

The Development and Testing of Novel Inorganic
Hydrous Oxide Ion Exchangers

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by

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Abstract

Novel composite inorganic hydrous oxide ion exchange materials have been developed based on Ti(IV), Mn(IV) and Si(IV). The materials are covered by a British Patent application. Laboratory scale synthesis of the hydrous oxides has been scaled up to pilot plant scale manufacture. A novel method of floc precipitation has been developed. A precipitate washing process quantified by conductivity measurements has led to a high degree of reproducibility in the consistency of products from different batches.

Fractional addition of Si(IV) hydrous oxide has produced materials with superior ion exchange capacities for several radioactive species, and greater physical, chemical and irradiation stabilities. Thermogravimetry and room temperature X-ray powder diffraction studies have revealed the materials to be homogeneous and of a highly amorphous nature. Surface area measurements, carried out by two methods, and microporosity measurements are also reported. The addition of silica has greatly increased the strength of Mn(IV) hydrous oxide and has shown a general increase in surface area. Attempts at elucidating the exact structure of the materials were made with high temperature XRPD. The physical strength of ion exchange materials has been determined by diamond indentation technique. The inorganic hydrous oxides have shown high resistance to irradiation doses of up to 1000 Mrads of γ -radiation.

Cationic/anionic exchange behaviour has been studied in an attempt to deduce the functionalities active in the ion

exchange processes. The ion exchange capacities and selectivities of the materials have been determined for Cs^+ , Sr^{2+} , Am^{3+} , Eu^{3+} , UO_2^{2+} and Th^{4+} . The ion exchanger performances with waste stream simulants, specified by BNF plc, have shown the materials to be suitable for decontaminating their radioactive streams.

Kinetic studies of several radioactive species were carried out to establish the ion exchange mechanism. Kinetic studies have revealed the predominance of particle diffusion as the rate controlling step at concentrations $\geq 10^{-3}\text{M}$ CsNO_3 . Kinetic tests carried out at 10^{-4}M CsNO_3 suggest this concentration to possibly have both particle and film diffusion control processes present together. Experimental data suggests the existence of film diffusion at lower concentrations. Kinetic tests at various temperatures were carried out to confirm the ion exchange sorption process to be a diffusional process and not a chemical reaction between the adsorber and the adsorbate.

Proposals for future work are also presented.

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- III. TG and DTA curves for hydrous oxides
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Nomenclature

C	total ion concentration	meq/cm ³
C	a constant	
D	diffusion coefficient	cm ² /sec
F	extent of reaction	-
K _i	dissociation constant of species i	-
K _d	distribution coefficient	cm ³ /g
K _A ^B	selectivity quotient	-
MW _i	molecular weight of species i	g
n	number of moles of associated water	-
P	rate of permeation	meq/m ² sec
P	partial pressure of adsorption gas	Pa
P _o	solution pressure of adsorption gas	Pa
q	total amount of solute entered/unit area	meq/cm ²
Q	total amount of adsorbate per particle	meq
r _o	radius of ion exchange particle	m
r _o '	radius of sphere of aqueous solution	m
RT	room temperature	°C
t	time	sec
V	solution volume	cm ³
V _{ads}	total volume (at STP) of adsorbed gas	cm ³
V _m	monolayer volume of adsorbed gas	cm ³
α _A ^B	separation factor	-
δ	thickness of Nernst film	m
ρ _i	density of species i	g/cm ³

symbols superscripted with ' denote parameters within the solid phase

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Chapter 1

Introduction

*1.1 Radioactive Decontamination by Ion Exchange 1.2 Ion
Exchange Process*

1.1 Radioactive decontamination by ion exchange

Decontamination of liquid wastes from the BNF plc plant at Sellafield is a matter of some national concern. The regulatory bodies have demanded more stringent controls on effluent discharge to the Irish sea and two major plants have been planned to deal with the discharges from the site. The first plant SIXEP, already in operation, treats effluent water from fuel storage plants to remove radioactive caesium. A second plant EARP is being built to treat large volumes of low active effluent arisings from the reprocessing plant and especially to remove traces of transuranic metals in the stream. Ion exchange is the process used in SIXEP for caesium removal.

Radioactivity in liquid wastes may be removed by one of several methods; evaporation, distillation, flocculation, filtration or ion exchange^{2,3,4,5}. Ion exchange has found application not only in water purification, the original major application, but also in many specialised fields: namely carbohydrate refining, metal, organic and pharmaceutical products recovery, analytical, agricultural and medical applications, as catalysts and in the 'clean-up' of radioactive waste.

All through the development and growth of the nuclear industry, the utilization of adsorption processes has created a demand for materials to be stable in intense radiation fields and high temperatures. For this reason ion exchange materials, in particular, the inorganics have played an integral part in radiochemical process and

development. The use of water as a process medium in nuclear plants of all descriptions, largely in cooling ponds for storage of irradiated fuel, give rise to the production of high, medium and low activity¹ liquid wastes. Typically, medium and low level liquid waste streams may contain the following radioisotopes, Cs¹³⁷, Sr⁹⁰, Co⁶⁰, Sm¹⁵¹, Tc⁹⁹, I¹²⁹, Kr⁸⁵, Eu¹⁵², U²³⁵, Am²⁴¹, Th²³⁹, and Pu²⁴². The maximum permissible levels of concentration in water⁷ of these and some other radionuclides are given in text⁸.

The presence of Cs¹³⁷ and Sr⁹⁰ in radioactive waste poses the greatest hazard due to the high levels of activity. Gluekauf⁹ has shown that the biologically weighted relative β -activity of mixed fission products reduces by five fold over a period of 25 years, to less than the maximum permissible levels, in the absence of Cs¹³⁷ and Sr⁹⁰. McKay¹⁰ has shown that after Cs¹³⁷ and Sr⁹⁰ the most hazardous radionuclide is Am²⁴¹. Jenkins¹¹ presents a comprehensive review on the actinide and fission product separation by ion exchange. The hazards associated with waste solution containing these three radionuclides would be greatly reduced by their removal, reconcentration and separate storage at the earliest stages of the decontamination cycle.

At Sellafield, there are a number of waste streams that still require treatment. Further streams may result from processing other types of wastes, for example americium bearing alumino-ferric floc⁶. The composition of some of these waste streams, however, precludes their treatment in

either SIXEP or EARP. For example effluents with a high magnesium content cannot be treated in SIXEP and those containing chelating agents such as citrate cannot be treated in EARP. These streams will require separate treatment plants to be built.

As a result of some previous work carried out in this laboratory⁹⁸, BNF plc decided to develop certain inorganic ion exchangers with a view to using them to treat other process streams that could be decontaminated in EARP or SIXEP. Inorganic hydrous oxides were utilized as suitable ion exchangers, which have been attested by many previous workers. However, there are two novel aspects about the present programme of work. The first is the use of mixed oxide exchangers such as those made from hydrous manganese oxide HMnO and hydrous silica HSiO. The second novel aspect is the development of hydrous uranium (IV) oxide and this is the subject of a separate study.

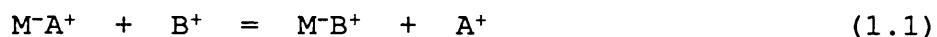
It was the primary objective of this study to synthesise and test novel inorganic composite hydrous oxide ion exchange materials having high selectivity and capacity for radionuclides (of the kind generated at the BNF plc fuel reprocessing plants), exceptionally high irradiation and thermal stabilities, high mechanical resistance to breakdown, and good chemical resistance throughout the pH range. The work presented here is not solely a study of inorganic ion exchange, the manufacture of these exchangers has also been studied with the aim of reproducibly providing bulk quantities of a variety of materials for use

in radioactive waste treatment. The decontamination of high volume low level radioactive waste streams, has been demonstrated in this study. Selectivity series and total effective capacity values are reported. Most properties were expected to better those for the synthetic organic resins, which are popular as they are readily available and possess high chemical stabilities but lack in performances in radiation and high temperature environments. Fracture toughness, specific surface area and microporosity parameters were determined which are vital in the optimum designing of large scale operating columns. Rudimentary work on ion exchange kinetics was carried out to determine the rate controlling steps in the ion exchange process and effects of temperature, particle size and type of counter-ions. However, it is also obvious that a variety of other sorption processes could be responsible for the removal of activity associated with multivalent ions at high pH. Some diffusional parameters were determined from the kinetic investigations to enable preliminary modelling of a continuous ion exchange operation.

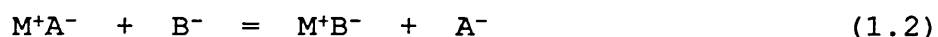
It is the practice in the nuclear industry to call these materials ion exchangers and this convention will follow here.

1.2 Ion Exchange Processes.

An ion exchange reaction may be defined as the reversible interchange of ions between a solid phase (the ion exchanger) and a solution phase. The ion exchange material therefore should ideally be chemically stable in the solution containing the exchangeable ions. The earliest critical observations of the ion exchange phenomenon were made by Thompson and Way¹², who investigated the ability of soil to absorb ammonia from ammonium sulphate and later discovered the selective behaviour of the soil, for example where Ca^{++} could be replaced by NH_4^+ but not by Na^+ . If an ion exchanger M^-A^+ carrying cations A^+ as the exchange ions, is placed in an aqueous solution containing B^+ ions, an ion exchange reaction may take place:



The equilibrium represented in the above equation is an example of cation exchange, where M^- is referred to as the fixed anion, and A^+ and B^+ are referred to as the counter ions. In much the same way anion exchange may take place with M^+ being the insoluble cationic complement of the ion exchange material M^+A^- and A^- , B^- being the anionic ions as depicted in equation(1.2),



The above equilibria obey the law of mass action and a thermodynamic equilibrium constant may be derived for the exchange¹³. The electroneutrality is preserved at all times in both the exchanger and solution phases and this in turn requires that the counter ions are exchanged in equivalent

amounts. A thorough understanding of the physical chemistry of the ion exchange equilibria must include not only the main exchange reaction but also the secondary effects such as the change of water content, penetration of soluble electrolyte from external solution, sorption of non-electrolytes and influence of the non exchange ions in the external solution on the equilibrium. There are two quantities that measure the extent of reaction in equation (1.1); (a) the distribution coefficient¹⁴, K_d and (b) the selectivity quotient^{14,15}, K_A^B both of which are experimentally determined quantities. The distribution coefficient is defined as the number of milliequivalent of an ion absorbed per unit mass of the exchanger divided by the number of milliequivalents of that ion per unit volume remaining in the solution at equilibrium. A K_d value therefore is the measure of the extent to which an ion is removed from the solution in the presence of the exchanger. The selectivity quotient refers to the counter ions (A^+ and B^+) concerned in the exchange and is equal to the ratio of the concentrations, at equilibrium, of the two ions in the solid phase divided by that of their concentration in the liquid phase. This is thus a measure of the selectivity of the exchanger for one species relative to the other. Besides the extent of reaction and selectivity of the exchanger in a given environment, the capacity of the exchanger for a given species or total milliequivalent capacity is an important parameter. The total capacity of an exchanger is the measure of its total content of

exchangeable ions, and is conventionally expressed in terms of total number of equivalents of ions per kilogram (milliequivalent per gram) of the exchanger in its dry state and in a given univalent ionic form. When quoting values for the distribution coefficient, selectivity quotient and the capacity it is important, particularly for inorganic exchangers, to specify pH of reaction and pretreatments if any. A small pH change may have a significant effect on the number of exchange sites available as a result of hydrolysis. Pretreatment, with say acid or alkali may affect the material capacity and selectivity.

Much work has been done on the kinetics of the ion exchange processes by various researchers. Earliest works by Boyd et. al.¹⁶ and later by Helfferich¹⁷ have put forward a comprehensive mathematical understanding of the ion exchange mechanism and are discussed in detail in a later chapter.

The most important features characterising an ideal ion exchanger are;

1. A hydrophilic structure of regular and reproducible form
2. Controlled and effective ion exchange capacity
3. Selectivity for specific species
4. Rapid rate of exchange
5. Chemical stability
6. Physical stability in terms of mechanical strength and resistance to attrition

7. Thermal stability

8. Consistent particle size and effective surface area compatible with hydraulic design requirements of a large scale plant.

Manufacturers of modern ion exchange materials, mostly organic, over the last 50 years have progressed a long way in meeting all these requirements. Inorganic ion exchange materials are custom made to conform to most of the above features. As a result inorganic ion exchange has become an established separation technique. With the systematic study of the ion exchange materials simplified through the availability of radioactive tracers of most elements, a detailed knowledge of adsorptive properties of the materials have become well defined.

Earliest work on inorganic ion exchangers by Kraus et. al.^{20,21,22} showed the feasibility of inorganic materials for ion exchange adsorption. Techniques and inorganic materials have recently been developed for the efficient removal of radioactive species such as Cs^+ , Sr^{2+} , Eu^{3+} , UO_2^{2+} , Am^{3+} and Pu^{4+} in the aqueous phase. The chemistry²³ of such species allows them to exist as ionic or anionic complex species in aqueous solutions, so it is possible to extract or separate these species from solution by treatment with an ion exchanger having an appropriate selectivity trend. Inorganic ion exchangers are, as compared with organic ion exchanger resins, stable at high temperature and under strong irradiation and have, in most cases, selective ion exchange properties for specific species. The inorganic

zeolites are not of universal application due to their chemical instability in both strongly acidic and strongly basic media^{18,19}.

In general, it is necessary to form inorganic exchangers into specifically shaped products of suitable size. In addition, such a shaped product is required to have strength in water, acid and alkali media. The resistance to physical breakdown should be sufficient to withstand operation inducing physical and osmotic forces on the material. These factors are of a vital importance where the inorganic exchangers are used in packed columns. In order to form inorganic ion exchangers into shaped products, known inorganic binders, such as silica sol, water glass may be used. However, such binders may render the material totally useless to alkali resistance and show markedly lower ion exchange capacity than the pure product. An optimum balance has to be found between ion exchange capacity and the physical strength of the material. The option of using chemically stable organic binders, such as natural and synthetic polymers, is not viable under high temperature and irradiation as shown by the work done by Kenna²⁴ on a sodium titanate loaded macroreticular resin.

Chapter 2

Literature survey

2.1 General Introduction 2.2 Hydrous Oxides

2.1 General Introduction

Inorganic ion exchangers can be categorised into two general types, depending on whether they absorb cations and therefore called cationic or absorb anions and called anionic exchangers. Since all the radioisotopes undertaken in this study are cationic species the emphasis of the literature survey is on cationic exchangers. Complexes of some of the isotopes can exist depending on the pH and the other elements present in the medium. A further sub-division of inorganic ion exchangers can be made into the naturally occurring and the synthetics. Broadly speaking the naturally occurring materials are mainly alumino-silicate minerals and can be categorised as clay minerals and zeolites. However, the synthetic inorganic ion exchangers may be classified into five categories:

i) Hydrous oxides of tri- and tetravalent metals; such as alumina, silica gels and titanium dioxide.

ii) Insoluble salts of polyvalent metals; titanium phosphate and zirconium phosphate.

iii) Insoluble salts of heteropolyacids; such as ammonium molybdophosphate.

iv) Complex salts based on insoluble ferrocyanides; such as sodium copper hexacyanoferrate.

v) Synthetic zeolites or permutites which are used in water softening.

The main emphasis of the account that follows is placed on the hydrous oxides and the factors that can affect their kinetic and ion exchange properties. It is intended to

provide the reader with information sufficient to serve as a guide in the field of ion exchange separation related to some inorganic ion exchangers. Where appropriate, principles and procedures involved in both the equilibrium and non-equilibrium ion exchange processes will be discussed. Influence of competing ions and the effects of solution pH is a recurrent theme throughout this study.

2.2 Hydrous oxides.

The principle of ion exchange for the hydrous oxides is the same as for the synthetic ion exchange materials and for the mineral exchangers first discussed by Gans²⁵: the skeleton of ion exchange material carries an excess charge which is covered by mobile counterions. Hydrous oxides have a unique selectivity specific to the metal ion forming the material matrix (the central metal ion) and may show the properties of both cationic and anionic ion exchangers. These substances are mainly amphoteric and their dissociation could be schematically represented by either of the two following schemes²⁶



Equation (2.1) represents anionic dissociation of exchanger in acidic media and equation (2.2) represents dissociation at a higher pH. At the isoelectric point of the oxide, where ionization would be at a minimum, we would expect virtually no exchange. The pH at which the exchange is negligible will depend on the values of the ionization (or the dissociation) constants K_1 and K_2 , which in turn depends on the chemical nature of the oxide substrate and possibly also upon the nature of the exchanging ions. The pH of the crossover point from cationic to anionic exchange may not be clearly defined²⁶.

The chemical characteristics of the fourth group (IVA and

IVB) elements exhibit an increase in electropositive character with increase in atomic mass²⁷. This can be explained by the corresponding increase in the diameter of their atoms which in turn lowers the force of attraction between the nucleus and electrons in the atom. The ionic size of the metal in the matrix can be correlated to its ion exchange behaviour and selectivity for different ions. This is demonstrated by Inoune and Yamazaki²⁸ who worked with oxides of Ti, Sn, Zr and Nb.

The hydrous oxides behave as ion sorbers due to the presence and pH-dependent dissociation of surface hydroxyl groups, as depicted in equations (2.1) and (2.2). To achieve any significant amount of anion uptake at high pH, mixed oxides have to be prepared with a net positive charge in the matrix. Typically this may be a pentavalent oxide 'doped' in a quadrivalent oxide matrix. In an oxide M_2O_n , if the metal ion M^{n+} is replaced by another ion of higher charge $M^{(n+1)+}$, the resultant matrix will attain a net positive charge. This is not to be confused with heteropolyacid salts, like tin tungstoarsenate, titanium and zirconium phosphate silicates etc. which are suitable for specific ion exchange and have high chemical and thermal stabilities. However the concept of mixed oxides, to enhance anionic and cationic exchange at high and low pH respectively, was studied earlier by Duwell and Shepard²⁹. Venkataramani³⁰ et. al. have shown that introduction of high valency metal ions in a matrix indeed enhances the anionic exchange at high pH. Bi(III)-Ti(IV), Bi(III)-Zr(IV) hydrous

oxide systems were prepared in differing ratios to illustrate such behaviour.

