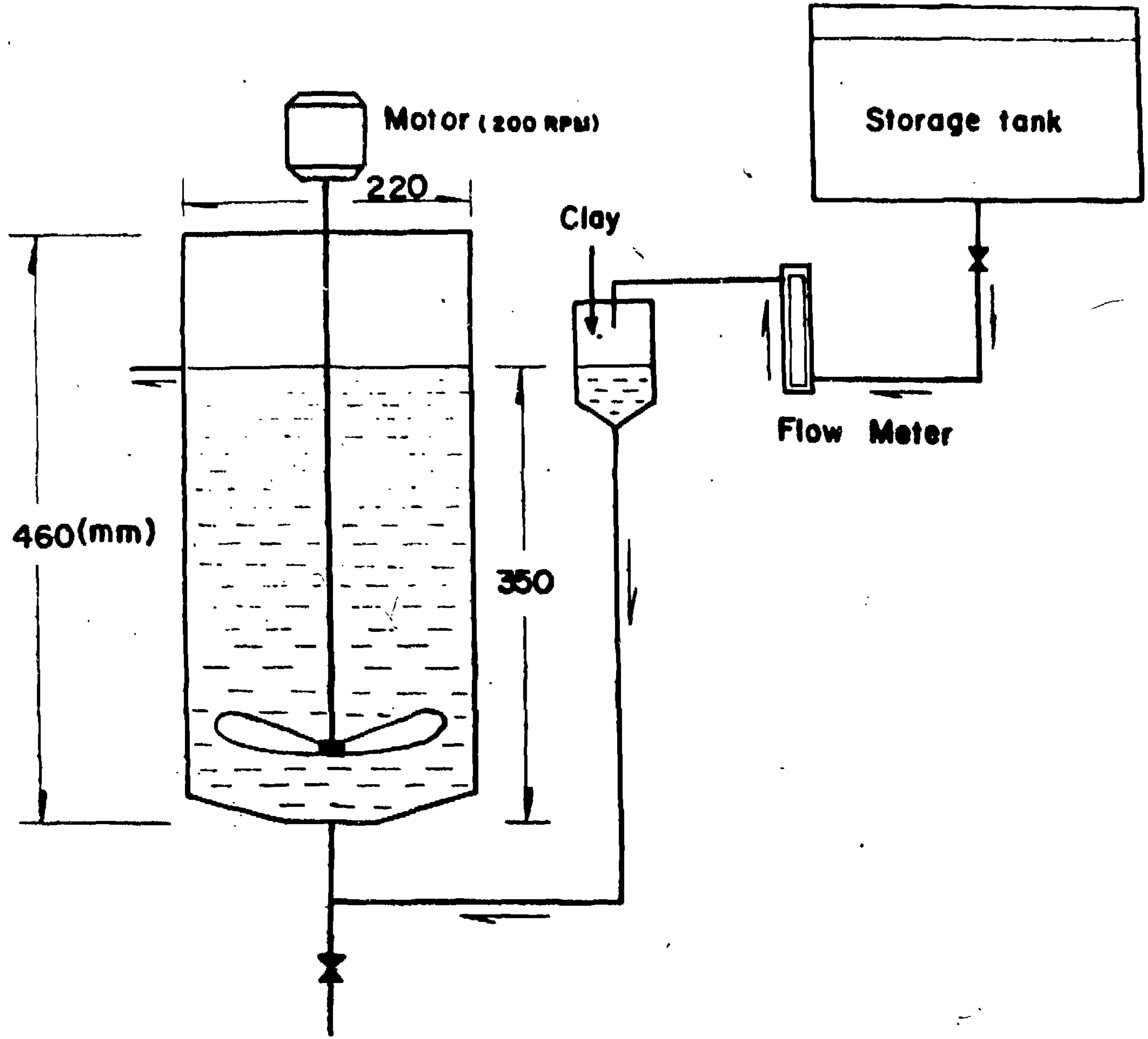


Fig. (12) Flow diagram of Model Test

