SUITABILITY OF LOCAL CLAYS FOR RADIOACTIVE WASTE DISPOSAL

A THESIS

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the Requirements for the Degree
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DECLARATION

It is hereby declared that:

1. the report presented in this thesis is the result of the original research carried out by the author;
2. this thesis has not been submitted in whatever form to any other institution, organisation or body for the award of any degree;
3. all sources of information have been specifically acknowledged by references.



S. A. Adeleye
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CERTIFICATION

This thesis entitled SUITABILITY OF LOCAL CLAYS FOR RADIOACTIVE WASTE DISPOSAL by SOLOMON AJIBADE ADELEYE meets the regulations governing the award of the degree of Master of Science (Chemical Engineering) of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

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DEDICATION

This thesis is dedicated to the Adeleye family for all they mean to me; to all who await the coming of OUR LORD JESUS CHRIST; and most especially to GOD who is my SOURCE.

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May God satisfy you all with His peace. Amen.

ABSTRACT

Six local clays namely Bomo, Bukuru, Kankara, Manjahota, Onibode and Upkor were studied for use as wasteform for fixation of strontium ion in radioactive wastes. The clays were characterized with respect to cation exchange capacity, organic carbon content and crystal structure. Then the most relevant properties of c]ay wasteforms: shrinkage, density and porosity were studied for Bomo clay and finally, the prepared wasteforms were tested for leaching characteristics.

Bomo clay had the highest cation exchange capacity (CEC) of 44.45 and 50.50 meq/l00g for raw and beneficiated respec-tively. It was followed by Bukuru clay. The other clays had rather low CEC values of between 26.1 and 15.32 meq/l00g lor both raw and beneficiated. Bomo clay contained quartz, illite and montmorillonite with some muscovite in the raw sample. While Bukuru clay contained predominantly quartz and disordered kaolinite. The other clays contained predominantly kaolinite, illite and quartz minerals. Bomo clay had the best characteristics for fixation and disposal of radionuclides.

The shrinkages of the wasteforms were generally higher for the beneficiated than for the raw samples. The bulk density ranged between 1.80 x $10^3$and 1.94 x 10^3 kg/m^3 and apparent porosity ranged between 17.2 - 24.2%.

For low strontium concentration of 1587.5 ug/g the mass fixed in clay mineral varied between 63.0 - 70.9 percent of the initial mass used for equilibration while 30.0-41.3 was obtained

for high concentration of 7875 ug/g. The highest percentage cation loading obtained were 50 and 73 of the total CEC of Bomo clay for low and high concentrations. Bomo clay gave promising result of over 99% retention of fixed strontium after 25 days of leaching. The cummulative mass leached for 25 days ranged between 9.0 ug/g for BL1 and 3.5 ug/g for sample BL3 for the low concentration and 20.0 ug/g for sample BH1 and 2.0 ug/g for sample BH3 for high concentration. For beneficiated sample, the mass leached decreased sharply as temperature increased from 800-1000 C. The most fixation was obtained by beneficiating the clay and firing to 1000 C for both low and high concentrations. However, considerable fixation was obtained by using a raw clay even at 800 C. The leach rate approximately obeyed the natural decay law: $R = R \quad e$ The distribution coefficient, a , generally increased with increase in temperature. The values ranged between 1632 for sample BL1 and 4516 for sample BL3 for low concentration and 2566 for sample BH1 and 20478 for sample BH3 for high concentration.

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CHAPTER ONE

INTRODUCTION

The nuclear industry has been established for over four decades and its continuous operation generates large amount of radioactive wastes. These wastes emit radiation which are known to cause clinically detectable effects in individuals and whose exposure to large populations are presumed to increase the incidence of both somatic, for example cancer, and genetic effects. They are therefore,biologically toxic and dangerous to man. Hence the radioactive wastes must be isolated from the environment. Radiation is greatly feared because it cannot be detected with ordinary human senses.

Radioactive wastes are generated from facilities in the nuclear fuel cycle and the application of radionuclides in medicine, research, industry and other fields. The nuclear fuel cycle includes nuclear power station, fuel fabrication plants, nuclear fuel enrichment processes, fuel reprocessing and decommissioning of nuclear installations. In Nigeria the waste generated are presently minimal; the main sources are two research centres, hospitals and industries. But the waste disposal problem will increase with the possible acquisition of nuclear fuel cycle technology. There is also the possibility of the discovery of radioactive waste dumps in the country, making it necessary to develop capability to condition and dispose the wastes.

Nuclear wastes can be classified by their form as solid, liquid and gas or by radiation level i.e. low, intermediate and high level wastes. In current disposal practice, low level wastes are released directly into the environment after certification. All other wastes are prepared for ultimate disposal in two main

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ways: they may be converted into a suitable solid form and liquid wastes may be stored in underground tanks. These methods are inadequate because leaching from the solid forms and leakage from the underground storage tanks are potential hazards. This has generated much interest in safer methods of disposal such as the fixation in non-leacheable ceramic waste forms, clays (Lee, Kim et al.1969, Spitsyn et al.1958, Saidl 1962, Nishuta et al.1956, Mistry et al.1965, Mitchell 1963, Sobolev et al.1968, Hatch 1952, 1953, Ginell et al.1954), glasses (Brodsky 1966, IAEA 1983), Zeolites (Dyer et al.1985, Kormaneni 1985) and other ceramics. In developing country like Nigeria, the use of clays is particularly attractive because it is inexpensive and widely available (Ahmed and Onaji 1987). However, the results available in literature on foreign clays cannot be directly applied in Nigeria because of the well known variability of the characteristics of the clays with locality. There is therefore, need to study the suitability of the local clays for waste management and this is the primary purpose of this study.

Liquid wastes are of interest in this work and the nuclides of main concern in such wastes are ^{90}Sr, ^{137}Cs, ^{106}Ru, and actinides. Fixation of strontium has been chosen for study because of the long half-life (30 years) of the nuclide and its tendency of biological accumulation and concentration from dilute solutions. In this study, several Nigerian clays are characterized mainly with respect to cation exchange capacity and crystal structure. This enabled the selection of one of the clays for study of fixation of strontium and its leaching from calcined waste forms.

CHAPTER TWO

LITERATURE REVIEW

In this chapter the hazards, classification and management of radioactive wastes, are first reviewed. Then the use of local minerals in the treatment of the wastes is described. Finally, the properties, classification and structure of clay minerals and the important properties of calcined waste forms are discussed.

2.1 Hazard of Radioactive Wastes

A radioactive waste is any material that contains or is contaminated with radioactive isotopes (radionuclides) at concentration or radioactivity level greater than the "exempt quantities" established by competent authorities and for which no use is foreseen. Radioactive wastes are hazardous because of the radiation they emit. They may emit three types of radiation namely alpha, beta, and gamma. These are ionizing radiation unlike other forms of radiation such as visible, infrared, ultraviolet light and radio waves which are non-ionizing. Ionizing radiations have the greatest effects on living and non-living things. The biological effects of these radiations are brought about through chemical changes in the cells caused by ionization, excitations, dissociations and atom displacements. The effect of such radiation in living tissues can disrupt normal biological processes. Radiation dosage above 1Sv is known to cause clinically detectable effects such as nausea and vomiting. Although there is no such effects in the individuals exposed up to 0.25Sv,

lower levels of exposure to large populations are presumed to increase the incidence of both somatic, for example cancer, and genetic effects. Because of the lack of unequivocal evidence, it is conservatively assumed that there is no threshold dose below which radiation dose does not induce cancer or genetic effects.

Biologically, not only the amount of radiation is important, but also its type: equal doses of radiation do not necessarily have equal biological effects. The relative biological effect of different ionizing radiation as measured by their quality factors are given in Table 1 (Friedlander et al.1981). The quality factor reflects the effect of

Table 1 Quality Factor for Various Types of Radiation

Radiation	Quality factor
X - and Y - rays	1
Electrons and position	1
Neutron, energy < 10 KeV	3
Neutron, energy > 10 KeV	10
Protons	1 - 10
Alpha particles	1 - 20
Heavy ions	20

different density of ionization along the path of radiation. The ranges of values in the table reflects the energy dependence

of linear energy transfer i.e. energy deposited per unit path length. The heavy ions have the greatest effect and x-rays have the least. The effect of the radiation on living organisms, whether from external radiation, or from ingested or inhaled radioactive material also depends on many other factors: density of ionization, the dosage rate, the localization of the effect and the rate of administration and elimination of the radioactive material. Since different radionuclides emit and yield different combination of radiations, they have varying relative biological effects as quantified by their biological significance (Table 2). The relative biological significance of each radionuclide is based on the yield and the maximum permissible concentration in drinking water. The maximum permissible concentration of ^{90}Sr (3×10^{-7} μCi/ml) is taken as a base for defining relative biological significance factors of each isotope. Thus strontium has attracted great interest as a public health hazard since it is the most biological significant radioactive fission products. Due to the fact that strontium is chemically similar to calcium it tends to deposit and concentrate in the bone tissue. Because of their biological toxicity the amount of radionuclide in the environment and organs of the body are seriously limited. The maximum permissible levels of selected radionuclides above the natural background in inhaled air, ingested liquids and in critical organs of the human body as listed by Friedlander et al.(1981), are given in Table 3.

Table 2 Biological Significance of Significant Non-Volatile Fission Products From Uranium-235 Fission

Isotopes	Radiations	Half life Years	*Relative Biological Significance
^{144}Ce	β , γ	0.8	3×10^{-2}
^{106}Ru	β , γ	1.0	3×10^{-2}
^{155}Eu	β , γ	1.8	1.5×10^{-3}
^{147}Pm	β , γ	2.6	1.5×10^{-3}
^{125}Sb	β , γ	2.7	3×10^{-3}
^{154}Eu	β , γ	16.0	1.5×10^{-2}
^{137}Cs	γ	22.8	1.5×10^{-2}
^{90}Sr	β	30.0	1.0
^{151}Sm	β	90.0	7.5×10^{-4}
^{79}Se	β	6.5×10^{4}	1.0×10^{-3}
^{99}Tc	β , γ	2.1×10^{5}	1.0×10^{-3}
^{93}Zr	β , γ	9.5×10^{5}	3.8×10^{-4}
^{107}Pd	β , γ	4.5×10^{6}	3.0×10^{-2}

* Bases ^{90}Sr in equilibrium with daughter ^{90}Y.

Table 3 Biologically Permissible Levels of Selected Radionuclides Above Natural Background

Nuclide	Occupational Exposure (Restricted Area)		General Public (Unrestricted Area)		
	In Air ($\mu Ci ml^{-1}$)	In Water ($\mu Ci ml^{-1}$)	In Air ($\mu Ci ml^{-1}$)	In Water ($\mu Ci ml^{-1}$)	In Critical Organ (μCi)
$^{3}H(H_2O)$	$5x10^{-6}$	$1x10^{-1}$	$2x10^{-7}$	$3x10^{-3}$	1000
$^{14}C(CO_2)$	$4x10^{-6}$	$2x10^{-2}$	$1x10^{-7}$	$8x10^{-4}$	300 (fat)
^{24}Na	$1x10^{-6}$	$6x10^{-3}$	$4x10^{-8}$	$2x10^{-4}$	7.1 (G.I. tract)
^{32}P	$7x10^{-8}$	$5x10^{-4}$	$2x10^{-9}$	$2x10^{-5}$	6.0 (bone)
^{35}S	$3x10^{-7}$	$2x10^{-3}$	$9x10^{-9}$	$6x10^{-5}$	90.0 (testes)
^{60}Co	$3x10^{-7}$	$1x10^{-5}$	$3x10^{-11}$	$3x10^{-7}$	10.0 (G.I. tract)
^{90}Sr	$1x10^{-9}$	$1x10^{-5}$	$3x10^{-11}$	$3x10^{-7}$	2.0 (bone
^{131}I	$9x10^{-9}$	$6x10^{-5}$	$1x10^{-10}$	$3x10^{-7}$	0.7 (thyroid
^{137}Cs	$6x10^{-8}$	$4x10^{-4}$	$2x10^{-9}$	$2x10^{-5}$	30 (whole body)
^{210}Po	$5x10^{-10}$	$2x10^{-5}$	$2x10^{-11}$	$7x10^{-7}$	0.03(spleen)
^{226}Ra	$3x10^{-11}$	$4x10^{-7}$	$3x10^{-12}$	$3x10^{8}$	0.1 (bone)
^{238}U	$7x10^{-11}$	$1x10^{-3}$	$3x10^{-12}$	$4x10^{-5}$	0.005
^{239}Pu	$2x10^{-12}$	$1x10^{-4}$	$6x10^{-14}$	$5x10^{-6}$	0.04(bone)

2.2 Classification of Radioactive Wastes

There are many bases for the classification of radioactive wastes but perhaps the simplest is to classify them by their physical states i.e. gases, liquids and solids. Other classifications could be based upon specific activity, type of reaction producing the radionuclides, chemical, physical, radiological and biological properties, types of radiation and the half life of individual radionuclides as well as sources of wastes. Each classification system is related to the disposal methods adopted.

2.2.1 Classification based on forms

Gaseous waste can be subdivided into several major categories: pure gases or vapours, combination of gases and solids, combination of gases and liquids and combination of gases, liquids and solids. The last three are usually considered gaseous waste because the gas is the carrier for the solid or liquid phase. Typical pure gases which might exist from routine operation are tritium and radon from tailing piles. The second category of gaseous waste is a gas containing solid particles. The solid or particulate matter in gas must be of such size that effluent gas can carry these particles into the atmosphere. An example of such gaseous waste is the effluent from chopping and milling operations. These solid particles are easily airborne in the atmosphere and when ingested by human beings can cause respiratory ailments, or if toxic, have more serious effects.

The third category is a combination of gases or liquids. The liquids are in small droplets and are carried by effluent gas stream to adjacent areas. Large quantities of water vapour, organic liquids etc, and small amounts of UF_6, HF, etc entrained in air are examples of this type of gaseous effluent.

Liquid wastes may contain gases or solid particles. Gases usually are separated and may be treated as gaseous waste. Solids may be separated by filtration or centrifugation. A pure liquid waste should be classified as aqueous and non-aqueous. Aqueous wastes are those containing high percentage of water with small amounts of dissolved inorganic or organic materials. Liquid wastes could be further classified as combustible and non-combustible.

2.2.2 Classification based on specific activity

Based on specific activities, radioactive wastes are classified as high, intermediate and low-level wastes. The specific activities defining the various levels of activity are often different in various countries and even different in various establishment of the same country; for example, high level in a research establishment may correspond to intermediate or even low-level in a reprocessing plant. A typical classification of liquid wastes based on specific activity is presented in Table 4 (IAEA 1984). There are three subdivisions of the low level wastes.

Table 4 Classification of Liquid Wastes

Category		Activity	Remarks
	1	< 37 KBq	No treatment required; released after measuring.
Low-level waste (LLW)	2	37 KBq to 37MBq	Treated, no shielding required.
	3	37 MBq to 3.7GBq	Treated, shielding sometimes required according to radionuclide composition.
Intermediate-level waste(ILW)	4	3.7GBq to 370TBq	Treated, shielding necessary in all cases
High-level waste (HLW)	5	> 370TBq	Treated; shielding necessary in all cases.

a Concentration of alpha activity is negligible.
$K = 10^3$, $M = 10^6$, $G = 10^9$, $T = 10^{12}$

2.2.3 Sundry Classification

On the basis of waste packaging, shipping, and possible disposal requirements, fuel cycle wastes can be grouped into four principal categories: spent fuel, transuranic wastes, non-transuranic wastes and ore tailings. The volume, radioactivity levels, thermal powers, and estimated number of shipments to possible disposal sites of the various waste categories are given in Table 5 based on the production of 1000 MW/year of electricity, after Kirk-Othmer (1981).

Classification based on chemical properties takes into account the pH, principal anions and cations, combustible and non-combustible, and ash content as well state of radionuclides

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Table 5 Fuel Cycle Wastes From the Production of 1000 MW.yr of Electricity

Category of Waste	Volume m^3	Activity GBq	Power KW	Number of shipments	Possible disposition
spent fuel	14	6.36×10^9	970	11	Surface storage or geological disposal
transuranic (TRU) Wastes					
high level solidified	3.1	6.29×10^7	960	2	geologic disposal
cladding hulls	2.7	7.4×10^5	10	2	geologic disposal
intermediate level	140/	4.4×10^6	0.057	66	geologic disposal
low level	480/	1.9×10^6	0.04	17	geologic disposal
non-TRU wastes					
noble gases	0.1	9.3×10^6	0.37	0.4	near surface storage
iodine	0.05	37		0.2	geologic or ocean disposal
carbon-14		7.10			geologic or ocean disposal
LWR tritium	140	2×10^4		9	deep wells
fission-product (FP)					
tritium	0.35	7×10^5	7×10^{-4}	1	near surface storage
low level	2,400/	7×10^4	0.007	180	burial grounds
ore tailings	42,000	1.9×10^4	0.011		surface storage

(Tables 6 and 7). A classification system based on physical properties considers type for example, paper and metal, bulk density and compressibility.

On the basis of the type of radiation: alpha, beta, and gamma, and half lives of radionuclides, wastes can also be grouped into other categories. The broad categories are the non-alpha and alpha bearing nulides (Table 7). First, there are relatively short half life isotopes for example ^{144}Ce and ^{106}Ru of 0.8 and 1 year half life respectively. These are extremely hazardous during the first 5 years but virtually harmless after 50 years. On the other hand are isotopes having intermediate half lives for example ^{137}Cs, and ^{90}Sr of 28.8 and 30 half life years respectively. These isotopes represent by far the greatest hazard after 50 years. While the third group are of the very long-lived isotopes for example ^{79}Se having 65,000 half life years (Table 2).

The last classification system is based on the sources of waste. Radioactive wastes generated in all nuclear operations, ranging from ore production to disposal of wastes and other applications of radioisotopes are discussed in the subsequent section.

Table 6 Characteristics Of The Principal Types Of Concentrate

Characteristic	Source	Nuclear power plants	Solvent washing at reprocessing facilities	Nuclear research centres
Physical:				
Nature		Concentrated solution with suspended solids		
Density (kg/m^3)		1.1 1.3	1.2	1.1 - 1.3
Dry solids content (wt %)		10 30	15	5 - 30
Chemical:				
pH		6 - 12	> 12	3 - 10
Principal cations		Lithium, sodium	Sodium	Sodium, calcium
Principal anions		borate, sulphate phosphate	Carbonate nitrate	sulphate, nitrate, phosphate, citrate
Radioactivity:				
Nuclides		Activation products, fission products	Fission products, transuranics	Activation products, fission products
Specific activity (Ci/m^3)		1 - 10	100 - 1000	1 - 20

Table 7 Characteristics of Typical Solid Wastes

	Combustible		Non-combustible	
Characteristic waste category	non-alpha	Alpha-bearing	Non-alpha	Alpha-bearin
Main sources	Nuclear power plants nuclear research centres, medical institutions	Fuel reprocess-ing plants, nuclear research centres	Nuclear power plants, nuclear research centres	Fuel reproce ing plants, nucl research cen
Physical:				
Type	Paper, cloth, and polymeric materials	Paper, cloth, and polymeric materi-als	Metal, glass, masonry, polymeric materials	Metal, glass masonry, polymeric materials
Bulk density (kg/m^3)	100 - 400	100 - 400	200 - 3000	200 - 3000
Compressibility (%)	50 - 85	50 - 85	0 - 60	0 - 60
Chemical:				
Ash content: (wt %)	2 - 15	2 - 15		
(vol%)	2 - 15	2 - 15		
Radioactivity:				
Nuclides	Activation products, fission products	Fission products transuranics	Activation products, fission products	Fission products, transuranics
Specific activity				
$\beta - \gamma$ (Ci/m^3)	0 - 0.5	0 - 0.1	0.0.1	0 - 0.1
α (Ci/m^3)	0 - 0.01	0 - 5	0.0.01	0 - 100

2.3 Sources of Wastes

Radioactive wastes are generated mainly from the nuclear fuel cycle of the nuclear reactor technology ranging from ore production to the disposal of radioactive wastes. A schematic diagram of a typical (light-water-reactor) nuclear fuel cycle is given in Fig. 1.

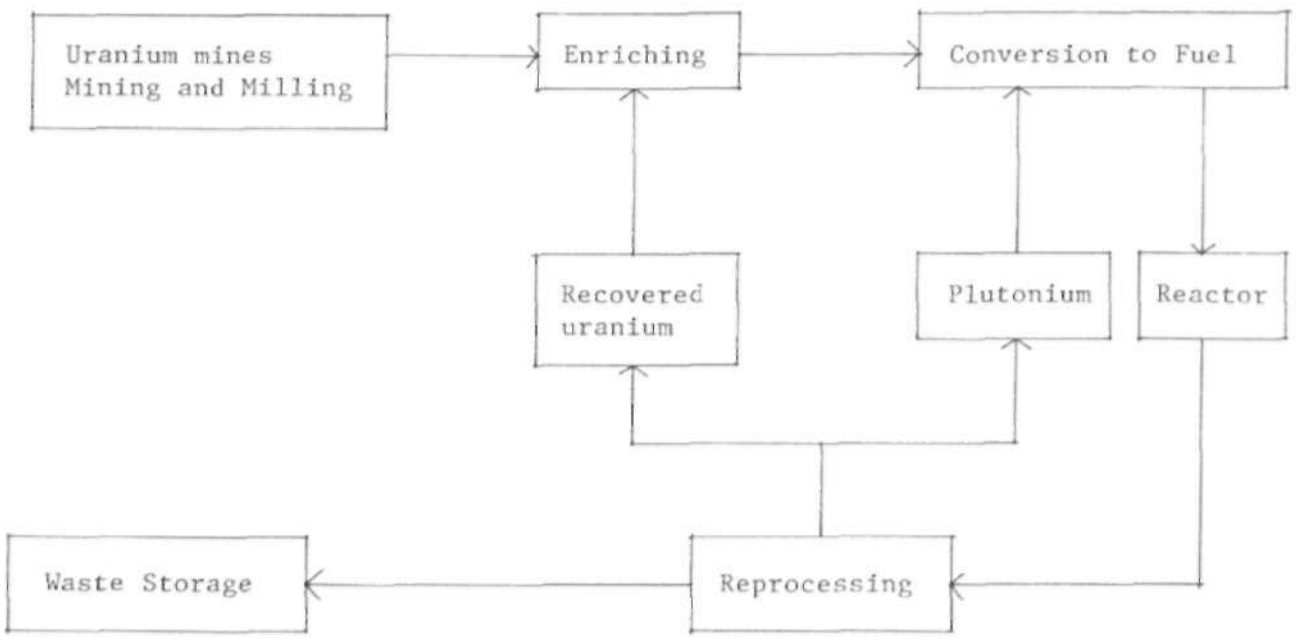


Fig. 1 Nuclear Fuel Cycle

The activities in the cycle include mining, milling, conversion, enrichment, fuel fabrication, reprocessing and waste disposal. They are also generated in other operations involving the application of radioisotopes such as research, medicine, remote

power sources etc.

2.3.1 Uranium mining and milling

Natural uranium containing about 0.71% of ^{235}U is obtained by mining both sub surface and open pit mines. The mined uranium ore is crushed and ground by wet method. These operations give rise to liquid wastes depending on the type of mines or extraction operation. These liquid arisings contain very small amount of the natural alpha activity from uranium in the ore.

A uranium mill extracts uranium from the ore. Milling present a greater problem since the uranium is separated from extraneous material to produce concentrate of about 85% U_3O_8 (yellow cake) which is the feed material for production of uranium hexaflouride. The process involves dissolution in acid, chemical extraction, settling, etc which produce liquid arisings contaminated with both chemicals and alpha activity with specific activity up to 370KBq/m^3. Large amount of solid waste tailings remain following the removal of the uranium from the ore. These "tailings piles" have a radiological impact on the environment through air pathway by continuous discharge of ^{222}Ra gas.

Liquid and solid wastes from milling operation will contain low-level concentrations of radioactive materials. Airbone radioactive releases include radon gas and particles of the ore and product of uranium oxide.

2.3.2 Uranium conversion to uranium hexafluoride

Uranium concentrate milled from the ore must be converted to volatile uranium hexafluoride in order to be enriched by the gaseous diffusion process. Two industrial processes are used for producing UF_6. The "hydrofluor process" consists of reduction, hydrofluorination and fluorination of the ore concentrates to produce crude UF_6 followed by fractional distillation to obtain a pure product. The wet solvent extraction process employs a wet chemical solvent extraction step at the head of the process to prepare high purity uranium feed prior to reduction, hydrofluorination and fluorination steps. Each method is used to produce roughly equal quantities of uranium hexafluoride feed for the enrichment plants.

Because no irradiated material is handled by conversion facilities, all radionuclides present occur in nature. They are radium, thorium, uranium and their respective decay products. Uranium may appear in gaseous effluent in several chemical forms. Possible chemical species are U_3O_8, UO_2, UF_4, UF_6 $(NH_4)_2$ U_2O_7, UO_2F_2. Thus uranium may be released as both soluble and insoluble aerosols. Liquid wastes from processes contain about 0.03% of the material processed.

2.3.3 Uranium enrichment

Natural uranium contains 0.7% of fissionable ^{235}U. Lightwater nuclear power reactors, however, utilize uranium that is enriched in ^{235}U to the range of 2-4%. This can be done in several ways, but the major processes in use today

are diffusion through a barrier or centrifugation. Such plants are usually large complexes containing many operations (analytical laboratories, decontamination etc) in addition to enrichment. The gaseous effluent stream bearing radioactive materials release uranium to the air and river water must probably as UO_2F_2. Unlike the milling and independent uranium conversion facilities, the radionuclides in the liquid wastes include fission products from irradiated uranium recycled through the enrichment process. Effluent data for uranium enrichment plants are minimal. Solid wastes consist of sludge from on site holding ponds. The sludge is collected and buried on site.

2.3.4 Fuel fabrication

Fuel fabrication facilities include a variety of operations including conversion of UF_6 to UO_2, sintering and finishing fuel pellets, tubing preparation and final assembly. The wastes generated contain large amount of chemicals for example nitrates, fluorides etc used in the UO_2 production and cladding treatment. The specific activities can be as high as 740KBq/m^3.

2.3.5 Nuclear power plants

Depending on the different types of reactors now operating commercially all over the world - light water reactors, heavy water reactors and gas cooled reactors - different waste streams arise. These streams are different both in

activity content and amount of liquid generated. Water cooled and moderate reactors generate more liquid waste than gas cooled plants. In all cases liquid waste will arise from decontamination operations.

Light water reactors: There are two types of light water reactors: pressurized water reactor (in direct) and boiling water reactor (direct). A light water cooled nuclear power station operates on the same principle as a conventional fossil -fueled (oil or coal) power station except that the heat generation is by nuclear fission rather than combustion. The heat liberated in either process is used to convert water into steam which is subsequently used for power generation. A schematic diagram of a typical light water reactor is shown in Fig. 2.