One of the most serious disadvantage in working with hydrous metal oxides is that different investigators frequently give inconsistent results because of the irreproducibility of the materials. Abe³¹, Ruvarac³², Veseley and Pekarek⁴² and Kraus et.al.³³ discuss extensively the preparation of various oxides. It is important, for making a reproducible product, to note preparation conditions; initial concentrations of reagents, reaction pH, and preparation history: ageing time and temperature etc. For example Alberti and Conte³⁴ and Abe and Ito ^{35,36} have shown the reduction in K_d values of zirconium phosphate as a function of drying temperature. The exchanger loses water upon heating which results in decrease of its surface area and in some cases changes in the crystalline form³⁷. Porosity and surface area are an intrinsic property of any hydrous oxide and depend on the conditions of preparation.

In the remainder of this section on hydrous oxides a short literature review on Ti(IV), Sn(IV), Mn(IV) and Si(IV) hydrous oxides is presented in order to develop a coherent comparative discussion of their properties.

2.21 Hydrous Titanium Oxide

In the periodic table, titanium belongs to the same group as zirconium, so that the hydrous oxide of Ti also can be expected to have good ion exchange properties. Hydrous titanium oxide (HTiO) is represented in various forms, two most common ones being $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ and $\text{TiO}(\text{OH})_2 \cdot n\text{H}_2\text{O}$. However, the material is a well characterised ion exchanger and is the object of considerable attention for its possibilities as an absorbent in the recovery of U from sea water^{38,39,40,41}. Literature on HTiO and its application has been thoroughly reviewed by Veseley and Pekarek⁴². More recently Gupta and Venkataramani⁴³ have studied the sorption of uranyl ions on HTiO and have reported a capacity of 0.65mmol UO_2^{2+} ions per gram of HTiO. Nakamura et. al.⁴⁰ have reported capacities in the region of 175-127mg U per gram of exchanger. Komatsu et. al.⁴⁴ have shown that the distribution coefficient value, K_d increases as uranium concentration decreases.

Inoune and Tsuji⁴⁵ have prepared HTiO by three methods to study the effect of preparation route on ion exchange behaviour. The three preparation systems they adopted were : (a) TiCl_4 -NaOH- H_2O , (b) ATS (ammonium titanyl sulphate monohydrate) -NaOH- H_2O and (c) TiCl_4 - NH_4OH - H_2O . The first system yielded a material with the highest stability and is the most common method adopted. Heitner-Wirguin and Albu-Yaron's⁴⁶ preparation by NaOH precipitation and air drying at room temperature also yielded a high capacity exchanger. System (c)⁴⁵ produced a fine powder unsuitable for column operation. This confirms an earlier observation

by Abe et. al.⁴⁷. The drying temperature determines the crystalline form of the material. Heitner-Wirguin and Albu-Yaron⁴⁸ carried out thermogravimetric, X-ray analysis and infrared spectral studies on HTiO. They reported the material to be amorphous up to a temperature of 400°C, losing approximately 28% of the interstitial water at 200°C. Regai and Selim⁶¹ report a total loss of 26% for HTiO prepared under similar conditions. Infrared studies⁴⁸ revealed three absorption bands which are characteristic of interstitial water and hydroxyl groups. The ion exchange capacity of HTiO decreases with an increase in drying temperature (and therefore crystallinity), but finely divided microcrystalline products formed during thermal hydrolysis are reported to have good absorption properties, especially with transition metals and lanthanides⁴⁹.

Since the oxides are liable to lose their exchange capacities at high temperatures due to the loss of the hydroxyl groups, the use of these materials in the environment of elevated temperatures, such as a reactor water 'clean-up' system, is limited. Inoune and Yamazaki²⁸ have however, shown that HTiO retains its ion exchange capacity up to a temperature of 160°C and it rapidly declines above a temperature of 324°C.

Hydrous titanium oxide prepared by method (a)⁴⁵ is an amphoteric exchanger with an isoelectric point (point of zero charge, PZC) at pH 5.5: anionic exchange below this pH and cationic above it. Ion exchange capacities for HTiO found in the literature vary quite considerably, they

depend on the method of preparation and on the absorption environment, particularly pH and temperature^{50,51}. The capacities for alkali metals and alkali earth metals are listed in Table 2.1.

Distribution coefficient values⁵⁴ for Sr^{2+} are about 104, however in the presence of competing ions and complexing anionic species this value will probably be lower than expected. Distribution coefficient values reported for Cs^+ and Sr^{2+} have been 151, 194⁴⁸ and 39, 269²⁸ respectively at $\text{pH} \approx 4.5$ to 6. The selectivity series for alkali metal cations^{48,54,56,28} is $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$, for alkali earth metal cations^{56,28} is $\text{Ba}^{2+} > \text{Sr}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ and that for bivalent transition elements^{56,28} is $\text{Zn}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+}$. On the basis of these results, HTiO has been utilized in the chromatographic separations of lanthanides from transition elements⁴⁹, and qualitative separations⁵⁶ of Cs^{137} - Ba^{133} and Cs^{137} - Sr^{85} systems. HTiO can be used for extraction of actinides. This has been reported by Talant⁵⁸ and Kennedy et. al.⁵⁹ The K_d values for U^{6+} , Pu^{4+} and Cm (oxidation state not reported) are 1.0×10^4 , 2.0×10^5 maximum and 1.0×10^6 respectively. Not much published literature is available on other heavy element separation with HTiO.

Surface area is very sensitive to conditions of preparation, heat treatment and storage (age). Nelson and Eggertsen⁶⁰ have shown that the surface area of titania gels depend on pH of preparation and found it to be $420\text{m}^2/\text{g}$ at pH 6, dropping drastically to $40\text{m}^2/\text{g}$, $< 2\text{m}^2/\text{g}$ at pH values of

9 and 10 respectively. Ragai and Selim⁶¹ have reported values ranging from 24 to 109m²/g over a pH range of 3.5 - 9.3 of preparation of precipitate. Inoune et. al.⁴⁵ have demonstrated that the pH of preparation only affects the physical properties of the ion exchanger and not its ion exchange characteristics. However this is contrary to data given by Ragai and Selim⁶¹ who show an increase in the ion exchange capacity as preparation pH is increased to 8 and a slight drop thereafter. Ragai and Selim⁶¹ tests however, were carried out with Co²⁺, Ni²⁺, Cu²⁺, Cr²⁺, and notably Inoune et. al.⁴⁵ carried out their tests with the uptake of Na⁺.

Table 2.1 : Ion exchange capacities of HTiO
for alkali and alkali earth metals

Ion	Capacity meq/g	Reference
Li^+	4.9 - 6.0	52
Na^+	2.4 - 5.1 1.27 - 5.45 3.5 4.5 - 3.4	52 51 28 50
K^+	2.3 - 4.3 3.4 - 4.5	52 50
Cs^+	3.9 - 1.25 3.4 - 2.8	52 50
Sr^{2+}	2.35 - 0.8 3.8 1.6 - 0.1	48 50 53
Ca^{2+}	2.3 - 1.92 6.95	48 51

2.22 Hydrous Tin oxide

Hydrous Tin oxide (HSnO) has two forms , the so called α - and β - stannic acids. The α -form is prepared by the normal hydrolysis reaction in aqueous solution at room temperature, eg. addition of alkali to a solution of a Sn(IV) salt or the acidification of a solution of a soluble stannate. The β -form is normally prepared by the oxidation of tin metal with hot nitric acid, but can also result from hydrolysis reactions in hot solution. X-ray diffraction^{62,64} data and Mossbauer parameters^{63,64} for the two forms are exactly identical with those for Sn(IV) oxide and on heating water is lost from both material forms by a continuous process⁷⁴ until dehydration is complete. It has been reported that the difference between the α - and β -forms is due to the differences in the degree of agglomeration and to the amount of adsorbed water in the tin dioxide particles. HSnO has been in general formulated as $\text{SnO}_2 \cdot n\text{H}_2\text{O}$ and occasionally referred to as stannic acid. Densities of 3.06 - 3.31 g/cm³ ⁶⁵ and 3.80g/cm³ ⁶⁴ have been reported for the differing preparation routes adopted. Due to the problems of irreproducibility Inoune and Yamazaki^{65,73} and Inoune et. al.⁷⁴ carried out a comprehensive study in the preparation of HSnO using eight systems to establish the best method to produce a material of high ion exchange capacity, chemical and physical stability. Infrared studies^{64,67,74} on the two forms of HSnO revealed peaks similar to those for hydrous titanium oxide⁴⁸. The α -form, however gave rise to two further peaks at 990cm⁻¹ and

1250cm⁻¹, which can be related to the coordinated water. The α -form HSnO is soluble in acidic solutions, whereas the β -form is more inert in concentrated nitric and sulphuric acid solutions^{64,65,67}. The stability in alkaline solution was low with increasing concentrations^{64,67,68} for both the forms. Kraus et. al.³³ and Amphlett¹⁴ have shown HSnO to be an amphoteric hydrous oxide. The pH titrations by Abe and Ito⁶⁹ demonstrate the amphoteric behaviour with a relatively low point of zero charge of $\approx$ pH 4 as compared to $\approx$ pH 5.5 for HTiO.

Alkali and alkali earth metal cations are weakly absorbed⁷⁶ at low pH, however trivalent cations like Al³⁺ and Cr³⁺ are more strongly absorbed. Column separations of bivalent transition elements with HSnO are commonly reported. Based on selectivities, the HSnO cation affinity series has been given as transition elements > alkaline earth metals > alkali metals. The affinity series shows that the selectivity is higher for the metal ions of a smaller crystalline radius than those of a large one. The respective orders of selectivities⁶⁸ for alkali and alkali earth metal cations are Li⁺ >> K⁺ > Rb⁺ $\geq$ Cs⁺ and Mg²⁺ > Ca²⁺ > Sr²⁺ $\geq$ Ba²⁺. Donaldson et. al.⁷⁶ found that for a sulphate-free exchanger, in nitrate media, the sorption of Ca²⁺, Sr²⁺ and Ba²⁺ is low and at equilibrium pH ($\approx$ 4) and the maximum sorption is 0.10 - 0.15 meq/g. A selectivity series for transition elements of Cu²⁺ > Zn²⁺ > Co²⁺ >> Fe²⁺ > Ni²⁺ > Mn²⁺ has been reported by various independent studies^{68,70,76}. The capacities for transition elements are

given in table 2.2 below.

Because of the high affinity shown by HSnO for transition elements chromatographic separations of transition metal(II) cations amongst themselves and from alkaline earth and transition metal(III) cations have been achieved⁷⁶. The HSnO has been utilized for selective ion exchange separation of anionic species^{71,72}. The HSnO has shown potential for selective separation and preconcentration of radioactive species. Radiochemical separation⁷⁵ of tellurium - selenium and molybdenum - technetium have been reported. The separation of actinides from fission products have been carried out by Inoune and Yamazaki⁷³. The distribution coefficient values for UO_2^{2+} are considerably higher than for transition elements. UO_2^{2+} removal by HSnO in the pretreated H^+ form has also been successfully demonstrated by Donaldson and Fuller⁷⁶.

Table 2.2 : Ion exchange capacities of HSnO
for transition metals

Ion	Capacity meq/g	pH
Cu^{2+}	1.56	2.83
Zn^{2+}	0.99	3.01
Co^{2+}	0.77	3.14
Fe^{2+}	0.70	3.28
Ni^{2+}	0.63	3.30
Mn^{2+}	0.55	3.20

from references 68, 70, 76

2.23 Hydrous Manganese oxide

The adsorption of metal cations^{42,77,78,79} on hydrous manganese oxide (HMnO) has been known for a long time and consequently the use of HMnO as an ion exchanger for the treatment of active waste streams is steadily increasing. An earlier review by Vesley and Pekarek⁴² shows that HMnO can exist in amorphous and crystalline forms and is an amphoteric exchanger with the point of zero charge (PZC) or the cross over point at $\approx$ pH 2.8⁸² and pH 2.25⁸⁷. Literature survey on the use of HMnO by various workers has shown that the ion exchange properties show almost as many variations as papers published, and the mechanism for adsorption is still uncertain. These variations can almost certainly be accounted to the wide variety of structural forms of manganese(IV) oxide that can exist.

The crystalline forms identified are α , β , γ , δ and ρ -MnO₂⁸⁴. Normally these are heterogeneous, so a sample may contain a mixture of forms. Bigliocca et. al.⁸⁴ described a method for preparing a tetragonal form of MnO₂ which they report could be α - or β -form; α -form has been produced by treatment of aqueous solution of MnSO₄ / H₂SO₄ with (NH₄)₂S₂O₈ and the β -form by the thermal decomposition of Mn(NO₃)₂. The γ -form can be produced by several different routes, (a) by the reaction, $3\text{Mn}^{3+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$, (b) by anodic oxidation using either an aqueous solution of the chloride⁸⁵, or of a 5-6% sulphate solution⁸³ and (c) by treatment of 2MnO_4^- with H₂O₂. The δ -form may be prepared by (a) treatment of an aqueous solution of MnSO₄ / H₂SO₄ with

potassium permanganate⁸³, (b) precipitation by the rapid addition of potassium permanganate to a basic solution containing H_2O_2 and (c) by reacting potassium permanganate with HCl . Information on preparation method for ρ -form has been very little, Bigliocca et. al.⁸⁴ report that one of their preparation methods yielded a material resembling $\rho\text{-MnO}_2$. The amorphous MnO_2 (HMnO) can be specifically prepared by (a) the treatment of ammoniacal solution of MnSO_4 with ammonium thiosulphate and (b) the addition of NaOCl solution to MnSO_4 solution⁸³.

The HMnO is chemically stable in strongly basic and weakly acidic solutions. Work carried out by various workers^{47,77,91} has shown the various forms of HMnO to be stable in the pH range 2-10 and above. Hunter⁹¹ reported a weight loss of 29% in Li-doped $\lambda\text{-MnO}_2$ in sulphuric acid at pH 2, this loss however, was entirely due to the release of Li from the matrix. Hunter⁹¹ has reported a density value of 4.49g/cm^3 for pure $\lambda\text{-MnO}_2$.

The structural and surface studies of synthetic and naturally occurring forms of HMnO are beyond the scope of this study. An empirical formula of MnO_x for HMnO has been proposed by several authors and the values for x have been 1.88⁸⁴ and 1.77-1.75⁴². The material is understood to contain some interstitial water, as Abe and Ito⁴⁷ have proposed $\text{MnO}_2:0.6\text{H}_2\text{O}$. The maximum capacity values suggest that there is only one $-\text{OH}$ group per two MnO_2 molecules⁴² and the total capacity decreases on heating. The heat treatment is limited by the $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3$ transformation between $440\text{-}470^\circ\text{C}$

resulting in total loss of ion exchange capacity. The ionic-sieve properties, common with zeolites¹⁰⁴, of HMnO prepared by different kinds of introducing ions have been exploited^{79,91} with very useful selectivity series for alkali and alkali earth metal cations.

As with nearly all other inorganic ion exchangers the adsorption data varies for HMnO depending on its ionic form. The adsorptive properties of cations on HMnO also depend on pH; increase in adsorption with an increase in pH has been widely reported^{77,78,80}. Hasany and Qureshi⁷⁷ have reported K_d values for a wide range of metal cations, Co^{2+} was found to have the highest distribution coefficient value of 876 at a molar concentration of 10^{-7}M with Cs^+ and Eu^{3+} having distribution coefficient values of 77 and 7.6 at 10^{-9}M and 10^{-8}M molar concentrations respectively. Hasany and Qureshi⁷⁷ also studied the influence of different anions (EDTA, citrate, fluoride, plus seven more) on the Co^{2+} uptake; EDTA yielding the lowest percentage adsorption. The explanation for this being that Co^{2+} forms a stable complex with EDTA in solution. Abe and Ito⁴⁷ have observed a maximum uptake of $0.3\text{meq K}^+/\text{g}$ at pH 12 for $\beta\text{-MnO}_2 \cdot 0.6\text{H}_2\text{O}$. Ooi et.al.⁸⁸ reported $\lambda\text{-MnO}_2$ to have capacity of $\approx 4.5\text{ meq Li}^+/\text{g}$ which is very much greater than that for the other alkali metals. The apparent adsorptive capacity increased in the order $\text{Na}^+, \text{K}^+, \text{Rb}^+, \text{Cs}^+ \ll \text{Li}^+$ at $\text{pH} < 7.0$. The affinity order changed to $\text{K}^+, \text{Rb}^+, \text{Cs}^+ < \text{Na}^+ \ll \text{Li}^+$ at $\text{pH} > 7.0$, probably due to the large steric effect for large unhydrated cations ($\text{K}^+, \text{Rb}^+, \text{Cs}^+$) at higher pH. A

selectivity series reported for divalent cations with δ - MnO_2 by Murray⁸⁹ is $\text{Mg}^{2+} < \text{Ca}^{2+} < \text{Sr}^{2+} < \text{Ba}^{2+} < \text{Ni}^{2+} < \text{Zn}^{2+} < \text{Mn}^{2+} < \text{Co}^{2+}$; the alkali earth series conforms with that given by Gray and Malati⁹⁰.

