



TREATMENT OF LOW-LEVEL RADIOACTIVE WASTE USING VOLCANIC ASH

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Abstract

The effective application of volcanic ash, an indigenous adsorptive material abundant in the Mt. Pinatubo area, in the removal of radioiodine from radioactive waste streams was demonstrated. Factors such as availability, low cost and comparative retention capacity with respect to activated charcoal make volcanic ash an attractive alternative in the conditioning of radioactive waste containing radioiodine. Chemical precipitation was employed in the treatment of low level aqueous waste containing ^{137}Cs . It was shown that there exists an optimum concentration of ferric ion that promotes maximum precipitation of caesium. It was further demonstrated that complete removal of caesium can be achieved with the addition of nickel hexacyanoferrate.

I. INTRODUCTION

The Science Act of 1958 created the Philippine Atomic Energy Commission, presently known as the Philippine Nuclear Research Institute (PNRI). The PNRI is under the control and administration of the Department of Science and Technology (DOST). In general, the PNRI is tasked with the control of peaceful applications of atomic energy. The Institute is therefore responsible for the regulation and safe use of all radioactive materials in the country. This responsibility includes the management of radioactive wastes generated by users of radioactive materials in industry, medicine and research.

The radioactive wastes produced by these users (i.e., 92 medical and 100 industrial) are mainly spent sealed sources. In addition however, liquid and solid wastes arise from the operation of the research reactor and various radioisotope applications in the Institute. With the anticipated increase in nuclear applications resulting from the projected operation of the TRIGA-converted 3 MW research reactor, the total volume of radioactive wastes will increase to an estimated 300 m³ after ten years.

Before 1988, storage of unconditioned radioactive wastes was the only option available for radioactive waste management. However, the PNRI proposed to develop an integrated facility for treatment, conditioning and storage of newly generated as well as accumulated radioactive wastes under the technical assistance programme of the IAEA.

The PNRI is currently implementing an IAEA TC project on the upgrading of its low level radioactive waste management facility. Technical assistance in the form of equipment supply, training and expert services were provided over a period of four years starting in 1991. Equipment totaling about US\$ 206,690, 22 man-months of fellowship training costing about US\$ 58,350 and expert services in the amount of US\$ 26,720 were provided by the IAEA over a period of 4 years. In addition to the expert services provided under the project, several missions including a WAMAP and an evaluation mission of the WAMAP were conducted in the last five years. Most of the recommendations of these experts and WAMAP missions have either been implemented and/or are in various stages of implementation.

The waste compactor provided by the IAEA had been commissioned and with the routine operation of the cementation facility, most of the solid compactable wastes have already been conditioned and stored in a newly constructed interim storage trench. The most urgent task now is to remove radioactive waste stored in the old trench and segregate, treat, condition and transfer the wastes to the new trench. In view of these

important tasks, a research contract proposal was submitted to the IAEA particularly concerning the treatment of liquid wastes prior to conditioning.

Problems in the treatment of liquid waste have been highlighted in the Philippines especially those containing ^{14}C , tritium and radioiodine. The project aims to conduct studies of options for a cost-effective treatment of radioactive wastes containing radioiodine, ^{14}C and tritium; to identify simple low cost processes required for reliable liquid waste treatment operations; to review current waste treatment technologies for possible adoption under local conditions using indigenous materials and to provide inputs in the design and construction of a radioactive waste treatment facility appropriate for the type and volume of wastes generated from nuclear applications.

Initially, treatment methodologies for liquid wastes containing radioiodine, ^{14}C and tritium were considered. With the commissioning of the chemical precipitation plant as part of an IAEA assisted Technical Cooperation project on the establishment of a waste management facility in the country and following the recommendations of the second Research Coordination Meeting in Istanbul, the project objectives were expanded to include the management of wastes contaminated with ^{137}Cs .