Nuclear power reactors generate radioactive materials as a consequence of the fissioning of uranium and by neutron absorption in the coolant and in structural materials which leads to radioactivity in these components. The important radionuclide produced by uranium fission are isotopes of noble gases krypton and xenon, the alkali metal cesium and rubidium, the alkaline earth barium and strontium and the halogens iodine and bromine. The coolant activation products are generally gases such as ^{41}Ar, ^{18}F, ^{13}N, ^{16}N, and $^{19}0$ which have short half lives in the range of several seconds to a few hours. The induced activities in the structural materials may have considerably long half lives and comprise a much wider range of elements including zirconium, manganese, nickel, iron, carbon, chromium, cobalt and copper. These radionuclides

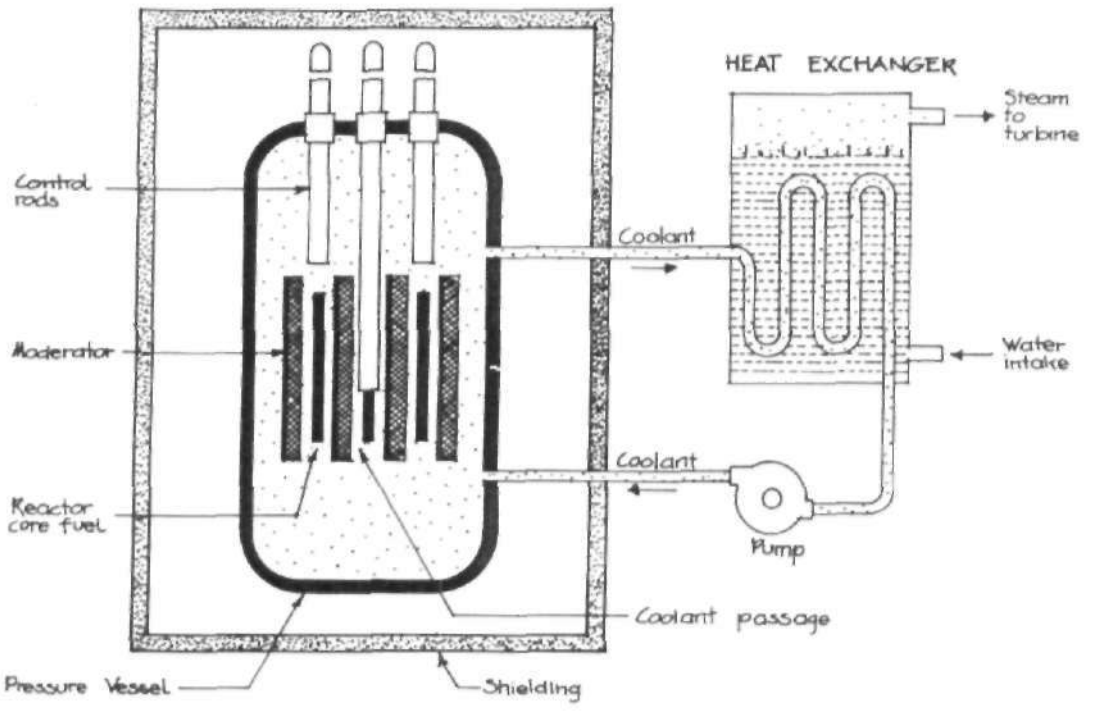


FIG. 2 ... Power Reactor.

usually remain fixed in the structural material but can enter the coolant as a consequence of corrosion and erosion in the pumps and other moving components. The volume and activity of low level radioactive waste generated in United States from commercial power reactors (Table 8) can be considered as a typical model. The total solid wastes generated was 35,563m^3/a in volume and 404,554 Ci/a (1.5MBq/a) specific activity for the commerical power reactor.

Heavy water reactors: Heavy water moderated reactors generate normally a low amount of liquid waste streams. Liquid wastes arise from the clean up system of the moderator circuit (high tritium values, the primary cooling circuit sump water and the different drains). Clean up system of this reactor works mainly with once-through ion exchange techniques, virtually no liquid concentrates are generated.

Gas cooled reactors: Gas cooled reactor produces only few liquid wastes in comparison to the other reactor types. The liquid wastes generated are from fuel cooling pond water and laundry drain and decontamination processes are in significant volume. However gas-circuit dryers generate relatively low volume. As oil is used as a lubricant and sealing material at some reactor sites, contaminated oil become liquid radioactive effluent. This problem arises especially at gas cooled reactors. Dougall and Newell (1970) reported that about 115m^3 radioactive oil was generated with an activity content of about 148 GBq tritium and 5.5GBq other radionuclides in one year.

Table 8 Low-level Radioactive Waste Generated in the United States of America

Commercial Power reactor wastes

Waste form	m^3/a	Ci/a	Typical radionuclides
Spent resins, filter sludges	17116	41316	^{51}Cr, ^{54}Mn, ^{59}Fe ^{58}Co, ^{60}Co, ^{65}Zn
Dry compressible waste and contaminated equipment	16653	2723	
Irradiated components	1794	360515	^{134}Cs, ^{137}Cs, ^{140}Ba ^{144}Ce
Total	35563	404554	

Institutional wastes (medical facilities and universities)

Waste form	m^3/a	Ci/a	Typical radionuclides and % total	
Biological	1803	209	^{3}H	29.1
Scintillation vials	9223	1081	^{14}C	8.9
Solidified and absorbed	1461	171	^{32}P	5.3
liquids			^{35}S	2.0
Dry trash	8761	1026	^{51}Cr	1.6
Total	21248	2487	^{57}Ga	0.1
			^{99}Tc	30.9
			^{126}I	3.5
			^{131}I	5.9

Industrial Wastes

Total	20397	473579	Misc.	12.7

2.3.6 Fuel reprocessing

This is the separation of reusuable fission material from unwanted fission products. Essentially all the radioactivity leaving a nuclear power reactor is transferred to the fuel reprocessing plant. In general reprocessing consists of dismantling reactor fuel in a manner that permits dissolution of the core material without dissolving the corrosion-resistant cladding. The resulting solution is subsequently treated by several cycles of solvent extraction or ion-exchange to recover, separate and purify the residual uranium and plutonium.

Normally reprocessing operations are carried out according to chemical Purex process. Basically, this process consists of dissolving the irradiated fuel in nitric acid and separating and purifying uranium and plutonium from the fission products using the solvent extraction technqiue (with diluted tri-butyl phosphate (TBP) in dodecane). Besides high-level wastes, large amounts of intermediate-level liquid wastes are generated in each step of the fuel-reprocessing operations from initial receipt of the fuel and storage in ponds until Pu - and U - extractions and purifications. The characteristics and amounts of such wastes are very variable according to the type of fuel reprocessed (Light water reactor, Gas cooled reactor, etc). Nevertheless, as a common feature, some typical waste streams are inevitably produced such as: cooling pond liquid wastes, decladding wastes, off-gas scrubber solutions, solvent wash alkaline wastes, second and third uranium and plutonium cycle wastes, oxalic liquor from Pu conversion, and plant decontamintion solutions.

The reprocessing of spent nuclear fuel generates large quantities of more radiotoxic material than all other operations of nuclear power cycle or nuclear industry in general.

2.3.7 Decommissioning

The type of wastes that are produced from decommissioning nuclear facilities is difficult to assess because of the uncertainties that exist in, for example, the status of the plants when the decision is made to decommission them, the level to which they must be decontaminated, and the provisions that may have been made in the design of the facilities to facilitate their eventual decommissioning. Decommissioning of a nuclear facility when it is no longer required will generate hazardous waste. This includes all materials in the reactor, equipment parts of the plant and miscellaneous contaminated small tools.

2.3.8 Nuclear research establishments, medicine and industry

The research establishments include universities, colleges and isotope laboratories. A great variety of effluents arise at such institutions depending on their activities. These include wastes from research reactors, radioactive-chemical laboratories, decontamination facilities, hot cells and pilot plant.

The liquid wastes generated in medicine, research and industry vary extensively in both chemical and radionuclide content. Each nuclear application produces a primary type of liquid waste depending on the particular operation being

conducted. The use of radionuclide in medicine, industry and university combined with those in nuclear research institution results in comparatively large volume of low-level wastes. The most common of these wastes are solid including contaminated equipment, tank, pipes, heat exchangers and pumps; protective clothing, gloves and paper; nuclear reactor equipment and residue or scrap from chemical or metallurgical operations. Other are contaminated concrete or asphalt blocks; precipitates, sludges or ion-exchange resins containing radioactive materials and filter from ventilation exhaust systems. IAEA (1984) provide evidence that the volume of liquid waste are large, the activity level do not normally exceed 10MBq/m^3 beta/gamma activity, although in special cases very small volume may exceed this value. The volumes and specific activities of liquid wastes of nuclear research establishments in different countries are presented in Table 9. The ranges of specific activity of low and intermediate level wastes were $4 \times 10^3 - 6.7 \times 10^9$ and $2 \times 10^6 - 3.5 \times 10^{12}$ Bq/m^3 respectively while the total average specific activity of all wastes produced in the Centre ranged between $10^3 - 3.4 \times 10^{10}$ Bq/m^3. The volume of wastes generated ranged from $34 - 8 \times 10^4$ m^3/a for low-level and $0.2 - 2.5 \times 10^4$ m^3/a for intermediate. The total volume of liquid wastes generated in research establishments ranged between $35 - 10^6$ m^3/a. The research establishments in Seibersdorf, Austria generated the least quantity of intermediate level while Hungary generated the least for low-level wastes. Hungary generated the least volume of wastes while united states generated the largest.

Table 9 Liquid Wastes of Nuclear Research Establishments

Country	Centre	Year	Low-level waste (Categories 2 & 3) Volume (m^3/a)	Low-level waste (Categories 2 & 3) Average specific activity (Bq/m^3)	Intermediate-level waste (Category 4) Volume (m^3/a)	Intermediate-level waste (Category 4) Average specific activity (Bq/m^3)	Total (Categories 1 - 4) Volume (m^3/a)	Total (Categories 1 - 4) Average specific activity (Bq/m^3)
Austria	Seibersdorf	1981	$3.8x10^3$	10^5	0.2	10^8	$5x10^4$	$1.5x10^4$
Belgium	Mol	1980	$8x10^4$	$<10^8$	$1.5x10^4$	10^8-10^{10}	$1.7x10^5$	10^8
Canada	Chalk River	1981	$3x10^3$	10^7	$2.5x10^4$	$2x10^6$	10^6	10^4
Canada	Whiteshell	1981	$4.5x10^3$	$2x10^7$	10-15	$3x10^{11}$	n.a	n.a
CSSR	Rez	1981	n.a	n.a	-	-	10^3	$3x10^4$
Denmark	Risø	1979	n.a	n.a	-	-	$3x10^3$	10^5-10^8
Finland	Espoo	1981	40	10^6	-	-	-	-
France	Cadarache	1982	$2.5x10^3$	$3.7x10^9$	n.a	n.a	n.a	n.a
France	F.A.R.	1982	$3x10^2$	$3.7x10^9$	5	$3.7x10^{11}$	n.a	n.a
France	Saclay	1982	$3x10^3$	$6x10^9$	$7x10^2$	$1.5x10^{11}$	3700	$3.4x10^{10}$
German Dem.Rep.	Rossendorf	1980	$6.5x10^2$	10^5	60	10^9 -10^{10}	$6.5x10^3$	$1.9x10^7$
Germany,Fed.Rep.	Karlsruhe	1980	$6.1x10^3$	$6.7x10^9$	270	$3.5x10^{12}$	n.a	n.a
Germany,Fed.Rep.	Jülich	1981	$4.6x10^3$	$4.6x10^7$	1.6	$4x10^{10}$	$3.65x10^5$	10^3
Hungary	All res. establish-ments	1982	34	$<3.7x10^9$	1		35	$4x10^5$ $4x10^7$
India	Trombay	1969	n.a	n.a	n.a	n.a	$1.5x10^5$	$6x10^5$
Italy	Ispra	1980	n.a	n.a	-	-	$2.5x10^3$	10^4x10^8
Italy	Casaccia	1979	n.a	n.a	-	-	$2.5x10^2$	10^4-10^8

Table 9 (Cont'd)

Country	Centre	Year	Low-level waste (Categories 2 & 3) Volume (m^3/a)	Low-level waste (Categories 2 & 3) Average specific activity (Bq/m^3)	Intermediate-level waste (Category 4) Volume (m^3/a)	Intermediate-level waste (Category 4) Average specific activity (Bq/m^3)	Total (Categories 1 - 4) Volume (m^3/a)	Total (Categories 1 - 4) Average specific activity (Bq/m^3)
Japan	Tokai	1969	906	8.5×10^6	422	5.4×10^8	n.a	n.a
Netherlands	Petten	1980	3.7×10^3	10^4-10^6	150	10^6	5×10^3	2×10^6
Norway	Kjeller	1981	4×10^2	10^7	-	-	-	-
Poland	Otwock-Swierk	1981	2×10^3	4×10^3-4×10^6	400	4×10^6-4×10^9	1.43×10^5	1.9×10^4
Sweden	Studsvik	1980	7×10^3	4×10^6	400	$> 10^8$	1.5×10^5	
Switzerland	Würenlingen	1981	5×10^3	10^4-10^6	0.5	$> 10^6$	2×10^4	1.9×10^6
UK	Harwell	1979	n.a	n.a	n.a	n.a	5.5×10^4	2.6×10^6
USA	BNL	1979	n.a	n.a	10^3	2×10^8	10^6	$<10^4$
USA	ORNL	1979	n.a	n.a	n.a	n.a	5×10^5	1.1×10^6
USSR	Moscow, "Radon"	1981	2×10^3	2×10^9	-	-	2.5×10^5	10^3
Yugoslavia	"Josef Stefan" Ljubliana	1981	-	-	-	-	10^5	4×10^4

Regarding organic liquids waste it is rare that their quantities are reported. But, the volume of scintillation counting liquids is surely the most significant part of this special wastes.

The use of radionuclide in medicine, industry, and University combined with those in research institutions results in a comparatively large volume of low-level solid waste and an accompanying small volume of intermediate waste (Table 8). An estimate of the amount of low-level solid waste produced at a research Centre is between 0.25 and 0.5m^3 annually per employee (IAEA 1970). The total solid waste generated was 20397 m^3/a in volume and 473 579 Ci/a (1.75MBq/a) for the institutional wastes.

The medical profession is rapidly developing diagnostic and therapeutic uses for both reactor-produced and cyclotron-produced radioisotopes. These uses will produce relatively small quantities of radioactive wastes. Radioisotopes are widely used in hospitals (Table 10). Liquid wastes generated are related to the kind of radiotherapeutic and diagnostic nuclear medicine techniques practiced; for example iodine waste is generated in diagnosis and treatment of thyreotoxics (Grave disease) (Choppin et al 1983, IAEA 1982).

Table 10 Uses of Some Radioisotopes in Hospital

Isotopes	Halflife	Main Uses	Amount μCi
^{131}I	8.04 dy	Diagnosis and Treatment	1 - 50
^{24}Na	15 hr	Human diagnostic tracer	1 - 1000
^{22}Na	2.58 yr	Human diagnostic tracer	1
^{32}P	14.2 dy	Treatment of blood disorder diagnosis	5000 - 10,000
^{80}Br	1.5 yr	"	10
^{82}Br	36 hr	"	10
^{137}Cs	30 yr	Sealed sources (Radiotherapy and Radiography)	10^3 - 10^6
^{132}I	2.26 hr.	Diagnosis and treatment of	
		(a) hyperthyrodism	50 - 10,000
		(b) thyroid carcinoma	10^5 - $1.5x10^5$
^{198}Au	2.7 dy	Therapy as colloid mental	1.5×10^5 per dose

hr. = hour, dy = days, Yr = years

2.4 Radioactive Waste Management

From the very beginning, the primary consideration in nuclear waste management and disposal options has been effective protection of the public and biosphere, for both the present and the future, from the radioactivity of waste materials. Wastes are characterized according to their different properties and sources in order to give safe handling and correct treatment. IAEA (1983) reported that one of the essential aims in the waste management is to reduce, as much as possible, the waste volumes to be stored or disposed of, and to concentrate and immobilize as much as possible the radioactivity contained in the waste. For proper waste management planning and objective conditioning adequate knowledge of the wastes on such as the source, type, form, radionuclide, and treatment and disposal as given in Table 11 is necessary.

The main objective of conditioning is to convert the waste into a form which is chemically and mechanically stable throughout the life time of the hazardous radionuclides it contains. At the same time the conditioned waste product should be sufficiently leach resistant and, the waste forms and their package should preferably be of relatively small volume and space in view of requirements of intermediate storage and final disposal (IAEA 1963, 1982, 1983).

2.4.1 Treatment and disposal of radioactive wastes

Gaseous wastes: gaseous wastes originates from chopping and dissolution operations. The most hazardous volatile

Table 11 Radioactive Waste Management

Source of Waste	Type of Waste radioactivity	Form of waste	Typical isotope	Treatment and disposal
Mining and Milling of Uranium ores	Nuclear activity	Solids	U-238 Radium -226 Thorium -230	Contain and open controlled pit
		Liquid	Radium -226	Treat and dilute
		Airborne	Radon-222	Ventilate and disperse
Uranium fuel Fabrication Plants	Nuclear activity	Solids Liquid	U-235 and 238	Decontaminate and contain concentrate and contain
		Airborne		filter and disperse
Reactor Operation	Activation and fission product activity	Solid	Cobalt-58 and 60 Fe-59, Manganese-59	concentrate and contain
		Liquid	Cerium-144, Cesium-137, Tritium, Strontium -90	Treat and dilute
		Airbone	Argon-41, Sulphur-33, Iodine-131, Xenon-133	Delay and disperse
Fuel reprocessing Plants	Fission product activity and transuranic	Solid	Americium -241, Strontium -90, Cesium-137	Concentrate and contain
		Liquid	Plutonium Cerium-144, Tritium, Zirconium -99	

Table 11 (Cont'd)

Source of Waste	Type of Waste radioactivity	Form of waste	Typical isotope	Treatment and disposal
		Airborne	Iodine -131 and 129 Krypton-85, Tritium	Dilute and disperse or contain
Production Use of Isotopes	Activation product activity and trans-uranic	Solid	Cobalt-60, Strontium 90 Cesium-137, Plutonium	Concentrate and contain
		Liquid	Tritium, carbon-14 Phosphous -34, Cerium-144	Treat and dilut
		Airborne	Iodine - 131	Dilute and disperse or contain

constituents are iodine and ruthenium fission products. The tritium and iodine formed in the reactor primary water are bled out of the primary loop into ventilation exhaust air. Air that leaks in and is purged out of the reactor core graphite gas atmosphere contains Argon-40 and is activated to Argon-41. In current practice the volatile radionuclides are discharged to the stack after scrubbling with sodium hydroxide. The hydroxide scrubbing removes the acidic nitrous oxides which pass through the recombination unit above the dissolver. The ventilation air and gases exhausted from the building pass through high efficiency particulate air filters (HEPA), Silver nitrate impregnated zeolite filters and/or charcoal filters impregnated by potassium iodide before being discharged to atmosphere from very high ventilation stack. For example, with these techniques the retention of iodine in the plant is greater than 99.5%. Ruthenium forms volatile RuO_4 in the dissolver. Almost all RuO_4 is retained in gas purification system. Of the noble gases radioactive xenon has completely decayed after 1 year cooling, but krypton contain ^{85}Kr with 10.7 year half life. Krypton in dry, clean air is effectively trapped on a charcoal filter at cryogenic temperature; however because of explosion risk (reaction between radiolytically formed ozone and carbon), the favoured process is condensation by liquid nitrogen followed by fractional distillation. The krypton is packaged as high pressure gas in steel cylinders. A process is being developed for storing the recovered noble gases in a sodalite-zeolite matrix at normal atmospheric pressure. The processes for separating and concentrating tritium is based on Vol-oxidation that is volatilization

by heating the chopped fuel at 400-600^{o}C, pyrochemical processing, isotopic enrichment and aqueous recycle techniques. The $^{14}CO_2$ is removed from head-end-off-gas streams by scrubbing with calcium hydroxide solution, reaction with barium hydroxide hydrate, sorption on molecular sieves and absorption in fluorocarbons.

Liquid wastes: Low-level liquid radioactive wastes occur most often as slightly contaminated solutions, generally much too voluminous to store. IAEA (1983, 1984) and Choppin et al. (1983) reported that these solutions are treated by distillation or chemical methods to remove the radioisotopes, and these purified liquids are then discharged after legal certification. Each waste stream is examined at its source for both volume and concentration reduction and possible pretreatment prior to combination with other streams. While it is desirable to operate only one treatment facility, it can be more economical to segregate streams, for example alpha - contaminated (Table 7), high salt stream etc requiring different processes. Concentrates from the treatment of alpha-contaminated waste streams may require more expensive conditioning and sometimes special storage and disposal. Thus, waste streams segregation is a necessity. Liquid wastes are normally converted into solid form to reduce the potential for migration or dispersion of radionuclide before disposal. Low-level radioactive wastes are usually discharged to ground water ways or public water ways or public sewerage, after they must have been established to fall within prescribed limit of safety with respect to their activity.

The intermediate level liquid waste results essentially from evaporating various streams from the chemical process, such as solvent clean-up, off-gas scrubbers, product concentration etc. It may contain appreciable amount of solids. The waste is neutralized and is stored in steel tanks at reprocessing site.

Presently there is no single handling and storage that is preferred for high level wastes. However, a number of methods are being proposed and practised. According to IAEA(1983), the practices include disposal by burial in deep wells, caves, old salt mines, the ocean, clay formations and underground tanks (Mantell 1975, Kirk-Othmer 1981). Evaporation is a common and effective method of reducing the volume of radioactive waste. Ion-exchange and co-precipitation can be used to decontaminate radioactive wastes. The generated wastes are treated to remove the radioactivity. Not all methods are, however appropriate for a specific type of source. The categories of wastes likely to be encountered from each of the primary sources and type of treatment which might be appropriate before wastes are immobilized is given in Table 12. The method selected always depends on the efficiency of removal of radioactive contaminants, available equipment, and techno-economic factors. The concentrates produced by the treatment of low and intermediate level waste, albeit of low specific activity compared with high level waste still require control. A matrix - bitumen, cement/concrete, polymer etc is commonly used for immobilizing sludges, evaporator concentrates and miscellaneous solid wastes. In the meantime the liquid waste remaining after decontamination treatment can be safely disposed

Table 12. Waste Treatments Appropriate To Wastes From Specific Sources

Waste Category	Appropriate treatment Prior to immobilisation																								
	Water removal (4.2)					Thermal & Chemical destruction (4.3)					Chemical adjust-ment(4.4)					Mechanical treatment (4.5)					Decontamination (4.6)				
source	A	B	C	D	E	A	B	C	D	E	A	B	C	C	E	A	B	C	D	E	A	B	C	C	E
Concentration:																									
Liquid wastes:																									
Sludges	x	x	x	x	x					x		x	x		x										
Ion-exchange media	x	x		x		x	x		x												x	x			
concentrates	x	x	x	x					x			x	x		x										
Solid wastes:																									
Combustible																									
non-alpha bearing						x	x	x	x	x						x	x	x	x	x					
alpha bearing							x	x	x								x	x	x						
non-combustible																									
non-alpha bearing																x	x	x	x	x		x	x	x	x
alpha bearing																	x	x	x						
Special Wastes:																									
Organic liquid	x	x	x	x		x	x	x	x	x				x											
Decanning residue																	x		x			x		x	
Other irradiated materials																	x		x			x		x	
Decommissioning wastes	x	x	x	x												x	x	x	x		x	x	x	x	
Wastes with Signficant ^{3}H and ^{13}C content	x	x		x					x			x	x								x				

Primary Sources of wastes A Nuclear power plants B-Fuel processing facilities C-Fuel enrichment and fabrication facilities. D Nuclear research Centre E-Other institutional and industrial sources

of into the environment in seas and rivers after it has been certified (IAEA 1970 and Elsden 1984) to have activity in the legal range for disposal.

Fuel processing generates high level liquid radioactive fission products containing 99.9% of radioactivity present in irradiated fuels. High level radioactive wastes have been stored historically in an interim basis as concentrated solutions in underground tanks. In nearly every case, some form of protection have been provided to ensure recovery in the event of tank leakage. This precaution is now a requirement for all interim tank storage, and true double containment will be provided for future interim tank storage (Mantell 1975). Prevention corrosion is very important with interim tank storage of high level radioactive waste solution. Mantell (1975) and Kirk-Othmer (1981) reported failure of fifteen and twenty six carbon steel tanks respectively but no failure of stainless steel have yet occurred. In most of the cases, actual leaks that occurred have been attributed to pitting (localized corrosion), which has often been enhanced by sludges in the bottom of the tanks. In some installations agitators (stirrers) are employed to ensure homogeneity of solution so that localized corrosion and others could be corrected. Gorman (1953), IAEA (1963) and Mantell (1975) described cases where the heat generated from fission products decay were removed by cooling coils. The cooling coils were provided to maintain the temperature of stainless steel tank below $60^{o}C$. According to Gorman (1949, 1953) the storage of these liquid wastes require continuous monitoring due to the presence of long lived radionuclides. IAEA (1963) and Mantell (1975)

indicated the need of maintaining one empty stainless steel tank, so that any liquid leaking from another tank can be immediately transferred from the vault sump around the loading tank into the empty spare tank. This precaution will avert any problem that may arise. Other workers (IAEA 1966) proposed burial of high level wastes in deep clay formation. Mantell (1975) agreed with this concept but in addition, adequate knowledge of the interation of radionuclide and geological media are required to tackle the problem of migration in repositories.

Solid wastes: Other low-level wastes occur initially as solids, and these are generally stored in burial sites, which are sometimes preceeded by compaction or incineration operations. Pretreatment of solid radioactive waste is mainly aimed at an appropriate preparation of the waste that facilitates the subsequent waste treatment steps. The administrative measures fix the rules for the very first steps of the solid-waste management i.e. collection, sorting, segregation and packaging for transport to better storage area, or directly to the treatment facilities. The next step is the size reduction and final volume reduction technqiues such as incineration, compaction and decontamiantion.

It is easier to handle store and transport solid than gas and liquid. Adequate management will therefore be to fix or immobilize the liquid radioactive waste and get it in convenient form that will enhance better storage and easier transport.

2.4.2 Fixation of radionculides

Immobilization involves processing radioactive wastes to a solid monolithic matrix. The primary purpose of the immobilization is to improve the safety associated with the subsequent management steps. The most widely used media for immobilization are cement and bitumen (IAEA 1963, 1972, 1983). Other matrix materials are clays zeolites, glass, ceramic and polymers. Calcination and vitrification are normally used for proper fixation of radioactivity. The process of fixation in cement consists of mixing cement with the waste, be it as a solution, slurry or solid and allowing to set in a suitable container. This fixation is carried out at ambient temperatures because of the hydraulic setting property of the cement. For bitumen matrix, the solutions, sludges or solids are mixed with the matrix at elevated temperatures. The bitumen based waste form is released into a suitable container, where it cools and solidifies. The same process of fixation applies to glass. Incorporation of radioactive waste in to polymeric fixation agents is achieved at both ambient temperatures or with hot liquids to $60^{o}C$ depending on the polymer used. Liquid and gaseous wastes may be decontaminated by adsorbing the radionuclides onto an adsorbent and then the solid exchanger is fixed. Zeolite and clays exhibits ion-exchange phenomena to a marked degree as such they are suitable for decontaminating of liquid wastes before fixation (Matsumura 1969, Shock 1961, Amphlett 1956, Emmon 1956 and Wahlberg et al 1962, 1965).

Suitable matrix must be selected taking cognisance of physical, chemical and radiochemical properties of the wastes. The choice of a matrix must take into consideration the following properties: Stability, compability and low cost. IAEA (1970 , 1972, 1983) and Elsden (1984) pointed out the standard criteria for judging the adequancy of immobilized waste form as follows:

- low leachability in natural waters
- long term chemical stability
- mechanical stability
- radiation resistance
- chemical compatibility with disposal environment.

Atkinson et al.(1984, 1986) studied adsorption of cation on to hardened ordinary portland cement paste using radio-tracer technique in batch equilibration experiments. They concluded that there were no evidence of chemical bonding of the cesium into cement paste. However, there was proof of chemical bonding of the strontium into solid phases of cement during setting. There is limitation in the use of cement because of the fact that the water/cement chemistry is not yet understood. Kormaneni (1985) and Dyer et al.(1985) worked on

zeolites for treatment of radioactive waste and their effects were monitored by x-ray diffraction technique. They concluded that zeolite in general showed good selective adsorption for cesium and strontium with clinoptiolite being particularly good. Additionally Kormaneni also found that the maximum ion exchanged ranged between 70-75% of cation exchange capacity. In general, for waste form containing zeolite the mechanism of adsorption involves additional step of exchange of Cs^{+} from the zeolite with Ca^{2+} from cement. Finally, it was shown that calcination can reduce leach rate of nuclide in both zeolite and cement based waste forms. In static leach test the kinetic behaviour is described by effective diffusion coefficient and depletion depth (Atkinson et al 1986) and these were found to be 2.3×10^{-11} cm^2/S and 0.25 μm respectively for ordinary portland cement/clinoptiolite based waste form. Matsuzuru and Moriyana (1982) have recently suggested that low strontium leachability may result from being incorporated in precipitated carbonates when carbon dioxide is dissolved in the leachant.

Of all the matrix materials studied thus far, clays stand out to be very attractive because of their widespread availability, low cost, ion-exchange properties, stability and compatability. Soil investigators are aware of the fact that certain cations may be sorbed by clay minerals in a non-exchangeable state. Potassium is the commonest ion that is "fixed" to a considerable degree and is the ion that has been studied extensively because of its importance in soil fertilization. Investigators have shown that illite will fix potassium and most of the potassium ion fixed in soils is probably due to the

action of this clay mineral. The potassium fixation in illite occurs by the emplacement of the potassium ion in this mineral. Wiklander (1950) showed that the amount of fixation in illite mineral varies with cation already adsorbed. Montmorillonite has some power to fix potassium ion but the power is less than that of illite and the ion is fixed in clay minerals only if the material is dried (Stanford 1947). Kaolinite has little power to fix potassium ion either in moist condition or after drying.