The HMnO has been tested for removal of heavy elements^{80,81}. Heavy metal cations tend to be adsorbed to greater extent than the alkaline earth metal cations, and this adsorption is less reversible for the former than for the latter. The results of adsorption measurements at different pH values indicate specific adsorption of heavy metals at $\text{pH} \leq$ cross over pH^{80} . Gadde and Laitinen⁸⁰ report that in a pH range 2 to 8, the extent of adsorption lay in the order $\text{Pb}^{2+} > \text{Tl}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+}$ and the order of capacities as a function of increasing metal concentration remained unchanged. The capacities reported were 0.56, 0.28, 0.24 and 0.17 respectively at pH 6, for the above mentioned series. Adsorption studies of radioactive Cs^{137} and Sr^{90} by Singh and Tandon⁷⁸ showed similar trends for pH and concentration variations as reported by Gadde and Laitinen⁸⁰. A significant drop in the Cs^{137} and Sr^{90} uptake was noticed in presence of other alkali and alkali earth metal cations.

2.24 Hydrous Silica

Hydrous silica (HSiO) has been widely used as an ion exchanger for many years. The ion exchange mechanism of HSiO has not been fully understood, however silica gel generally acts as a weakly acidic cationic exchanger^{92,93}. The pH titration curves for HSiO given by Abe and Ito⁴⁷ show such a trend and the maximum uptake of K^+ is 1.5meq/g at pH 10.2. Anionic uptake by HSiO has also been reported by Parks⁹⁴.

Like most inorganic ion exchange materials the chemical composition and ion exchange properties of HSiO depend on the method of preparation. Factors related and affecting the ion exchange characteristics like specific surface area and porosity may vary widely. High surface area HSiO may be prepared by (a) the controlled acid extraction of metal silicates and subsequent vacuum activation at 200°C⁹⁵, and (b) by soaking of preheated silica in hot hydrochloric acid leads to an increase in its silanol group content as well as its porosity⁹⁶. HSiO with a porous structure is obtained by hydration of xerogels⁹⁷: $Si-H + H_2O \rightarrow Si-OH + H_2$. The storage of silicic acid xerogels makes their structure denser and decreases their adsorption activity, probably as result of the influence of moisture. HSiO can also be prepared by treating waterglass (sodium silicate) with a mineral acid (HNO_3)⁹⁸.

Heat treatment and its effects have been extensively studied on HSiO. The adsorption ability decreases gradually in the temperature range of 100°C to 300°C, thereafter to

1000°C it increases significantly⁴². This is explained by the transformation of the original compound to a compound with a higher capacity; the surface area decreases from 580 to 25 m²/g, mean particle size increased from 5 to 105 nm and mean total pore volume increased from 0.74 to 2.31 ml/g. The HSiO is stable in acid solution and is soluble in high alkaline solutions, pH > 10.5.

The high electron affinity of the tetravalent Si⁴⁺ ion results in a very low basicity for the hydroxyl groups. The hydrogen atoms of the latter are readily replaced by cation even in acid solutions, particularly those ions which readily coordinate with oxygen. The adsorption mechanism on silica gel is mostly interpreted in terms of ion exchange^{99,100,101}:



There are some suggestions that beside this mechanism physical adsorption and ion exclusion from small pores may also occur even for alkali metal ions⁴². The affinity for the cations increases, going from univalent to tetravalent elements. For elements of same charge, the adsorption is enhanced by decrease in crystallographic diameter. The series for alkali, alkali earth metals and tervalent cationic species are Rb⁺ > K⁺ > Na⁺ > Li⁺, Ba²⁺ ~ Sr²⁺ < Mg²⁺ < Be²⁺ and In³⁺ < Ga³⁺ < Al³⁺ ¹⁰². The adsorption of multivalent cationic complexes of U, Pu and Th have been reported with the pH ranges favoured for the extraction being from 1 to 2.5¹⁴ and from 2.5 to 2.9⁴² and that the sorption processes are irreversible. The sorption of

complexes such as $\text{Zn}(\text{NH}_3)_4^{2+}$ and $\text{Zn}(\text{en})_3^{2+}$ are used to determine the surface area of HSiO .

The chromatographic separations of individual elements from a combination has been reported by several workers and is summarised by Vesley and Pekarek⁴². The removal of Cs^+ and Sr^{2+} from waste waters is also reported⁴².

Chapter 3

Development of Manufacturing Technique

*3.1 Introduction 3.2 Reproducibility Studies on Hydrous
TiO₂ and SnO₂ 3.3 Preliminary Tests 3.4 Manufacture
of Hydrous MnO₂ using Capillary Reactor 3.5
Development of Composite Inorganic Hydrous Oxides 3.6
Effects of Drying Temperature on Ion Exchange Properties*

3.1 Introduction

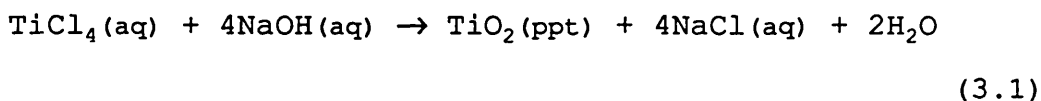
The aim of the study on manufacturing was to develop a reliable technique by which the hydrous oxides may be produced on a 'pilot-plant' scale with good reproducibility. The work reported here has been presented in the chronological order of its development. Initially the main interest was on the manufacturing technique followed by work on the development of novel mixed (or composite) hydrous oxide ion exchangers. Work on a composite hydrous oxide has already been reported - a combination of hydrous silica and manganese hydrous oxide⁹⁸. As metals can have their properties enhanced by alloying, it was hoped that an analogy would follow with the mixed hydrous oxides. Hydrous silica was chosen to be the binary constituent as it is known to be promising cationic exchanger and recognised inorganic binding material^{14,98}. In determining the best composition of HTiO:HSiO and HSnO:HSiO composite exchangers the emphasis was not entirely on the ion exchange properties of the exchangers but also on their chemical stability and physical strength. The thermal and radiological degradation properties of inorganic ion exchangers are generally well recognised¹⁰³, so these aspects were not considered in the development stages of the composites, but are covered separately in this study.

One of the problems often reported by previous workers has been the lack of reproducibility in successive batches of material with identical properties. The manufacture of inorganic ion exchangers on a large scale has also been

neglected. The preparation routes adopted were those reported to yield the overall best ion exchanger; for HTiO it was system (a) $\text{TiCl}_4 + \text{NaOH}$ as reported by Inoune and Tsuji⁴⁵, HSnO was prepared by system (5) $\text{SnCl}_4 + \text{NaOH}$ as recommended by Inoune and Yamazaki⁶⁵ and the HMnO was prepared by the reduction of KMnO_4 with H_2O_2 as investigated by Labayru⁹⁸. The HSiO, as the binary constituent, was prepared by the acid hydrolysis of sodium silicate solution ($\text{Na}_2\text{SiO}_3 + \text{HNO}_3$).

3.2 Reproducibility studies on HTiO and HSnO exchangers

Initial laboratory batches of Sn(IV) and Ti(IV) hydrous oxides were prepared by rapid addition of sodium hydroxide solution to the stirred solutions of the respective metal tetrachloride. In the production of hydrous Ti(IV) oxide (and Sn(IV) oxide) the following reaction occurs:



The quantity of alkali added was stoichiometrically sufficient to give an alkaline precipitate. The stirring was continued for 15 minutes, the products were filtered under suction using a Buchner funnel and washed repeatedly. Washings from filtrate were periodically checked for salt (sodium chloride) content by a simple flame test for Na^+ . The residual cake was then dried at 110°C overnight. The resulting material was subsequently crushed and sieved to obtain the required mesh size fractions.

Attempts were also made at preparing the precipitates by controlling the product pH. It was noted that the pH value read was a function of speed at which the respective precipitate was being stirred - the higher the speed higher the pH. From this variation in pH values it was concluded that:

- (a) the pH values of a floc is meaningless with an ordinary pH electrode and therefore attempts at preparing precipitates at a given pH were abandoned.

(b) the production of exchangers by batch production is unsuitable because of the increased chance of an incomplete reaction. It was feared that in batch production method the precipitate was formed on large particles which act as nucleation sites for further precipitate formation. The nucleation sites may entrap the initial reagents creating problems in pH measurement and precipitate washing. This mechanism was believed to explain the increase in pH with stirring speed- releasing the entrapped reagent (NaOH) from the colloid at higher shear rates.

The pH/stirrer speed relationship also means that reproducing exactly similar products would be somewhat impossible, unless the contacting regime can ensure complete mixing. This would certainly become cumbersome with a large batch. All these constraints led to the development of the capillary reactor, a continuous method for preparing the oxide precipitates with much more consistency.

3.21 The Capillary Reactor

The capillary reactor (CR) is basically an inverted "Y" shaped arrangement of narrow perspex tubes.(figure 3.1a). Stoichiometric quantities of reactants are made up to equal volumes, pumped through at equal flow rates and mixed in the 'reaction capillary'. As more reagents are pumped at 0.5-1.0 ml/s using a peristaltic pump from the lower ends, the precipitate already formed in the small control

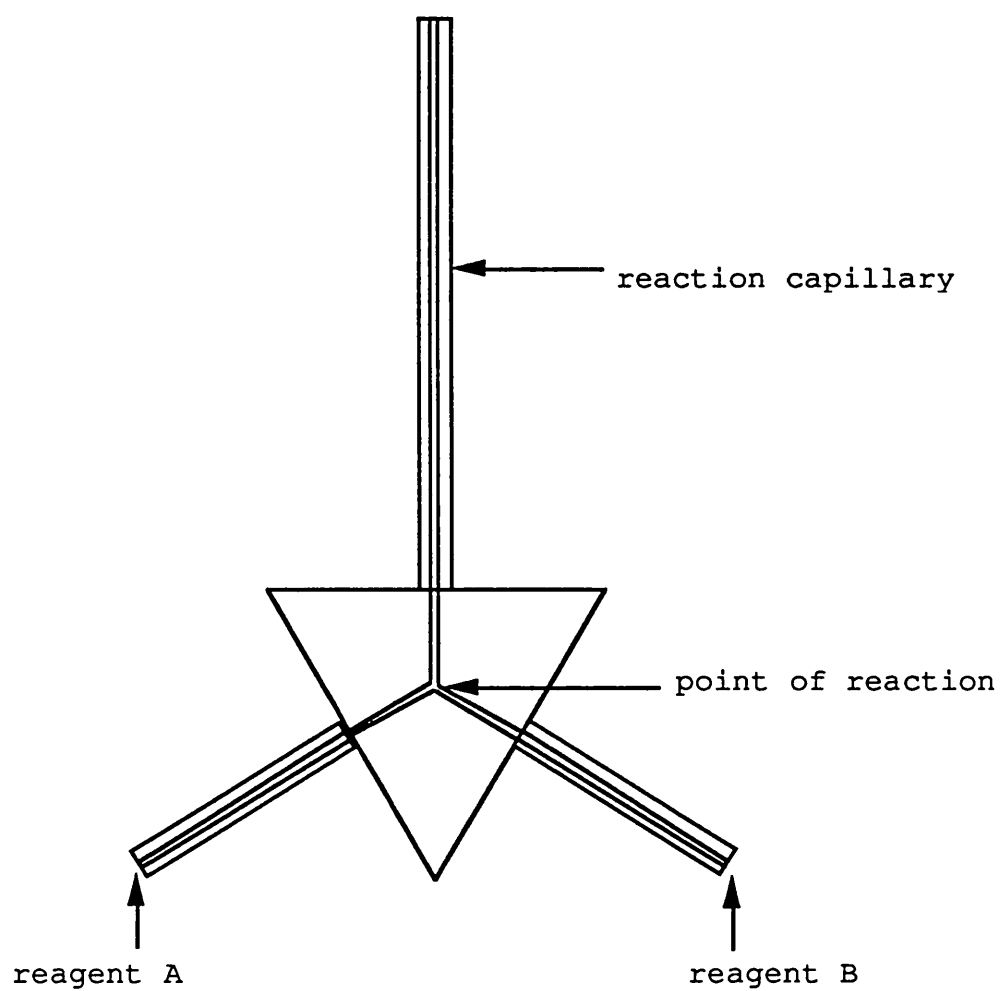


Figure 3.1a The capillary reactor

volume (at the 'point-of-reaction') is pushed forward thus preventing the formation of large precipitate particles which may entrap the reagents. However, due to the small internal diameter ($\approx 3\text{mm}$), the reaction capillary ($\approx 84\text{cm}$) invariably blocked from time to time. To overcome this problem distilled water under pressure was flushed periodically through the two feed tubes. The rate of flushing and synchronisation of the water pulses was controlled by means of a two way air actuated slider valve, a modified version of the type used by Booker and Streat¹⁵⁶. The whole operation was controlled by a microcomputer. A simple program can be written for a given set of reacting reagents to calculate the optimum flow rates, if the concentrations, temperature, viscosity and other parameters are known. See figure 3.1b. The slurry in the collection vessel may be stirred for complete homogenisation. For large scale production several capillary reactors, fed from the same stock solutions, may be used in parallel. In this way large quantities of reagents may be passed through in a day. The maximum batch size so far successfully manufactured has been 100g. Although the slurry production is continuous, the washing procedure described below can only be carried out in batches. In a later section on HMnO manufacture, a capillary reactor setup, with capillary reactors in series, was devised to increase the HMnO yield for given amount of H_2O_2 .

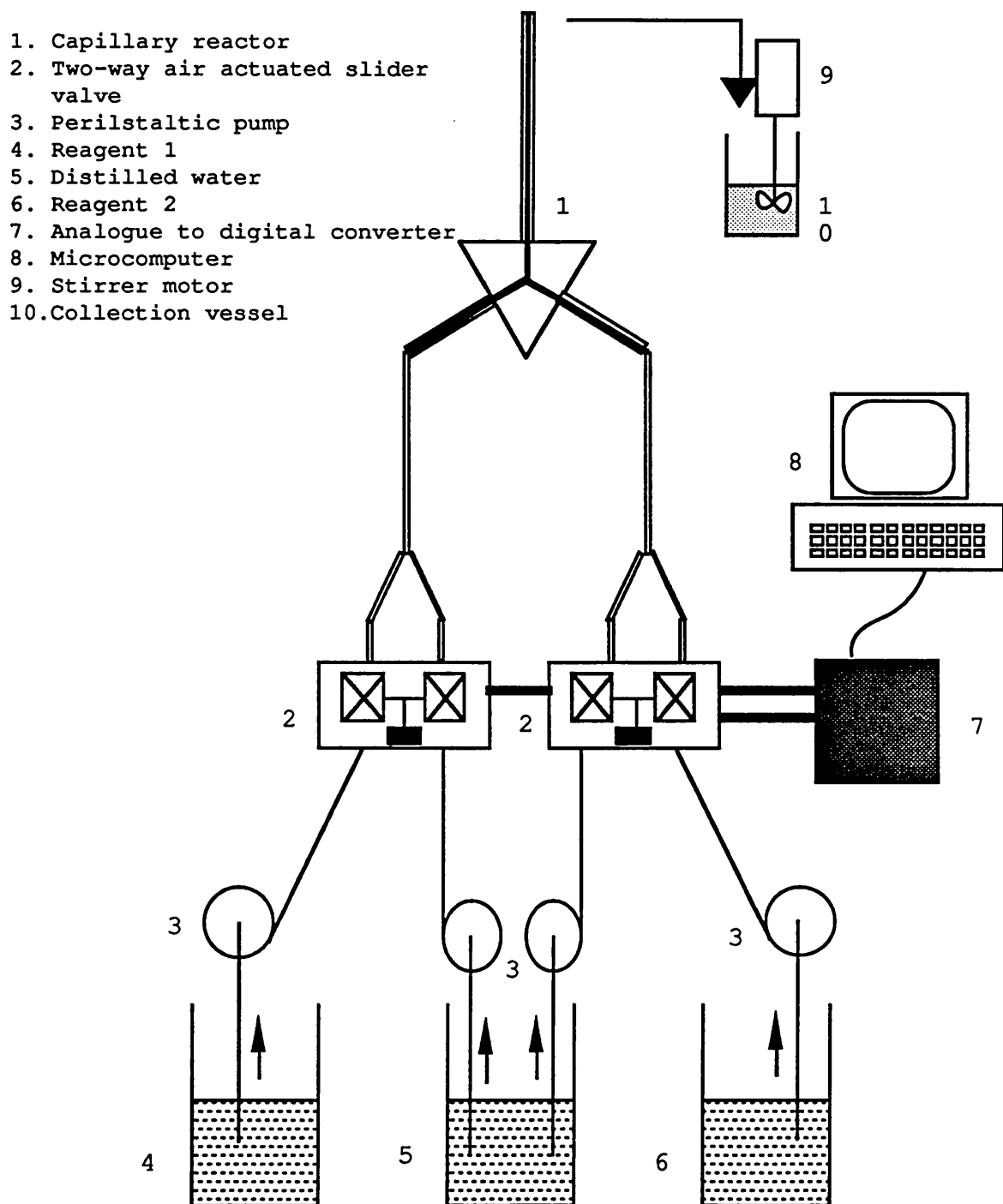


Figure 3.1b Capillary reactor setup for large scale manufacture of hydrous oxide precipitates (Not to scale)

3.22 Washing Technique

It was found with the earlier batches of hydrous oxides that after overnight drying at 110°C the products were particularly disappointing in physical state, being very soft and brittle. Despite prolonged washing sodium was still apparent in the end product. With the Buchner funnel method of filtration it was difficult to establish the number of bedvolumes of wash water required to wash the NaOH and NaCl concentration down to a predetermined suitable value. Another drawback with this method was that the total wash time was excessively long. As a result all further solid- liquid separations were carried out on a large capacity centrifuge, an 'MSE - model GF8', which made it possible to know exactly the volume of wash water required.