2. METHODOLOGY

2.1. ^{131}I , ^{14}C and ^3H - BEARING WASTES

An extensive literature study on current treatment technologies for radioactive liquid wastes containing radioiodine, tritium and ^{14}C was undertaken to identify those which can be adopted locally in conjunction with utilization of indigenous materials.

Experimental runs of selected treatment processes were conducted. Radioiodine adsorption using volcanic ash and activated carbon were conducted following the methodology and procedures outlined below.

Activated carbon (commercial grade, powdered) and volcanic ash from Mt. Pinatubo sampled at Porac, Pampanga around 20 km from the site of the volcano were used as adsorbent materials for radioiodine. 50 g (activated carbon) and 60 g of volcanic ash with different mesh size (32 mesh and 60 mesh) were weighed and soaked separately for 5 hours with continuous stirring in a liter of 10% w/w sodium hydroxide solution. The activated carbon and volcanic ash were then filtered off and washed thoroughly with water before drying in an oven at 80-100°C.

A glass column with a length of 34 cm and 1.25 cm in diameter was used in the experimental test runs. The dried pretreated activated carbon/volcanic ash was packed in a glass column with glass wool placed at the bottom and on top of the pretreated activated carbon/volcanic ash.

100 mL of synthetic waste spiked with ^{131}I was poured into the packed column of pretreated activated carbon/volcanic ash and the eluate was controlled at a rate of 10 mL per 10 minutes. One mL samples were taken from each eluate for G-M counting.

Similarly, treatment methods for ^{14}C and tritium were identified. Basically, the waste will be absorbed in sawdust and incinerated, provided however that the radioactive waste does not contain alpha-emitting radionuclides and the activity of other radionuclides is below 1×10^{-10} Bq/mL of waste. The ash which will contain both ^{14}C and ^3H which are long lived, will then be immobilized by cementation for interim storage. Wastes with activity beyond the set limits will be absorbed in sawdust, immobilized by cementation and stored in the interim storage facilities.

A locally fabricated incinerator is currently being installed and is expected to be fully operational in the middle of 1996. It is planned to use incineration for wastes containing ^{14}C and tritium subject to certain conditions.

Experimental runs will be conducted to validate theoretical computations in order to determine the maximum concentration limits for incineration of ^{14}C and ^3H wastes (i.e., 1.37×10^{-7} Bq/kg for combustible ^{14}C wastes and 3.66×10^{-6} Bq/kg for combustible ^3H wastes).

Further experimental runs will also be carried out for other treatment methods for specific radionuclides. It is also planned to chemically precipitate ^{14}C in aqueous waste by carbonate precipitation. The precipitate will then be conditioned by cementation. The supernatant liquid which is expected to be non-radioactive (following complete removal of ^{14}C as carbonate) will be neutralized prior to sewage disposal. The chemical precipitation plant is currently being installed. Cold runs will be conducted prior to the commissioning of the plant scheduled in the middle of this year.

2.2. WASTES CONTAMINATED WITH ^{137}Cs

Chemical precipitation was used in the treatment of low-level aqueous waste. Precipitation was achieved by using the ferric hydroxide process. Finely divided ion exchange material was added in order to maximize the decontamination of specific radionuclides.

The use of nickel hexacyanoferrate as a specific ion exchange material for caesium removal was investigated using the lowest possible concentration which would yield a high decontamination result. A small amount of polyelectrolyte was added to aid in the particle agglomeration of the precipitate so as to produce a floc that will ensure efficient separation. About 100 mL of actual aqueous waste known to contain ^{137}Cs radionuclide with an activity of about 170-180 Bq/mL was used in every experimental test.

Different concentrations of ferric ion in the form of ferric chloride were added at pH2 with vigorous stirring in every experimental test and neutralized to pH7 with either nitric acid or sodium hydroxide solution to determine the optimum concentration needed in the ferric hydroxide precipitation process.