Clay mineral exhibits one or more useful adsorption or chemical reaction with radioactive or stable trace elements. Lee, Kim et al have evaluated the suitability of clay minerals for use in adsorption of radionuclides. There is considerable evidence provided by Mitchell (1963), Hatch (1952, 1953), Ginell et al. (1954) and Sobolev et al. (1968) indicating that montmorillonite clays were found to be the best natural agents for adsorption of radioactive isotopes strontium, cesium, cobalt, ruthenium and other fission products. For a given clay, the maximum amount of any one cation that can be taken up is constant and is known as cation exchange capacity (C.E.C.), measured in milliequivalent per 100 grams. According to Mistry et al. (1966) the highest cation exchanged during equilibration for clays corresponds to between 70-75% of the total cation exchange capacity. The ionic exchange capacity of clays is considerably increased by calcination. The alteration of crystal lattice begins at 800^{o}C at temperature radioactive waste fixation is greatly enhanced. Above 800^{o}C the mechanism of fixation is determined by changes in the crystal lattice and also by gradual vitrification of clay minerals. According to Sawhney (1964) fixation of Cesium by mica occurs at crystal edges where cesium ion replace

potassium ion and thus become a part of the stable mica structure. Spitsyn et al (1958) suggested that fixation of cations by clay during calcination is analogous to the diffusion of ions within a crystal lattice or the formation of strong chemical bond between a cation and a clay. The extent of fixation of fission products (Amphlett 1956, 1958, Hatch 1952, 1953, Ginell 1952, Sobolev et al.1968, IAEA 1983) to clay minerals by heat treatment gave promising results. About 99% of the activity of the immbolized calcined (1000^{o}C) waste form was retained after washing in distilled water and dilute nitric acid. The findings of these investigators demonstrated effectiveness of calcination of clay minerals showing only 0.2% of adsorbed radioactivity leached in natural waters. Saidl (1962) agrees with Spitsyn's concept and further suggested that nuclides are probably incorporated in silicates crystal lattice between two oxygen atom with a replacement of one silicon atom. Other workers studied the formation of insoluble mineral cancrinite produced by reacting clays with concentrated alkaline salt solution. This resulting structure acts as a trap for water, fission products and other minor constituents. These in coming constituents are usually trapped in cages and in channels enclosed by the cages. The waste form is subsequently fired at about 800^{o}C to convert it to nepheline, a durable aluminosilicate mineral.

2.4.3 Disposal of radioactive wastes

Solidification of radioactive wastes accomplishes a needed reduction in their volume, and generally reduces the mobility and often when calcined the susceptibility to leaching

by water of soluble radionuclides. However, it does not change th radioactivity or the danger from radiation emanating from it. The solidified wastes still must be separated from man and his environment for as long as the radiation may be harmful. This period of time varies widely. Solidified wastes containing radioisotopes with short half lives need to be stored only few decades. On the other hand, wastes containing significant quantities of transuranic element or of long lived fission products such as strontium-90 and cesium-137 must be stored so that they cannot contact man and his environment for many centuries. Gilmore (1977) reported the deep rock disposal concept, in which the wastes are buried in a hole drilled into deep, dry, geologically inactive crustal rock. Several authors have discussed and analysed the liquid waste emplacement in mined cavity concept for disposal and its modification (Gilmore 1977). Work still continues on aspects of heat generation from radioactive decay, material selection, migration of radionuclides etc but conclusions have not yet been reached. Salt mines are favoured as permanent storage sites because they are known to have long been quite free of water; however, doubts about their suitability have not been completely dispelled.

2.4.4 Burial ground for low-level radioactive wastes

A number of burial grounds have been established for direct burial of solid low-level wastes in developed countries. For each burial ground a hazard analysis is required to establish the safe operation under all conceivable circumstances. The purpose of this hazard analysis is to ascertain that the material surrounding the waste must be able to retard water access and

retain the radioactive materials when leached from waste. It is also aimed at establishing a maximum concentration of radio-isotopes that can be buried at each location.

This form of storage appears to be acceptable for the foreseable future. However, the possible pathways where by burial waste can get to the biosphere are as follow:

(i) erosion of overlying material resulting in waste exposure

(ii) intrusion of man

(iii) leaching and seepage into ground water systems

(iv) excavation activities

The important natural phenomenon for bringing buried wastes to the biosphere is transport of underground water. Umar (1987) reported the general acceptance that the intrusion by man is a very likely phenomenon for periods less than 100 years despite the restriction on burial sites.

Introducing a proper backfill material will act as a very effective chemical and mechanical barrier preventing free migration of radionuclides released from the waste containers. The proper backfill materials should satisfy the following properties:

(i) low permeability/solubility to ground water

(ii) long term thermal stability

(iii) thermal conductivity equal to or greater than that of the surrounding rock.

(iv) no unfavourable chemical interaction with waste container or waste form

(v) good adsorption properties to retard movement of radionuclide.

Some of the material to be used as "backfill" includes clay minerals, synethetic materials eg mixture of magnesium oxide and silica gel, inorganic metal carbonates and phosphates, graphite and zeolites (Choppin et al.1983, Sobolev et al. 1968, and Umar 1987).

The performance of a burial ground or the degree to which it provides containment of radionuclides is determined by monitoring programs conducted during and after operation of burial ground. Monitoring programs are commonly included in a larger environmental monitoring program conducted as part of the overall laboratory operations.

Although burial of solidified wastes in geologic formations seems to be the favoured method of ultimate waste disposal; more exotic schemes have been suggested, including rocketing into space and injection under the earth's crust, but at present such methods appear to be neither technically nor economically feasible.

2.5 Clay

Clays are recognized as being agglomerates of several mineral types, each of which has a limited range of chemical composition. It is difficult to define clay precisely, because of the wide variety of materials that have been called clays. In general, clay is a natural, earthy, fine grained material which develops plasticity when mixed with a limited amount of water (Grim 1953). Clay constituents are basically silica, alumina and usually appreciable quantities of iron, alkalies and alkaline earths.

The term clay has no generic significance. It is used for material that is the product of weathering, has formed by hydrothermal action, or has been deposited as a sediment. According to Grim (1953) it is convenient to use the expression clay minerals for any fine-grained, natural, earthy argillaceous material. Clay mineral occur in a great variety in nature and are found in commercial workable deposits all over the world.

2.5.1 Constitution of clays

Generally there are five important constitution characteristics of clay minerals: clay composition, non-clay mineral composition, organic material, exchangeable ions and soluble salts, and texture.

Clay composition: This refers to the identity and relative abundance of the clay mineral components. In order to make complete clay mineral determinations, it is necessary to fractionate the clay grade to concentrate minor constituents so

that adequate analytical data can be obtained. These clay minerals are determined in their natural states. For example, care must be taken to ensure that the analysis reveals the natural hydration state of minerals and their ion-exchange composition.

Non-clay mineral composition: This refers to the identity and relative abundance of non-clay minerals, and the particle size distribution of individual species. Large flakes of mica, feldspar and other minerals are very abundant in some clay minerals. The non-clay content in mineral is generally known to be concentrated in particles coarser than about 2 microns, but, there are materials in which they are much finer grained for example bentonite and Wyoming (Gruner 1940, Roth 1951).

Organic material: This refers to the kind and amount of organic material contained in the clay mineral. Most of the organic material occur in clay materials in two ways: it may be present as organic materials adsorbed on the surface of the clay mineral particles, or it may be present as discrete particles of wood, leaf matter and spores. The discrete particles may be present in any size from large chunks easily visible to the naked eye to particles of colloidal size which act as a pigment in clay minerals. According to Hesse (1971) organic material contributes to the physical condition of clay mineral by holding moisture and by affecting structure. It is a direct source of plant nutrient elements. Organic material is directly involved in the availability of such elements due to its own cation exchange capacity. Since organic material embraces the whole non-mineral fraction of soil, analytical results depend in part upon the mean size of sieve used in the

preparatory stage, however macro-organic material is largely excluded by fine grinding and sieving (0.5mm) of sample.

Exchangeable ions and soluble salts: Some water soluble salts are entrained in the clay at the time of formation or may have developed subsequently as a result of weathering or alteration processes as in the oxidation of pyrite to produce sulphates. Common water soluble salt found in clay minerals are chlorides, sulphates and carbonates of alkalies, alkaline earths, aluminium and iron.

Texture: The textural factors refer to the particle size distribution of constituent particles, the shape of particles, the orientation of the particles in space and with respect to each other and the forces tending to bind the particles together.

2.5.2 Structure of clay minerals

Clay minerals are classified on the basis of structure into amorphous minerals such as allophanes and the crystalline minerals such as kaolinite, halloysite, montmorillonite, illite, chlorite and attapulgite (Fig. 3). The atomic structures of these clay minerals have been studied in considerable detail by numerous investigators based on the generalization of Pauling's work for structure of the micas and related minerals. Two general structural units are involved in the atomic lattice of most of the clay minerals. One unit consists of two sheets of closely packed oxygen or hydroxyl in which aluminium, iron, magnesium atoms are embedded in octahedral coordination so that they are equidistant from six oxygen or hydroxyls. The second unit is built of silica tetrahedrons. A silica atom is equidistant from four oxygen or hydroxyl in

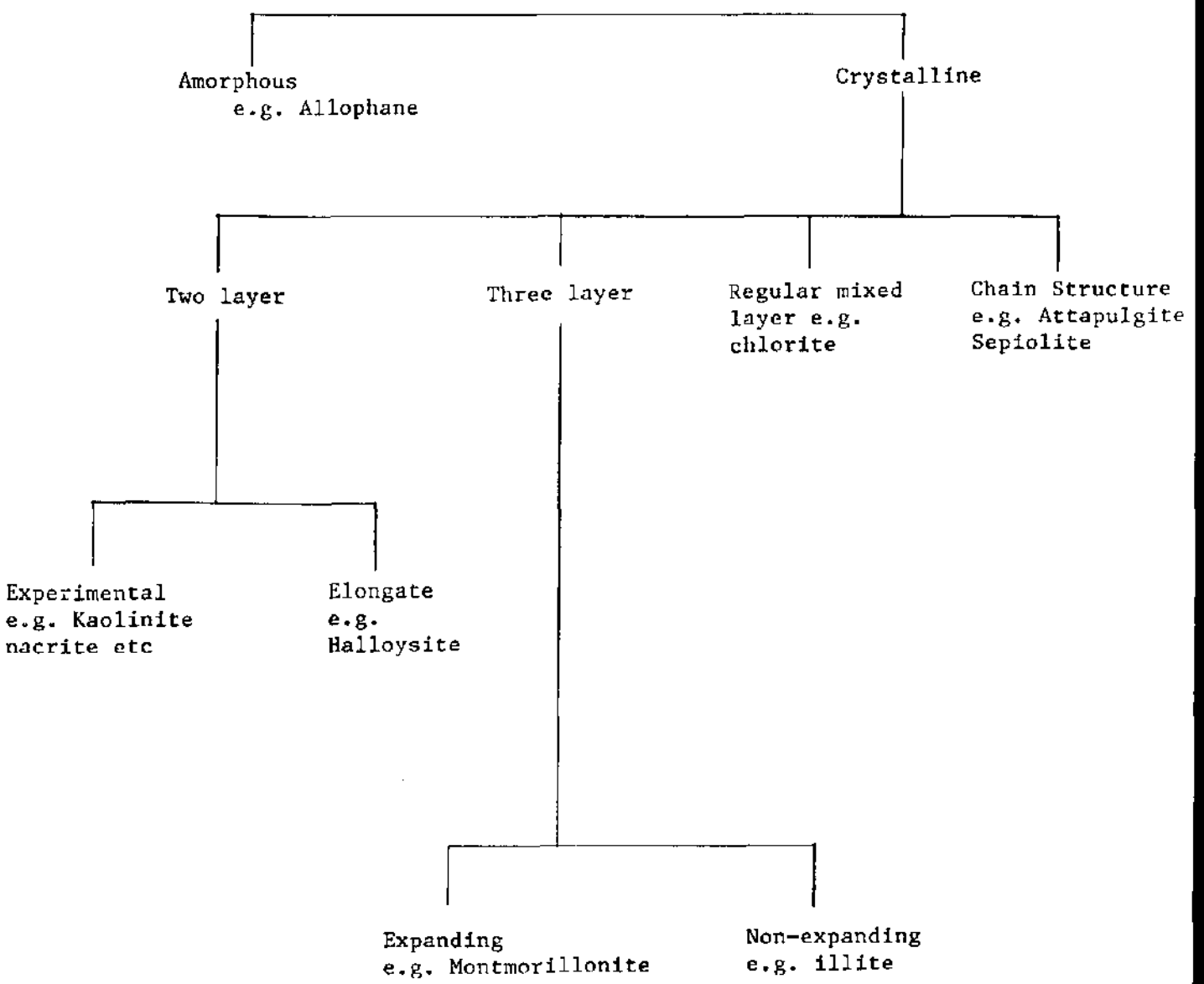


Fig. 3 Classification of clay minerals Grim (1953)

each tetrahedron to balance the structure. The active oxygen are those with only one link to silicon and hence are those at the edges of the chains and at the tips of the tetrahedron. The structural configuration of the basic units vary in the different clay minerals.

Allophane minerals: The allophane minerals are amorphous to x-ray diffraction by definition. According to Grim (1953) the study of allophane minerals is particularly difficult because of the problem of separating them from intermixed crystalline materials, as such very little study has been done on the structure. The variation in composition is therefore unknown.

Kaolinite minerals: Pauling did the pioneering work on the structure of kaolinite minerals while Gruner did more detailed studies which were lately revised by Brindley et al (1946). The basic structural unit in the silicate layer are silicon-oxygen tetrahedral sheets and aluminium hydroxide octahedral sheets. The structural formula is $Si_4Al_4O_{10}(OH)_8$. The plane between the units layer is a cleavage plane. The tetrahedral and octahedral sheets are superimposed in different ways to form the so called 1:1, 2:1, and 2:1:1 layer types as shown in Fig. 4. However in kaolinite cleavage is not so pronounced as it is in other clay minerals where oxygen planes are adjacent at unit boundaries so that there is no hydrogen bonding (i.e. a bond connecting hydrogen of one molecule to the oxygen of the other). The presence of weak forces (Fig. 5) existing between the individual units in the c-axis direction makes kaolinite mineral disperse readily in water.

Halloysite minerals: There are two forms of halloysite minerals with formulae $Si_4Al_4O_{10}(OH)_8$ and $S_{14}Al_4O_{10}(OH)_8 \cdot 4H_2O$.

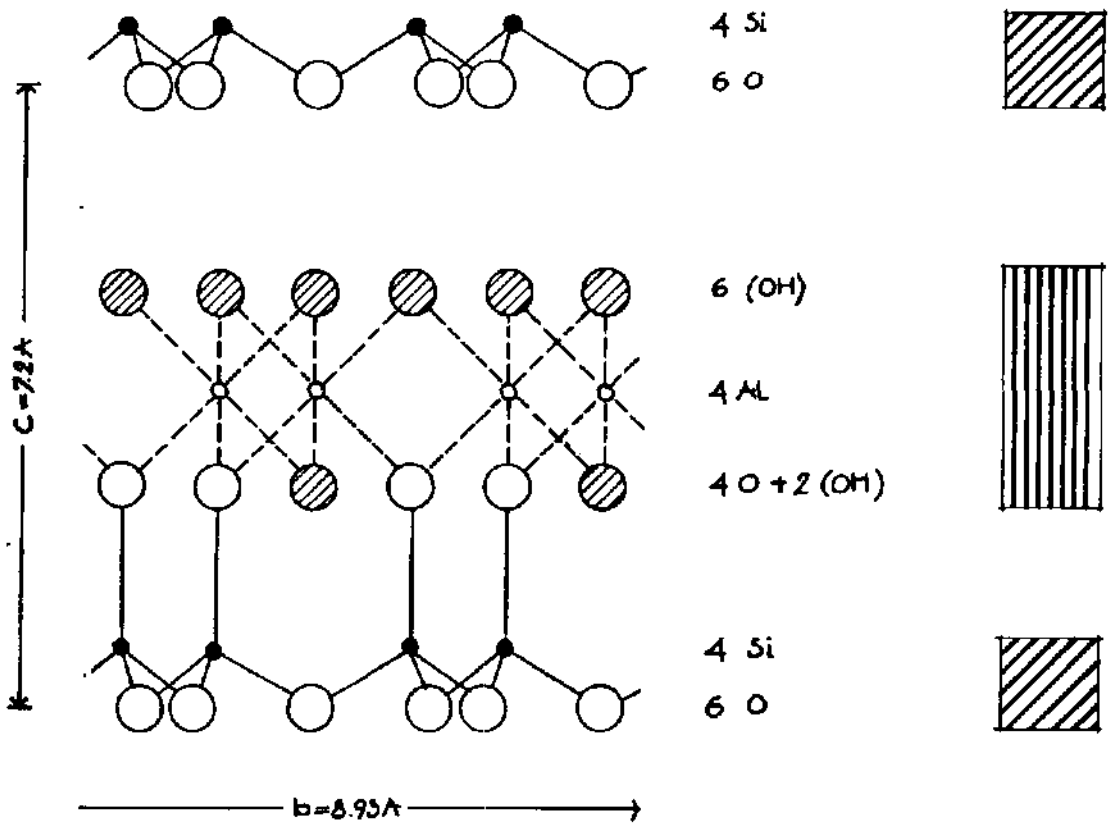


Fig. 4 ... Diagram of the Crystal Structure of Kaoline, after Gruner. Grim (1953).

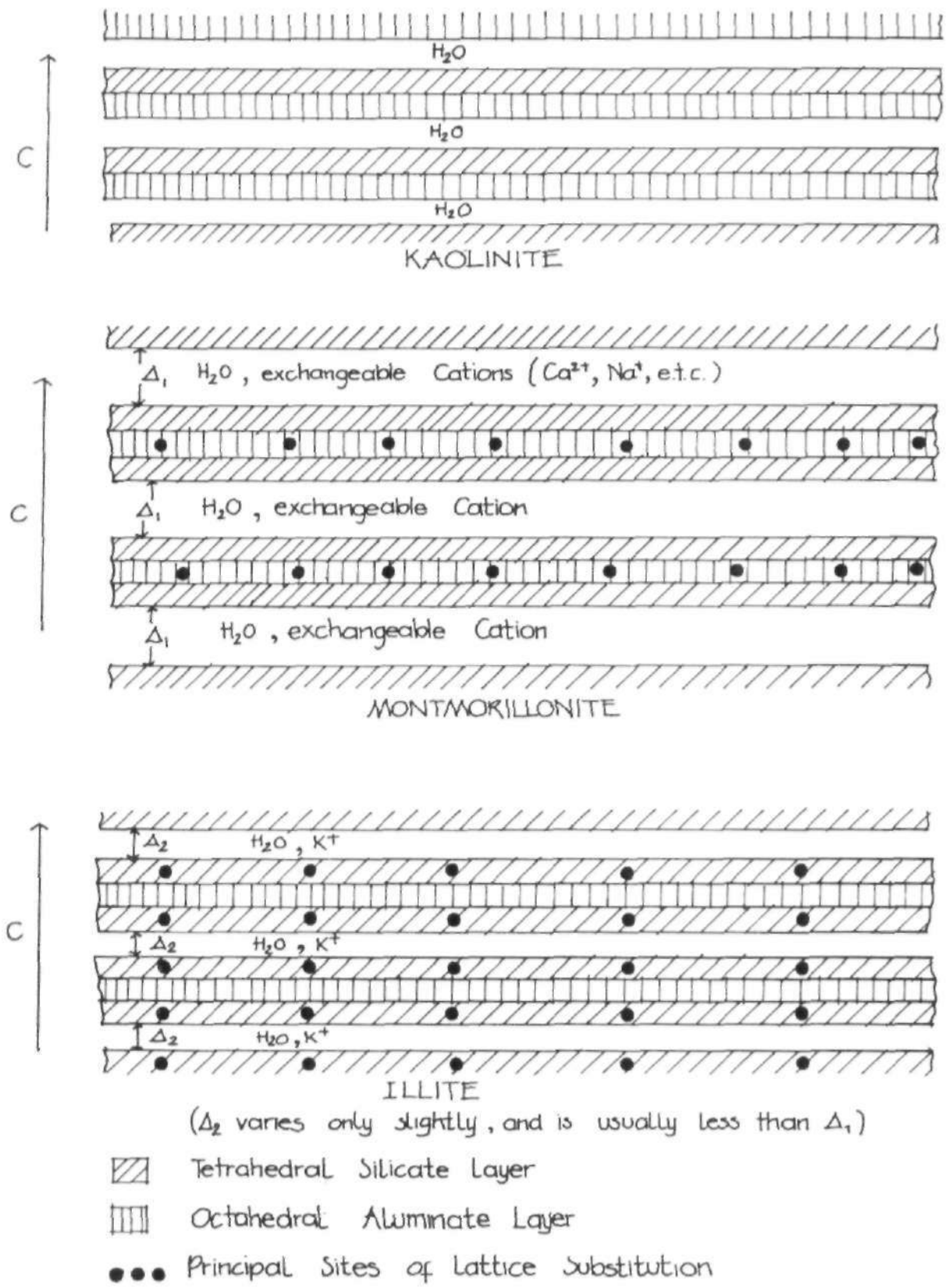


FIG. 5... Diagrammatic Representation of Three Important Layer-Lattice Structures Characteristic of Certain Clay Mineral. Arrow indicates C-axis.

The later form dehydrates to the former at relatively low temperature (60-70^{O}C). Various structures for halloysite minerals have been suggested by investigators (Grim 1953). Hendricks et al (1938) have shown that earlier suggested structures were not in conformity with the observed intensitites of the basal reflections or with the very easy dehydration of the mineral. His subsequent works showed that molecule in this layer had a definite configuration. Diffraction data for halloysite are not suited for detailed structural study, but the intensities of the basal reflections are in conformity with Hendricks' suggested structure (Grim 1953).

Montmorillonite minerals: The montmorillonite mineral structure generally accepted was suggested by Hofmann et al.,in 1933 and later modified by other investigators (Grim 1953). The montmonillonite structure is derived from that of the prototypes pyrophyllite and talc as given in Fig. 6 by substitution of certain ions for other ions. Montmorillonite is an example of a diooctahedral smectite and is represented by the formula $Al_{2-x}\ Mg_x Si_4 O_{10}(OH)_2$. This formula suggests that the substitution of ions for the lattice ions is limited to the octahedral sheets. Most of the time, the substitutions are by ions of lower valency thereby producing an excess of charge which causes the basal faces to be essential electronegative. The outstanding characteristic of the montmorillonite structure is that water and other polar molecules, such as certain organic molecules (for example amines, alcohol, crude oil etc) can enter between the unit layers causing the lattice to expand in c-direction (Fig.5) because of the weak Vander Waal binding forces between the layers and the hydration of the cations. The

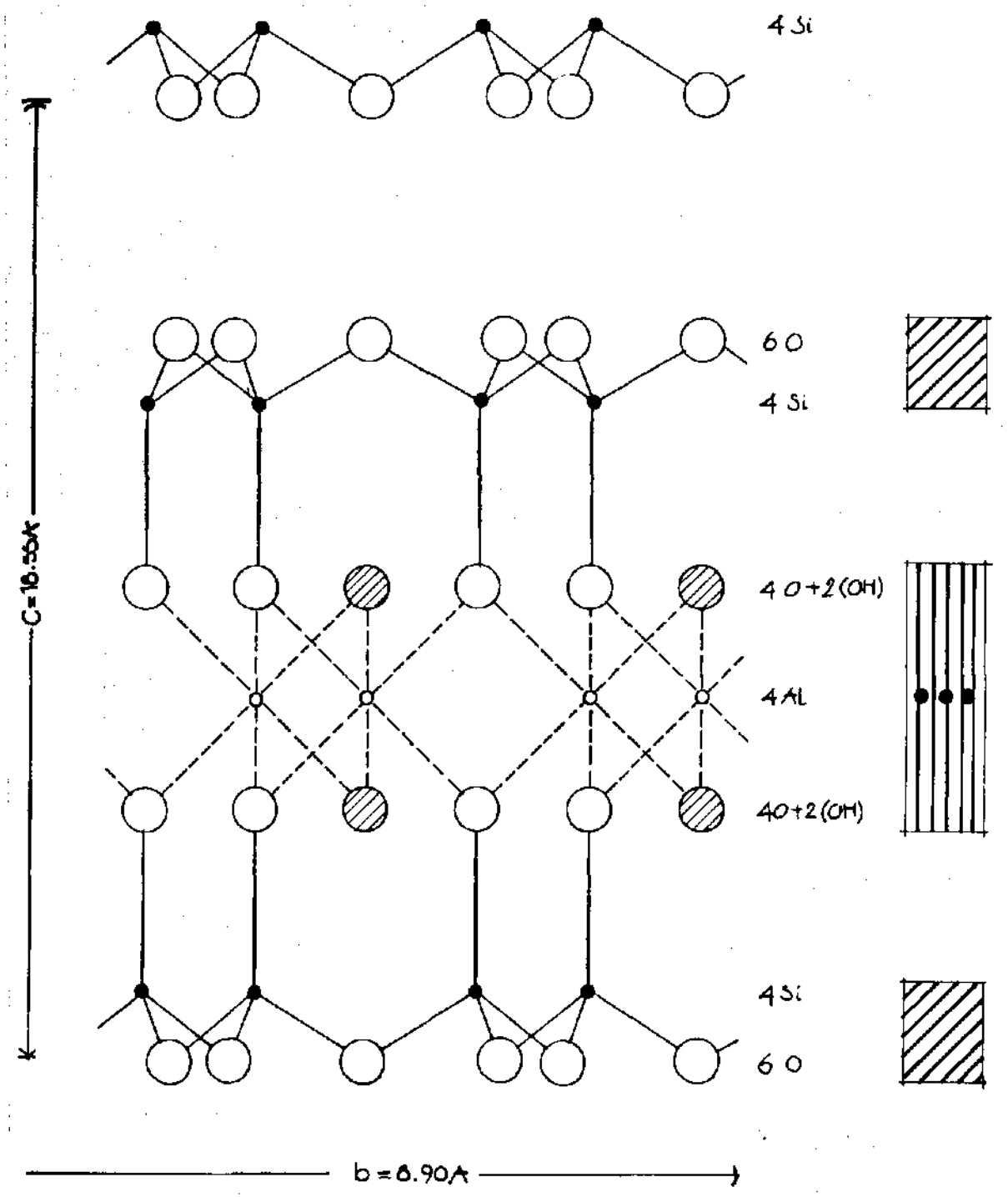


Fig. 6 ... A Diagram indicating the Crystal Structure of Pyrophyllite, after Pauling. Kerr (1951).

very high cation exchange capacity of the montmorillonites is thus adequately explained by the high degree of substitution and lattice expansion. The structural formula is $Si_8Al_4O_{16}(OH)_{12} \cdot H_2O$ (inter layer).

Illite minerals: The basic structural unit is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedron in each silica sheet point toward the centre of the unit and are combined with the octahedral sheet in a single layer with replacement of hydroxyl and oxygen. The unit is the same as that of montmorillonite except that some of the silicons are always replaced by aluminium and the resultant charge deficiency is balanced by potassium ion. The structural formula is $K_2(Si_6.Al_2)\ Al_4O_{20}.(OH)_4$. The charge distribution within the layer of the well crystallized mica is:

K^+	1^+
$6O^{2-}$	12^-
$3Si^{4+}Al^{3+}$	15^+
$4O^{2-}$	10^-
$4Al^{3+}$ (Diooctahedral)	
6R(Trioctahedral,	
$R=Mg^{2+}$, Fe^{2+}, Fe^{3+}	
Li^+, Ti^{3+})	12^+
$4O^{2-}$ $2(OH)^-$	10^-
$3Si^{4+}$ Al^{3+}	15^+
$6O^{2-}$	12^-
K^+	1^+

The illite clay minerals differ from well crystallized micas. The silica-to-alumina molecular ratio of the illites is higher than that of well crystallized micas and the net unbalanced charge deficiency is reduced by 2 per unit cell to about 1.3. In well crystallized micas one-fourth of the Si^{4+} are replaced by Al^{3+}, whereas in illites only one-sixth are replaced frequently (Grim et al.1937).

2.5.3 Ion exchange in clay minerals

Thompson (1850) and Way (1850) were the first to systematically study cation exchange in soils. The materials responsible for this phenomena were identified by Lemberg and later Weigner as clays, humic acid, zeolites and glauconites (Helfferich 1962). Kelly (1948) made a detailed review on the history of cation exchange, while Helfferich (1962) gave a clear cut picture of the phenomena and their physical causes.