Attempts were made at relating the pH of supernatant solution with the NaOH concentration retained in the precipitate. These were found unsuitable as the range of pH values over consecutive washes depended on the concentrations of the starting reagents and therefore there was no set final pH value to aim for in the washing process. It was therefore decided to use the correlation between the conductivity of the supernatant and its salt concentration. A conductivity meter (Phillips Alpha 800) was acquired to give an overall ion concentration in the supernatant. The concentrations of the salts were determined from a conductivity/concentration calibration

curve for the electrode. The results of a typical wash for HTiO precipitate are given in table 3.1, it was determined with repeated batches that suitably consistent exchangers were obtained for conductivity readings of the supernatant solutions $< 2000 \mu\text{Siemens}$ ($< 0.02\text{M NaOH}$), whatever the concentrations of the initial starting reagents. The degree of washing was therefore independent of concentrations of starting reagents, which was not the case in measuring the pH of the supernatant solutions.

Table 3.1 Typical washing data for HTiO precipitate
reagent strengths : 0.1M TiCl_4 and 0.4M NaOH

Solution	Conductivity $\mu\text{Siemens} (\times 10^3)$	[NaCl] M	pH
First supernatant	126.2	$> 1\text{M}$	12.5
After wash 1	81.8	0.91	12.4
wash 2	33.0	0.33	12.2
wash 3	12.1	0.15	12.0
wash 4	4.72	0.05	11.9
wash 5	2.48	$< 0.05\text{M}$	11.8

As an alternative to washing the precipitate through a Buchner funnel, freezing as a means of salt removal was attempted. Salt has no solubility in solid ice¹¹³, owing to this property the freezing of seawater to remove brine is a

well established field^{108,109}. Although the removal of NaCl was successfully achieved by freezing, the Ti(IV) oxide material after drying at 110°C overnight was found to be a very soft powder with no ion exchange properties. This was probably due to the loss of hydroxyl and interstitial water, during freezing, as active functionalities in the ion exchange process.

Various batches of HSnO were made to determine the best concentration of the starting reagents and to compare the capillary reactor method of preparing hydrous oxides to the traditional method. Equal volumes of 0.1M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (BDH analar grade), 0.4M NaOH (BDH analar) as "weak" solutions and 1M $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, 4M NaOH as "strong" solutions were respectively pumped through the capillary reactor. Similarly equal volumes of weak solutions were mixed in beakers and stirred for 15 minutes to give the same amount of precipitate. All precipitates were washed, with 600ml of distilled water per wash, down to similar conductivity values ($< 2000 \mu\text{siemens}$) and dried overnight at 110°C. The results for the washings are given in table 3.2a, 3.2b and 3.2c.

Table 3.2a Wash data for HSnO precipitate
(by capillary reactor, weak solutions)

Solution	Conductivity ₃ μSiemens (x10)
First supernatant	21.7
After wash 1	4.8
wash 2	1.4

Table 3.2b Wash data for HSnO precipitate
(by capillary reactor, strong solutions)

Solution	Conductivity ₃ μSiemens (x10)
First supernatant	74.1
After wash 1	16.1
wash 2	1.9
wash 3	0.9

Table 3.2c Wash data for HSnO precipitate
(by batch method, weak solutions)

Solution	Conductivity ₃ μSiemens (x10 ³)
First supernatant	24.2
After wash 1	7.9
wash 2	2.2
wash 3	0.7

The conductivity reading of the supernatant solution prior to the first wash was indicative of the "completeness" (or "incompleteness") of the reaction. If the first value is high, it implies that the reaction is incomplete in that there are more ions in solution, which should have been precipitated. From the results the following points may be concluded that:

- (a) the capillary reactor gave the lowest conductivity reading for the supernatant prior to first wash, therefore indicating that the reaction is complete as compared to batch method.
- (b) a stronger solution precipitate required more washes than a weaker one.
- (c) homogeneity achieved with the capillary reactor gives consistency in the appearance and properties

of materials.

The washing technique presented here is quantified; for a given mass of precipitate the amounts of distilled water per wash and therefore total volume of water is known and the final concentration of salt present is also known. Bashir and White¹¹⁰ have formulated a semi-continuous washing theory on the optimisation of counter current washing of ion exchange flocs; the theory gives the value for the number of washes required, by presetting the degree of washing (ratio of final and initial concentrations of soluble ions) and total volume of wash water that would be required, see appendix II. The approach adopted in the study can be used in the early stages of process design and development, as an aid to planning of laboratory and pilot plant work and ultimately to ensure that full scale process designs are optimised. In an other study White¹¹⁴ has presented a simple theory on co-current washing regime using the Ti(IV) oxide production as an example.

3.3 Preliminary Tests

Throughout this study the interest has been in the removal of radioactive isotopes from BNF plc waste stream simulants - in particular, 'EARP', the Enhance Actinide Recovery Plant, and 'THORP', the Thermal Oxide Reprocessing Plant. A series of ion exchange tests with 'standard' contacting solutions, EARP and THORP simulant feeds (specification given in appendix I), were carried out to examine the ion exchange properties of the materials. Tests to determine the physical strength were also carried out on a comparative basis to determine which preparation method gave the strongest material.

3.31 Ion exchange tests

0.5g portions of the materials in 420-600 μ m mesh size, were weighed out in 1oz glass bottles with bakerlite screw top lids. 15cm³ aliquots of solutions EARP and THORP were added to each bottle. The bottles were sealed and placed on a rotary mixer for 24 hours. At the end of this period 6cm³ samples were taken, centrifuged and then 5cm³ were taken and analysed by gamma-spectrometry^{105,106} for 241-ameridium, 85-strontium, 134-caesium using their 60, 514 and 605keV respective gamma peaks. 1cm³ from the 5cm³ samples was taken for analysis of 242-plutonium by alpha-spectrometry¹⁰⁷ via TTA extraction. The distribution coefficient, K_d values given in the results were calculated using the following definition:

$$K_d = \frac{(C_I - C_F) \cdot V}{C_F \cdot m} \left[\frac{\text{cm}^3}{\text{g}} \right] \quad (3.2)$$

where C_I and C_F are initial and final radioactivity concentrations in the solution respectively, V , the volume of solution in cm^3 and m , the weight of the exchanger in g. The distribution coefficient obtained were taken to be equilibrium values as was shown in the chapter on kinetics of ion exchange.

The ion exchange results are given in tables 3.3a and 3.3b for HSnO tested with EARP and THORP feeds respectively. The results for HSnO show that the method of preparation and varying the strengths of reagent does not have a significant impression on the ion exchange properties, as reported by Inoune and Yamazaki⁶⁵.

Table 3.3a : Ion Exchange tests for HSnO with
EARP simulant feed

Sample	Am ²⁴¹		Pu ²⁴²		Sr ⁸⁵		Cs ¹³⁴		pH
	% ext.	Kd	% ext.	Kd	% ext.	Kd	% ext.	Kd	
HSnO Batch weak	19.7	7	46.3	26	0	0	0	0	1.1
HSnO CR weak	22.8	9	84.2	160	0	0	0	0	1.2
HSnO CR strong	42.5	22	78.4	109	0	0	0	0	1.2

Table 3.3b : Ion Exchange tests for HSnO with THORP simulant feed

Sample	Am ²⁴¹		Pu ²⁴²		Sr ⁸⁵		Cs ¹³⁴		pH
	% ext.	Kd	% ext.	Kd	% ext.	Kd	% ext.	Kd	
HSnO Batch weak	92.7	381	77.2	102	100	∞	28.5	12	8.1
HSnO CR weak	72.7	80	51.6	32	100	∞	28.9	12	7.9
HSnO CR strong	78.7	111	60.2	45	100	∞	27.4	11	7.8

3.32 Mechanical Properties.

For mechanical properties test, a simple crusher developed by Labayru⁹⁸ comprising of a cylinder and a piston was used. A known mass is impounded several times by the piston under which a known mass and mesh size material is placed. The mass of material remaining of the same size after the impacts is taken to be an indication of the strength of the material. In repeated tests 0.5g portions of the materials, in the mesh sizes 1000-600 μ m, were taken and the results for the tests are presented in table 3.4.

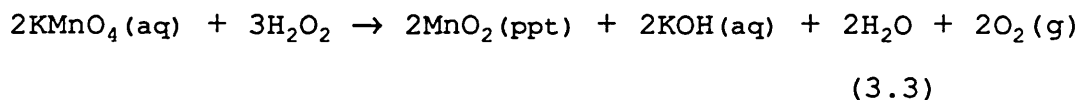
The Labayru crusher test shows that HTiO is stronger than HSnO and HMnO. Allowing for the inherent inaccuracies involved with this basic crusher, after repeated tests it however showed that the capillary reactor product is in general stronger than the batch method and that the weak solution product is better than the stronger solution. This was also noticed in the appearance; the stronger solution product was milky whereas the one from the weaker solution was lustrous glassy material. An accurate fracture toughness determination by a different technique is described in the physical properties chapter.

Table 3.4 : Mechanical properties test results
for various batches of HSnO and HTiO
prepared by different methods.
CR - capillary reactor

Sample	Initial mass/g	Final mass/g	% loss
HSnO Batch weak	1.0021	0.5971	40.42
HSnO CR weak	1.0000	0.6389	36.11
HSnO CR strong	1.0016	0.6285	37.24
HTiO CR weak	1.0009	0.9393	6.15
HMnO CR weak	1.0008	0.7512	24.94

3.4 Manufacture of HMnO using Capillary Reactor

Before the introduction of the capillary reactor, the HMnO was normally prepared by permanganate reduction using hydrogen peroxide, which may be represented by the following reaction:



The potassium permanganate (BDH analar grade) was dissolved in luke warm water and allowed to cool. A stoichiometric amount of hydrogen peroxide (BDH analar, 6% w/v) made up to an equivalent volume was slowly mixed with the permanganate and stirred continuously. A vigorous reaction led to the formation of dark brown / black MnO_2 on the surface of solution and evolution of gas. When preparing MnO_2 in beaker up to 7 or 8 times more H_2O_2 was used than stoichiometrically required. The reason for this was the catalytic decomposition of H_2O_2 :



In the reduction reaction (3.3) the effective decomposition given by equation (3.4) cannot be totally eliminated, however by reducing the contact volume of the reagents (KMnO_4 and H_2O_2), it can be drastically reduced. The capillary reactor found its most useful application here.

The modified two- and three-stage capillary reactor

systems were devised in order to minimise the quantity of H_2O_2 used. Fig 3.2a shows two capillary reactors in series; the product of the first enters the second as the permanganate reagent. Figure 3.2b is a three-stage reactor setup. HMnO was prepared using the one-, two- and three-stage reactor systems and the batch method to determine which method gives the maximum yield. The experimental details are as follows:

Solutions of stoichiometric amounts (9.091g) of KMnO_4 for a 5g sample of MnO_2 were made up to 250ml for each test. 250ml aliquots of H_2O_2 containing various stoichiometric strengths of H_2O_2 were prepared (where 1:1 ratio = 48.92ml 6% w/v BDH H_2O_2). For various tests from one to six times the stoichiometric amounts of H_2O_2 were used. The results are presented in table 3.5

The table shows that one, two and three 250ml aliquots, each containing twice the stoichiometric amount required, were used for batch and the one-stage capillary reactor system making the total amounts of H_2O_2 used equal to two, four and six times the stoichiometric amount. In the two-stage system one and two times the stoichiometric amount required were used making the final amounts equal to two and four times in total. Similarly, in the three-stage system one and two times the stoichiometric amount required were used making the final amounts equal to three and six times in total. After completion of each run the products were allowed to settle and 10ml samples of the supernatant were filtered through a $0.22\mu\text{m}$ millipore filter to monitor

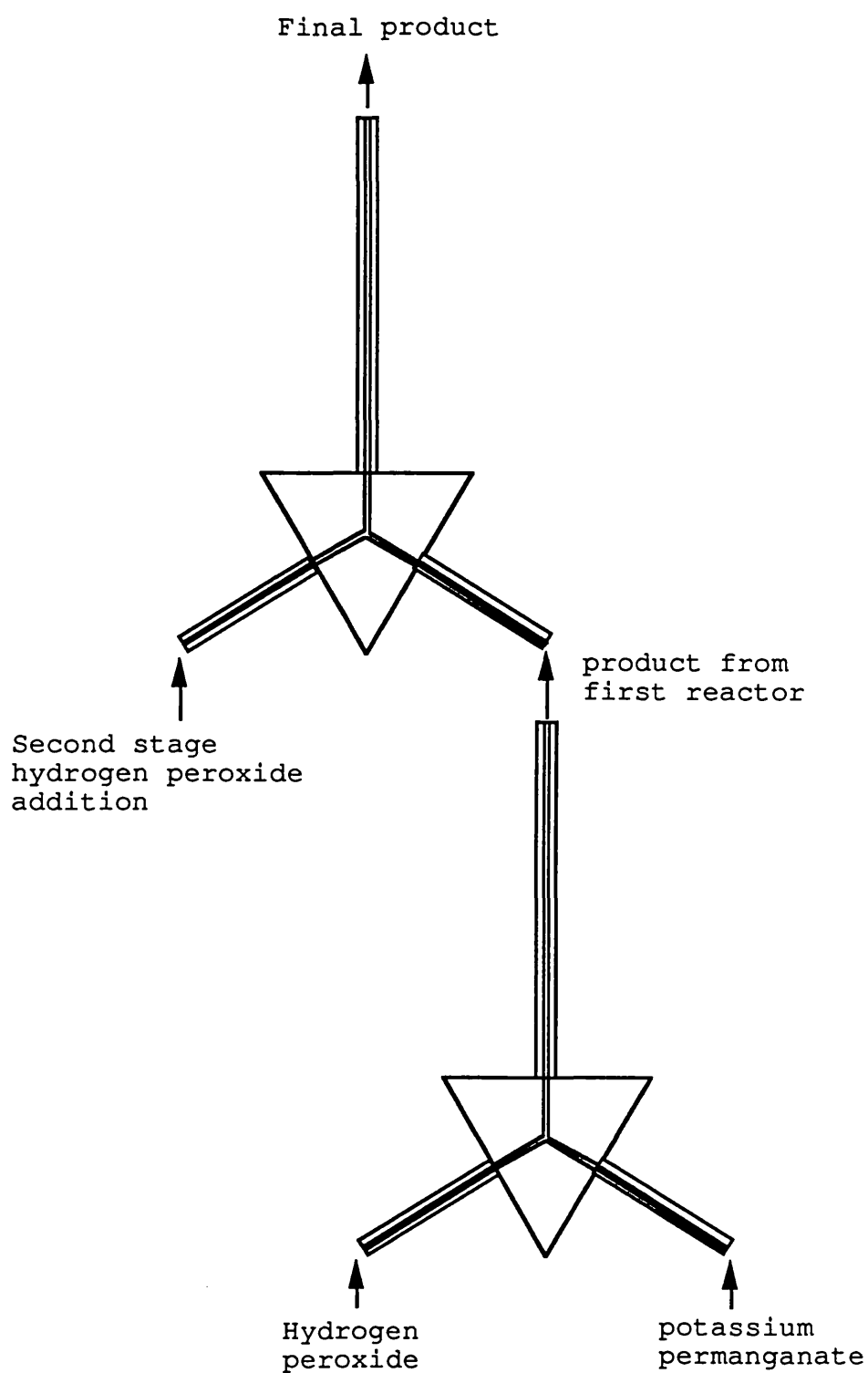


Figure 3.2a A two-stage capillary reactor setup
for HMnO preparation

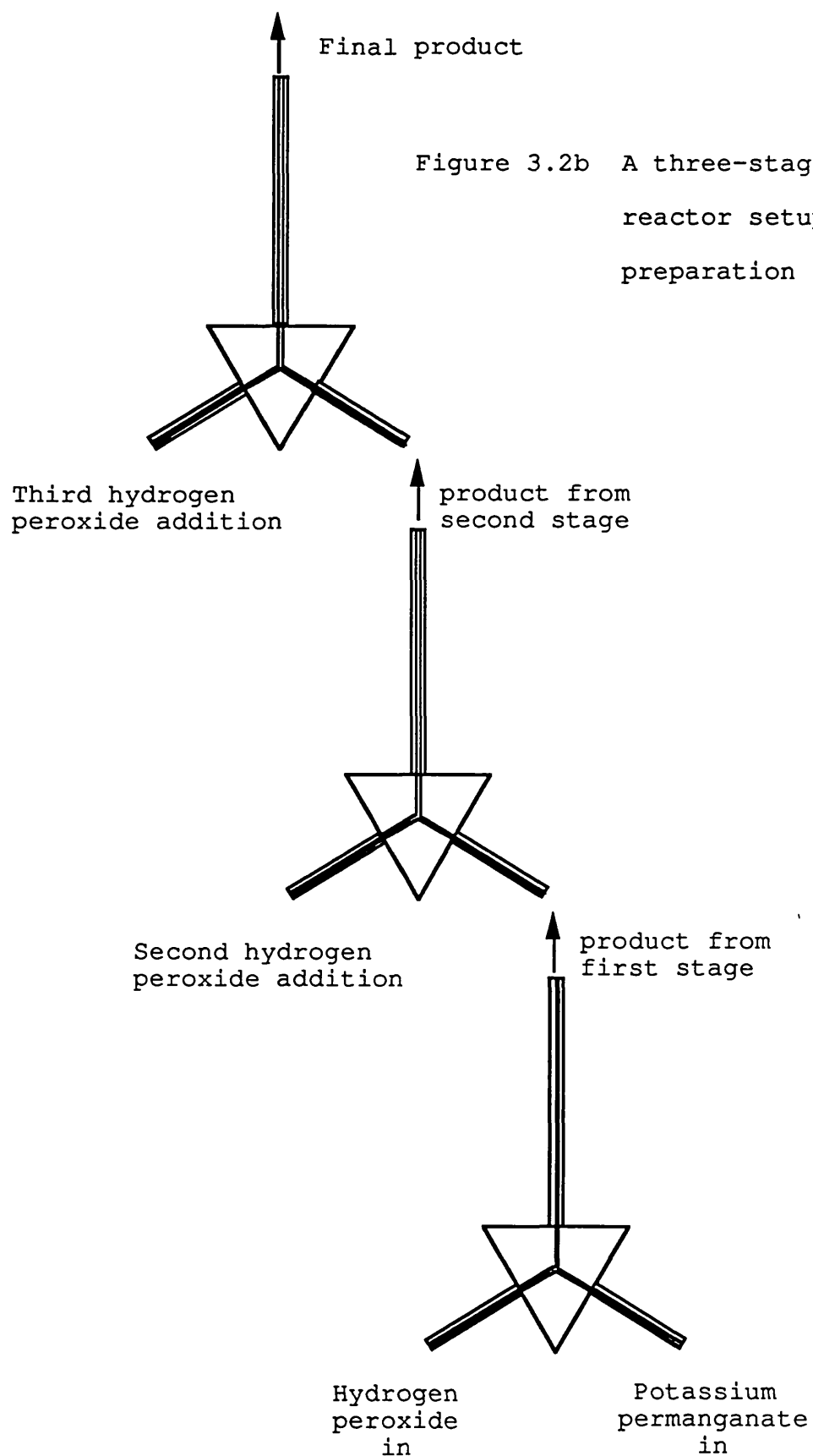


Figure 3.2b A three-stage capillary reactor setup for HMnO preparation

the amount of unreacted permanganate still remaining in solution. This was done spectrophotometrically¹¹¹ using the 528nm spectrophotometric peak characteristic of permanganate. All samples were washed and dried under similar conditions and the results of the yields are given in table 3.5.