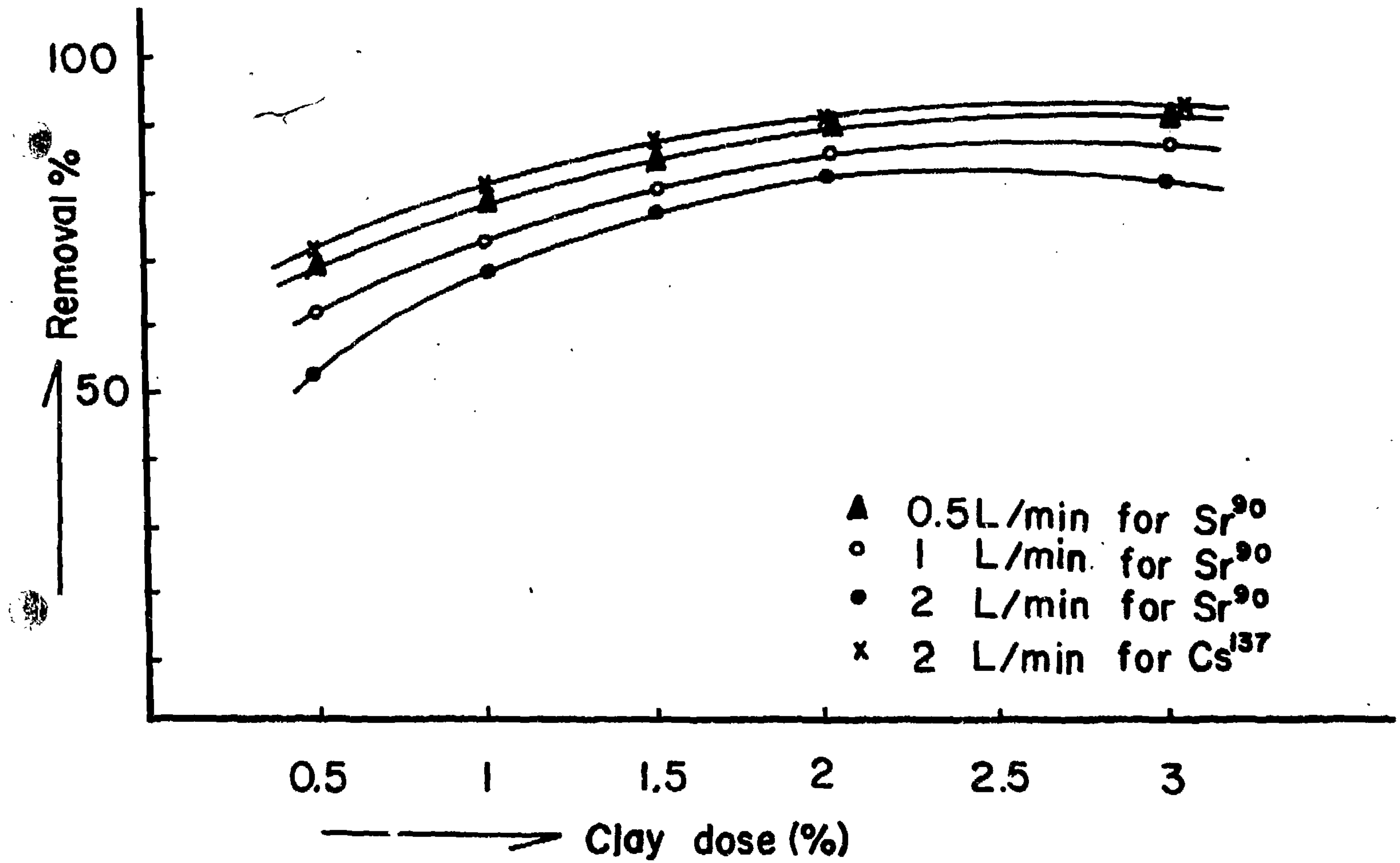


Fig (13) Model Test With flow control

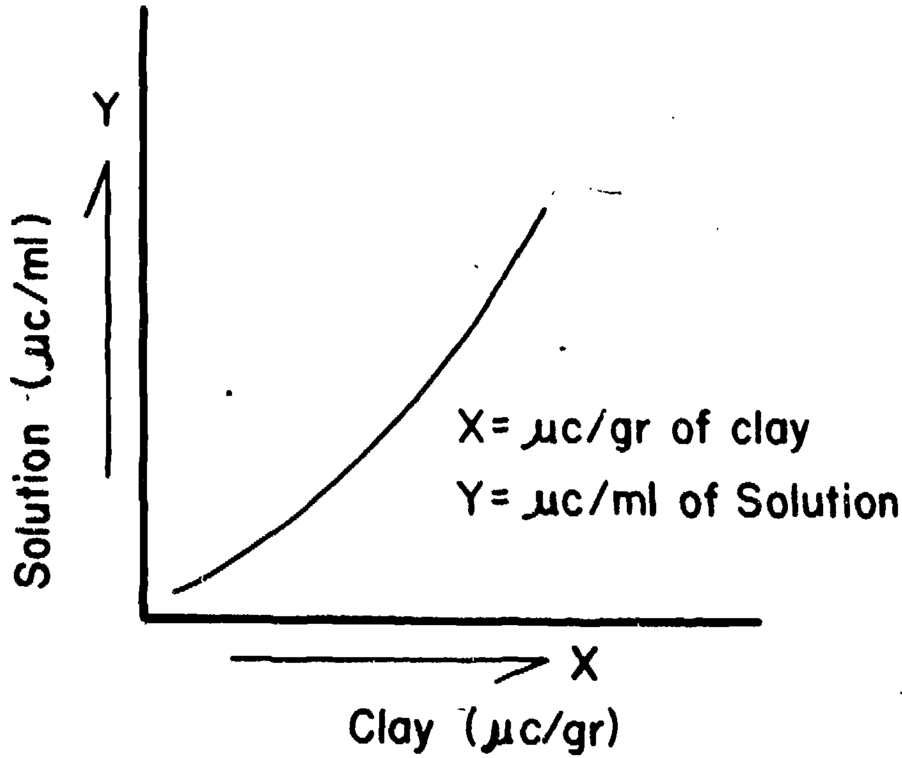