The property of sorbing certain anions and cations and retaining them in an exchangeable state is exhibited by clay minerals. The exchangeable ions are held around the outside of the silica - alumina clay mineral structural unit, and the exchange reaction generally does not affect the structure of the silica-alumina pocket. The commonest exchangeable cations in clay minerals are Ca^{2+}, Mg^{2+}, H^{+}, NH_4^{+}, K^{+} and Na^{+}, while the commonest anions are SO_4^{2-}, Cl^{-}, PO_4^{3-} and NO_3^{-}.

Considering the factors influencing cation exchange capacity, there is no single capacity valve that is characteristic of a given group of clay minerals. Because of this capacity values are rigorously comparable only if they have been obtained by the same standard procedure on material of

comparable textural and structural attributes. However a range of capacities are shown in Table 13 for each group.

Table 13 Cation Exchange Capacity of Clay Minerals

Clay Mineral	Cation exchange capacity (meq/100g)			
	Grim (1953)	Amphlett (1956)	Seedhouse (1957)	Johnson (1949)
Kaolinite	3-15	3-15	2-5	3-5
Halloysite $2H_2O$	5-10			3-10
Halloysite $4H_2O$	40-50			
Montmorillonite	80-150	80-150	50-150	60-100
Illite	10-40	10-40	20-40	20-40
Vermiculite	100-150	100-150		
Chlorite	10-40			

The property of ion exchange and exchange reaction are of very great fundamental and practical importance in many fields in which clay minerals are studied and used for example, oceanography, soil science, geology, and applied art and construction.

Causes of cation exchange: There are three main reasons identified for cation exchange capacity in clay minerals namely broken bonds, substitution and hydrogen exposed by hydroxyls. Broken bonds around the edges of the silica-alumina units create unsatisfied charges, which would be balanced by adsorbed cations. The number of the broken bonds and hence exchange

capacity due to this cause would increase as the particle size decreases. Lattice distortion tends to increase broken bonds, and the exchange capacity increases as the degree of crystallinity decreases. Johnson (1949) has recently argued that the total exchange capacity of montmorillonite results from broken bonds, but his evidence is not convincing(Grim 1953).

Substitution in the lattice structure of trivalent aluminium for quadrivalent silicon in the tetrahedral sheet and of ions of lower valence, particularly magnesium, for trivalent aluminium in the octahedral sheet result in unbalanced charges in the structural units of some clay minerals. Sometimes such substitutions are balanced by lattice changes, for example, hydroxyl for oxygen or by filling more than two thirds of the possible octahedral positions, but most often they are balanced by adsorbed cations. Exchangeable cation resulting from lattice substitutions are found mostly on cleavage surfaces. In clay minerals, replacement into octahedral layers are probably the major substitutions causing cation-exchange capacity. In some cases cations held by forces due to substitutions of aluminium for silicon seem to be substantially non-exchangeable e.g. potassium in mica. In montmorillonite and vermiculite, substitution within the lattice causes about 80 per cent of the total cation exchange capacity.

The hydrogen of exposed hydroxyls may be replaced by a cation which would be exchangeable. Some hydroxyl groups are exposed around the broken edges of all the clay minerals, and cation exchange due to broken bonds would, in part at least, be replacement of the hydrogen of exposed hydroxyls. The presence of the sheet of hydroxyl on one side of the basal

cleavage plane is considered to be the cause of exchange capacity in kaolinite and halloysite (Grim 1953).

Factors affecting cation exchange: There are five basic factors which affect the cation exchange capacity in clay minerals: environment of the exchange reaction, clogging of cation exchange positions, temperature, particle size and grinding. Cation exchange usually takes place in an aqueous environment, and the ions generally have considerable solubility. However, it has been shown that clays may take ions from water suspensions of very insoluble substances and resistant minerals by means of ionic sorption reaction and in the presence of relatively little water.

The development on exchange position reduces the exchange capacity of montmorillonite clays. This is partly due to damaging of the montmorillonite lattice, and also partly due to clogging of the exchange position by aluminium. Dion (1944) has pointed out that Iron (III) oxide alone or in the hydrated form may serve to reduce the cation-exchange of clay minerals by a clogging action. Hendrick (1944) pointed out from his studies that large, flat organic ions adsorbed on the basal surface of montmorillonite may be of sufficient size to blanket more than one exchange position and thereby reduce the exchange capacity of montmorillonite.

Kelly (1948) has shown that the effect of temperature on cation exchange is generally small. On the contrary, Weigner reported a small negative temperature coefficient, and subsequent workers found that the exchange reaction is accelerated somewhat by raising the temperature. Although Chapman and Kelly (1930) pointed out that the disadvantages of heating

overweigh the advantages because of the increased solubility of certain constituents at higher temperature. The exchange capacity is reduced on heating, but the reduction is not uniform and varies with cation present. For example, the calcium montmorillonite shows gradual loss of cation exchange capacity on heating to 300°C (from 93 to 41 meq per 100g) and an abrupt drop from 41 to 12 meq per 100g between 300 and 390°C (Grim 1953).

The cation exchange capacity of kaolinite and illite increases as the particle size decreases. Because the exchange capacity is due primarily to broken bonds, an increase is to be expected with decreasing particle size. However, the cation exchange capacity does not change substantially with particle size. Johnson (1949) reported that there is no variation in the 87-14 mμ particle range. This is due to the fact that substitution of certain atoms within montmorillonite lattice by metals of lower valency accounts for the ion exchange in this mineral.

Kelly and Jenny (1936) have shown that grinding of the clay minerals and many other non-clay minerals, caused an increase in cation exchange capacity. The grinding causes a variation in particle size and surface area and an increase in the number of broken bonds.

Kinetics of cation exchange: The kinetics of cation exchange reaction are influenced by a number of factors for example, concentration, surface area of the solid, pore size and nature of the cations. Kunin has studied kinetic of cation exchange and has recognised three diffusional process involved: 1) the diffusion of cation in the solution phase, which did not

generally influence the kinetic of exchange unless the solid was non-porous or the solution was viscous. 2) the diffusion of cation through the film formed at the interphase junction by the exchange of cations between those present initially at the surface of the particle with those of the solution immediately in contact with the particle and 3) the diffusion of cations through the crystal phase (Kunin 1960).

The last diffusional process is normally the rate controlling step at high ionic concentrations for clay minerals, while at low concentrations (<0.01 N>) the second diffusional process may play an important role.

The exchangeable cations sited at the edges of the clay particles have been found to exchange more readily than those sited between the lamina in the clay. Consequently the exchange kinetics of kaolinite clay, which has all its exchangeable cation sited at the particle edge and because of its ready dispersion in suspension, are much faster than in montmorillonite or illite which have most of their exchangeable cation sited in between the clay layers. Because illite groups are resistant to swelling, cation exchange rate follows the order Kaolinite > Montmorillonite > illite. Input of an extra energy of activation may be required in exchange accompanied by swelling such as montmorillonite.

2.5.4 Effect of heat on clay minerals

One of the characteristics of a clay is that when mixed with water it forms a coherent mass that is capable of being moulded to any desired shape, i.e. it is plastic. When a plastic clay is dried, shrinkage occurs; if drying is too

rapid and uneven, the shrinkage may give rise to cracks in the product. When completely dry, clays have a considerable strength which is further enhanced by firing. A mass of plastic clay which is being allowed to dry undergoes shrinkage as shown in Fig. 7. As drying proceeds, water evaporates from the outer surface and the particles of clay are drawn closer together by surface tension forces. Eventually, the clay particles will come into mutual contact, Fig. 7(b) forming a loosely packed assembly. When this stage has been reached further contraction is not possible and no further shrinkage therefore occurs. The residual water contained in the voids between the particles and water content at this stage is known as the critical moisture content. Further drying now results in loss of water from the pores of the body, the water being drawn to the surface by capillary attraction. Thus, the original pack is maintained and air replaces water in the pores, resulting finally in a dry, porous body, Fig. 7(c). The total shrinkage undergone by a clay article depends on the difference between the critical moisture content and the initial moisture content. However, in practice the latter is adjusted to suit particular forming process so as to produce correct consistency.

For pure clay minerals further heating produces the following effects. After removal of adsorbed water at just over $100^{o}C$, kaolinite decomposes above about $450^{o}C$ losing its hydroxyl groups as water. Work done by White and Others (Worrall 1975) have shown that dehydration follows approximately a first order reaction. If the temperature is not too high, the residue can be rehydrated to kaolinite. This

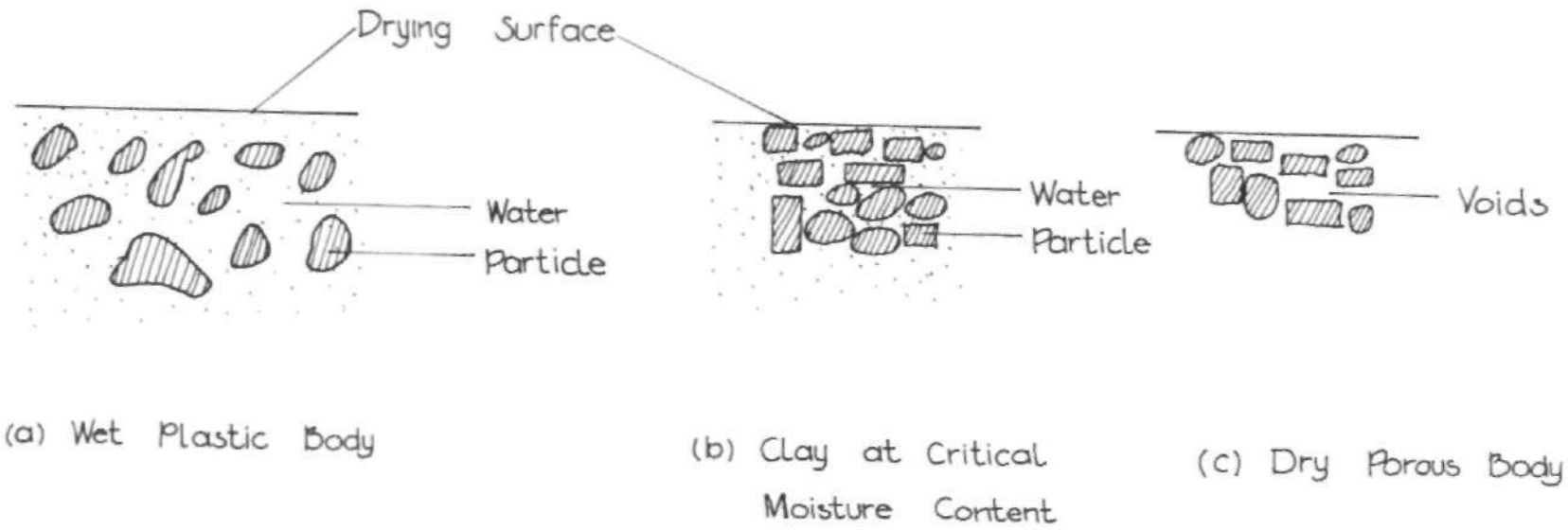


FIG. 7... Behaviour of Clay Particles on Drying

This product is refered to as Metakaolin:

$$\underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} \xrightarrow{450^{\circ}C} \underset{\text{Metakaolin}}{Al_2Si_2O_7} + 2H_2O \qquad (1)$$

At still higher temperature metakaolin undergoes further reactions to form crystalline compounds, the end product being free silica (cristobalite) and mullite, $3Al_2O_3 .2SiO_2$. Earlier work based on x-ray diffraction, indicated that at 1000°C a spinel type compound was formed, thought to be $\gamma - Al_2O_3$. Recent x-ray work strongly suggests that mullite are formed at higher temperature (1150 - 1300°C). More recent accurate measurements of the unit cell dimensions of the spinel compound have been shown that it is probably not $\gamma - Al_2O_3$ but silica-aluminium spinel, of formula $2Al_2O_3.3SiO_2$. This latter compound looses silica by a progressive diffusion of silicon ion from the lattice, resulting in a multiple-like compound, $Al_203.SiO_2$, as an intermediate stage, and by further loss of silica, true mullite $3Al_2O_3.2SiO_2$ is formed. The entire process is represented by the following chemical equations:

$$\underset{\text{Metakaolin}}{2(Al_2O_3 . 2SiO_2)} \xrightarrow{925^{\circ}C} \underset{\text{Silicon spinel}}{2Al_2O_3 . 3SiO_2} + SiO_2 \qquad (2)$$

$$\underset{\text{Silicon spinel}}{2Al_2O_3 . 3SiO_2} \xrightarrow{1100^{\circ}C} \underset{\text{pseudo-mullite}}{2(Al_2O_3.SiO_2)} + SiO_2 \qquad (3)$$

$$3(Al_2O_3.SiO_2) \xrightarrow{1400^{\circ}C} \underset{\text{mullite}}{3Al_2O_3.2SiO_2} + \underset{\text{cristobalite}}{SiO_2} \qquad (4)$$

The liberated silica forms cristobalite as noted but the transformation is commonly believed not to occur below 1350°C.

Because of the many different substitutions in montmorillonites, there is a wide variation in their chemical compositions and therefore in the final products of heating. As with kaolinite adsorbed water is lost at about 105°C from external surfaces, but a much higher temperature from 120 to 300°C is required to remove the inter-layer water, depending on the nature of exchangeable cations. At about 650°C the hydroxyl groups are removed as water, the exact temperature varying with the type of montmorillonite. The initial dehydration products in this case are probably amorphous alumina and silica. On heating to still higher temperatures, a spinel phase appears and the final products of heating to 1400°C are given mullite and cristobalite. The montmorillonite group of minerals may be considered to be derived from pyrophyllite (or talc) by substitution, and if pyrophyllite is taken as a "model" substance, the dehydration reaction may be written:

$$3[Al_2Si_4O_{10}(OH)_2] \xrightarrow{650^{\circ}C} 3Al_2O_3.2SiO_2 + 10SiO_2 + 3H_2O \qquad (5)$$

Illites, particularly those present in British fireclays, have dehydration characteristic remarkably similar to those of kaolinite. The major evolution of water occurs between 350 and 600°C, thus there is a small loss of water below 100°C. Grim and Brindley have reported that the structure of illite is not completely destroyed until a temperature of 850°C is attained.

Clays of highest quality do contain significant amounts of constituents other than the clay minerals. Largest amount of such accessory minerals in most cases in quartz, others are mica, titania-bearing minerals, pyrite, feldspar and siderite. These accessory minerals affect the behaviour of clays on heating. Quartz could change to cristobalite at about 1250^{o}C. Some of the oxides present in accessory minerals lower the temperature at which liquid formation occurs and may increase the amount of liquid at a given temperature. The alkalies, soda and potash are especially potent in this respect, as they react to form a highly viscous-liquid at very high temperature but below the melting temperature provided the body consist only of alumina and silica. In pure clays however, a very small amount of potash is sufficient to lower the melting temperature normally quoted as 985^{o}C (Harbinson-Walker 1950). In alumina-alumina-silica liquid, accessory minerals containing lime, magnesia, and iron oxide dissolving wholly or in part, as in amorphous and crystalline silica; this behaviour also hold at very high temperature.

2.6 Properties of Clay Wasteforms

The physical properties of free and fired clays are controlled by factors relating to the particle size and size distribution, particle shape, particle orientation, composition, moisture content, and temperature. Therefore, their properties vary widely with type of clay, processing etc. The properties are numerous but only density, shrinkage and porosity, which are most relevant to the present work are discussed in this section.

2.6.1 Drying and firing shrinkage

Drying is the moisture loss of a newly moulded clay sample. The shrinkage resulting from this process of drying or firing of moulded sample is known as drying shrinkage. The bodies are dried very slowly to prevent warping, cracking, and to thoroughly prevent explosion during firing.

The rate at which the drying takes place during the shrinkage period depends on three factors: temperature of the surrounding air, moisture content of air, and velocity of air. The overall drying shrinkage can be reduced by controlling the initial water content.

Drying shrinkage is more commonly expressed in linear relations than volumetric. In reporting drying linear shrinkage the basis on which calculation is made must be clearly stated. The basis of calculation could be based on formed dimensions or dried basis. If based on formed dimension then, the percentage linear drying shrinkage (%LDS) is given by

$$\%LDS = \frac{Lo - Ld}{Lo} \times 100, \qquad (6)$$

waere Lo is the length of the sample when formed and Ld is the length of the dried sample. If on the other hand the calculation is based on dried dimension of sample then

$$\%LDS_D = \frac{Lo - Ld}{L_d} \times 100, \qquad (7)$$

Excessive shrinkage may cause warpage, distortion and/or possibly cracks of the moulded clay sample. It is imperative to have drying shrinkage as small as possible. The firing

shrinkage of moulded sample is normally based on dried unfired dimension. So that percentage linear firing shrinkage (LFS) is given by

$$\% \text{ LFS} = \frac{Ld - Lf}{Ld} \times 100, \qquad (8)$$

where L_f is the fired dimension.

2.6.2 Bulk density

Bulk density is the ratio of mass of material to its bulk volume. The close relationship between porosity and bulk density has been shown by Norris et al (1979) to justify the use of bulk density measurement to establish vitrification characteristics of fired bodies. The other density measurements used in testing are apparent solid density, true density and apparent specific gravity. Apparent solid density measures the density without the open pores in the moulded sample. The true specific density measures the density without both closed and open pores. The difference between the two provides an indication of the proportion of closed pores present in the moulded sample.

2.6.3 Porosity

Porosity is a phase that is almost always present in ceramics and is characterized by volume fraction of pores present. Apparent porosity is defined as the ratio of the volume of open pores to bulk volume of the material expressed as a percentage. Apparent porosity is determined by liquid immersion method and is directly related to many other physical

properties of a refractory including resistance to chemical attack.

For a given class of refractory, those with the lowest porosity have the greatest strength, thermal conductivity and heat capacity (Shreve et al 1977). However such refractories have low resistance to thermal shock. If V_o is the volume of open pores of a refractory and V_b is the bulk volume, its apparent porosity Pa may be calculated:

$$P_a = \frac{V_o}{V_b} \times 100 . \qquad (9)$$

2.7 Diffusion in Wasteforms

In addition to their uses as wasteforms, clay minerals are also likely to be further used in technology of radioactive waste disposal for construction of trenches for low level waste disposal and for back filling. Consequently, to understand and predict the migration of radionuclides and other species through wasteform (leaching) it is necessary to have some knowledge of the diffusion of aqueous ions through these porous material when they are saturated with water in general.

It is possible to define diffusion through a water saturated porous medium by parameters which characterize the transport. With the assumption that diffusion only takes place in aqueous phase and that only ions adsorbed on to (absorb into) the solid phases can move by desorption into liquid with which they are in equilibrium. For the above system (model) various different diffusion coefficients could be

defined being careful of the specific one being considered at any time.

In the free liquid phase the diffusion coefficient D is defined by Fick's law (Crank 1970, Perry et al 1975, IAEA 1970).

$$J_x = - D \frac{dc_l}{dx} , \qquad (10)$$

here C, is the concentration in the liquid, J_x is the flux per unit $\frac{\text{area}}{}$ of medium, D is diffusion coefficient in free liquid and x space coordinate measured normal to the section. When the liquid is constrained by pore structure of porous medium, a similar diffusion coefficient D_p is defined

$$J_x = D_p \frac{dc_l}{dx} , \qquad (11)$$

for diffusion coefficient within the pores. The diffusion coefficient within the pores D_p is less than (10) for two reasons: the diffusion paths, being constrained by the pores structure are full of twists and bends (tortuous) compared to *diffusion in the free liquid.*

- the diffusion path are unlikely to be of uniform cross-section and may become very constricted at certain points. This leads to constrictivity σ , and tortuosity τ to describe the porous medium (Atkinson 1984).

$$D_p = D \frac{\sigma}{\tau^2} \qquad (12)$$

Experimentally it is easier to work in terms of average flux per unit area of medium, leading to another diffusion coefficient

D_i called intrinsic diffusion coefficient (Atkinson 1984).

$$< J_x > = D_i \frac{dc}{dx} \qquad (13)$$

and

$$D_i = D \frac{\varepsilon \sigma}{\tau^2} \quad , \qquad (14)$$

where ε is the volume fraction of porosity. The quantity $\varepsilon \sigma^2 / \tau^2$ is known as the diffusibility of the medium D_L and is a particularly useful parameter to measure for characterizing the transport properties of the medium. Whilst ε and τ are properties of the porous medium alone, σ depends both on the porous medium and the diffusion process.

The release of nuclide from waste forms could be studied in a leach test. There are many variations of the test such as the soxhlet, "ISO", low flow, static and crushed equilibrium (Atkinson et al 1986). In a static test a cylinderical waste form is immersed in a container of leachant as sketched in Fig. 8 (a)

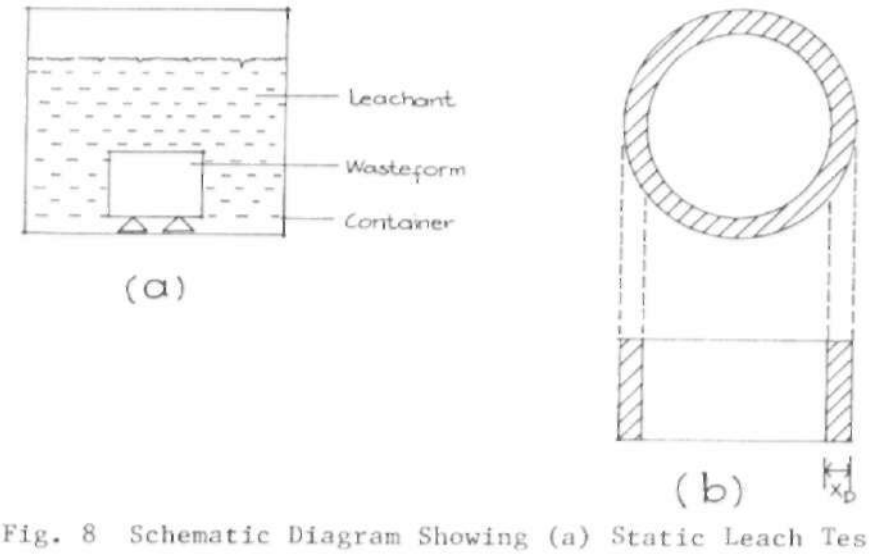


Fig. 8 Schematic Diagram Showing (a) Static Leach Test
(b) Depletion Depth

the results of such a test is expressed in terms of an equivalent depletion depth, X_D; given by the expression

$$X_D = \frac{A_I\ (t)}{A_s\ (o)} \cdot \frac{V_s}{S_s} \qquad (15)$$

where A_I (t) is the total activity which has been leached into the liquid up to time t, A_s (0) is the total activity of solid sample at t = o, V_s is the volume of the solid sample (including internal porosity), and S_s is its geometrical surface area. Thus X_D is the depth of sample (from the surface) in which the quantity of radionculide initially present was equal to that which has been leached into solution. This does not necessarily imply that there is no radionuclide present within this depth after leaching, since this depends on leaching mechanism. Measured mass of radionuclides may be related to the activities as follows: The initial mass of radionuclide in waste form

$$M_o \propto A_s(0). \qquad (16)$$

The leach rate R $= \frac{M_o - M_t}{S_s t}$, (17a)

where M_t is the mass of radionuclide in wasteform at time t.

$$M_o - M_t = R \cdot S_s t \cdot \propto A_L\ (t) \qquad (17b)$$

From Equations (15), (16) and (17b)

$$X_D = \frac{R\ S_s t}{M_o} \cdot \frac{V_s}{S_s},$$

$$X_D = \frac{R \cdot t}{\rho a}, \qquad (18)$$

where ρ_a is the apparent density of porous medium defined by

$$\rho_a = \frac{M_o}{V_s} \tag{19}$$

For porous materials, the kinetic of leaching often approximate to those of a diffusion controlled process (Atkinson 1984, 1986). For such a process parabolic leaching kinetics is expected which may be characterized by an effective diffusion coefficient, D_{eff}

$$D_{eff} = \frac{\Pi}{4} \cdot \frac{X_D^2}{t} \tag{20}$$

Effective diffusion coefficient here is based on the average concentration of radionuclide within the waste form taking into account the reduction in intrinsic diffusion in the liquid phase by chemical sorption of radionuclide on the solid. The intrinsic diffusion coefficient D_i based on the concentration of radionuclide in the liquid phase is given by

$$D_i = \alpha D_{eff} \tag{21}$$

where α is given by

$$\alpha = \frac{< c >}{C_L} , \tag{22}$$

$< c >$ is the average concentration of radionuclide in the waste form and C_L is the average concentration in the liquid phase.

While D_{eff} characterizes the overall chemical and physical effects in the transport of the radionuclide in porous

material, α and D_i relate to chemical sorption and physical transport in the pores respectively. The equilibra are conveniently expressed as a distribution coefficient, α, describing the partitioning of radionuclide between the water-saturated solid sample and the surrounding liquid. In terms of the parameters measured in static test, α, is given by equation (Atkinson et al.1986),

$$\alpha = \frac{A_s(\infty)}{A_L(\infty)} \cdot \frac{V_L}{V_s}, \qquad (23)$$

$$\alpha = \frac{M_s(\infty)}{M_L(\infty)} \cdot \frac{V_L}{V_s} \qquad (24)$$

and is sometimes used to describe diffusion and chemical interactions in porous media.

The other approach in studying the diffusion process is from a leach rate perspective. In this case diffusion process is taken to have a leach rate obeying Fick's first law (IAEA 1970)

$$\frac{Q}{t^{\frac{1}{2}}} = C^{te} \qquad (25)$$

where Q is the total activity entering the solution from unit surface area, t is period of time, and c is the concentration. The diffusion coefficient is given by

$$D = \frac{\left(\frac{Q}{t^{\frac{1}{2}}}\right)^2}{\quad}, \qquad (26)$$

where C_o is the concentration of radionuclide material in the mixture.

$$\text{Leach rate, } R = \frac{\text{activity leached}}{\text{total activity}} \Big/ \left(\text{surface area of sample} \times \text{mass of sample} \times \text{time}\right)$$

relating above relation to mass "leaching"

$$R = \frac{\text{mass leached}}{\text{initial mass}} \Big/ \left(\frac{\text{surface area}}{\text{mass}}\right) \text{time}$$

$$= \frac{-\frac{dm}{m}}{S_s \int m\,dt}$$

$$-dm = R\,S\,dt$$

$t = 0 \quad m = m_o$ = initial mass of sample

$$M = M_o - R\,S_s\,t$$

$$R = \frac{M_o - M_t}{S_s t}$$

The equation is the same as equation (17a)

$$\text{But } Q = Rt \tag{27}$$

From equation (14)

$$D = \Pi \frac{R^2 t}{4\,Co^2}, \tag{28}$$

Rearranging equation (26)

$$R^2 = \left[\frac{4Co^2 D}{\Pi}\right] \cdot \frac{1}{t}, \tag{28a}$$

While equations (18) and (20) gives

$$R^2 = \left[\frac{4 D_{eff} \rho^2}{\Pi}\right] \cdot \frac{1}{t}. \tag{29}$$

CHAPTER THREE

EXPERIMENTAL

The experimental procedures used in the course of this study are described in this chapter. A description of the method of sample preparation and the procedure for mineralogical characterization by cation exchange capacity and x-ray diffraction is presented. The method used in determining the pfefferkorn test, density, porosity and dimensions of fired sample are explained. Detailed reports of equilibration, drying and calcination experiment are given. Finally the method used in studying leach test is described.

3.1 Sample Preparation

Large lumps of clays were broken up by hand and ground by employing mechanical grinder with desired sieve (attached) fixed in place. After grinding, the clay was screened through 2mm (10 mesh) sieve and approximately one kilogramme of clay was selected by quartering. About half of the selected clay was sieved to ensure that all the sample was < 200 mesh particle size. The fine material was removed during crushing so that coarser particles can be crushed more efficiently, avoiding over-crushing. The two sets of < 60 mesh and < 200 mesh sieve sizes of clay samples were prepared for Bomo, Bukuru, White Zankara, Majaota, Onibode and Upkor clays.

3.2 Identification of Clay Minerals

Clay minerals exist for most part only in very fine particles and same form of the powder method usually must

be used to obtain complete characterization. It is very important that the identity of the materials to be used for waste treatment be known. As such characterization was done using total cation exchange capacity and x-ray powder diffraction as structurally sensitive tools.

3.2.1 Total cation exchange capacity

The total cation exchange capacities were determined for Bomo, Bukuru, white Kankara, Manjahota, Onibode, and Upkor clays for both raw and beneficiated samples using ammonium acetate method (Black 1965, Worrall (1963), Hesse 1971).