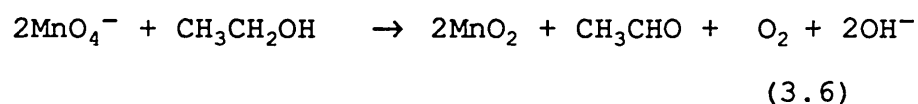
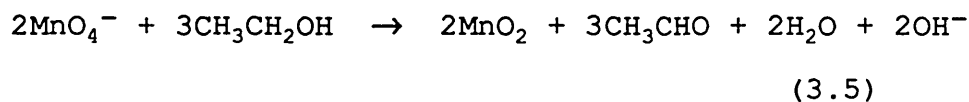
The results show that the maximum yield is from sample 5, a one-stage reactor system using twice the stoichiometric amount of H_2O_2 . The second highest yield is attained by sample 6, the one-stage system using six times the stoichiometric amount of H_2O_2 , whereas the remaining systems have a relatively low yields. The tests clearly demonstrate the effectiveness of the capillary reactor in preparing HMnO with respect to the traditional batch method, which show less than half the yields. It is believed that if the control volume at the point-of-reaction can be further reduced the yield may still be higher, however this has practical problems. Although the maximum yield is only 32% of theoretical, there is however an equivalent to 46% saving of H_2O_2 over the corresponding batch method. The two- and three-stage setups could give higher yields if the MnO_2 at the 'inlet' of the second and third stages is filtered in an intermediary process. This was demonstrated using the basic one-stage capillary reactor in a semi-continuous mode; for each run the product was allowed to settle and the unused permanganate recycled. The process was repeated 6 times using 6 times the stoichiometric amount of H_2O_2 to give a final product mass of 11.6g. This mass was obtained in making 10g, excess mass was due to water of hydration.

Table 3.5 Yield tests for HMnO manufacture prepared at varying strength of H₂O₂ and by different methods.

Sample	SYSTEM	Total reagent in all stages/ Stoichimetric	YIELD	
			g	%
1 2 3	BATCH B2 B4 B6	2 4 6	0.592 0.747 0.826	11.8 14.9 16.6
4 5 6	1-STAGE CAPILLARY 1S2 1S4 1S6	2 4 6	1.048 1.612 1.578	21.0 32.2 31.6
7 8	2-STAGE CAPILLARY 2S1 2S2	2 4	0.758 1.165	15.2 23.3
9 10	3-STAGE CAPILLARY 3S1 3S2	3 6	1.035 0.937	20.7 18.7

3.41 Mn(IV) oxide preparation by Alcohol precipitation.

Manganese dioxide was also precipitated from the permanganate using absolute alcohol. Two possible alcohol precipitation reactions may be represented as follows:



The product after drying and washing was found to have very little ion exchange capability and had no physical strength. The washing procedure was quicker requiring only two washes. Large volumes of alcohol were required when made in a batch process and therefore for higher yields the method proved too expensive.

3.5 Development of composite inorganic hydrous oxides

Work on a composite inorganic hydrous oxide based on Mn(IV) and Si(IV) has already been studied and an optimum composition of 83% HMnO : 17% HSiO has been reported⁹⁸. A series of tests were carried out on a variety of HTiO:HSiO and HSnO:HSiO composites to determine the optimum percentage of HSiO with respect to ion exchange properties and chemical stability in acidic, neutral and alkaline media. All ion exchange tests were carried out using the THORP and EARP simulants, chemical tests were carried out in pure distilled water (pH 6.0) and distilled water treated with NaOH and HNO₃ to simulate the pH values corresponding to THORP and EARP simulant feeds. The tests were designed to monitor the material performance as close as possible to the real working conditions. All preparations were carried out to stoichiometry to obtain 10g samples of the composite hydrous oxides. The precipitates were made using the capillary reactor and washings carried out as described earlier with the final conductivities less than 2000 μ Siemens. The ion exchange tests, as described in section 3.31, with the EARP and THORP feeds and the results for various compositions of HTiO and HSnO are given in tables 3.6 and 3.7 respectively.

Table 3.6 : Ion Exchange tests for various compositions of Sn and Ti composites with EARP Feed.

Sample	Am ²⁴¹		Pu ²⁴²		Sr ⁸⁵		Cs ¹³⁴		pH
	% ext.	K _d	% ext.	K _d	% ext.	K _d	% ext.	K _d	
Sn 80%	45.2	24.7	84.2	160	3.4	1.1	54.6	36	1.03
Sn 85%	19.9	7.5	74.8	89	2.7	0.8	30.2	13	1.03
Sn 90%	51.5	31.9	52.7	33.4	6.6	2.1	20.6	7.8	1.03
Sn 95%	43.2	22.8	60.2	45.4	6.8	2.2	5.6	1.7	1.05
Sn 100%	35.5	16.5	65.1	56.0	8.6	2.8	8.4	2.8	1.08
100% Si	95.3	608	96.4	803	92.3	360	86.0	184	10.1
Ti 50%	100	inf	100	inf	98.4	1845	98.8	2470	9.57
Ti 60%	100	inf	99.6	7470	98.6	2113	99.1	3303	9.77
Ti 70%	97.1	1004	98.3	1735	98.7	2278	97.7	1274	8.47
Ti 80%	96.1	739	99.1	3303	99.2	3720	95.3	608	8.72
Ti 90%	98.5	1970	99.2	3720	99.3	4256	91.7	331	7.90
Ti 100%	100	inf	100	inf	100	inf	87.3	206	10.31

Table 3.7 : Ion Exchange tests of various compositions of Sn and Ti composites with THORP Feed.

Sample	Am ²⁴¹		Pu ²⁴²		Sr ⁸⁵		Cs ¹³⁴		pH
	% ext.	K _d	% ext.	K _d	% ext.	K _d	% ext.	K _d	
Sn 80%	32.7	14.6	29.5	12.6	99.4	4970	89.7	261	7.82
Sn 85%	8.9	2.9	35.6	16.6	99.3	4256	70.9	73.1	8.05
Sn 90%	34.6	15.9	31.7	13.9	100	inf	79.1	114	7.44
Sn 95%	1.7	0.5	32.8	14.6	99	2970	60.6	46.1	7.80
Sn 100%	15.5	5.5	10.0	3.3	99.1	3303	38.5	18.8	7.92
100% Si	9.2	3.0	27.1	11.2	98.0	1470	96.2	760	10.94
Ti 50%	62.1	49.2	71.2	74.2	94.2	487	99.2	3720	11.64
Ti 60%	81.6	133	93.5	432	98.5	1970	98.4	1845	11.79
Ti 70%	86.7	196	99.6	7470	98.4	1845	97.8	1334	12.11
Ti 80%	85.0	170	97.9	1399	99.0	2970	94.5	516	12.32
Ti 90%	57.0	39.8	93.6	439	98.3	1735	87.1	203	12.23
Ti 100%	56.4	38.8	94.5	516	94.6	525	86.7	196	12.37

At first glance comparing the K_d values of the pure exchangers with those of the composites show that compositing with HSiO does indeed enhance the sorption process. The results show that HSnO and its composites are generally good exchangers at high pH and had low K_d values in the acidic EARP feed. HTiO was in general a good ion exchanger throughout the pH range. The Cs^{134} uptake was found to increase with increasing HSiO percentage for both materials in the two feeds. Sr^{85} uptake peaked at 20% and 10% HSiO in the THORP feed for HTiO and HSnO respectively and in the EARP feed it was maximum for pure HTiO and generally low for HSnO. Am^{241} uptake peaks were observed at 10% HSiO in HSnO in both the contacting solutions and at 30% HSiO in HTiO in THORP and 50 % HSiO in HTiO in EARP. The Pu^{242} uptake was maximum for HTiO at 30% HSiO in THORP and 40% in EARP, HSnO was low in both the feeds. All these conflicting values were not conclusive enough to arrive at a suitable final composition without considering the results for the chemical stability tests.

For chemical stability tests accurately weighed 0.5g portions of exchangers, mesh size 420-250 μ m were placed in 1oz glass bottles with bakerlite lids. 30ml of THORP and EARP simulated distilled water solutions and distilled water were added to the bottles. The bottles were sealed and vigorously shaken at regular intervals over a period of 27 days. The pH of the solutions were regularly adjusted to starting pH values and the pH profiles recorded. The pH profiles together with the ion exchange results were merely

intended to observe the nature of ion exchange behaviour of the materials, which is covered in a later section. Preliminary atomic absorption analysis with the solutions revealed almost no solubility. So the bottles were placed in a water bath at 60°C for three days to simulate adverse working conditions. All final atomic absorption analysis were carried out only when a pH equilibrium had been achieved i.e. final pH equalled starting pH, so that the dissolution, if any, would be for the material at the 'working' pH values. The atomic absorption analysis was carried out on a Perkin-Elmer 4020 machine and results are given in tables 3.8, 3.9 for EARP and THORP feeds respectively and table 3.10 for water. The Si presence observed in the high pH solution was not surprising as silica is soluble in alkali solutions. The high Si content in the EARP feed can only be explained due to the unbonded silica present in the exchanger. The results show that for HSnO:HSiO composite the maximum stability was at 15% HSiO and for HTiO:HSiO was good at ≈30% HSiO, in all the three test solutions.

From the ion exchange and chemical stability tests, it was decided that the optimum compositions for Ti(IV) and Sn(IV) based composites were 70%HTiO : 30%HSiO and 85%HSnO : 15%HSiO. Described below are the methods for preparing, the above composites, based on stoichiometry.

Table 3.8 : Chemical stability in EARP feed simulant of various compositions of HSnO and HTiO composites.

Sample	ppm of Ti/Sn in solution	ppm of Si in solution
Sn 80%	1.6	23.7
Sn 85%	1.1	0
Sn 90%	0.5	13.6
Sn 95%	2.0	3.8
Sn 100%	5.7	-
100% Si	-	69.5
Ti 50%	2.6	164
Ti 60%	3.8	136
Ti 70%	0.5	110
Ti 80%	0	135
Ti 90%	0	58.5
Ti 100%	0	-

Table 3.9 : Chemical stability in THORP feed simulant of various compositions of HSnO and HTiO composites.

Sample	ppm of Ti/Sn in solution	ppm of Si in solution
Sn 80%	97.8	41.7
Sn 85%	19.3	0
Sn 90%	55.7	20.3
Sn 95%	49.7	5.8
Sn 100%	53.9	-
100% Si	-	> 411
Ti 50%	0.1	435
Ti 60%	0.4	259
Ti 70%	7.5	159
Ti 80%	0	96.7
Ti 90%	0.8	41.1
Ti 100%	4.6	-

Table 3.10 : Chemical stability in distilled water of various compositions of HSnO and HTiO composites.

Sample	ppm of Ti/Sn in solution	ppm of Si in solution
Sn 80%	0.2	23.1
Sn 85%	0.4	0
Sn 90%	0	11.0
Sn 95%	0.2	2.5
Sn 100%	4.1	-
100% Si	-	44.9
Ti 50%	6.5	69.2
Ti 60%	1.1	86.8
Ti 70%	0.5	86.0
Ti 80%	0.5	45.6
Ti 90%	0.6	24.4
Ti 100%	0.6	-

3.51 Preparation of hydrous Ti(IV) and Sn(IV) oxide composites using the capillary reactor

The amounts given below are to make 10g of 70% HTiO : 30% HSiO composite ion exchanger, the method for preparing the Sn(IV) composite is similar. The BDH TiCl₄ solution was in 4.11 M HCl and hence the amount of NaOH required was much greater than calculated from the stoichiometric equation (3.1). A stoichiometric amount of the titanium tetrachloride for a 10g sample of the composite hydrous oxide was equivalent to 110.8ml of the BDH 15% w/v TiCl₄ 'Analar' solution. The total mass of NaOH required was 31.15g, NaOH contribution from Na₂O in the sodium silicate solution (waterglass) was also taken into consideration. 7.12g of waterglass were required to give 30% HSiO. The waterglass solution (BDH GPR) has a density of 1.5 ml/g. The NaOH was slowly dissolved in distilled water in a cool water bath. 4.75ml of waterglass was added to caustic soda solution and the final solution made up to 2 litres. The 110.8ml of TiCl₄ was also made up to the same volume and thoroughly stirred. Both solutions were passed through the capillary reactor to give 4 litres of slurry. The slurry was washed down to 1700 μ Siemens and dried at 110°C overnight with a final mass of 12.6g. The dried product was crushed and wet sieved into various fraction sizes. It was observed under a microscope that dry sieving gave rise to agglomeration of fine particles. As a consequence there was an apparent need to centrifuge contacting solutions after an ion exchange test. This effect was almost

negligible in wet sieving. Wetting the material after drying and measuring the various fractional sizes has been used as a physical strength test by previous workers, as illustrated on hydrous Sn(IV) oxide by Donaldson and Fuller⁶⁴.

The preparation of 85%HSnO:15%HSiO composite was in essence the same as the above procedure. A final mass of 13.0g was achieved, which includes the water of hydration.

3.52 Preparation of hydrous Mn(IV) oxide composite using capillary reactor

10g sample of 83%HMnO:17%HSiO was made by dissolving 15.085g of BDH analar grade KMnO_4 in distilled water. The solution was gently heated to accelerate the permanganate dissolution and then allowed to cool before 3.71ml of waterglass ('BDH, GPR') was dissolved in the permanganate solution. 1.43ml of 1M HNO_3 was added to this solution to precipitate silica from waterglass. The whole solution was made up to a final volume of 2 litres. A stoichiometric amount of H_2O_2 , 27.05ml of 6% w/v BDH hydrogen peroxide, was made up to 2 litres. Both solutions were passed through the capillary reactor. The products were allowed to settle and the unreacted permanganate recycled. The process was repeated (5 times) until almost all the permanganate had been reacted. The final precipitate was washed with distilled water. In the first two washes it was observed that there was still a little unreacted permanganate

present in the floc which had totally diminished on the third wash. Finally, the cake was dried overnight at 110°C and wet sieved to fractional sizes. Total yield was 91%.

100g batches of the composites have been regularly made with high degree of reproducibility. The mass throughput is restricted by the capacity of the centrifuge and the vast amounts of distilled water required; a 100g sample may typically require between 30 - 35 litres of distilled water.

3.6 Effects of drying temperature on ion exchange properties

A series of batch tests were carried out to determine the effect of drying temperature on the ion exchange properties of a hydrous oxide, HSnO was used for this experiment. A 100g batch of HSnO was prepared in the usual manner using the capillary reactor and washed. The washed precipitate was equally divided into four equal portions to be dried at four different temperatures - room temperature, 64°C , 110°C and 210°C . The sample dried at room temperature was placed in glass beaker and covered with perforated layer of polystyrene. The sample took 9 days to dry to a consistent low hardness throughout with an average laboratory temperature of $20^\circ\text{C} \pm 2.0$. The sample dried at 64°C was dried in a closed oven over 4 days. The remaining two portions were dried overnight in an oven.

The results for the ion exchange tests are given in tables 3.11 and 3.12. The ion exchange tests were carried out in the usual manner; with the sample mass of 0.5g in size $420\text{--}210\mu\text{m}$ wet sieved, volume of solution 15ml and contacting time 24 hours.

It is quite apparent from the results that over the temperature range considered there is no profound change in the ion exchange characteristics of HSnO . The relatively high values for Pu^{242} uptake in the THORP feed may be due to the precipitation of Pu (as plutonate²³) on to the exchanger rather than pure ion exchange (of PuO_2^{2+}).

On the basis of these results it was decided to dry the

hydrous oxides at a temperature of 110°C, sufficient to dry off loosely bound surface water and retain most of the interstitial water which may partake in the ion exchange process.