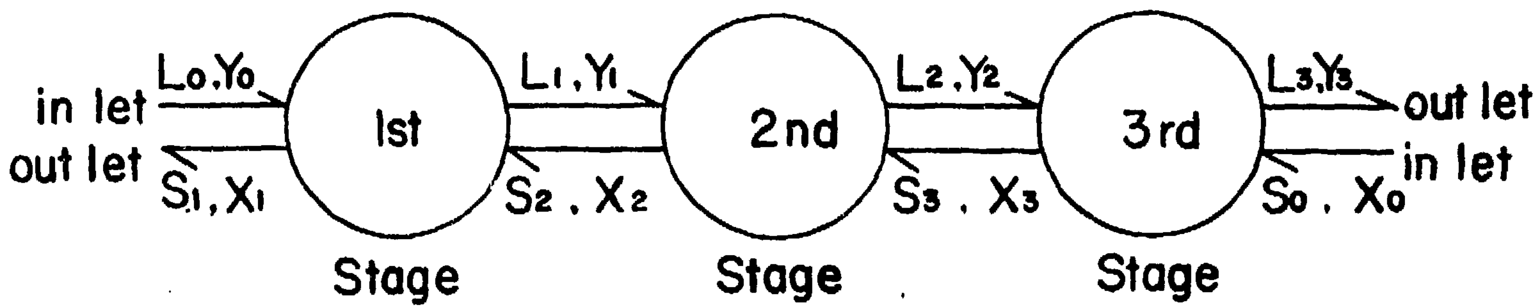
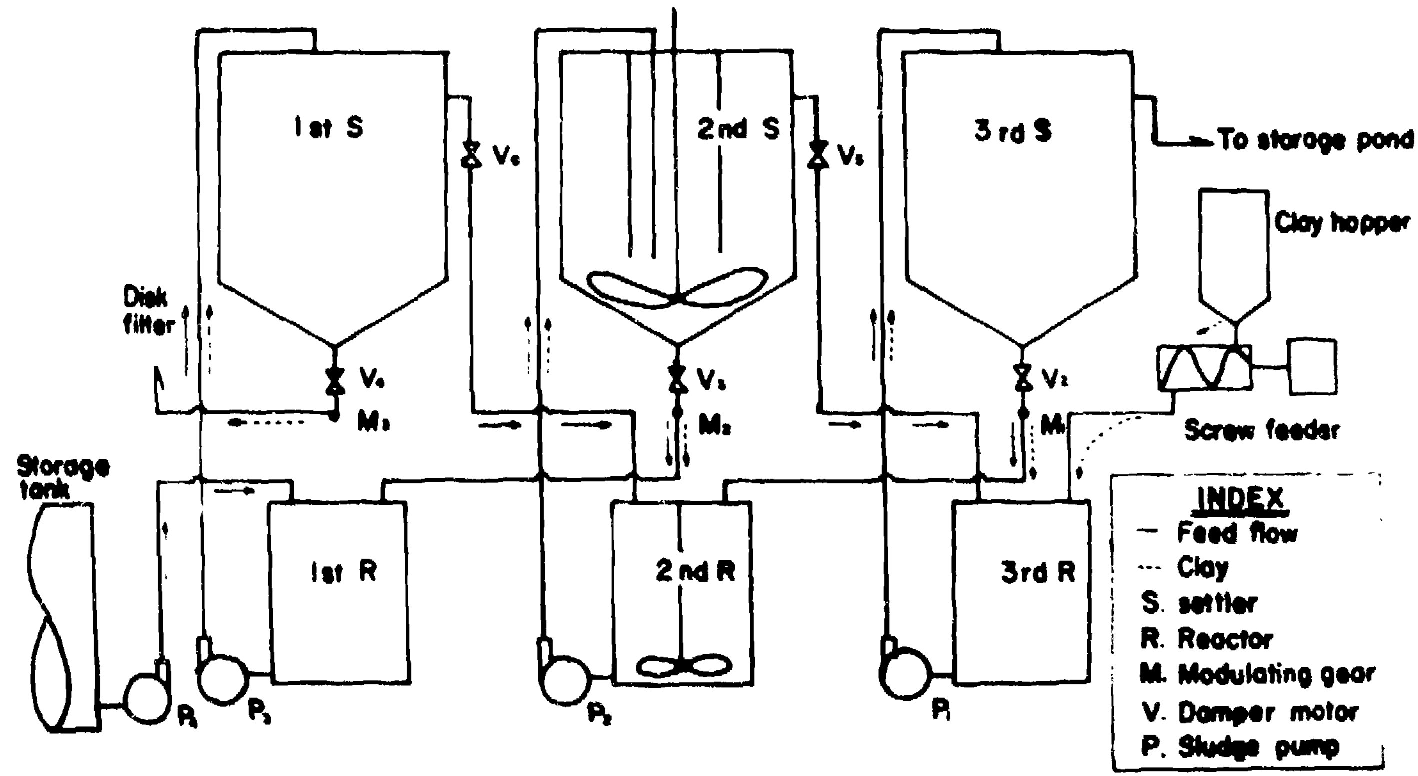