The Mettler balance model P163N was used for weighing. 10g of each clay sample was weighed in a bottle and mixed with 50ml portion of IN - ammonium acetate. The sample bottle was stoppered and agitated on mineralogical roller and allowed to stay overnight for equilibration. After the sample had stood overnight, the content of bottle was transferred to bunchner funnel fitted with moist Whatman No. 42 filter paper and filtered. The filterate was then leached six successive times with 25ml portions of ammonium acetate. The leachate was transferred to a volumetric flask where the ammonium saturated filterate on the buchner funnel was leached with 100ml methyl alcohol. Five portions of methyl alcohol were passed through the filter to remove excess ammonium acetate and, when the washings were free of ammonium ions, the clay was transferred to Kjeldahl distillating assembly. 30ml of IN sodium hydroxide, 300ml distilled water, 10ml of 10% sodium chloride, zinc granules and 5 drops of antifoam were added to clay and filter paper which

was quantitatively transferred in Kjeldahl flask. The flask was connected to the condenser and the liberated ammonia was steam distilled into 50ml of 4% Boric acid solution until 150 ml of distillate was collected. The distillate was titrated to give first tinge of purple with 0.2N hydrochloric acid, using 10 drops of methylene blue-methyl red mixed indicator and 3 drops of bromo-cresol green. Blank solutions were prepared same as sample except no clay.

The titrated figure was corrected for the blank and the cation exhcange capacities were calculated.

3.2.2 Organic carbon content

The percentage organic carbon was determined for twelve sample to ascertain what is solely responsible for the cation exchange capacity using Walkley-Black method (Black 1965, Hesse 1971).

2g of each clay sample was weighed into a 250ml erlenmeyer flask and 10ml portion of IN - potassium dichromate was added. The flask was swirled gently to disperse the soil. 20ml of concentrated sulphuric acid was added and then swirled gently until soil and reagent were mixed. The flask was placed on a sheet of asbsetos for 30 minutes. 100ml of distilled water was added and then the suspension was filtered into another erlenmeyer flask. The clear solution was titrated with 0.5N ammonium ferrous sulphate using 3-4 drops of indicator giving a colour change from green-dark green-blue-red.

A blank solution was made in the same manner but without clay, to standardize the ammonium ferrous sulphate using 10ml of IN potassium dichromate.

3.2.3 X-ray powder diffraction

X-ray powder diffraction is the most powerful and useful mineral identification tools. It has been used widely for structural analysis of crystalline solid studies. Collimated x-ray of fixed wavelength are permitted to strike a powdered sample. Only certain atomic planes of the crystalline substances in the sample will be in proper orientation relative to the incident x-ray beam such that Bragg condition of $n\lambda = 2d\sin\theta$ is satisfied.

where n - is the spectral order of diffraction

λ - is the wavelength of x-ray used

d - is the distance between the like planes of atoms in the substance

and θ - angle of diffraction

Because the wavelength of the X-ray is fixed, the variable is d, the interplanar spacings, which are unique to a given mineral structure. To identify the mineral phases in the sample, the d and intensity values were compared with diffraction data file for minerals (JCPDS 1974).

The Philips (PW1390) X-ray diffractometer used has the following parameters (characteristics):

Radiation	:	Cu Kα
Wavelength	:	1.5418^{o}A
Tube voltage	:	40 Kv
Tube current	:	30 mA
Exposure	:	37 minutes

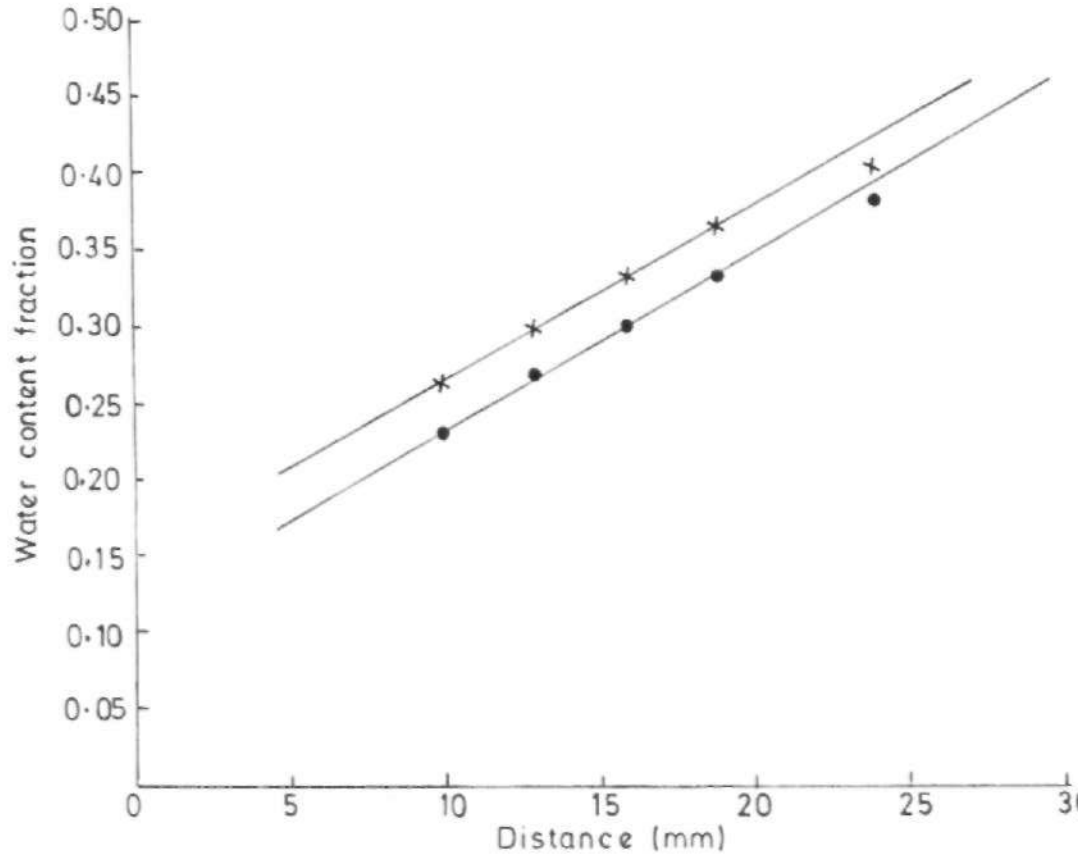
3.2.4 PfefferKorn test

On the basis of the foregoing investigation of cation exchange capacity, organic carbon content and crystal structure of Bomo, Manjahota, Kankara, Onibode, Bukuru, and Ukpor clay minerals; Bomo clay was chosen as the best for fixation of strontium for onward disposal, because it has properties close to clays already used in other countries. For example, it has the highest C.E.C of 50.50 meq/100g.

60g of Bomo clay sample was weighed into a container and known amount of water was added. The clay was rammed properly and made into cylinderical mould. The cylindrical mould was deformed in pfefferkorn apparatus by dropping the flat headed plunger weighing 780 gram on to it from a height of 6cm. The distance travelled was repeated for various moisture content taking 16, 18, 20, 22 and 24g of water for 60g of clay. A graph of distance travelled (pfefferkorn height) was plotted against moisture content (Fig. 9), the latter expressed as the percentage of water on weight of dry clay. The plasticity of the clay was determined being the moisture content corresponding with 15mm pfefferkorn height. The results were 32 and 29% for raw and beneficiated clay mineral respectively. These % water content were used for casting of moulded samples.

3.3 Cation Loading and Fixation

100g of raw and beneficiated Bomo clay were weighed into different polyethylene containers. Two standard solutions of 2.888 and 14.444 g/l strontium chloride were prepared. 250ml of 2.888g/l solution was added to the 100g clay in each polyethylene container. The caps were replaced.



FIG·9: RELATIONSHIP BETWEEN PERCENTAGE WATER CONTENT AND PFERFFERKORN HEIGHT

Reference samples were prepared for each of the clays using 250ml distilled water. The total weight of the 100g clay, 250ml portion of strontium chloride/distilled water and container was noted in each case. The mixtures were equilibrated by shaking on Edmund shaker for 24 hours at 25°C. After equilibration, the solid and solution phases were separated by sedimentation and filtration. The small portion of solution left on the clay was allowed to evaporate naturally. The weight of the mixture was monitored by weighing at interval until the water content correspond to the value determined by *Pfeffekorn test. The Sr-loaded samples were moulded in a* cylindrical moulds.

The solid samples after thermal treatment were prepared for leach test by placing in the dessicator for two hours. The dimensions and weight of solid samples were measured. The Atomic Absorption was used to determine the amount of strontium ion that went to the drain, hence amount fixed in the clay minerals. The same experiments were repeated for 14.444g/l concentration.

3.4 Drying and Firing of Samples

The moulded samples were dried naturally for 5 days at 25°C after which they were dried for 24 hours at 110°C in Gallenkamp electric oven. They were cooled to room temperature in a dessicator in which they were subsequently stored before firing. The Sr-loaded samples were heated at various temperatures 800-1000°C in a furnace (Carbolite Type FSF3 - PD), the soaking period being 4 hours in each case. Forty moulded

samples were prepared in all. The typical firing and cooling schedules are shown in Fig. 10. Dry to fired shrinkage: The height and diameter of three samples of each batch were determined with vernier calipers. The fired height and diameter of the same sample were determined after successful firing. The shrinkage length was calculated as a percentage of dry length and recorded.

3.5 Density and Porosity

Two samples of each of the raw and beneficiated Bomo clays were selected for test. The test samples were heated in boiling water for a period of two hours. The saturated mass of each of the test samples was determined after they were carefully wiped dry with moistened cloth. The suspended mass of each specimen immersed in water was determined and values for the dry mass, saturated mass, and suspended mass for each sample were used to calculate bulk density and apparent porosity in accordance with British Standard Institution.

3.6 Leach Test

The leach test that was used was a static one. The wasteform was immersed in 250ml leachate which was distilled water contained in a 500ml closed polyethylene container (Fig.11) and maintained at a temperature of 25 ± 5^{o}C. The chemical analysis of the solution was carried out using atomic absorption spectrometry (Unicam SP 1900). This was a non-destructive technique which was appropriate for use because experiments required the return of leachate after analysis.

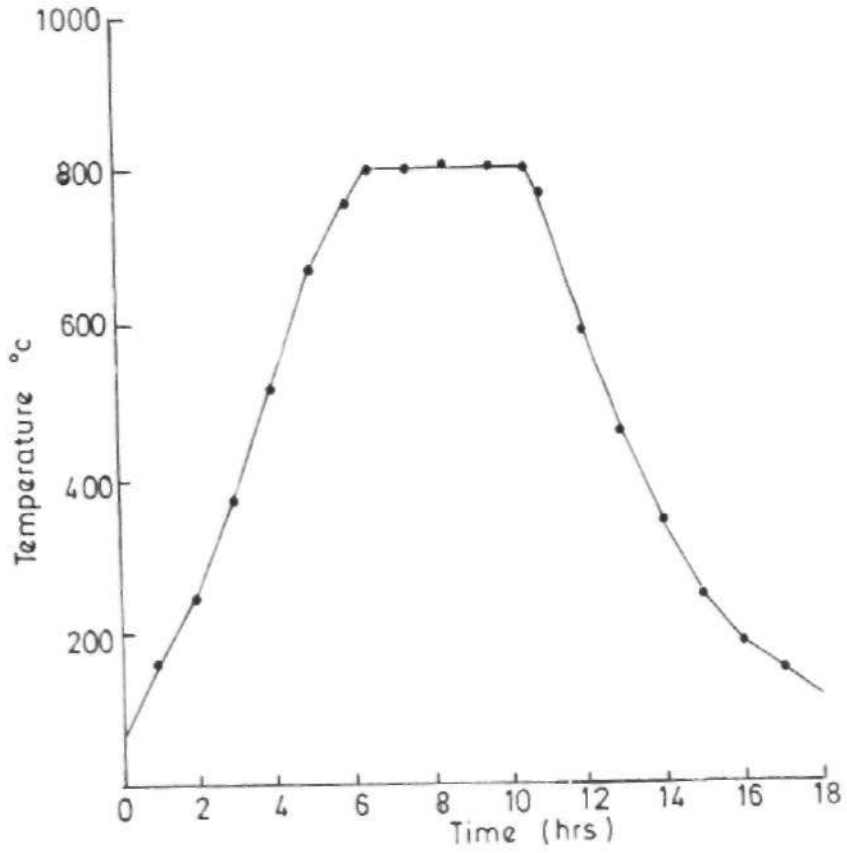


FIG.10: FIRING AND COOLING SCHEDULE FOR CLAY SAMPLES

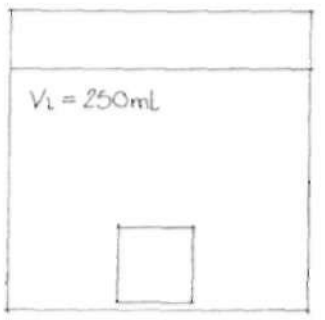


Fig. 11 *Static Leach Test*

The leachate was sampled for 25 days. The experiment was repeated for different cation loading and thermal treatment for both the raw and beneficiated samples. The ratio of volume of leachant to exposed "geometric" surface area of sample averaged 0.16m which was within the recommended range of 0.10 and 0.20 m (Atkinson et al.1984, 1986, ISO 1982).

CHAPTER FOUR

RESULTS AND DISCUSSION

The results of this investigation are discussed in this chapter. First, the cation exchange capacity (C.E.C.), organic carbon content and crystal structure of the clays are discussed. Then the shrinkage, fired weight loss, density, porosity, cation loading and leaching of the wasteforms are presented.

4.1 Cation Exchange Capacity

The quadruplicate determinations of the C.E.C. for the raw and beneficiated clay samples are given in Table A.1 in Appendix A. The mean values for the clays are presented in Table 14. Bomo clay had the highest C.E.C. of 44.45 and 50.50 meq/100g for the raw and beneficiated respectively. It was followed by Bukuru clay with C.E.C of 35.10 and 35.05 meq/100g for the raw and beneficiated respectively. The other clays: Kankara, Manjahota, Onibode and Ukpor clays, had rather low C.E.C. values of between 26.1 and 15.32 meq/100g for both raw and beneficiated. Bomo and Bukuru clays are highly plastic stoneware clays whereas the others are kaolins, thus the differences of the mineralogical composition of the two groups may explain their marked differences in C.E.C.

The effect of beneficiation on CEC was quite varied. While the CEC of Bomo and Ukpor clays increased, that of Onibode decreased on beneficiation. The changes in the

Table 14 Cation Exchange Capacity, Organic Carbon Content And Mineralogy Of Some Nigerian Clays

Laboratory number	Source/Location	*Mean Cation Exchange Capacity meq/100g	% Organic carbon content	Mineralogy by Cation Exchange Capacity	Mineralogy by X-ray diffraction
		RAW SAMPLES			
1	Bomo, Kaduna State	44.45	0.229	illite, Montmorillonite	Quartz, Kaolinite, illite-montmorillonite
2	Bukuru, Plateau State	35.10	0.239	Disordered Kaolinite	Quartz, Kaolinite
3.	Kankara, Katsina State	17.55	0.219	Kaolinite	Kaolinite
4.	Manjahota, Plateau State	18.80	0.259	Kaolinite	Quartz, Kaolinite
5.	Onibode, Ogun State	26.10	0.449	illite, Kaolinite	Kaolinite
6.	Ukpor, Anambra State	14.20	0.409	Kaolinite	illite, Kaolinite
		BENEFICIATED SAMPLES			
7.	Bomo, Kaduna State	50.50	0.419	Montmorillonite	Quartz, Montmorillonite
8.	Bukuru, Plateau	35.05	0.419	Disordered	Quartz, Kaolinite
9.	Kankara, Katsina	16.95	0.369	Kaolinite	Kaolinite
10.	Manjahota, Plateau State	19.45	0.479	Kaolinite	Kaolinite, illite
11.	Onibode, Ogun State	15.32	0.419	Kaolinite	Kaolinite, illite
12.	Ukpor, Anambra State	17.10	0.409	Kaolinite	Kaolinite

*Cation Exchange Capacity of Clay Samples (Appendix A)

CEC of Bukuru, Kankara, and Manjahota clays were small; their CEC were probably constant with beneficiation. The beneficiation removed the coarse materials of > 200 mesh from the raw clays. Such coarse materials may be of two types. One type may be the non-clay materials which are usually coarse. The second type were probably undispersed aggregates of clay particles since the individual clay particle are very fine, usually < 10 μm in size. Most non-clay materials have a low CEC and therefore contribute little to the total CEC of clays, whereas the fine clay particles have relatively large CEC. Therefore, the removal of non-clay material is expected to increase the CEC of clays and the removal of clay aggregates should decrease the CEC because of the increased proportion of fine non-clay materials. Anyone or both of these effects may have contributed to the changes in CEC observed. However, the removal of non-clay material was predominant for Bomo and Ukpor and the removal of clay aggregate was predominant for Onibode clay. For Bukuru, Kankara and Manjahota clays, the constancy of the CEC with beneficiation may be due to the inter play of the factors. The fact that little coarse material was removed for the Kankara and Onibode clays which were in powder form instead of hard lump also contributed.

4.2 Organic Carbon Content

The organic content for both raw and beneficiated clays are given in Table 14. Kankara clay had the least content of organic carbon of all the clays in both raw and beneificated forms. Of the raw samples, Onibode clay had the highest

content of organic carbon of 0.449% and of the beneficiated samples, Manjahota clay had the highest content of 0.479%. The organic matter is distributed among the coarse and fine fractions. Where it is constant, the distribution is equal but otherwise it is more or less in the fine fraction. The general trend was that the percentage organic carbon increased after beneficiation by drying sieving except for that of Ukpor which was constant and Onibode which decreased. It can be concluded that the major constituents which form the seat of the ion-exchange reactions are the clay minerals because of the low level of organic matter in the clays (<0.479%).

4.3 Crystal Structure

The mean CEC obtained for the clays (Table 14) were compared with standard ranges in literature for various clay minerals as in Table 13 (Johnson 1949, Grim 1953, Seedhouse 1957, Worall 1975 and Olphen et al. 1979) to deduce the mineralogy based on CEC as presented in Table 14. The CEC for most of the clays fell within the standard ranges for each of the mineral type except for Bukuru clay. The high CEC of Bomo clay suggested the presence of illite and montmorillonite. Bukuru clay might be disordered kaolinite in which partial replacement of its trivalent Al and divalent Mg produces an overall deficiency of positive charge which is balanced externally by other cations, for example Ca^{2+}, resulting in the high CEC ranged between 30-40 meq/100g (Worall 1975). However, the clay could also be a mixture of Kaolinite and illite and/or montmorillonite. Kankara, Manjahota, Onibode and Ukpor clays are essentially well

crystallized kaolinites. Both raw and beneficated Ukpor and Kankara gave this crystal structure. Raw Onibode and beneficiated Manjahota clays should contain in addition to Kaolinite, some amount of illite and/or montmorillonite because their CEC were slightly greater than that of pure kaolinite.

The x-ray powder diffractograms of clay minerals analysed are shown for each of the sample in Figs. 12 - 23. The principal crystalline phases in the samples were identified by using Search and Powder Diffraction Data Manuals of Joint Committee on Powder Diffraction Standard (JCPDS 1974).

From the x-ray diffraction pattern of a sample of raw Bomo clay (Fig. 12), Quartz was identified by the peaks giving d spacing of 3.34 and 1.98 ^{o}A; Kaolinite was identified by the peaks 2.33, 3.72 and 2.56^{o}A (cf 12 - 447) while illite-montmorillonite was identified with 4.53, 3.32, and 2.60 ^{o}A. Traces of muscovite minerals was also identified with 2.83, 2.98 and 3.30 peaks. For beneficiated Bomo clay mineral shown in Fig. 12 crystalline quartz was identified in the sample by peaks at 3.34; 2.45, and 2.12^{o}A. The peaks 3.23 and 2.49 were used to identifying montmorillonite. However muscovite mineral was removed after beneficiation, since it likely occurs in flakes or aggregate.

The x-ray diffraction pattern in Fig. 14 reveals that quartz is the principal crystalline species in Bukuru clays. Kaolinite was also identified in the sample by peaks 7.20, 2.28, 2.13 and 1.82^{o}A. There is also a trace of illites. The diffractograms Figs. 14 and 15 gave the same mineralogy of kaolinite, quartz and illite. There were no significant changes in the clay minerals present in both raw and benefici-

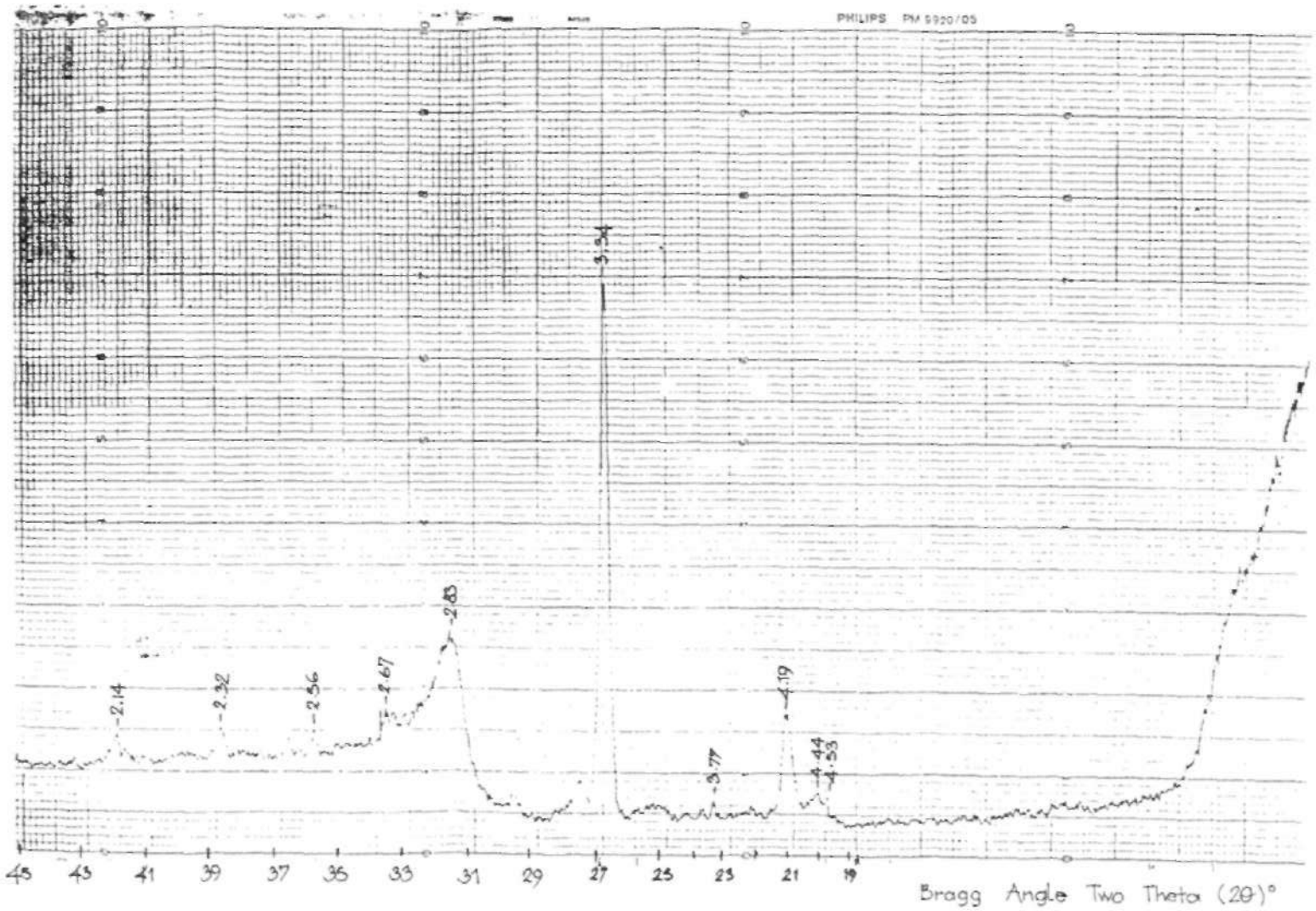


Fig 12... X-ray Diffraction Pattern of Raw Bomo Clay.



Fig 13... X-ray Diffraction Pattern of Beneficiated Bomo Clay.

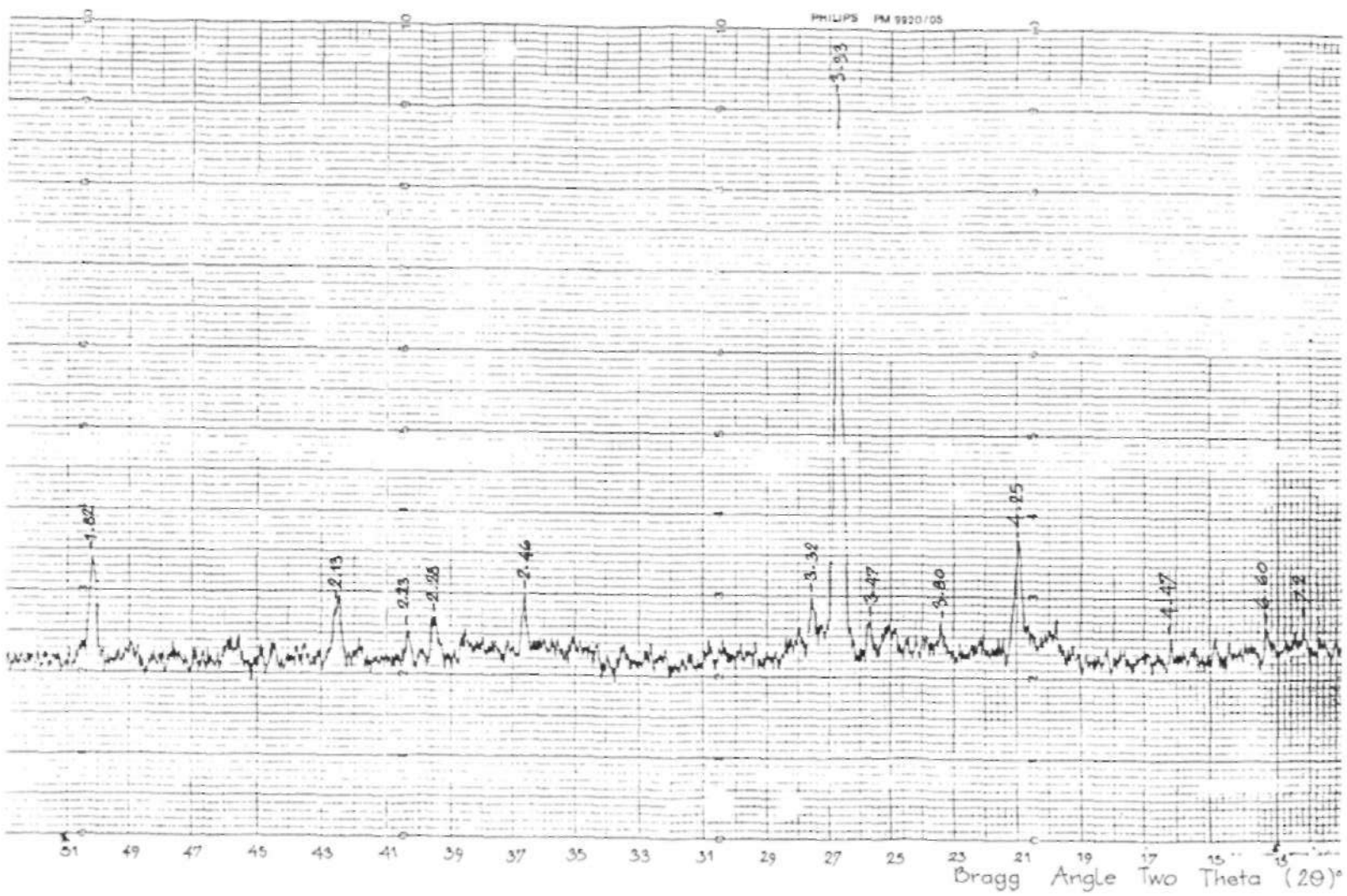


FIG. 14 ... X-ray Diffractogram of Raw Bukuru Clay.