Table 3.11 : Ion Exchange performances of HSnO dried
at various temperatures with EARP feed

Drying temperature	Am ²⁴¹		Pu ²⁴²		Sr ⁸⁵		Cs ¹³⁴		pH
	% ext.	K _d	% ext.	K _d	% ext.	K _d	% ext.	K _d	
RT	51.6	32.0	38.4	18.7	0	0	0	0	1.92 1.87 1.83
64	23.1	9.0	36.1	16.9	0	0	0	0	
110	37.1	17.7	40.9	20.8	0.7	2.4	0	0	
210	34.8	34.8	39.2	19.3	0	0	0	0	

Table 3.12 : Ion Exchange performances of HSnO dried
at various temperatures with THORP feed

Drying temperature	Am ²⁴¹		Pu ²⁴²		Sr ⁸⁵		Cs ¹³⁴		pH
	% ext.	K _d	% ext.	K _d	% ext.	K _d	% ext.	K _d	
RT	44.4	24.0	59.4	43.9	100	∞	27.9	11.6	
64	31.5	13.8	36.5	17.2	100	∞	25.6	10.3	7.87
110	61.7	48.7	36.0	16.9	100	∞	25.2	10.2	8.30
210	55.0	36.7	28.0	11.9	100	∞	24.6	9.8	9.80

Chapter 4

Ion Exchange Properties

*4.1 Introduction 4.2 The pH Titration Curves 4.3 Cation
Exchange as a function of pH 4.4 Capacity
Determinations 4.5 Selectivity Tests 4.6 Ion Exchange
Tests with Various Simulant Feeds.*

4.1 Introduction

Having developed techniques to make the materials reproducibly, various experiments were undertaken to characterise the materials with respect to the nature of the ion exchange processes occurring at different pH values. Total ion exchange capacity values were determined and the ability for the ion exchangers to undergo reversibility was also demonstrated. Experiments to illustrate the change in selectivity series of ions were also carried out at different pH values. Finally the ion exchange performances of the materials with several low level radioactive waste stream simulants were carried out to find the best working environment.

4.2 The pH titration curves

The pH titration curves are often determined to characterise the functional groups of the ion exchangers. Such tests can also reveal the type of exchange occurring over a pH range from acid to alkali - either anionic, cationic. The ion exchange of inorganic materials is usually pH dependent; classical theory indicates that the hydrous oxides are cationic exchangers at high pH and anionic at exchangers at low pH. A pH titration curve, with the exchanger present, compared with a blank is useful method of assessing this possible kind of behaviour in a qualitative manner. The pH verses acid added curve usually deviates quite significantly from the blank, as is shown schematically in figure 4.1.

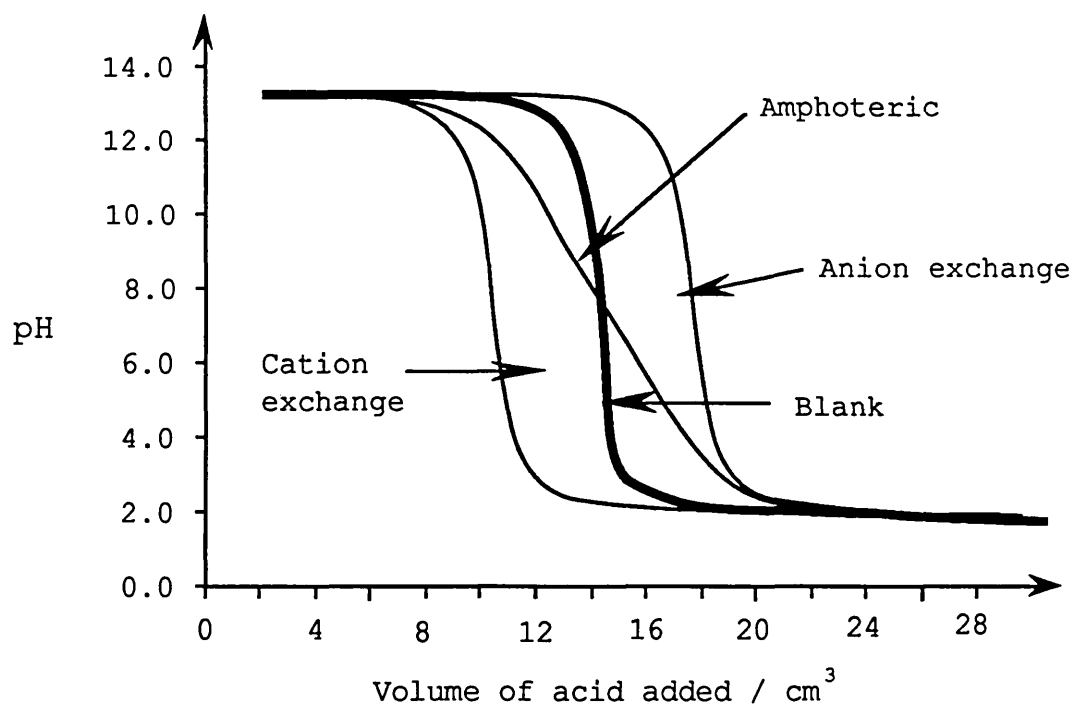
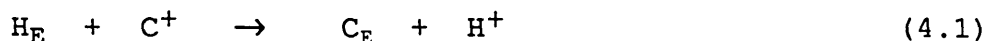
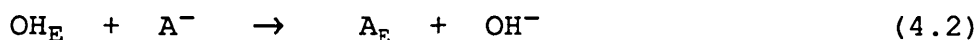


Figure 4.1 Acid Base titrations with inorganic hydrous oxides

If cation exchange occurs the overall reaction in the solution involves the transfer of H^+ in to the solution:



The subscript refers to the ion on the exchanger. This means that the pH will fall relative to blank, as shown in figure 4.1. If anion exchange occurs:



then the titration curve lies above the blank throughout the pH range studied. Certain exchangers may exhibit both cationic and anionic behaviour in which case the curve cuts over the blank. This is the classical behaviour of a hydrous oxide with cation exchange at high pH and anion exchange at low. When the blank is cut by the titration curve it can be taken to indicate the possible change in exchange properties.

The shape of the pH titration curve depends on various factors, eg. ageing, the chemical species to be measured, co-ion present, ionic strength, ratio of solution to sample, temperature etc. When the exchanger exhibits large steric and ion-sieve effects (as some crystalline forms of $HMnO$), the shape of the curve much depends on the chemical species in the system. Abe³¹ has illustrated some of these effects in his review paper. Unlike the work considered here, Abe³¹ reports not only the cationic behaviour but also the anionic.

The aim of the pH titration work in this study was to investigate the type of exchange occurring over a pH range and deduce the active functionalities in the process. The materials used in these experiment were $HTiO$, $HTiO:HSiO$

composite, HMnO, HMnO:HSiO, HSiO and HSnO. All materials were freshly prepared by the capillary reactor method as described in chapter 3, except for pure HSiO which was prepared by batch method.

Experimental:

15ml aliquots of 0.1M solution of a metal hydroxide and 0.1M solution of salt of same metal were mixed together and 0.25g of the exchanger, mesh size 400-250 μ m wet sieved, were added. This was stirred for 5 minutes and pH measured using a 'Phillips 5400' pH meter. Aliquots of 0.1M hydrochloric acid were added to the flask and stirred for 5 minutes, with the exchangers equilibrating. At the end of the 5 minutes pH was recorded and the process was repeated. Aliquots of hydrochloric acid were varied from 5ml to 0.5ml depending on the position on the curve; large aliquots on the very low and high pH value and smaller additions nearer to the point of inflexion. 0.1M hydrochloric acid was added in the titrations to the following initial solution systems:

- (a) 0.1M NaCl, 0.1M NaOH,
- (b) 0.1M KCl, 0.1M KOH,
- (c) 0.1M CsCl, 0.1M CsOH,
- (d) 0.03M SrCl₂, 0.03M Sr(OH)₂ (due to low solubility of Sr(OH)₂ - 0.03M HCl was added in this case), and
- (e) 0.1M NaClO₃, 0.1M NaOH.

Strontium hydroxide was unstable and tended to precipitate out with time as the insoluble carbonate. Graphs of pH versus total amount of acid added were plotted

and compared with blank run obtained in the absence of exchanger.

The results are presented in figures 4.2 to 4.7. The blank is represented by the continuous line and the pH titration curves in the presence of the exchanger by the dotted lines.

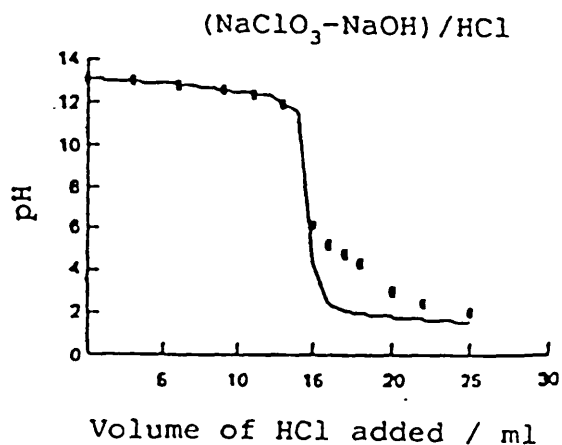
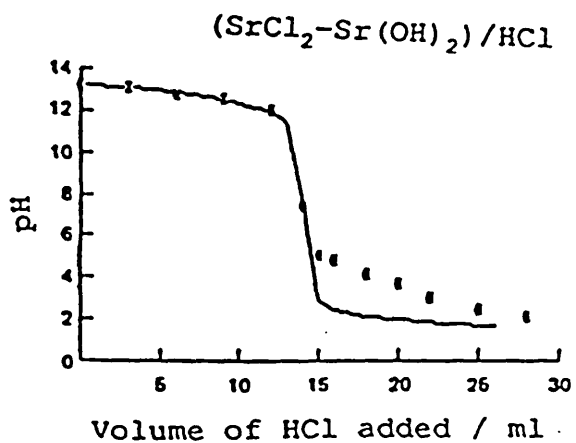
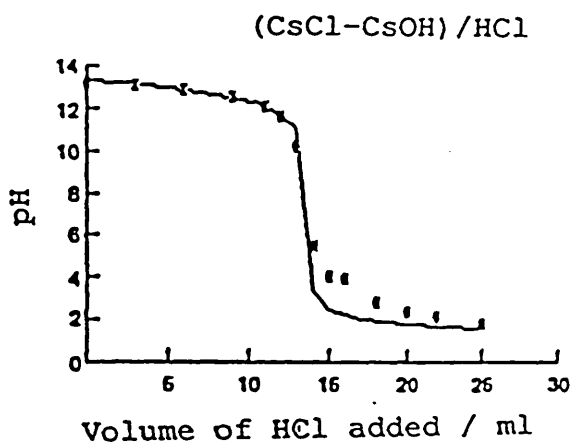
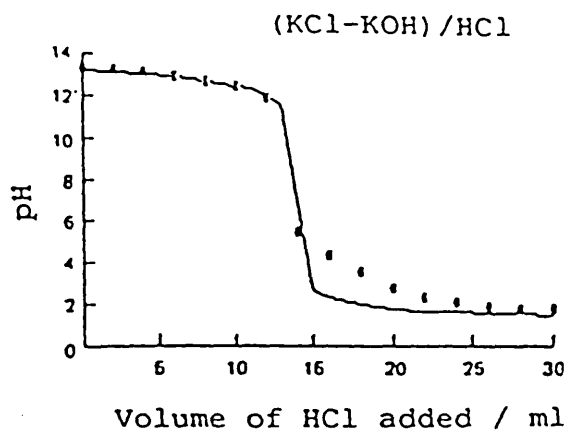
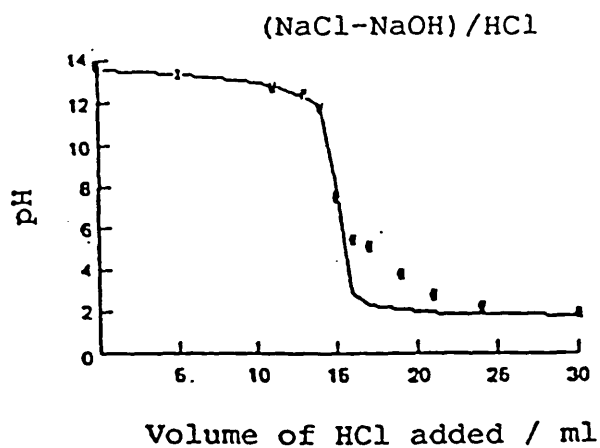


Figure 4.2 HTiO pH titration curves

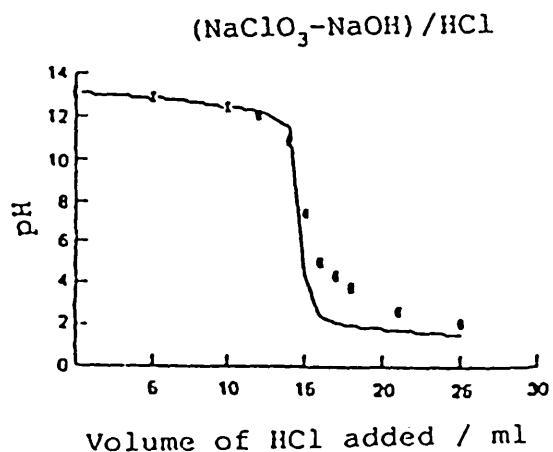
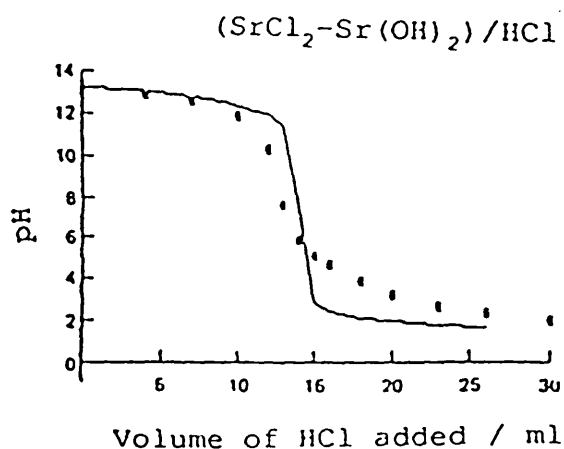
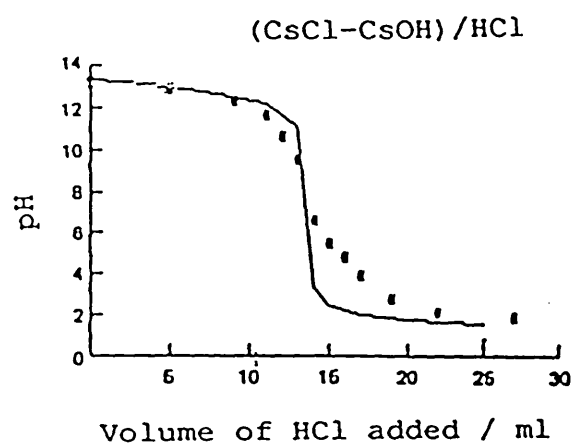
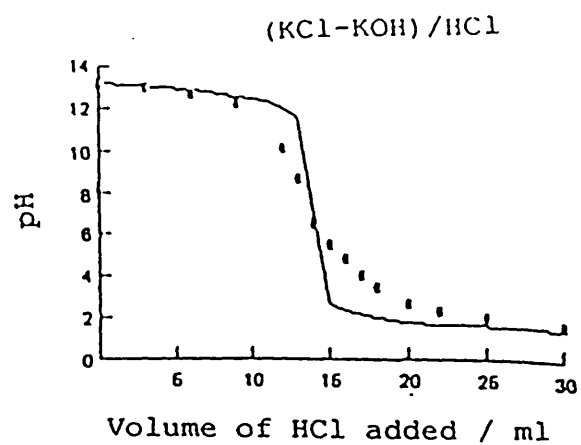
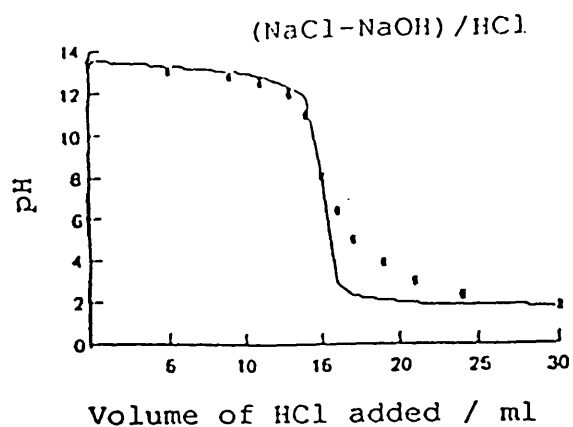