Fig (14) Equilibrium state between dilute solution and clay



Fig(15) Flow diagram of 3-stage counter current



Fig(16) Block Diagram of Waste Plant

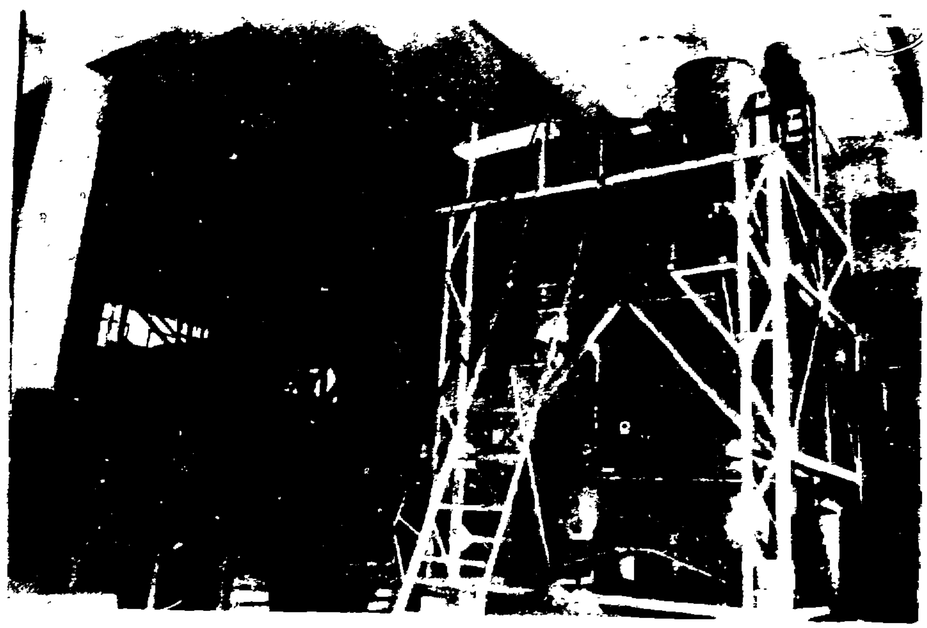


Fig. (17) Three stage liquid waste treatment facilities

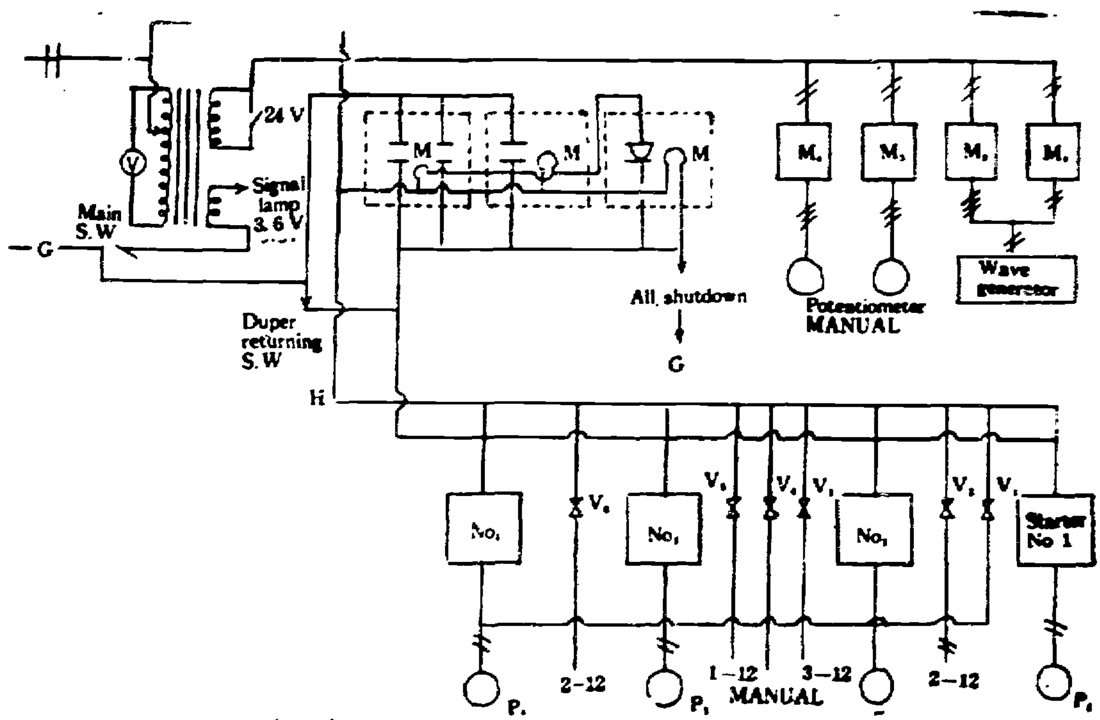


Fig.(18) CIRCUIT DIAGRAM OF CONTROL SYSTEM

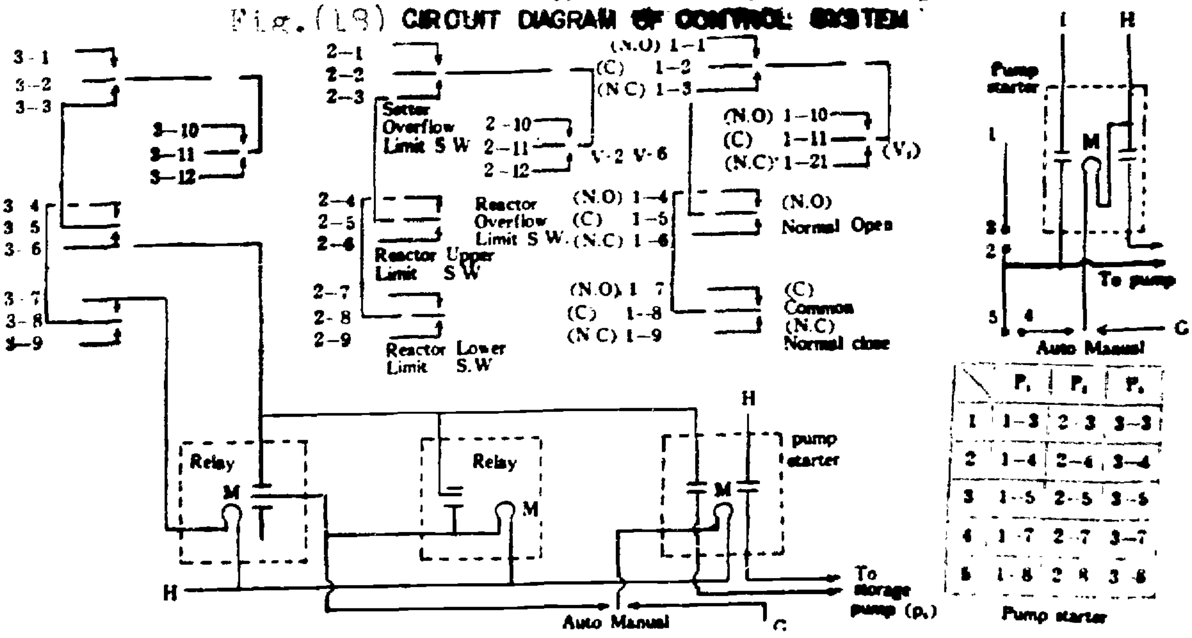


Fig.(19) CIRCUIT DIAGRAM OF MICRO SWITCH AND PUMP STARTER OF CONTROL SYSTEM

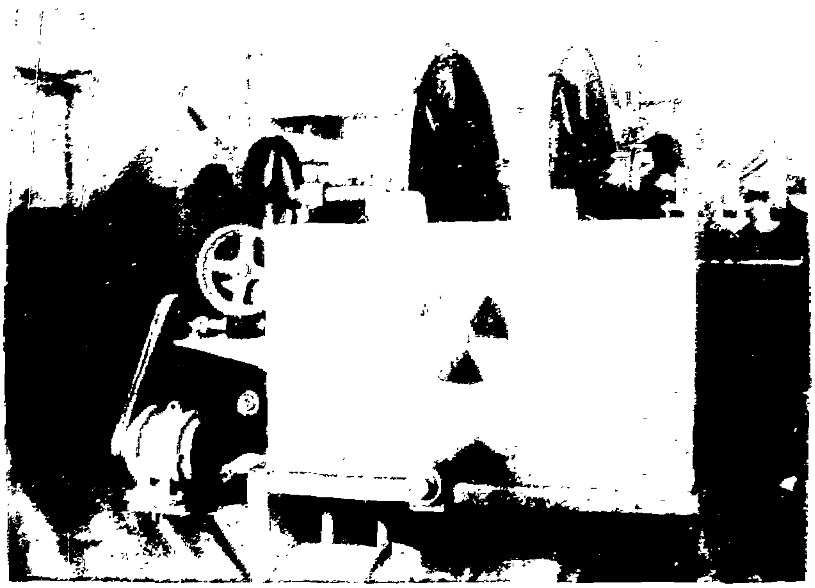


Fig.(20) Disc fieter

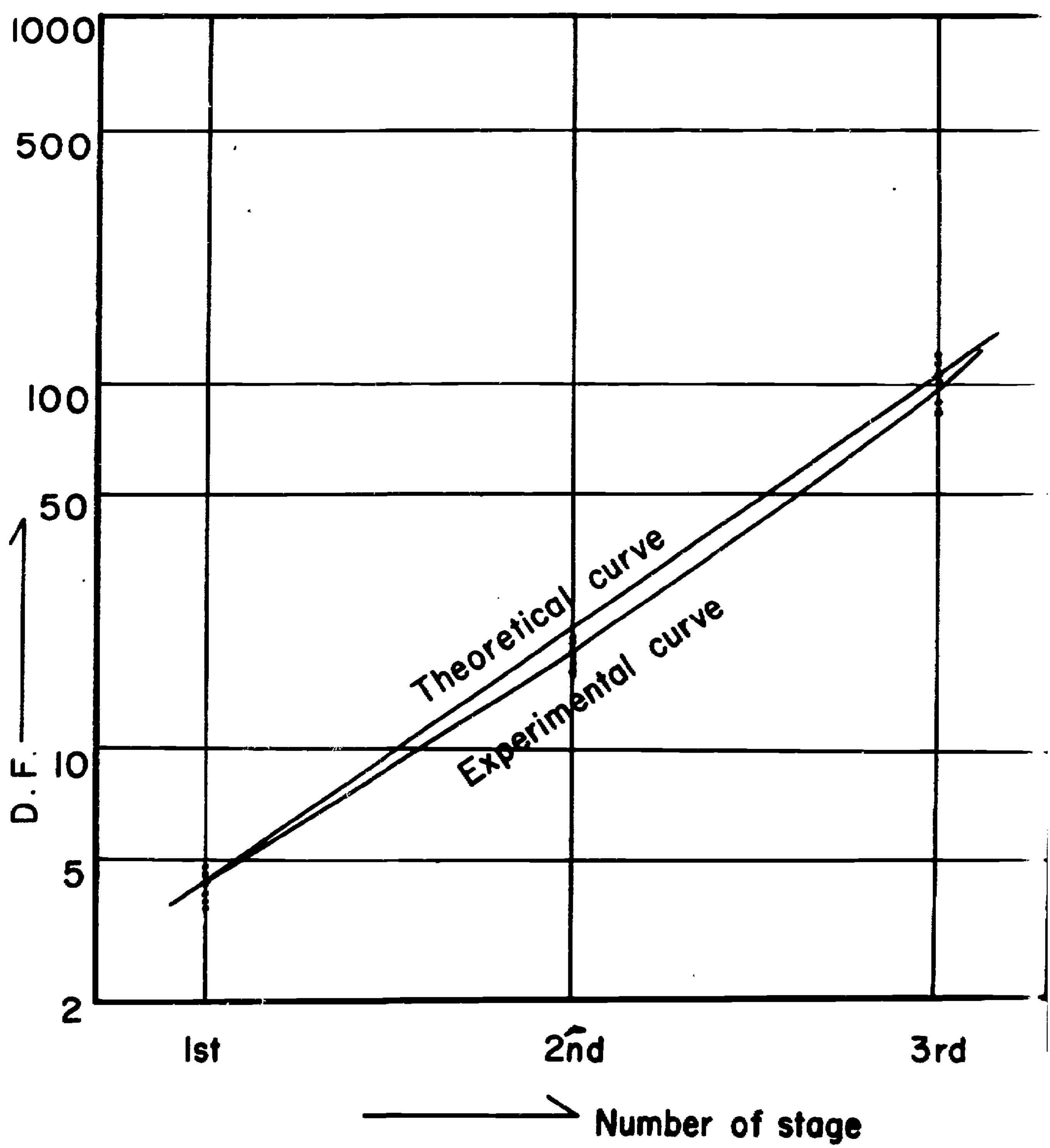


Fig (21) D.F. Value of Sr^{90} in each stage

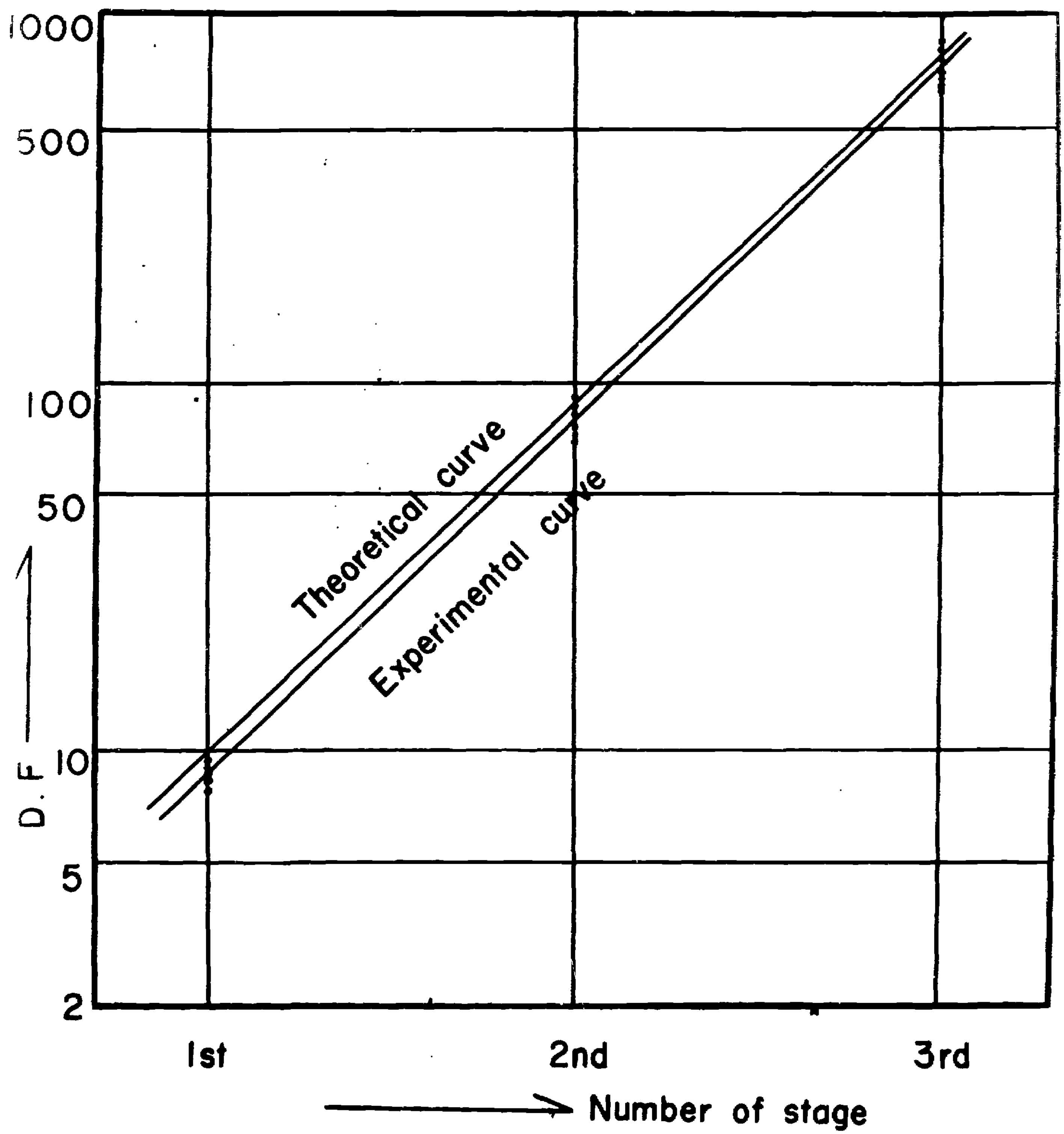


Fig (22) D.F Value of Cs^{137} in each stage

Summary

Title

Utilization of Korean clays and minerals for radioactive liquid waste treatment and disposal

Research Institute

Reactor Engineering Division, Atomic Energy Research Institute, Seoul, Korea

Principal Scientific Investigator