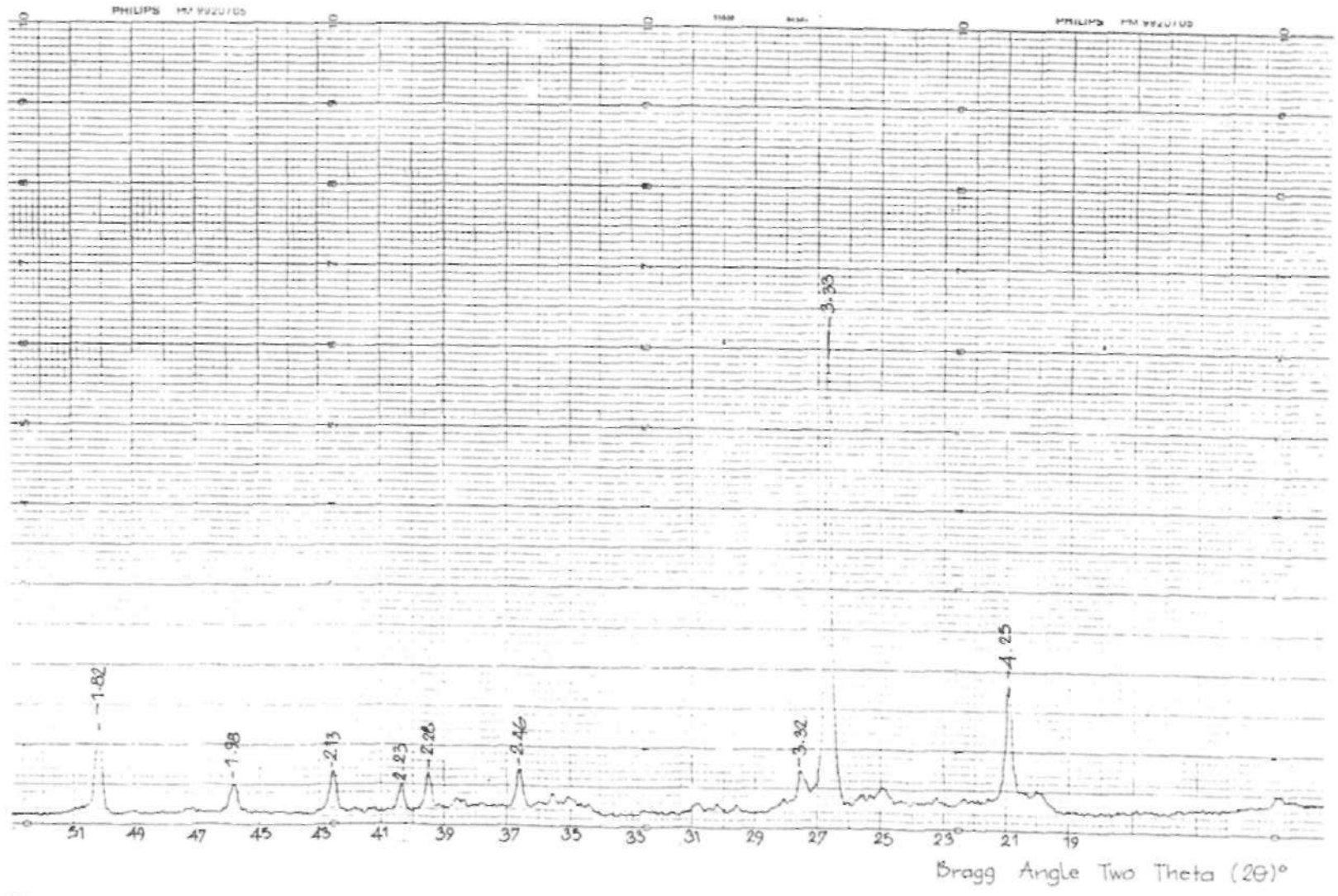


FIG. 15... X-ray Diffractogram of Beneficiated Bukuru Clay.

ated.

For raw Kankara clay (Fig. 16) the peaks at 7.2^{O}A, 3.56, and 2.33^{O}A correspond to kaolinite minerals and a trace of quartz identified by peaks 3.34 and 2.55. The x-ray pattern of beneficiated Kankara clay sample (Fig. 17) reveal that kaolinite is the principal mineral in the clay and this agreed with the results of differential thermal analysis (DTA) carried out on the same clay by Ahmed (1986).

The x-ray pattern of raw Manjahota clay minerals is shown in Fig. 18. Kaolinite was identified by peaks at 7.1, 3.56, 2.48 and 2.32 ^{O}A. Crystalline quartz was also identified by peaks at 3.33 and 4.23 ^{O}A. After benefication (Fig. 19) the x-ray diffraction pattern became more pronounced and showed that the clay contained kaolinite.

The raw Onibode clay mineral diffractogram (Fig. 20) showed the presence of kaolinite as principal constituents. The following peaks of 7.2, 4.35, 4.19, 3.59 and 2.56^{O}A were used in this identification. Trace of illite mineral was also identified. The same mineralogy contained in the raw sample was identified in the beneficiated (Fig. 21), however the peaks were more pronounced.

Figs. 22 and 23 shows raw and beneficiated diffractograms respectively of Ukpor clays. Kaolinite and illite were identified in both raw and beneficiated. However, the beneficiated clay sample revealed that kaolinite was the principal mineral in Ukpor clay. The mineralogical analysis of Ukpor clay thus obtained agreed with that of Nwajagu and Aneke (1986).

The clay mineralogy suggested by cation exchange values were generally confirmed by the x-ray diffraction studies.

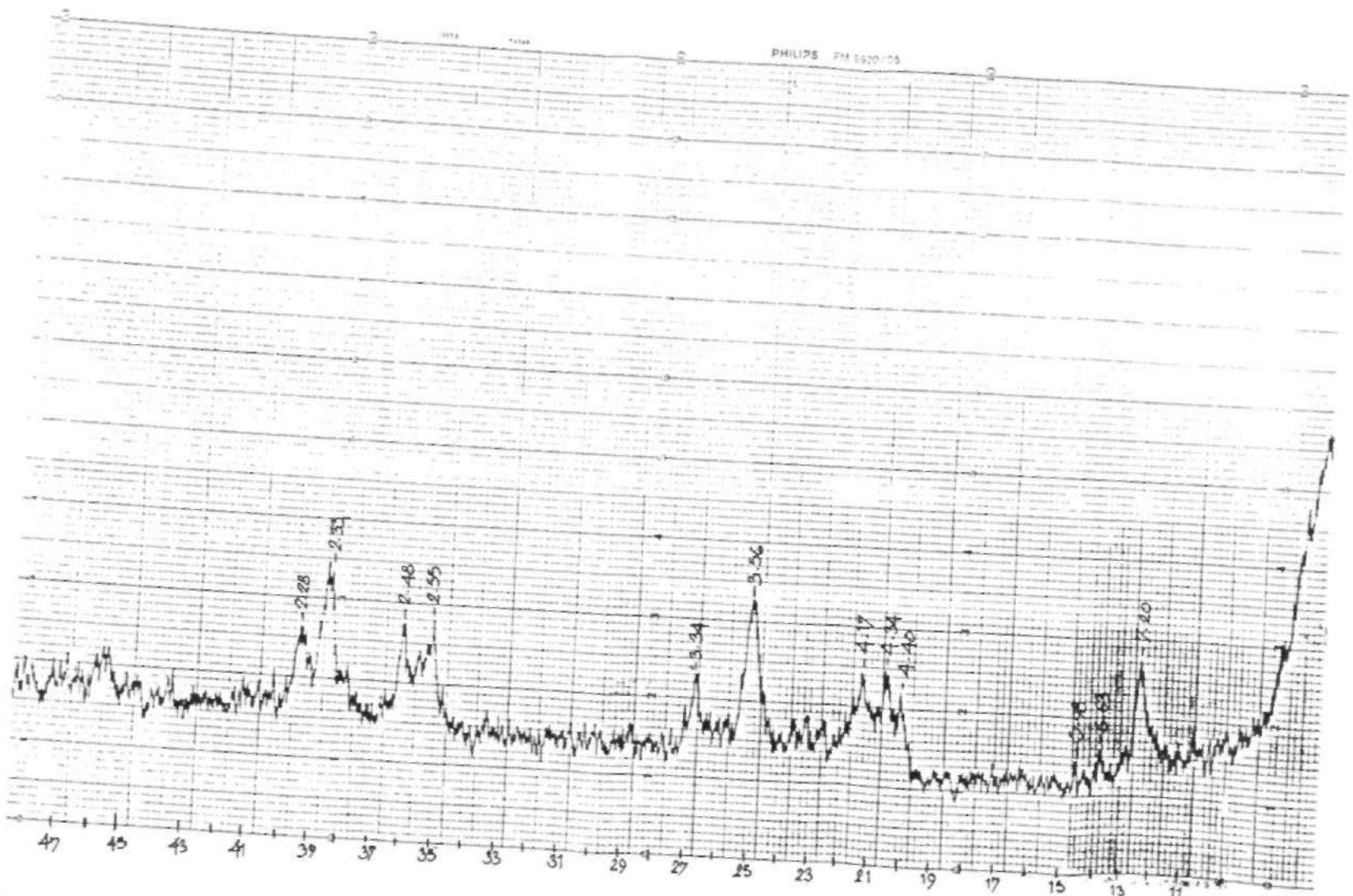


Fig. 16 ... X-ray Diffraction Pattern of Raw Kankara Clay.

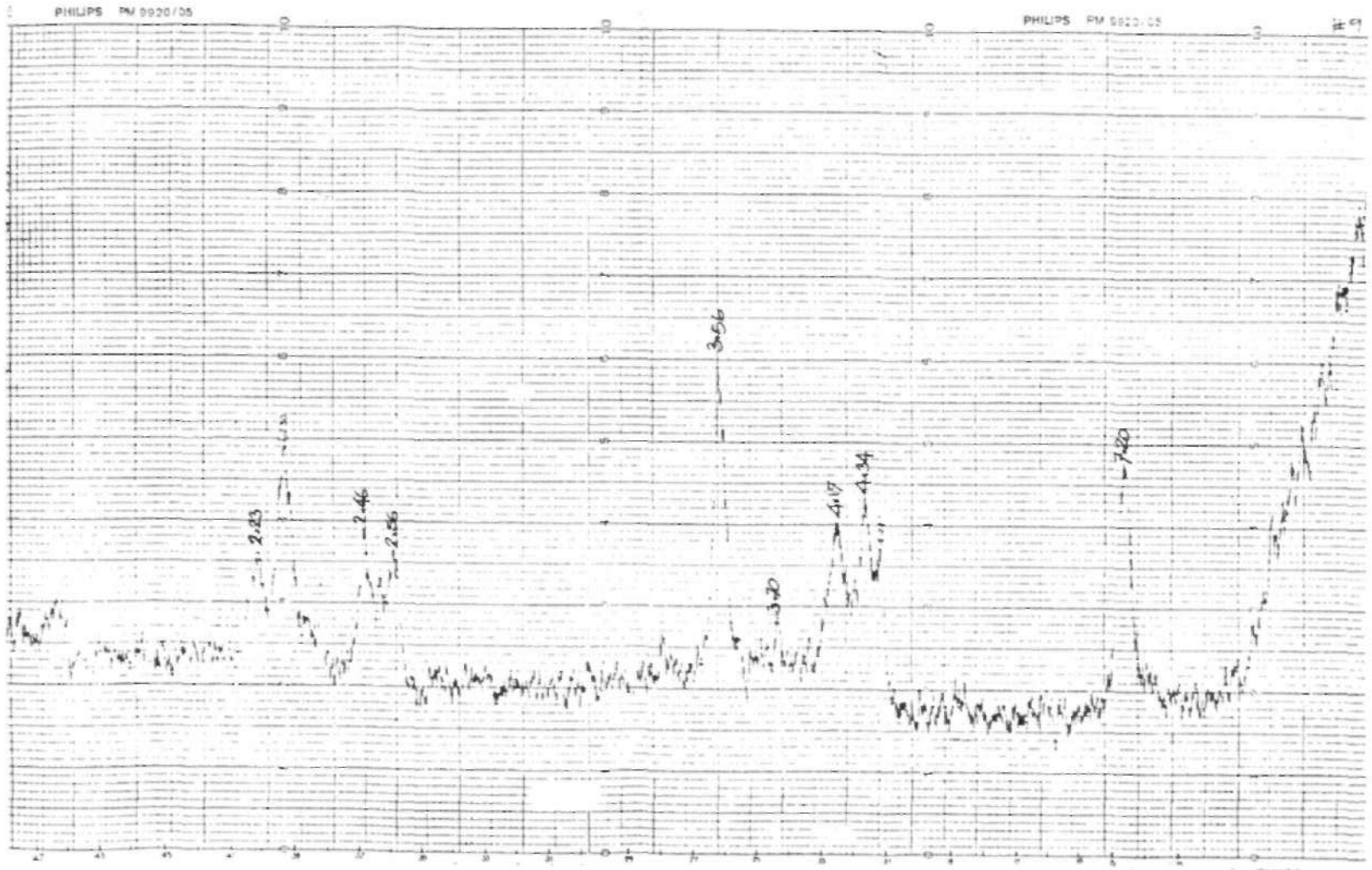


FIG. 17... X-ray Diffraction of Beneficiated Kankara Clay.

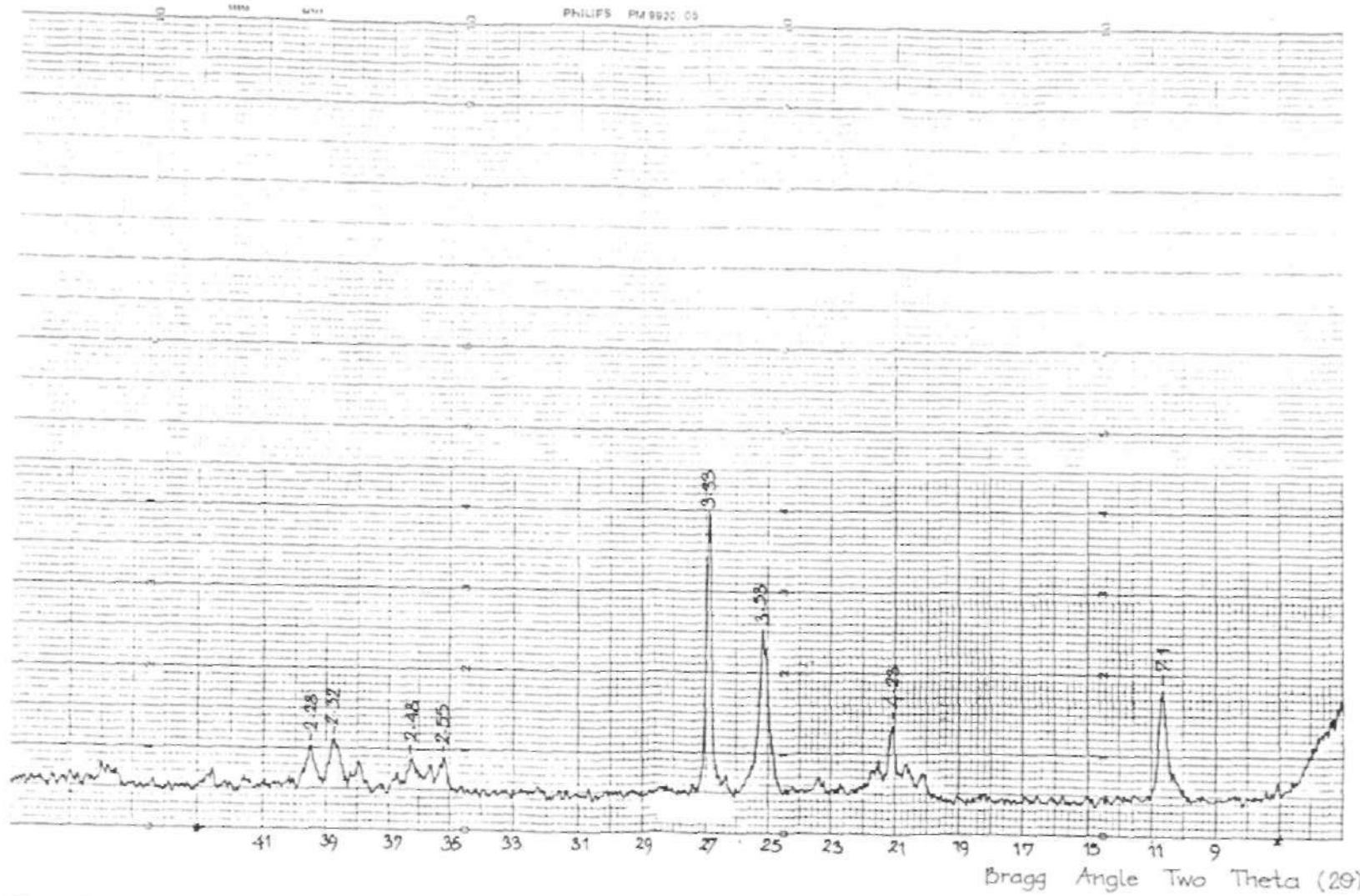


FIG. 18... X-ray Diffraction Pattern of raw Manjahota Clay

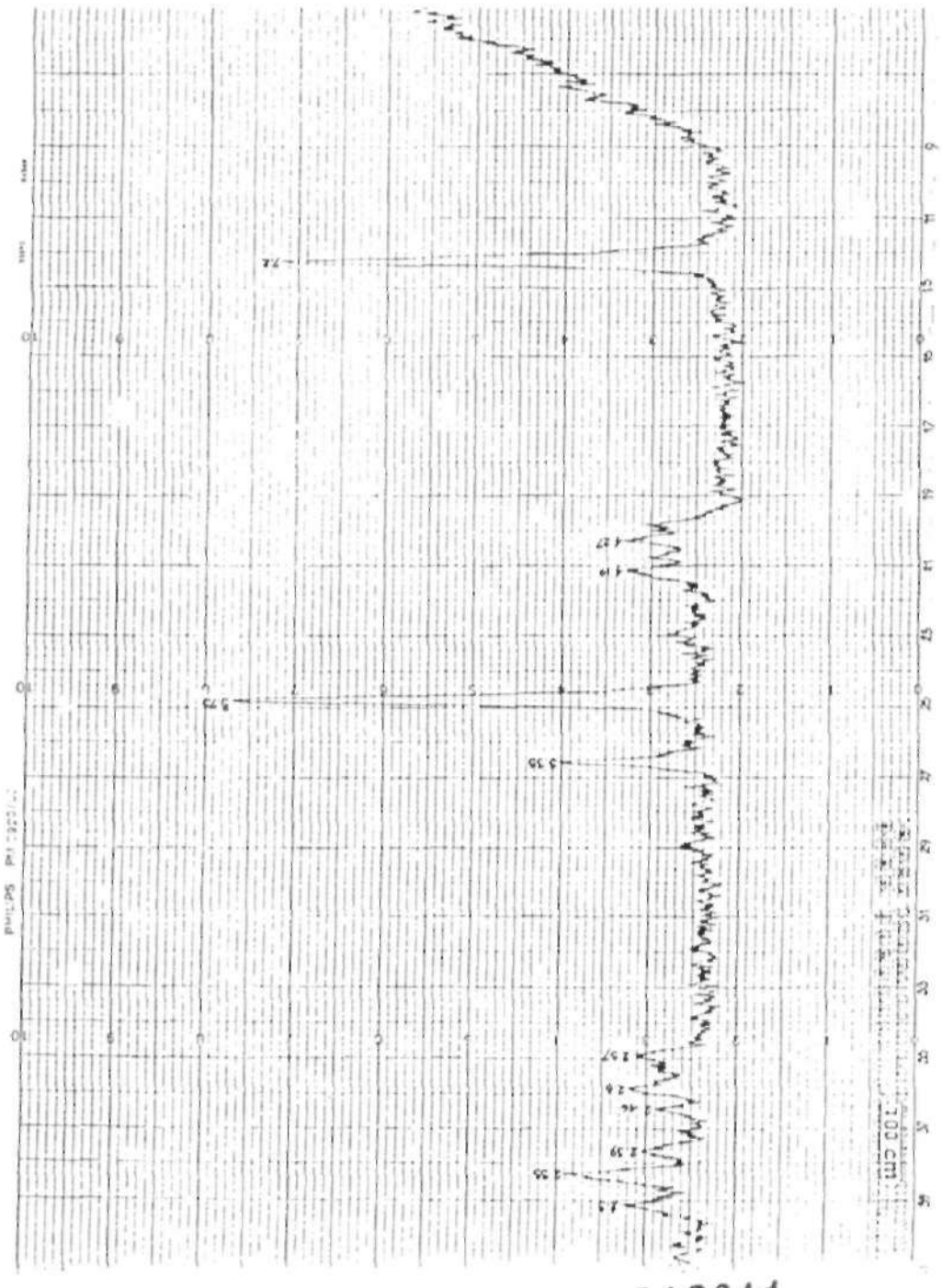


Fig. 19... X-ray Diffraction Pattern of Beneficiated Manjahota Clay.

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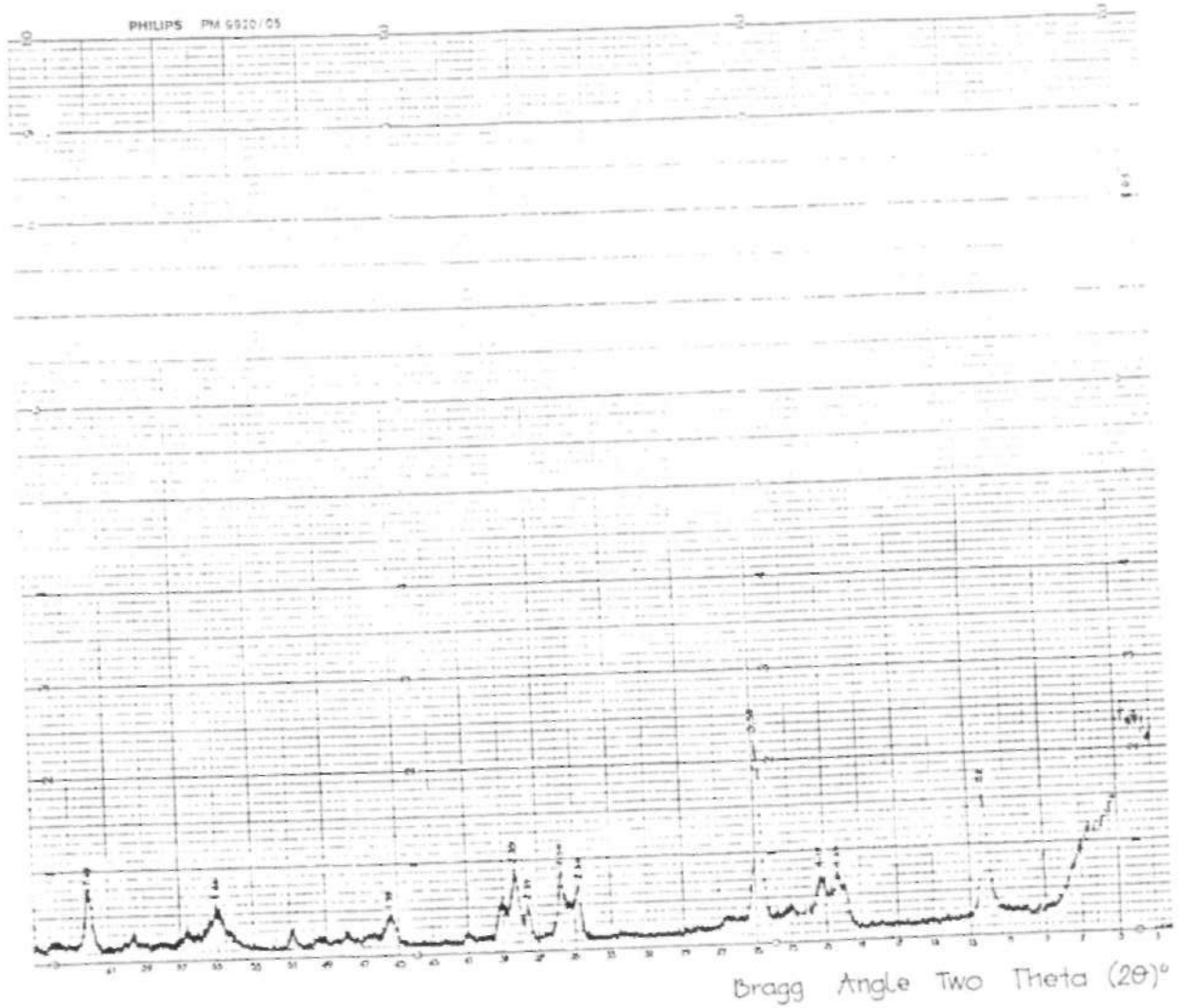


Fig. 20... X-ray Diffractogram of Raw Onibode Clay.

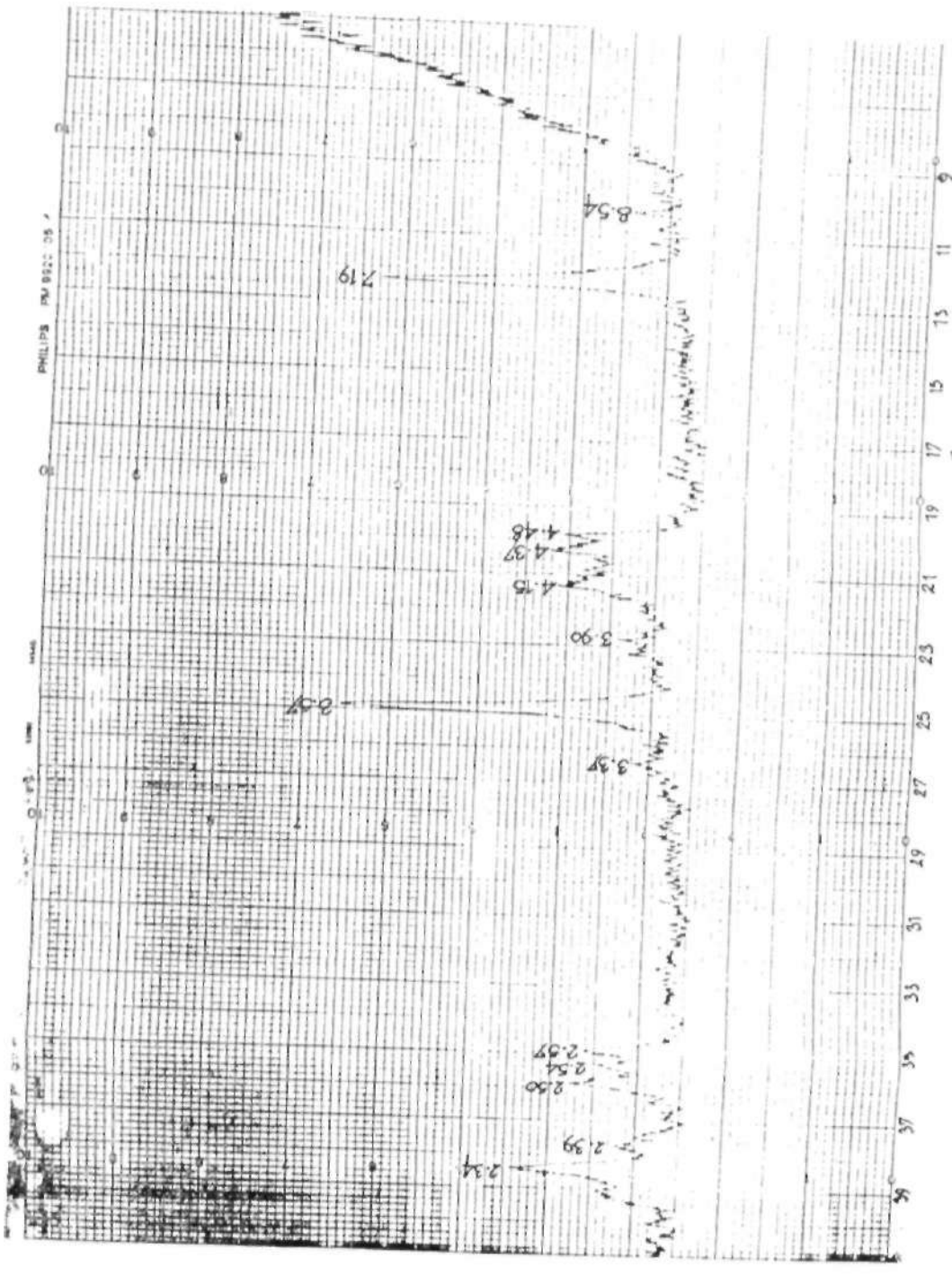


Fig. 21... X-ray Diffractogram of Beneficiated Onibode Clay.