Figure 4.3 HTiO:HSiO pH titration curves

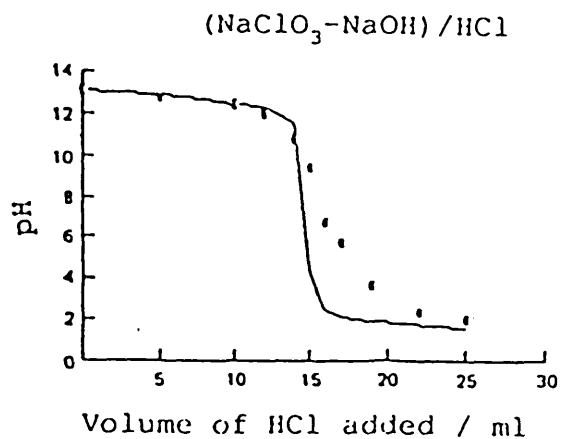
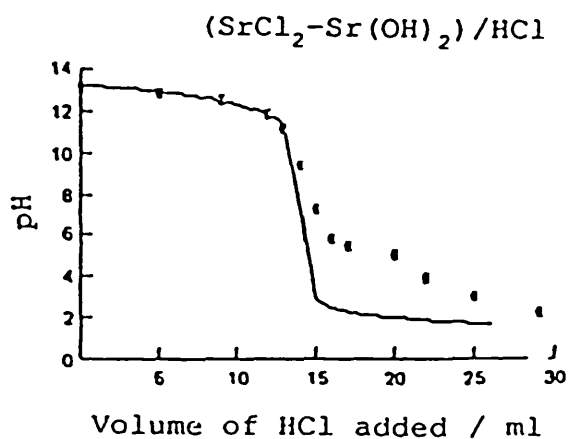
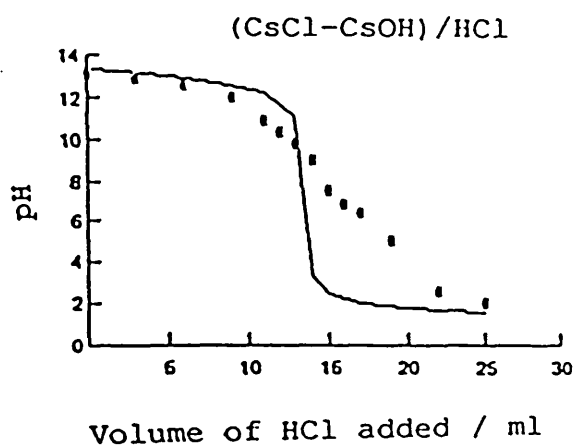
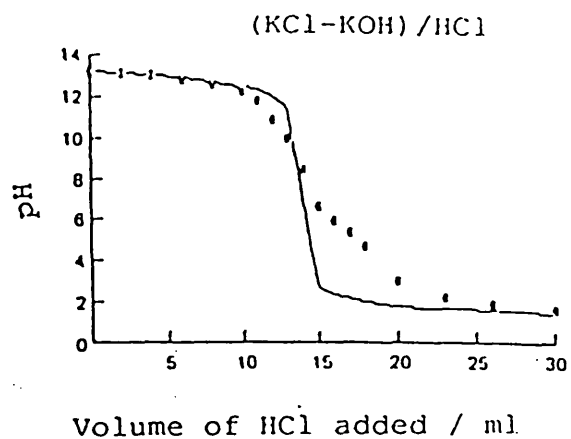
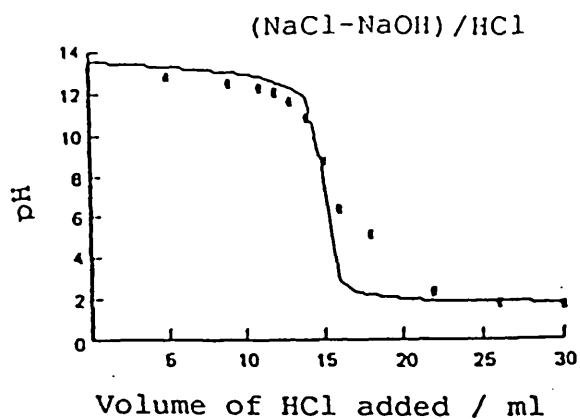


Figure 4.4 HMnO pH titration curves

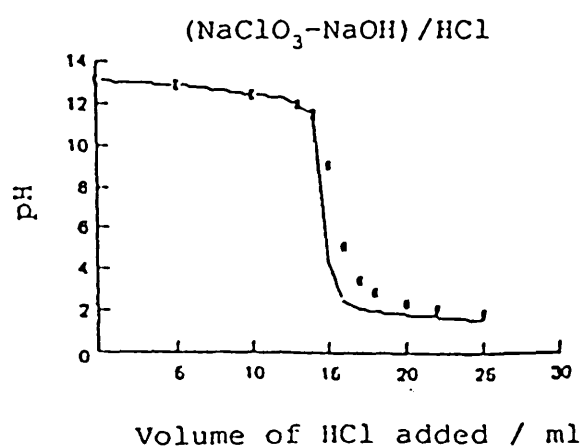
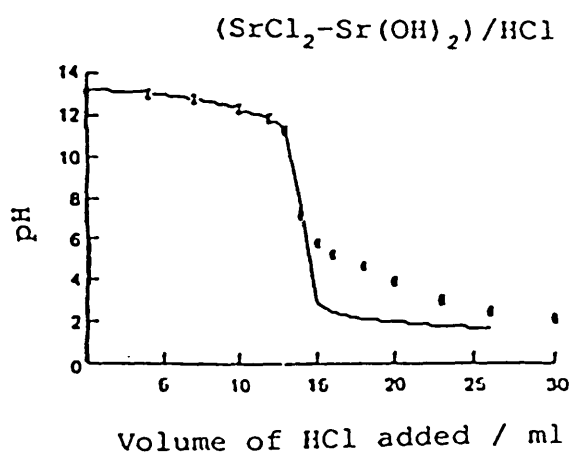
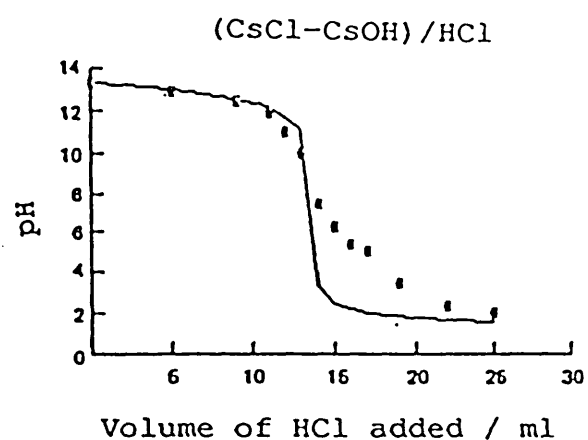
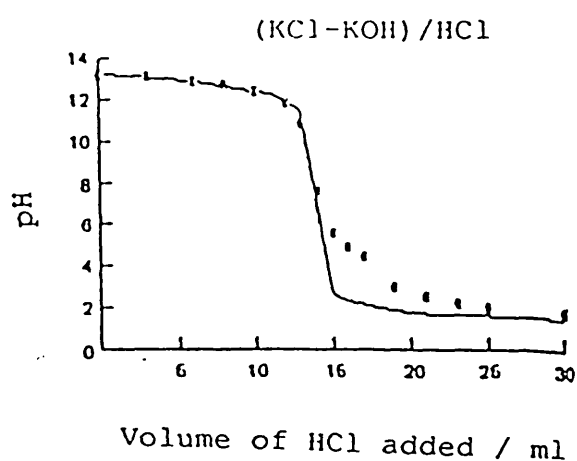
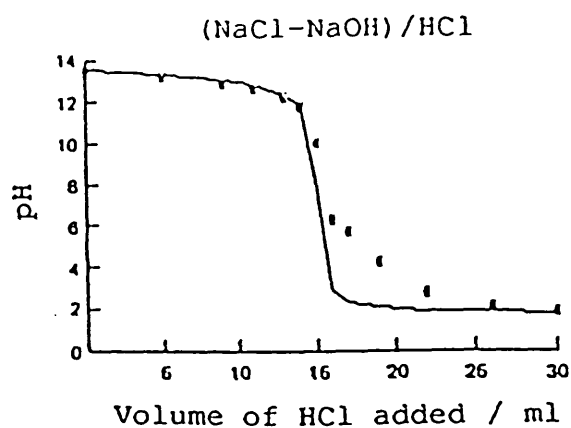


Figure 4.5 HMnO:HSiO pH titration curves

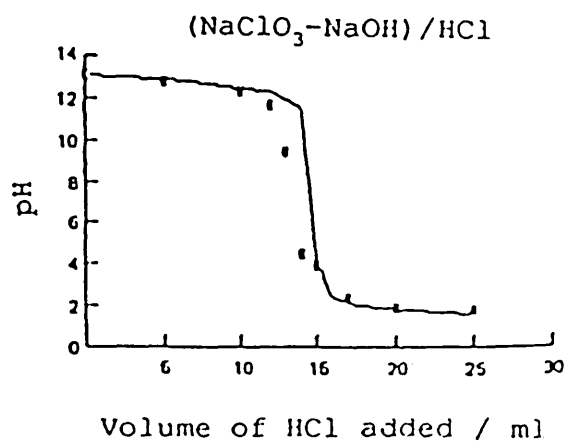
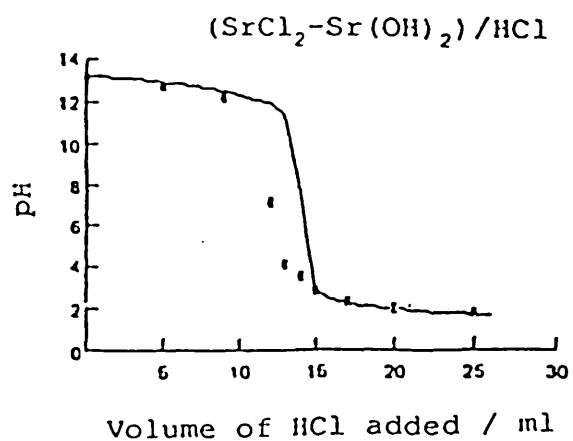
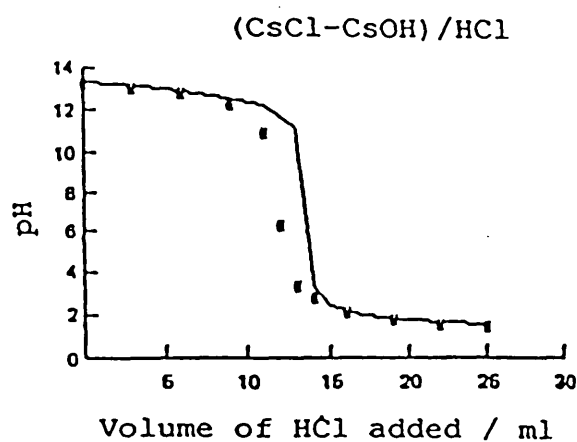
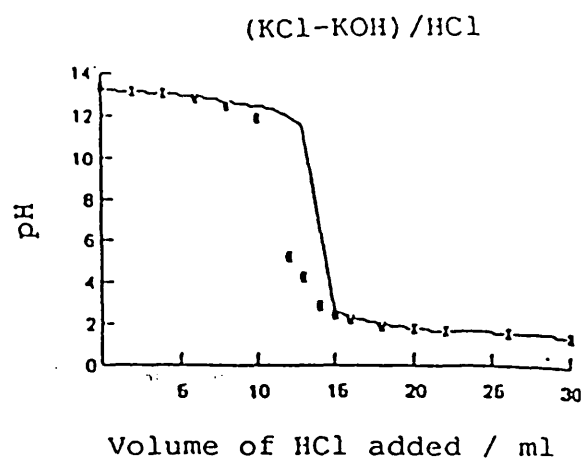
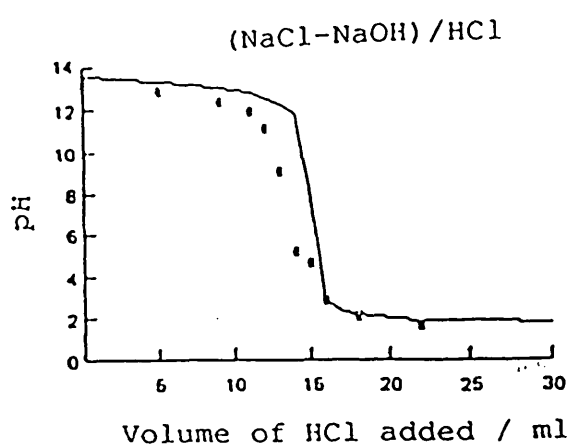


Figure 4.6 HSno pH titration curves

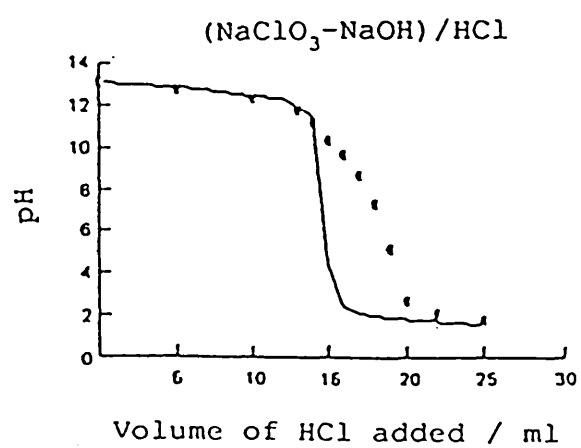
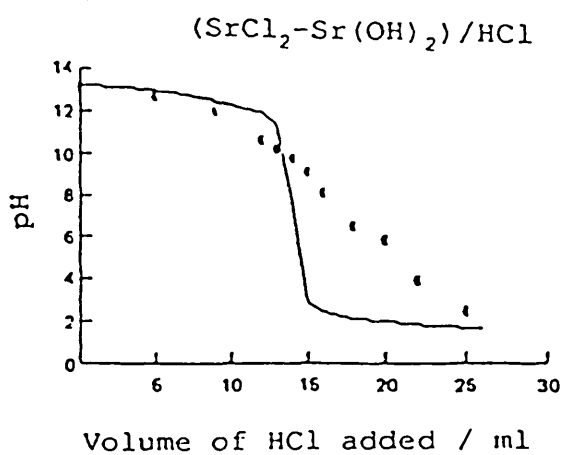
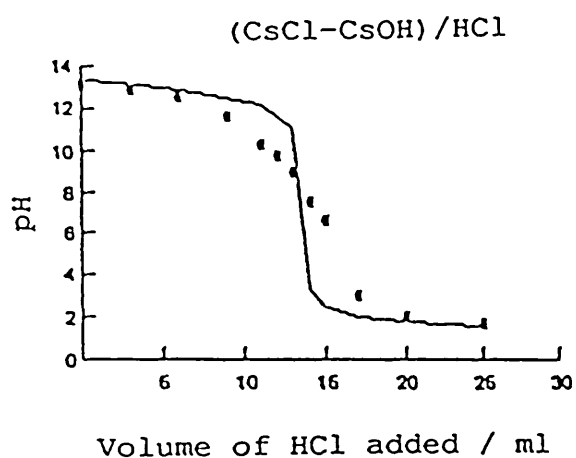
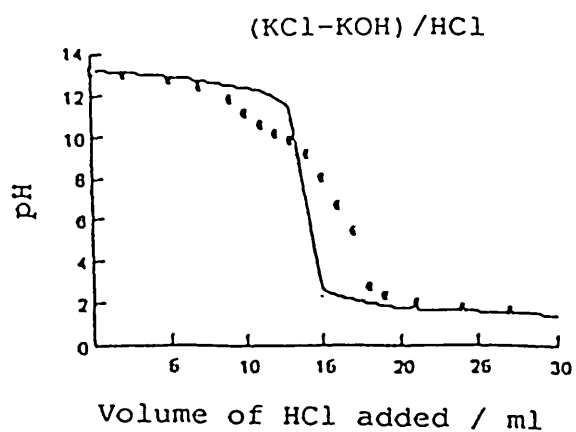
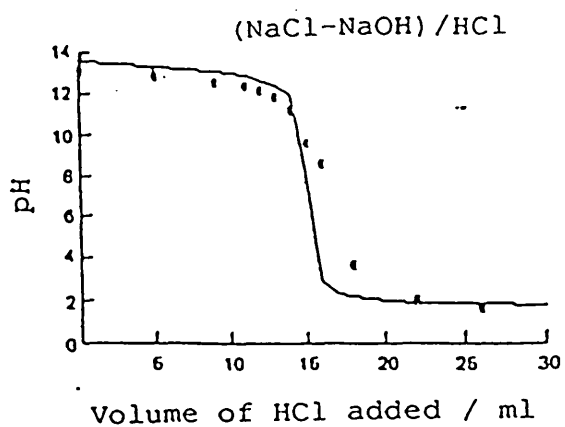


Figure 4.7 HSiO pH titration curves

The HTiO:HSiO composite (figure 4.3), HMnO (Figure 4.4), HTiO (figure 4.2) and HSiO (figure 4.7), all show cationic behaviour. However, in comparing these curves to the classic acid/base titration curve (figure 4.1) it also appears to exhibit apparent anionic exchange. HSnO showed only cationic exchange (figures 4.6). In nearly all the cases only one inflexion point is observed indicating monofunction behaviour. If there had been more than one inflexion, each would have corresponded to a functional group.

The HTiO is observed to be an anion exchanger. This observation is based on the profile obtained in the presence of the exchanger. However, comparing figures 4.2, 4.3 and 4.7 it is clear that the HSiO in the composite does indeed have an affect on the ion exchange characteristics, as pure HSiO clearly exhibits both cation and anion throughout the range of systems considered.

The HTiO:HSiO apparently shows constant anion exchange abilities for all the systems but varying cation exchange abilities - that of Na appears quite poor. The pH at which the overall exchange on material is zero (zero point of change) varies in the range 6-8. Where Na is present there appears to be little if any cation exchange taking place.

The HMnO apparently shows good capacity for anions, however some of this "capacity" may be due to dissolution of the material. It shows good capacity for alkali metals, especially caesium, but relatively poor capacity for strontium. The PZC varies in the pH range 9-11.

The HMnO:HSiO exhibits similar behaviour to HMnO for Cs

and Sr systems. In the sodium and potassium systems it exhibits greater anion exchange. Surprisingly, the HSiO content in the composite does not appear to have any apparent affect on the ion exchange behaviour as with HTiO:HSiO.

The HSiO shows strong cation and anion exchange, depending on the pH, in all cases except that of Na, when cation exchange is weak.

Finally HSnO is a good cation exchanger, irrespective of ionic size or charge , of the elements tested, down to pH 4.0.

The chlorate ion was used as an alternative anion and to see if oxidizing agents had any effect on the ion exchange processes. The oxidizing agent seems not to have any effect on ion exchange properties of any of the hydrous oxides.