After determining the optimum concentration of ferric ion needed in the solution, different concentrations of potassium ferrocyanide and nickel nitrate mixture at a ratio of 1:1 was added in every test specifically to determine the effective concentration of the mixture needed for the removal of ^{137}Cs radionuclide at a controlled low stirring rate. pH was maintained between 9 and 10 by the addition of small amounts of sodium hydroxide in order to provide good levels of caesium removal. An anionic polyelectrolyte was added at a low stirring rate after pH adjustment to produce a larger floc that will either settle or otherwise be removed by filtration. Experimental runs, at different values of pH in the precipitation of caesium were also conducted between pH 9 and 10.

3. RESULTS AND DISCUSSIONS

3.1. ^{131}I

The following data were obtained from experimental test runs.

EXPERIMENT 1

60 g pretreated volcanic ash (32 mesh)
volume of synthetic waste = 100 mL
initial count of synthetic waste = 22140 cpm
pH7-8

Residence time (minutes)	Eluate volume (mL)	Eluate (counts/min)	Adsorption (%)
10	10	18378	17
20	10	14398	35
30	10	10395	53
40	10	11390	49
50	10	8381	62
60	10	6394	71
70	10	6083	72.5
80	10	6578	70

EXPERIMENT II

60 g pretreated volcanic ash (60 M)
 volume of synthetic waste = 100 mL
 initial count synthetic waste = 20910 cpm
 pH9-12

Residence time (minutes)	Eluate volume (mL)	Eluate (counts/min)	Adsorption (%)
10	10	17029	18.6
20	10	20274	3.0
30	10	17676	15.5
40	10	15537	25.7
50	10	16136	22.8
60	10	16723	20.0
70	10	5968	71.5
80	10	23209	-

EXPERIMENT III

50 g pretreated powdered activated carbon
 volume of synthetic waste = 100 mL
 initial count synthetic waste = 12349 cpm
 pH7-8

Residence time (minutes)	Eluate volume (mL)	Eluate (counts/min)	Adsorption (%)
7200	10	1981	84.0
7210	10	1550	87.4

NOTE: The long residence time of synthetic waste in the pretreated activated carbon was due to the slow rate of penetration of the synthetic waste in the finely powdered pretreated activated carbon. A coarser grain of the activated carbon will be used in the succeeding experiments.

$$\% \text{ adsorption} = \frac{\text{initial counts} - \text{eluate counts}}{\text{initial counts}} \times 100$$