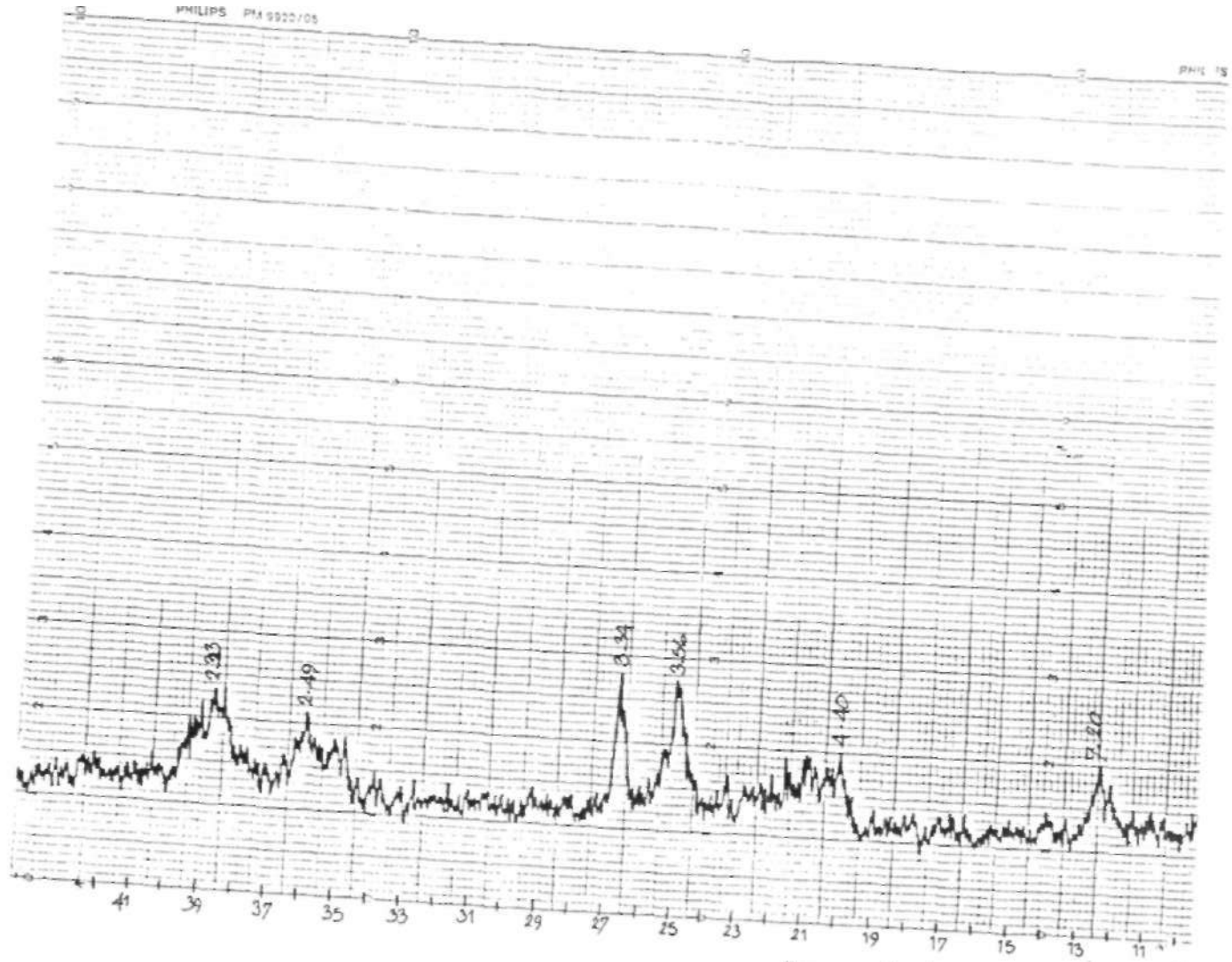


FIG. 22... X-ray Diffractogram of Raw Upkor Clay.

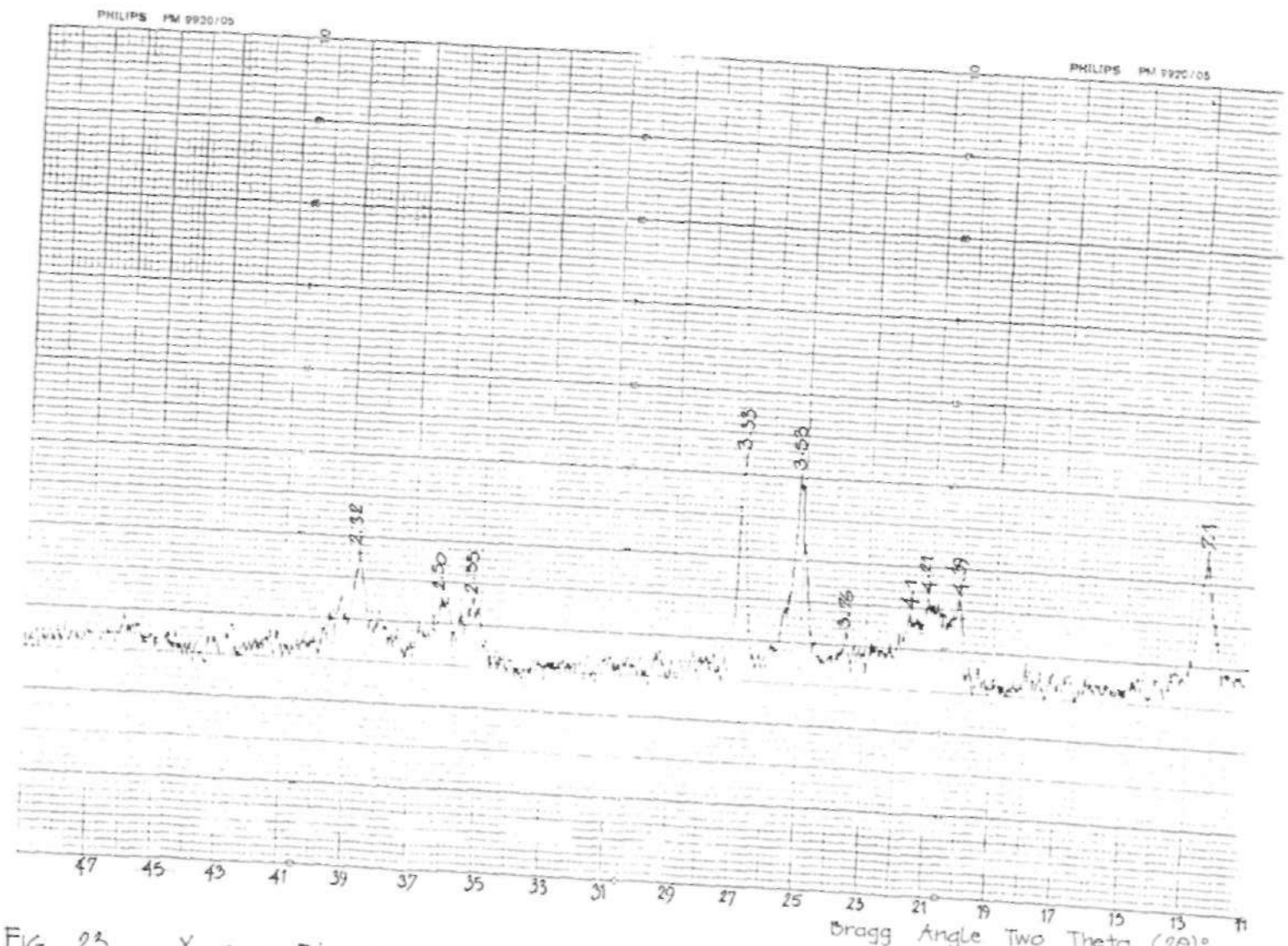


FIG. 23... X-ray Diffractogram of Beneficiated Upkor Clay.

In summary Bomo clay was found to contain quartz, illite and montmorillonite. However, the montmorillonite must be in small amounts because of the CEC value which was much less than expected for pure montmorillonite mineral. The raw sample had muscovite mineral which was removed in coarse fraction after beneficiation while Bukuru clay was predominantly quartz, and disordered kaolinite. The other clays: Kankara, Manjahota, Onibode and Ukpor are predominantly kaolinite, with illite and quartz minerals.

Thus Bomo clay appeared to have the best characteristics for fixation and disposal of radionuclides. The CEC was the highest at 50.50 meq/100g and it contained the mineral constituent, montmorillonite, most suitable for radioactive waste disposal.

4.4 Shrinkage And Fired Weight Loss

The linear drying shrinkage, fired shrinkages, fired weight loss, and soaking temperature for Bomo clay are given in Table 15 while the formed, dried and fired dimensions are presented in Table A.2 in Appendix A. The shrinkages of the fired bodies are based on formed dimensions (LDS_F) and dried dimensions (LFS_D). The shrinkages were generally higher for the beneficiated than for the raw samples due to the removal of non-plastic coarse fractions. A typical non-plastic in the raw samples is quartz which in ceramic bodies remains essentiall inert during heat treatment and acts as a skeletal framework to minimize shrinkage. Excessive shrinkage is undesirable in wasteforms because it could lead to cracks and/or warpage which will increase leaching.

The fired weight loss, calculated as a percentage of the dry weight for Bomo clay calcined at 800, 900 and 1000^{o}C

Table 15 Shrinkage And Fired Weight Loss of Clay Wasteforms

Sample number	$\%LDS_F = \frac{L_{fr}-Ld}{L_{fr}}$	$\%LFS = \frac{L_d-L_f}{L_d}$	% Fired Weight loss	Soaking Temperature ^oC
R1	0.36	0.35	4.92	
B1	0.58	0.58	5.23	
RL1	-	0.31	5.23	
BL1	0.85	0.30	5.39	800
RH1	-	0.29	5.51	
BH1	0.56	0.56	6.27	
R2	0.29	0.57	8.54	
B2	0.71	0.72	7.32	
RL2	0.30	0.30	7.32	900
BL2	0.58	0.59	8.08	
RH2	0.32	0.96	6.90	
BH2	0.59	0.90	8.33	
R3	0.29	0.59	7.83	
B3	0.59	0.59	8.44	
RL3	0.31	0.63	7.97	1000
BL3	0.28	0.56	7.33	
RH3	0.33	0.66	7.30	
BH3	0.54	0.54	8.64	

Key R - Raw Sample
B - Beneficiated sample
L - Low concentration of radionuclide
H - High Concentration of radionuclide

1 Calcined at 800^oC
2 Calcined at 900^oC
3 Calcined at 1000^oC

averaged 5.43, 7.75 and 7.92% respectively. A uniform trend of beneficiated clay giving higher values of weight loss than the raw was observed at different temperatures and concentrations. The fired weight loss represented the loss in weight from expelled hygroscopic and constitutional water contained in the clay and from gases resulting from decomposition reaction during firing. The weight loss appears to have levelled out with temperature as expected because of the completion of the relevant changes with temperature and time.

4.5 Density And Porosity

The bulk density and apparent porosity for the calcined clay wasteforms are shown in Table 16. The bulk density ranged between 1.80×10^3 and 1.94×10^3 kg/m^3 and the apparent porosity ranged between 17.2 - 24.2%. The values fall within the ranges obtained for fired clays of $1.96 - 2.36 \times 10^3$ kg/m^3 and 9 - 22.5% for bulk density and apparent porosity respectively (Chester 1973). They indicate poor densification. The apparent porosity of the raw clay decreased with increase in soaking temperature, showing increased sintering and vitrification, but it levelled out between 900 and 1000^{o}C. For both the raw and beneficiated samples, the bulk density was essentially constant with soaking temperature. This was probably because the densification processes were not intense enough in the temperature range of 800-1000^{o}C. The bulk densities of beneficiated samples were generally less than those of the raw samples at the same temperatures probably because the

Table 16 Bulk Density and Apparent Porosity of Calcined Wasteform

Sample number	Bulk Density $D_B \times 10^3$ kg/m^3	Percentage Apparent Porosity (Pa %)
R1	1.94	24.22
B1	1.88	20.00
R2	1.93	18.57
B2	1.87	17.26
R3	1.92	18.64
B3	1.84	18.22

denser coarse minerals such as muscovite (density = 2.76 - 3.0 x 10^3 kg/m^3) were removed from the samples leaving higher proportion of less dense, finer clay (density = 2.35 - 2.63 x 10^3 kg/m^3). Another factor could be the effect of higher initial green density resulting from the greater variation in sizes (fine, medium and coarse materials) in the raw sample.

fraction.

4.6 Cation Loading and Leaching Test

4.6.1 Cation loading and mass leached

The masses of strontium fixed initially and retained after 25 days of leaching are summarized in Table 17. For low strontium concentration of 1587.5 µg/g the mass fixed in clay mineral varied between 63.0 - 70.9 percent of the initial mass used for equilibration while 30.0 - 41.3 was obtained for the high concentration of 7875 µg/g. The highest percentage cation loading obtained in this work were 50 and 73 of the total CEC of Bomo clay for low and high concentration respectively. This may be compared with the results of Mistry et al (1965) where the highest cation loading corresponded to 70 and 75% of the total cation loading capacity for U.A.R. clays. The cation loading at high concentration agrees with that of Mistry et al.. The higher loading at higher concentration should be due to the increased driving force. This suggests preference for higher concentrations to fully utilise the exchange capacity of the clays. However, this has its limitations. A major one relates to the residual mass of radionuclide after equilibration.

The low concentration used for equilibration corresponded to 36.49 meq/100g or 70% of the total CEC. That of the high concentration was 181 meq/100g or 350% of the total CEC. The residual mass left in these solutions after equilibration were 30% of the initial for low concentration and 70% for high concentration. Hence considerable activity was left

Table 17 Mass of Strontium Fixed In Calcined Wasteform

Sample Number	Mass fixed in Wasteform M_2	Mass retained after 25 days of leaching M_3 µg/g	Percentage $\frac{M_2}{M_0}$ %	Percentage retention $\frac{M_3}{M_2}$ %
Low concentration (Mo) 1587.5 µg/g				
RL1	1100.0	1093.25	69.3	99.4
RL2	1125.0	1118.75	70.9	99.4
RL3	1037.5	1032.75	65.4	99.5
BL1	1000.0	991.0	63.0	99.1
BL2	1037.5	1032.75	65.4	99.5
BL3	1100.0	1096.50	69.3	99.7
High Concentration (Mo) 7875.0 µg/g				
RH1	2375.0	2371.5	30.0	99.8
RH2	3000.0	2995.75	38.1	99.8
RH3	3000.0	2995.75	38.1	99.8
BH1	3250.0	3230.0	41.3	99.3
BH2	2500.0	2488.25	31.7	99.5
BH3	3000.0	2998.0	38.7	99.9

unadsorbed at the higher concentrations which may require rather inconvenient recyclying and/or reprocessing.

The Bomo clay gave promising result of over 99% retention (Table 17) of strontium after 25 days of leaching. The result agrees with the findings of Hatch (1952), Amphlett (1956) and Spitsyn et al (1958) who studied clays calcined at temperature between 800-1000^{o}C, using distilled water, natural waters, and dilute nitric acid as leachant in their leaching tests.

The mass of strontium leached from the fired clay samples are plotted as a function of time for 25 days of study for the low and high concentrations in Figs. 24 and 25 respectively. The effects of firing temperature, concentration, raw and beneficiated clay minerals are shown. In both figures beneficiated clay mineral fired at 800^{o}C (Samples BL1 and BH1) gave the highest mass leached, while the same clays fired at 1000^{o}C (Samples BL3 and BH3) had the least at alltimes. The cummulative mass leached for 25 days ranged between 9.0 µg/g for sample BL1 and 3.5 µg/g for sample BL3 for the low concentration and 20 µg/g for sample BH1 and 2.0 µg/g for sample BH3 for high concentration. For beneficiated samples the mass leached decreased sharply as temperature increased from 800-1000^{o}C. These sharp changes cannot be attributed to the change in diffusion properties of the wasteform such as porosity solely as those changes were minimal due to poor densification. The changes are likely to be largely due to the actual fixation of the nuclide in the waste form by chemical reaction which increased with temperature. This view is supported by the findings of Spitsyn et al. (1958) on the fixation of Sr on montmorillonite. The workers observed that up to the beginning of alteration in the crystal lattice (T=800^{o}C), the fixation is controlled by the formation of slightly soluble chemical combinations of strontium and the adsorbent. Above 800^{o}C the process is determined by changes in the crystal lattice and by a gradual vitrification of the mineral. The changes of mass leached with temperature were smaller for the raw samples for low and high

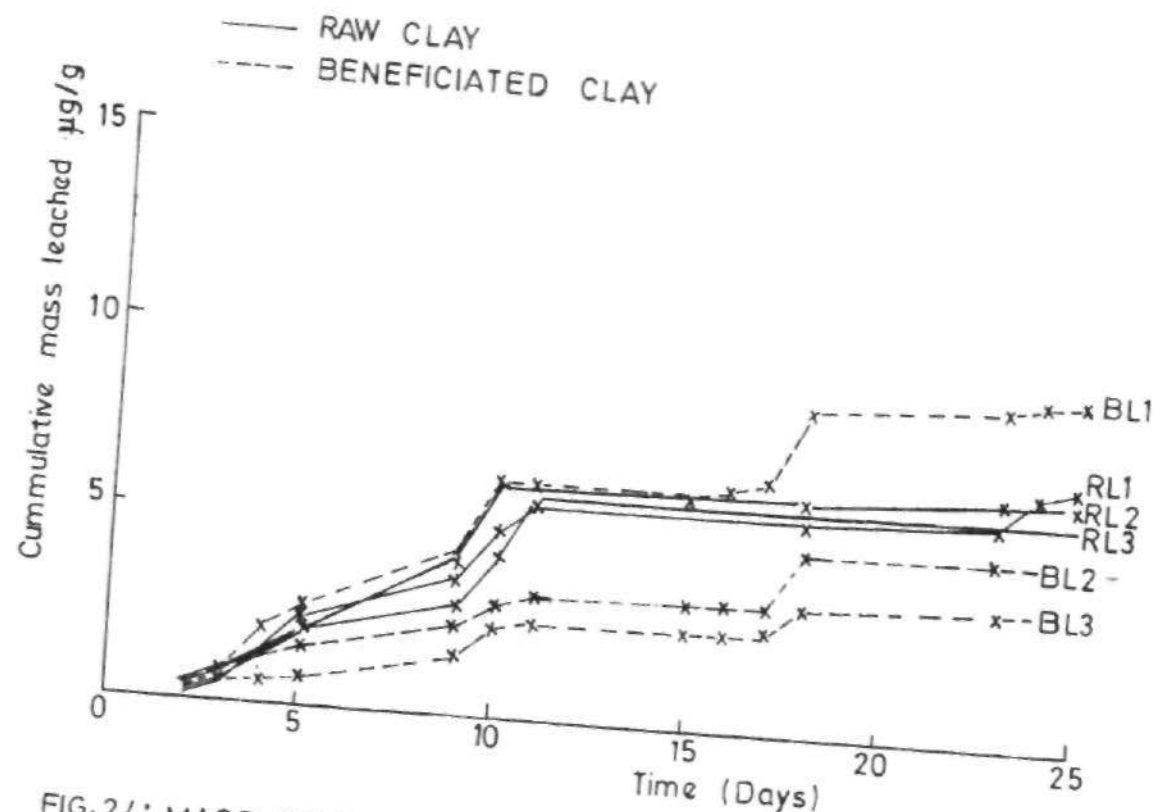


FIG. 24: MASS OF Sr LEACHED FROM CALCINED WASTEFORM AS A FUNCTION OF TIME (LOW CONCENTRATION)

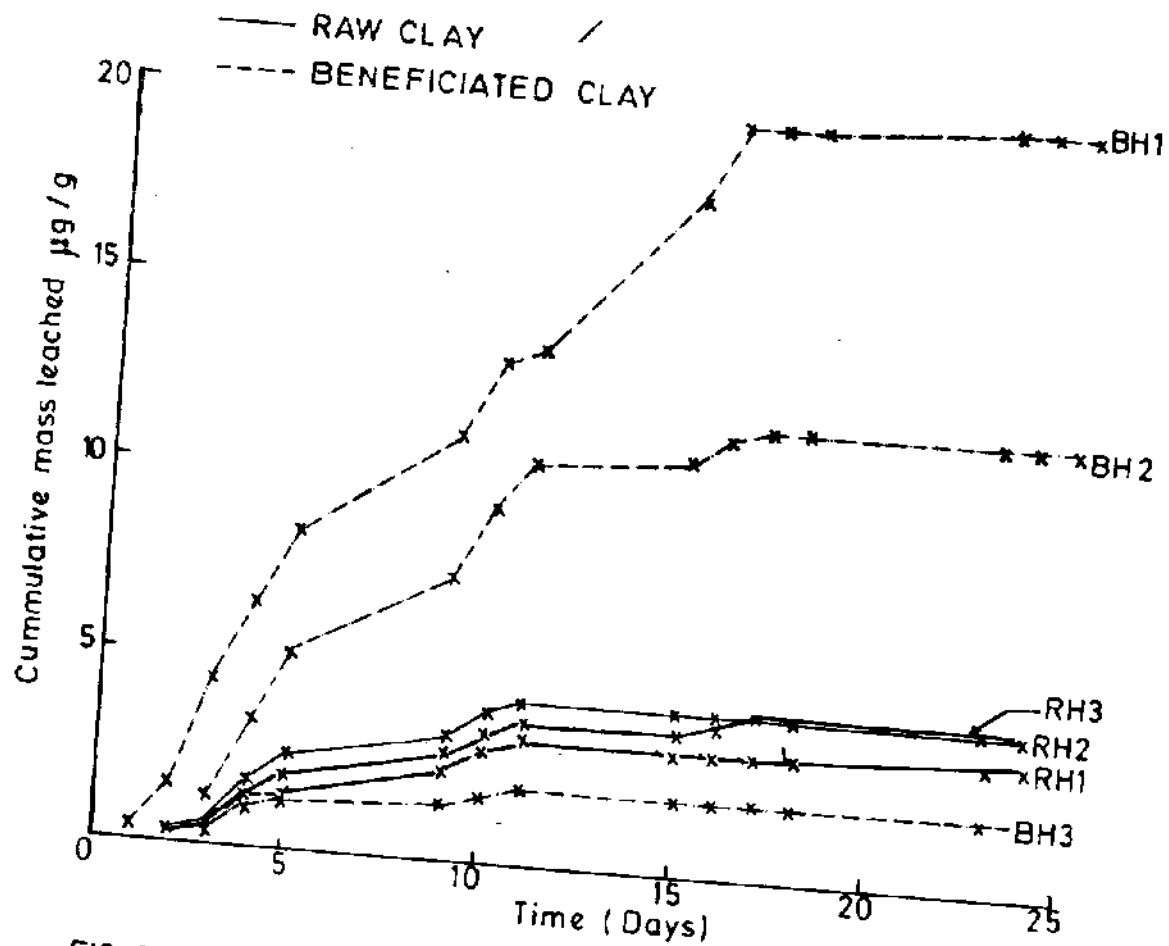


FIG. 25: MASS OF Sr LEACHED FROM CALCINED WASTEFORM AS A FUNCTION OF TIME (HIGH CONCENTRATION)

concentrations. There was generally a decrease with the temperature for low concentrations and times > 25 days, whereas the variation was rather erratic for high concentrations. Nevertheless, considerable fixation was achieved with the raw samples: the mass leached ranged between 3.5 and 6.5μg/g for temperatures between 800 and 1000°C and the two concentrations. In these raw samples two opposing effects might be operative. One is the presence of fluxing impurities in the coarse material which caused substantial fixation at lower temperatures. The other is the presence of coarse inert materials which do not contribute to fixation, lowering the fixation especially at higher temperatures. Thus the most fixation was obtained by beneficiating the clay and firing to 1000°C for both low and high concentrations. However, considerable fixation was obtained by using a raw clay even at 800°C. The additional costs of beneficating and firing to 1000°C need to be compared with the benefit of increased leach resistance in choosing the raw or beneficiated samples for fixation uses.

4.6.2 Depletion depth

The depletion depth of clay based waste form is plotted as a function of time for 25 days, for low and high concentration in Figs. 26 and 27 respectively. The values of depletion depth ranged from 0.268-0.321 μm for samples RL3 and RL2 respectively for low concentration (Fig. 26) and 0.599 μm for sample RH1 and 0.884 μm for sample RH2 for high concentration. The graphs thus obtained are similar to those of Atkinson et al.

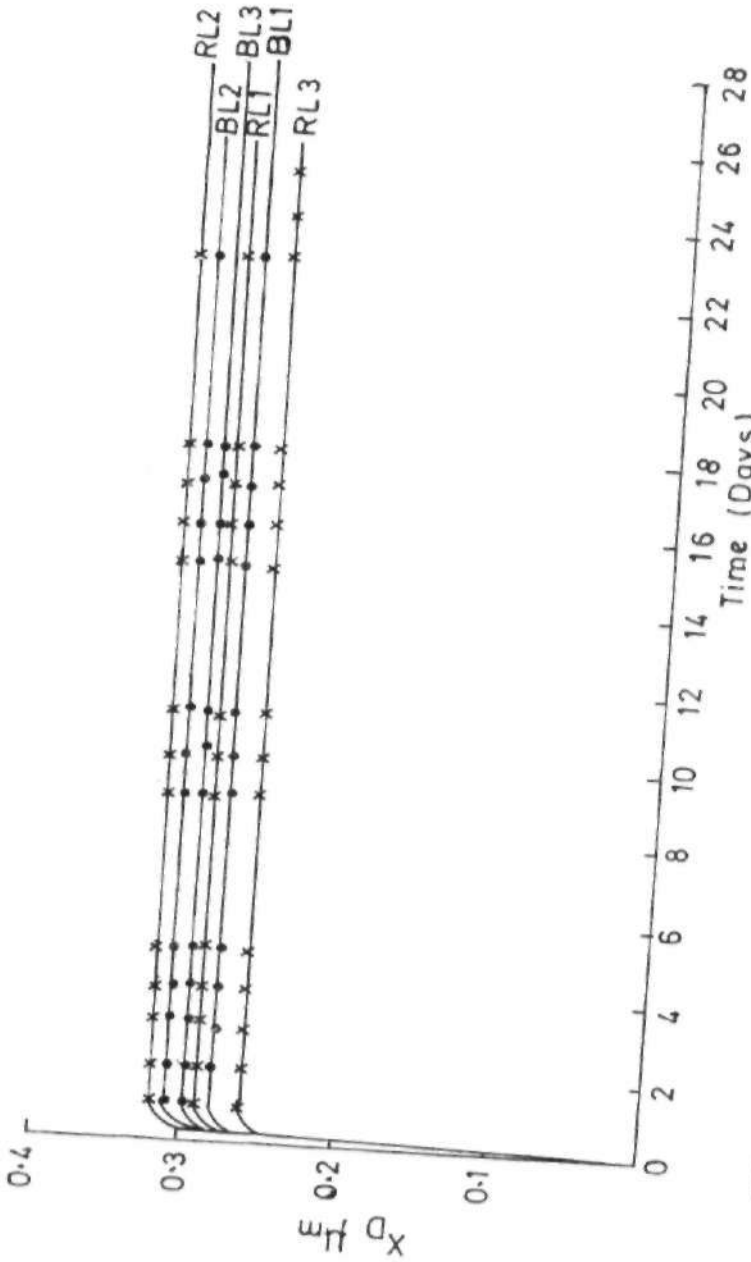


FIG. 26: DEPLETION DEPTH AS A FUNCTION OF TIME FOR LEACHING OF Sr FROM CALCINED WASTEFORM (LOW CONCENTRATION)

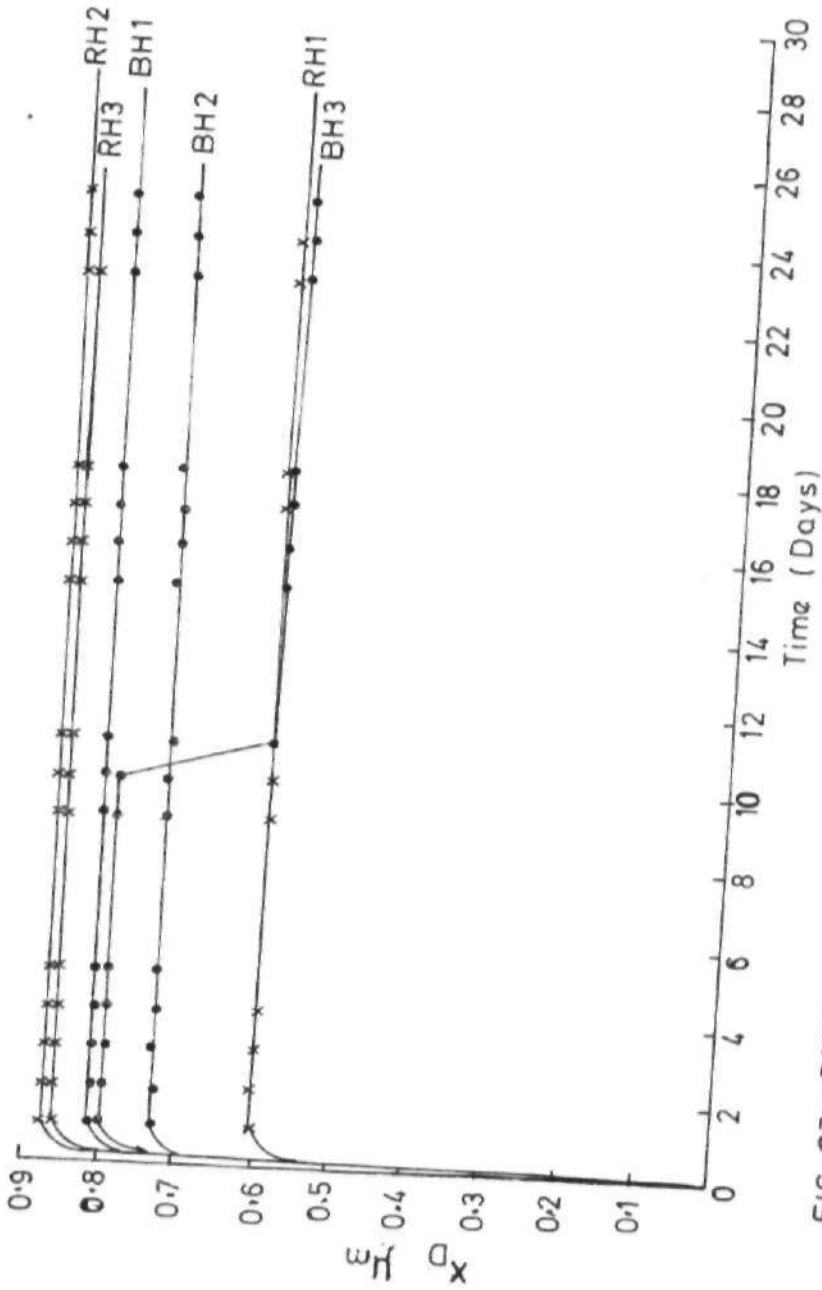


FIG. 27: DEPLETION DEPTH AS A FUNCTION OF TIME FOR LEACHING OF Sr FROM CALCINED WASTE FORM (HIGH CONCENTRATION)

(1986) who worked on leaching of cesium from OPC/clinoptilotile waste form in static study.