Sang Hoon Lee

Period of Contract

1 October 1967 - 14 December 1969

Scintific Background of the Project

One of the most economical method of treating the radioactive liquid waste at low level and medium level may be the clay adsorption of radionuclides. The Korean Atomic Energy Research Institute had been applying the sorption method .

The decontamination factor, however, has been fluctuated so much that there have been a great deal of difficulties in practising the method. This may be from the non-uniformities of the local clays and the waste qualities as well as the lack pretreating the clay, the sorption characteristics and the effetive application.

This Atomic Energy Research Institute has been operated a three -stage liquid waste treatment facility which process the low level liquid waste (10^{-3} μc/ml – 10^{-6} μc/ml). The study dealts with not only fundamental on local clay minerals (chemical, X-ray, sorption study etc) but also determining a optimum conditon in the operation of three-stage unit.

Experimental Method

The representative clay minerals such as Kaolin, Montmorillonite and Vermiculite groups were selected. The mineralogical studies were carried out by colour, size distribution, pH of the aqueous suspension, cation exchange capacities, X-ray analysis and chemical composition

As the pre-treatment method calcination and non-calcination, treatment with hydrochloric acid, sodium hydroxide or sodium chloride were used in the treatment simulated waste solution.

In batch experiments the uptake of Sr-90 and Cs-137 from sample solutions (distilled water plus Sr-90 or Cs-137) was defined. During experiments, different pH and clay dose were applied. In other experiments adsorption of Sr-90 and Cs-137 as a function of pH was defined. Decontamination with clay minerals was then applied for the treatment of the plant through the fundamental adsorption studies, plant design criteria and Model test.