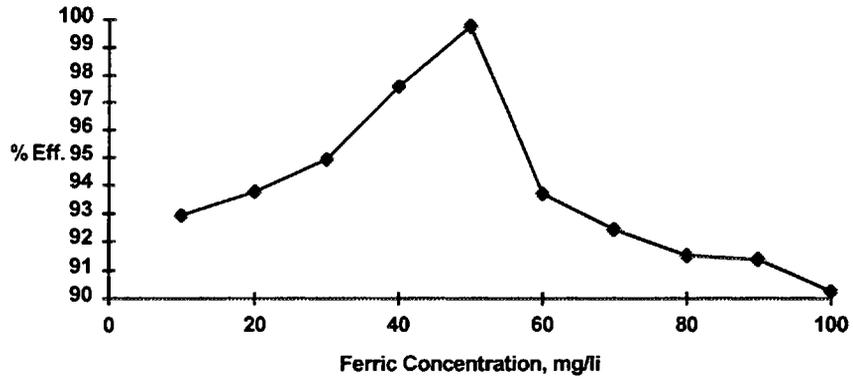


Figure 1
Ferric Concentration vs. Efficiency

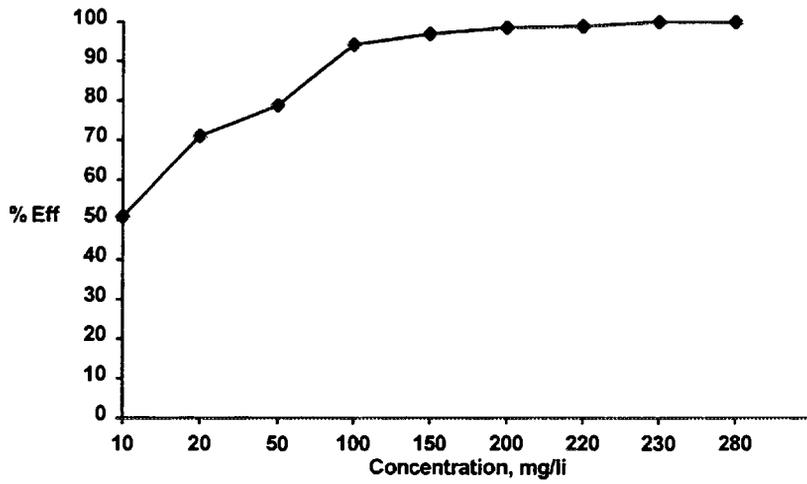


Figure 2
Hexacyanoferrate Concentration vs Efficiency

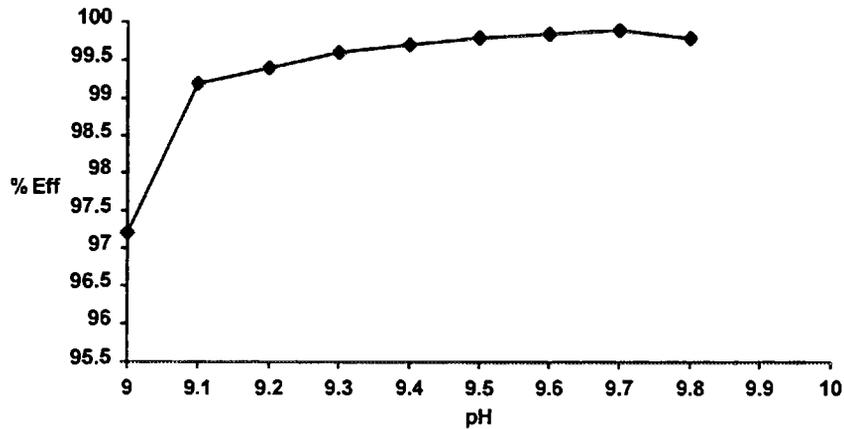


Figure 3
pH vs Efficiency

Results indicate that volcanic ash, which is an indigenous material can also be used to effectively adsorb radioiodine. Initial results showed a 65 - 70 % adsorption for volcanic ash and 80 - 85 % for the normally used activated carbon.

3.2. ^{137}Cs

Results are presented in Figures 1 - 3. As shown in Fig.1, there is indeed an optimum ferric ion concentration (50 mg/L) that promotes maximum precipitation. The degree of precipitation decreases significantly at higher concentrations of the oxidizing agent. There is a marked improvement in precipitation efficiency at hexacyanoferrate concentrations up to 100 mg/L (Fig. 2). Above this value, caesium removal increases only slightly up to a maximum value of 280 mg/L where 100% efficiency is achieved. Fig. 3 shows that a pH range of 9 to 10 does not have a significant effect on efficiency precipitation.

4. CONCLUSIONS

1. Effectively good retention (i.e., 65 - 70%) of radioiodine by volcanic ash has been demonstrated. This adsorptive capability is comparative with the 80 - 85% retention by activated carbon. Considering availability and cost factors, the results are encouraging for the use of the indigenous material in the conditioning of radioactive waste containing iodine.
2. The adsorptive properties for radioiodine of lahar - which has replaced the volcanic ash abounding in the Mt. Pinatubo area - need to be investigated further using the same parameters and conditions of earlier experiments with the original volcanic ash.
3. There exists an optimum concentration of ferric ion (i.e., 50 mg/L) that promotes maximum precipitation of caesium. A precipitation efficiency of 99.78 % was achieved in this case.
4. Precipitation of caesium is enhanced with the addition of nickel hexacyanoferrate. 100 % removal was achieved at a hexacyanoferrate concentration of 280 mg/L.
5. Maintaining pH of the solution between 9 and 10 does not have a significant effect on the efficiency of caesium precipitation.

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