The depletion depth increased sharply and then levelled out on the average after one day for low concentration and 0.79 day for high concentration for the period of study. The higher driving force of high concentration is a possible explanation for the faster rise and levelling out compared with low concentration. However, the difference is not more than a quarter of a day in all cases. The reason for the strange leaching behaviour of BH3 (Fig. 27) was not obvious.

4.6.3 Leach rate

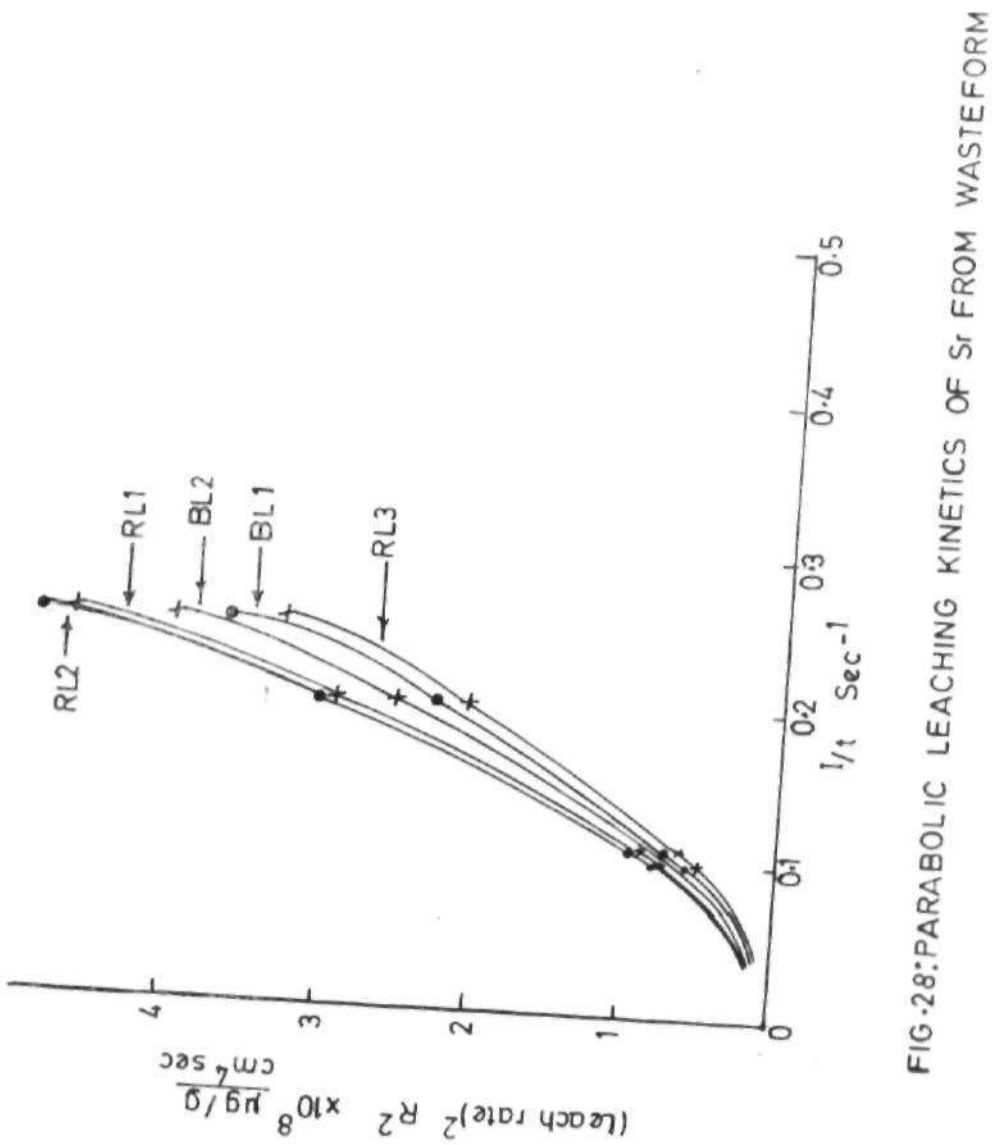
The leach rate of fired clay based wasteforms was monitored for 25 days for low and high concentration and a summary of results for these samples are presented in Table 18. A typical plot of leach rate as a function of time is shown in Fig. B.1 in Appendix B. Also a typical graph of the square leach rate as a function of reciprocal time (R^2 versus 1/t) is plotted in Fig. 28 for low concentration. The other plots are shown in Fig. B.2 in Appendix B. Curves, rather than straight lines were obtained, showing that the static leach test could not be described by parabolic leaching kinetics. However, plots of natural log (ln R) versus time - typical one's are shown in Fig. 29 - gave straight lines for long times indicating that the rate approximately obeyed the decay law given by

$$R_t = R_{to} \; e^{-\lambda t} \qquad (29)$$

where R_{to} is the amount leached at time t=0 (the constant

Table 18 Summary of Leaching Kinetics for Low and High Concentrations

Time in days	LEACH RATE, R X 10^{-4} $\mu g/g$ $cm^2 sec$											
	RL1	BL1	RH1	BH1	RL2	BL2	**RH2**	**BH2**	**RL3**	BL3	RH3	BH3
1	8.59	7.64	17.78	24.26	8.81	8.00	24.20	19.29	7.33	7.77	24.01	21.20
2	4.29	3.82	8.89	12.13	4.40	4.00	12.10	9.65	3.66	3.38	12.00	10.60
3	2.86	2.55	5.93	8.08	2.93	2.67	8.08	6.43	2.44	1.94	8.00	7.06
4	2.15	1.91	4.44	6.06	2.20	2.00	6.06	4.82	1.83	1.55	6.00	5.29
5	1.72	1.52	3.55	4.84	1.76	1.60	4.85	3.85	1.46	0.86	4.80	4.24
9	0.95	0.85	1.97	2.69	0.98	0.89	2.69	2.14	0.81	0.78	2.66	2.35
10	0.86	0.76	1.78	2.41	0.88	0.80	2.42	1.92	0.73	0.70	2.40	2.12
15	0.78	0.69	1.61	2.20	0.80	0.73	2.20	1.75	0.66	0.52	2.18	1.41
16	0.57	0.51	1.18	1.61	0.58	0.53	1.62	1.28	0.49	0.48	1.60	1.03
17	0.53	0.47	1.11	1.51	0.55	0.50	1.52	1.20	0.46	0.46	1.50	0.97
18	0.50	0.45	1.04	1.42	0.52	0.47	1.43	1.13	0.43	0.43	1.41	0.91
23	0.48	0.42	0.99	1.34	0.49	0.44	1.35	1.07	0.41		1.33	0.86
24	0.37	0.33	0.71	1.05	0.38	0.35	1.05	0.83	0.32		1.04	0.67
25	0.34			1.00 0.96	0.36 0.35			0.80 0.77		**0.34**		0.62



FIG·28: PARABOLIC LEACHING KINETICS OF Sr FROM WASTEFORM

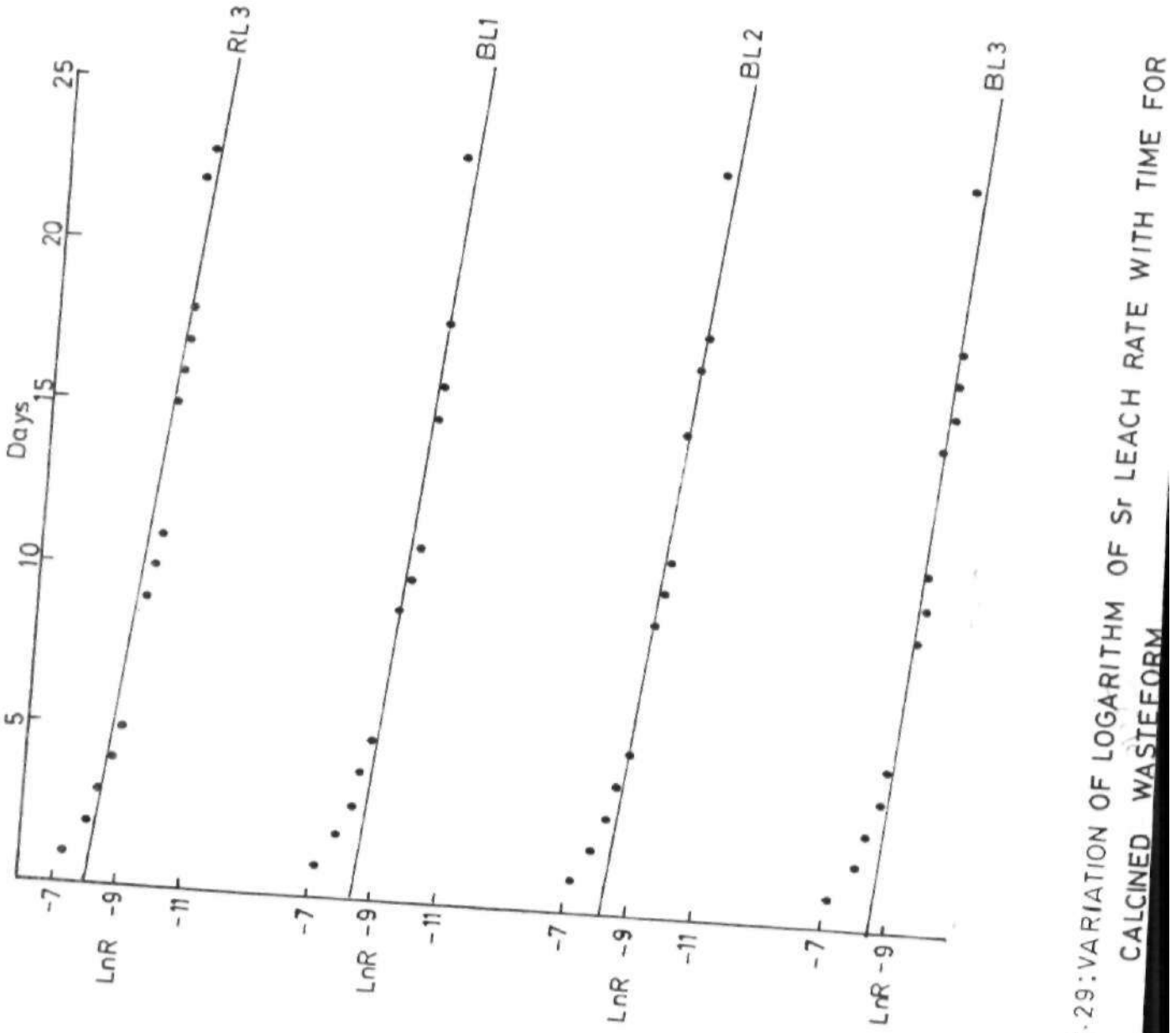


FIG. 29: VARIATION OF LOGARITHM OF Sr LEACH RATE WITH TIME FOR CALCINED WASTEFORM

depends on the initial concentration); λ is decay constant and t is time. It was also observed that 50% of the total amount leached out in 25 days had actually leached within 5 days. This was true for all the samples.

The decay constant, λ and constant R_{to} obtained by linear regression and the distribution coefficient, α , are presented in Table 19. The values of R_{to} and α obtained for low concentration were generally smaller than those for high concentration, because of the lower dirving force in the former. There was no particular pattern in the variation of λ with materials or temperature. The distribution coefficient generally increased with increase in temperature. This shows that the higher the fixation the higher the value of distribution coefficient, which explains low leachability of samples BL3 (Figs. 23 and 24). The values thus ranged between 1632 for sample BL1 and 4516 for sample BL3 for low concentration and 2566 for sample BH1 and 20478 for sample BH3 for high concentration. The range of values of the distribution coefficient obtained was within those obtained by Atkinson et al. (1986) and Umar (1987) working on cement and clays respectively (Table 20).

Table 19 Parameters Used In Characterizing Leaching of Wasteform

Sample Number	Mean Depletion depth μm	R_{to} $x10^{-4}$	λ $x10^{-6}$ sec^{-1}	distribution coefficient, α
RL1	0.290	4.52	1.28	2575
BL1	0.281	2.25	1.11	1632
RH1	0.817	7.62	1.42	10768
BH1	0.599	7.10	1.19	2566
RL2	0.321	5.0	1.37	2791
BL2	0.306	2.80	1.37	2556
RH2	0.884	11.13	1.46	11083
BH2	0.737	6.11	1.04	3247
RL3	0.268	3.35	1.19	3266
BL3	0.298	2.49	1.13	4516
RH3	0.878	7.10	1.05	11748
BH3	0.814	7.46	1.29	20478

Table 20 Distribution Coefficients Measured By Other Workers

Wasteform (Sr)	Distilled Water	
	Umar (1987)	Atkinson et al (1986)
Natural Surrey Earth	1232	-
Wyoming Bentonite	615	-
Natural illite	415	-
Natural Fulbent	882	-
Ammonium Surrey	1572	-
Sodium Surrey	578	-
Calcium Surrey	1464	-
Magnesium Surrey	1138	-
Calcium illite	430	-
Magnesium illite	509	-
Soil 1	21137	-
Soil 2	1278	-
Sand	34	-
Peat	142658	-
OPC	-	150
OPC/Clinoptilolite	-	1500

CHAPTER FIVE

CONCLUSION

Based on the results obtained from this study the general conclusions are as follows:

1) Bomo Clay had the highest CEC of 44.45 and 50.50 meq/100g for raw and beneficiated respectively. It was followed by Bukuru clay. The other clays: Kankara, Manjahota, Onibode and Ukpor clays, had rather low CEC values of between 26.1 and 15.32 meq/100g for both raw and beneficiated.

2) The major constituents which form the seat of the ion-exchange reactions are the clay minerals because of the low level of organic matter in the clays (< 0.479%).

3) The clay mineralogy suggested by CEC values were generally confirmed by the x-ray diffraction studies. In summary, Bomo clay was found to contain quartz, illite, and montmorillonite. However, the montmorillonite must be in small amounts because of the CEC value which was much less than expected for pure montmorillonite mineral. The raw sample had muscovite mineral which was removed in coarse fraction after beneficiation while Bukuru clay was predominately quartz and disordered kaolinite. The other clays: Kankara, Manjahota, Onibode and Ukpor were predominatly kaolinite, with illite and quartz minerals.

4) Bomo clay had the best characteristics for fixation of radionuclide and disposal among the clays studies because it contained the most suitable mineral constituent, montmorillonite.

5) The shrinkages of waste forms were generally higher for the beneficiated than for the raw samples.

6) The bulk density ranged between 1.80×10^3 and 1.94×10^3 kg/m^3 and the apparent porosity ranged between 17.2 - 24.2%. Bulk densities of beneficiated samples were generally less than those of raw samples.

7) For low strontium concentration of 1587.5 μg/g the mass fixed in clay mineral varied between 63.0 - 70.9 percent of the initial mass used for equilibration while 30.0 - 41.3 was obtained for the high concentration of 7875 μg/g.

8) The highest percentage cation loading obtained in this work were 50 and 73 of the total CEC of Bomo clay for low and high concentrations. The residual mass left in these solutions after equilibration were 30% of the initial for low concentration and 70% for high concentration.

9) Bomo clay gave promising results of over 99% retention of strontium after 25 days of leaching.

10) The cummulative mass leached for 25 days ranged between 9.0 μg/g for sample BL1 and 3.5 μg/g for sample BL3 for the low concentration and 20 μg/g for sample BH1 and 2.0 μg/g for sample BH3 for high concentration. For beneficiated sample, the mass leached decreased sharply as temperature increased from 800-1000^{o}C. The most fixation was obtained by beneficiating the clay and firing to 1000^{o}C for both low and high concentrations. However, considerable fixation was obtained by using a raw clay even at 800^{o}C.

11) The values of depletion depth ranged from 0.268 - 0.321 μm for samples RL3 and RL2 respectively for low concentration and 0.599 μm for sample RH1 and 0.884 μm for sample RH2 for high concentration.

12) Leaching approximately obeyed natural decay law:

$$R = R_t \cdot e^{-\lambda t}$$

The values of R_{to} and λ obtained for low concentration were

generally smaller than those for high concentration. They increased with increase in temperature. The values of α ranged between 1632 for sample BL1 and 4516 for sample BL3 for low concentration and 2566 for sample BH1 and 20478 for sample BH3 for high concentration.

CHAPTER SIX

RECOMMENDATION

1. Bomo Clay has been successfully studied for fixation and disposal of strontion ion, however further studies could be aimed at optimization of other commercially available clays and laterites, deposits.

2. A radionuclide like cesium could be studied with the available clays and laterites to understand fully its ion-exchange and leaching mechanisms.

3. Leaching of radionuclides could be studied with natural waters in order to understand the mechanism of the process. Other leaching methods could be simulated for repositories near run-offs.

4. Soxhlet leach test is suggested to be able to determine effective diffusion coefficient.

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APPENDICES

APPENDIX A

Table A.1 Cation Exchange Capacity of Clay Samples

Laboratory number	Number of Observations 1	2	3	4	Mean	Standard deviation
1	50.80	33.60	44.20	49.20	44.45	2.02
2	43.00	30.00	34.40	33.00	35.10	1.63
3	18.00	17.40	17.00	17.80	17.55	0.18
4	22.00	16.40	16.40	18.60	18.80	0.93
5	25.20	27.40	27.40	25.80	26.10	0.32
6	14.00	14.40	14.40	14.80	14.20	0.24
7	47.40	57.00	50.80	46.80	50.50	1.14
8	34.40	37.80	34.40	33.60	35.05	0.55
9	17.60	15.20	17.00	18.00	16.95	0.52
10	17.30	22.00	19.60	18.90	19.45	1.09
11	20.90	12.90	13.80	14.40	15.32	1.68
12	17.30	17.1	16.80	17.20	17.10	0.13

Table A.2 Formed, dried and Fired dimensions

Laboratory No.	Dimension at forming			Dimension after firing at 110°C			Dimension after firing		
	Hcm	Dcm	Wg	Hcm	Dcm	Wg	Hcm	Dcm	Wg
R1	2.81	2.98	33.76	2.80	2.97	33.76	2.79	2.96	32.10
B1	3.44	2.87	42.33	3.42	2.87	40.13	3.40	2.86	38.03
RL1	3.24	2.93	44.18	3.24	2.93	42.46	3.23	2.93	40.24
BL	3.39	2.91	44.00	3.36	2.91	41.88	3.35	2.88	39.62
RH1	3.44	2.90	44.74	3.44	2.89	42.63	3.43	2.88	40.28
BH1	3.60	2.89	46.99	3.58	2.88	44.78	3.56	2.88	41.97
R2	3.51	2.92	44.37	3.50	2.90	41.81	3.48	2.89	38.24
B2	2.80	2.84	34.22	2.78	2.83	32.53	2.76	2.81	30.15
RL2	3.30	2.89	42.69	3.29	2.89	41.00	3.28	2.87	38.00
BL2	3.42	2.88	41.66	3.40	2.86	39.73	3.38	2.84	36.52
RH2	3.14	2.98	40.55	3.13	2.99	38.67	3.10	2.94	36.00
BH2	3.37	2.89	42.32	3.35	2.89	40.20	3.32	2.88	36.85
R3	3.41	2.90	44.31	3.40	2.90	42.03	3.38	2.93	38.74
B3	3.41	2.98	46.51	3.39	2.98	43.26	3.37	3.00	39.61
R1	3.19	2.98	44.67	3.20	2.98	42.66	3.18	3.00	39.26
BL3	3.61	2.93	44.20	3.59	2.93	42.11	3.57	2.90	39.02
RH3	3.06	3.01	40.13	3.05	3.01	38.23	3.03	3.00	35.44
BH3	3.70	2.92	46.72	3.68	2.92	44.88	3.66	2.90	41.00

APPENDIX

B

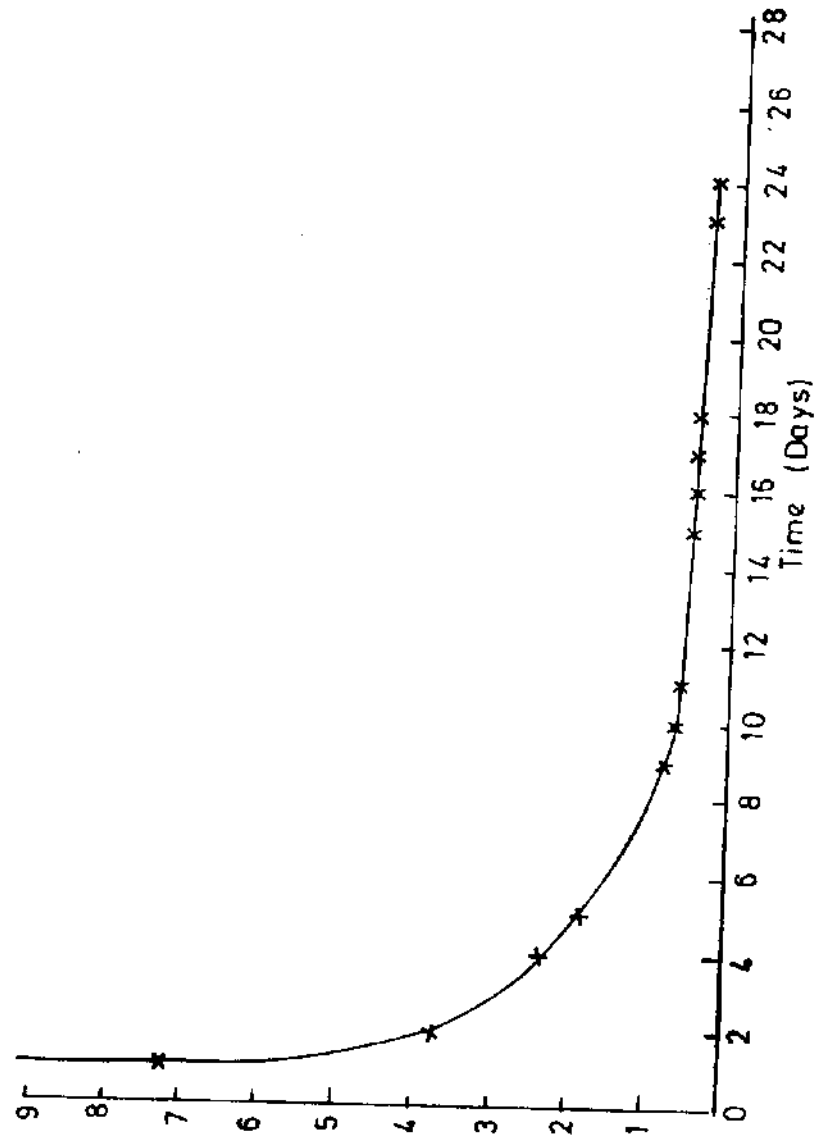


FIG. B.1: LEACH RATE OF Sr FROM WASTEFORM (RL3)

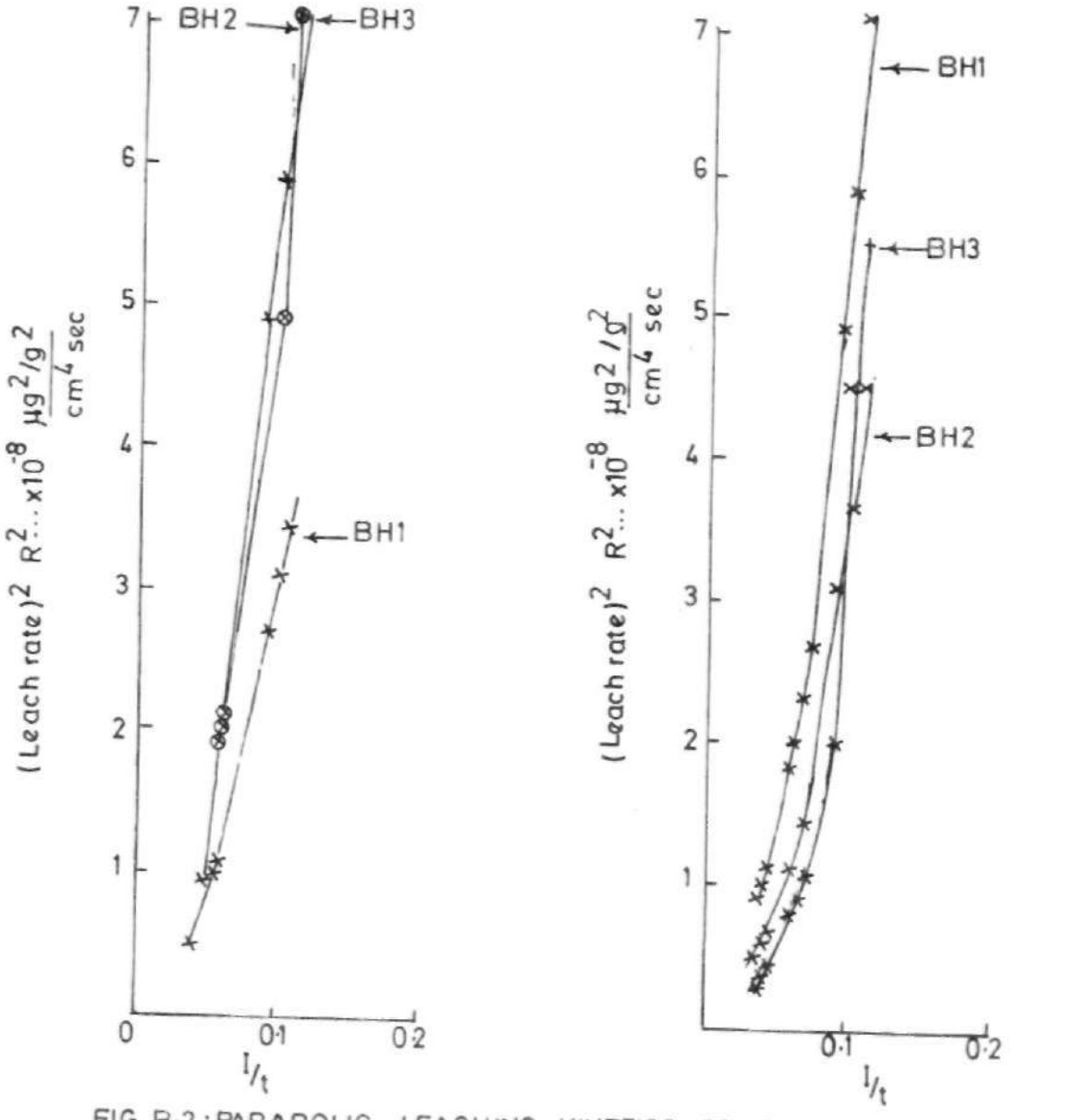


FIG. B·2 : PARABOLIC LEACHING KINETICS OF Sr FROM WASTEFORM