Results Obtained

1. The representative clay samples such as Yong-Il acid clay, Ha-Dong clay and Chong-Yang Vermiculite have base exchange capacities of 56.1, 15.4 and 70.8 Meq/100 gr respectively. And their chemical compositions are SiO2 for Yong-Il acid clay and Ha-Dong clay, and SiO_2 and MgO for Chong-Yang Vermiculite.

2. Maximum removal percent on 2% of Yong-Il acid clay treated by dilute hydrochrolic acid (less than 1%) was found to be 95%, while 93.2% of removal of Cs-137 on 2% raw Vermiculite and maximum 97.88% of removal on 2% Vermiculite treated by 1M NaCl were obtained at the wide range of pH.

3. 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 by 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 indicated to be 90-95% and over 99%. The affinity of Vermiculite on Sr-90 was inferior than Cs-137.

4. Considering the problems of disposal of the clay sludge and practical waste treatment, 2% dosage of clay and 2 liter per minuite of flow rate of feed solution would be appropriate in the Model test.

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

Conclusions

Preliminary studies of this contract covered mineralogical studies and their soption characteristics of long-lived nuclides such as Sr-90 and Cs-137. The representative domestic clay minerals such as Yong-Il acid clay, Ha-Dong clay and Chong-Yang clay were selected as a groups of Montmorillonite, Kaoline and Vermiculite in this project.

Extensive works on plant application and its economic problems were concentrated to find an optimum operation conditions of the plant through the fundamental adsorption studies, plant design criteria and model test.

Paper published on workdone under the contract

S.H. Lee and S. K. Kim

Use of Korean clay minerals in the treatment of radioactive liquid waste.

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