On the basis of these qualitative pH titration tests it is apparent that some of the exchangers can sorb anions. However, this phenomenon needs to be reasserted with tests to investigate anion exchange behaviour with changing pH. Work done by Mancilla and White¹⁶⁰ has shown successful uptake of iodate (IO_3^-) ions by HTiO, HMnO, HSnO and HSiO. In the same study it was also shown that HSiO also adsorbed iodide (I^-) ions. The results presented by Mancilla and White¹⁶⁰ and those reported by Abe³¹ give strong backing to the supposition that some of these oxides can sorb anions. Nevertheless, it is proposed that qualitative tests dedicated to anion exchange behaviour be carried out to authenticate the behaviour exhibited by the titration curves. The tests should also reveal the point of zero

charge values for the respective hydrous oxide.

4.3 Cation exchange as a function of pH

The results of the pH titrations have shown the character of the ion exchangers and their active functional groups. It was reported that, for example, HTiO is predominantly an anion exchanger at low pH, but at this pH it has not been conclusively proven that it does not sorb cations. The object of studying the variation of distribution coefficient as a function of pH was to illustrate this fact. Ideally, a comparative study of the two types of exchange at low pH should have been carried out to show the predominance of anionic over cationic. Since (radioactive) cationic species are of interest in this work only the cation exchange over the pH range was studied.

The materials used for these experiments were HTiO:HSiO composite and pure HTiO as examples of amphoteric and predominantly anionic exchangers. The materials were of the same batch as those used in pH titration tests. 0.1g portions of each exchanger were contacted with an aliquot each of the 10^{-4}M CsNO_3 and 10^{-4}M $\text{Sr}(\text{NO}_3)_2$ solutions spiked with radioactive Cs^{134} and Sr^{85} respectively; the bottles were sealed and placed on a rotary mixer for 5 hours. After this period, the bottles were taken off and the pH values adjusted from pH 1 to 12 with nitric acid and sodium hydroxide and the bottles replaced for overnight mixing. The following day the pH values were measured again and repeated adjustments were made if and when necessary. Some pH values took 5 days to adjust to the required equilibrium value. Once the required pH values had been attained 6cm^3 aliquots were extracted and centrifuged. 5cm^3 of this were

used to determine Cs and Sr concentrations by gamma spectrometry¹⁰⁵ using their 605 and 514 keV peaks respectively.

The results are given in figures 4.8a, 4.8b and 4.9a, 4.9b for HTiO and HTiO:HSiO composite respectively. The results show that despite the predominance of anion exchange, as revealed by the pH titrations, there is indeed considerable cationic capacity at low pH. A comparison of the results shows that the maximum K_d values are higher for the composite than for the pure material. This was not surprising as the composite has shown greater amphotericity. Another observation was the lower K_d value of HTiO for Cs at pH 1.0 as compared with the composite; this is indicative of the greater predominance of anionic exchange of HTiO. However this was not so apparent with the strontium solution and could be related to the higher charge density of the Sr^{2+} ion.

Figure 4.8a pH dependence of cationic exchange

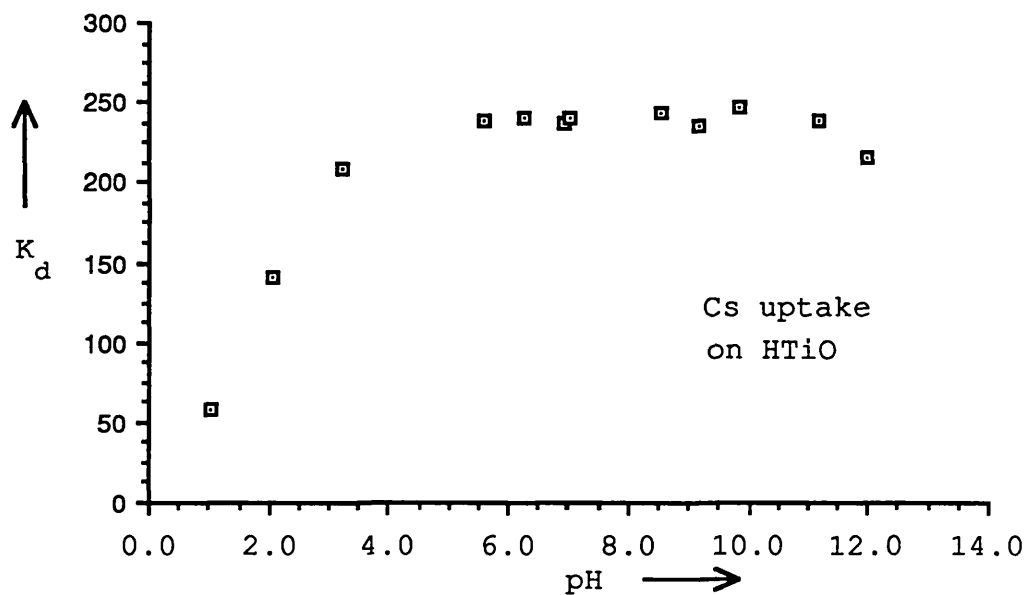


Figure 4.8b pH dependence in cationic exchange

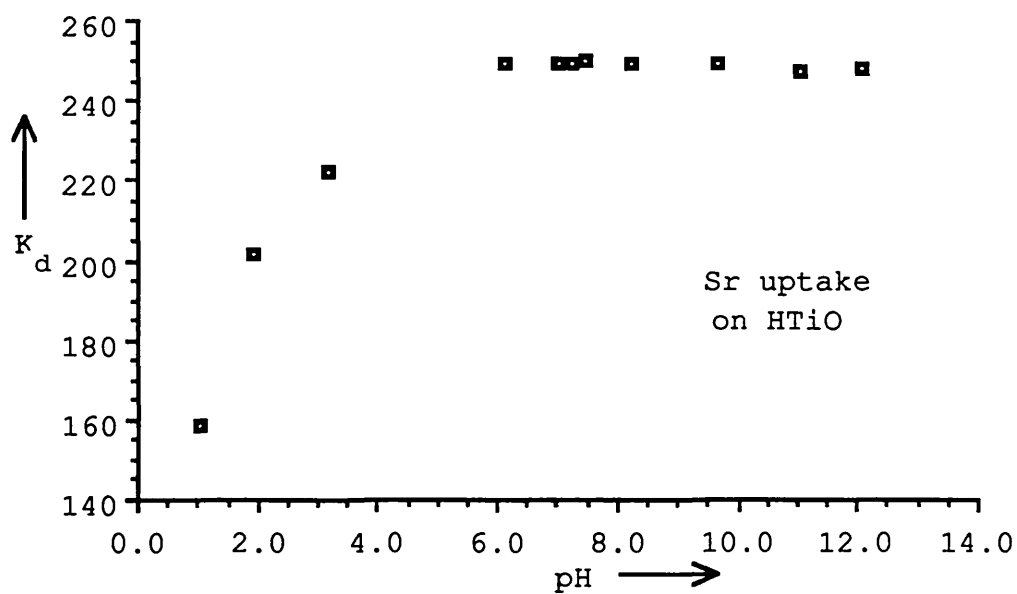


Figure 4.9a pH dependence of cationic exchange

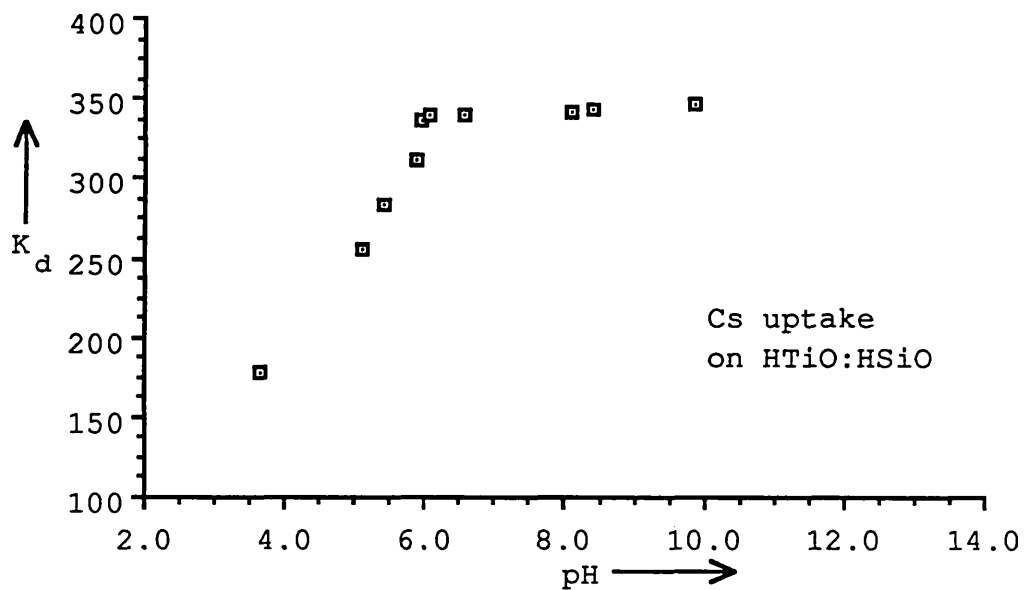
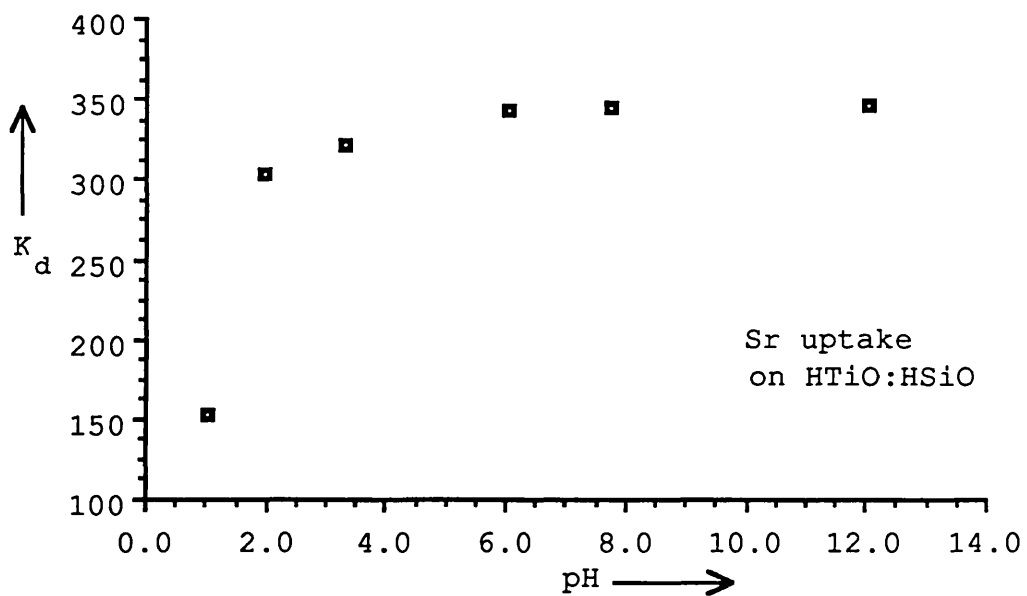


Figure 4.9b pH dependence of cationic exchange



4.4 Capacity determinations

A series of column tests were carried out to determine the total effective ion exchange capacity of the materials. Fresh batches of materials were prepared as described in an earlier chapter. All solutions used for these tests were made up to 10g/l concentration of the cation of interest. Reversibility of the ion exchange process was also investigated and illustrated by loading and eluting strontium and uranyl ions from loaded columns of titanium composite hydrous oxide. The preliminary ion exchange tests on the exchange materials with THORP and EARP were indicative of the materials possessing reasonably high ion exchange capacities. In light of these results it was decided to have a high concentration (10g/l) for the contacting solutions. The elutions were carried out with various strengths of nitric acid.

The batch capacity tests¹⁰⁶ only give the effective non-equilibrium capacity, in a state of incomplete exchange. The total effective capacity can readily be determined by a column operation where equilibrium conditions prevail. Since the rate of exchange is controlled by film and particle diffusion processes, which are slow, the rapid passage of solution through a column will lead to incomplete sorption, or alternatively, will require a proportionately longer column for complete sorption. Normally a compromise between the two has to be adopted.

4.41 Loading

A 'pyrex' glass column 15cm long and 1cm internal diameter with a sintered disc (number 4) at the lower end with a regulating tap at the bottom was used. The column was graduated. The mesh size for all materials used was 210-105 μ m, wet sieved. Dry material was poured into the column and gently tapped, to allow it to settle to a dry volume of 3cm³. 3cm³ portions of materials were then accurately weighed and these weights used in subsequent experiments. The weights of 3cm³, dry volume, of HTiO, HTiO:HSiO, HMnO, HMnO:HSiO and HSnO were 4.21g, 2.88g, 3.77, 4.58, and 6.17g respectively.

An accurately weighed sample (3cm³) was slurried with distilled water in the column. The air below the sintered disc was pushed upwards by washing the column briefly by an upward flow of distilled water with sufficient velocity to cause the ion exchanger bed to become fluidised - this removed any air bubbles that might have caused channelling. Material was allowed to settle and form a bed supported on the sintered disc. If the materials are dry-sieved then invariably fines would float in the water above the bed and have to be carefully removed. The level of the flexible capillary, at the outlet for test solution, was adjusted such that there was $\approx 1.5\text{cm}^3$ water head above the bed - the water level must not be allowed to expose the bed, in that case the above procedure needs to be repeated. The column was now ready to receive the contacting solution. Drop wise addition of the contacting solutions, at approximately 0.33ml per minute was achieved using a peristaltic pump,

the flexible capillary required slight readjustment to give a steady state condition with a constant head. 5cm^3 (≈ 1.67 bed volumes) samples were collected every 15 minutes and analysed for the isotopes using their respective γ and α peaks. Cs^{134} , Sr^{85} , Eu^{152} and U^{235} were analysed using their 605, 514, 344 and 185keV γ/β peaks and Th^{232} was analysed for its 4.39MeV α -peak via a TTA extraction¹¹⁵ method. The pH values were also recorded for each sample collected to ensure that the pH was within the range of solubility of the species being extracted (obtained from Pourbaix diagrams) and were also monitored to avoid chemical precipitation.

The results obtained were plotted as percentage extraction (y-axis) versus volumes passed through (x-axis) and the ratio of the areas under and above the curve were used to determine the total ion exchange capacity. A typical breakthrough curve of HTiO for Sr uptake is given in figure 4.10a, and the capacity values were determined in the usual manner. The overall capacities as meq per unit volume and as meq per unit mass of exchanger are presented in Table 4.1.

Although no dissolution of the materials was visible, fines caused blockage of the sintered disc. Due to this the capacity determination tests for HMnO and HMnO:HSiO composite with europium solution were abandoned.

Determination of Th by Asenazo method¹¹⁶ was attempted, as it is less time consuming than α -spectrometry, but was found to be inaccurate at low Th concentrations. Th^{232} determination was eventually carried out by TTA method.

The results show, in general, that the composite materials have higher overall capacities than their pure counterparts. In some cases Ti composite and Mn composite have much better capacity for Sr than their respective pure oxides. Mn composite has a high capacity for Th^{4+} of 1.16 meq/cm³ where Ti composite only has 0.72 meq/cm³.

The HSnO has the highest capacities for Sr^{2+} and Eu^{3+} and surprisingly low capacity for Cs^+ . This difference was noticed earlier in the pH titration curves of Cs and Sr.

An interesting set of results is the UO_2^{2+} capacities by all the hydrous oxides. All values are very similar, except for Ti composite, perhaps indicative of surface adsorption mechanism which allows only a specific number of UO_2^{2+} ions to adhere to the surface to completely cover it, beyond this the ion attraction is negligible to attract any further UO_2^{2+} ions.

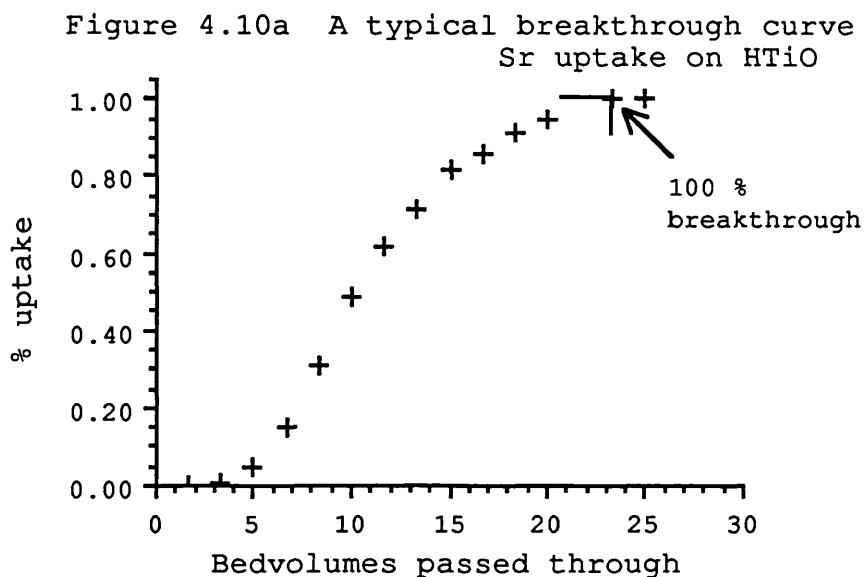


Table 4.1 Total effective ion exchange capacities of the hydrous oxides for various radionuclides

Ion Exchanger	Cs ⁺		Sr ²⁺		Eu ³⁺		UO ₂ ²⁺		Th ⁴⁺	
	meq/cm ³	meq/g	meq/cm ³	meq/g	meq/cm ³	meq/g	meq/cm ³	meq/g	meq/cm ³	meq/g
HTiO	2.11	1.51	4.29	3.06	2.34	1.66	0.96	0.68	—	
HTiO:HSiO	1.42	1.48	2.85	2.97	2.46	2.56	1.24	1.30	0.72	0.75
HMnO	—	—	1.31	1.04	—	—	0.41	0.33	—	—
HMnO:HSiO	1.36	0.96	1.52	1.00	—	—	0.66	0.43	1.16	0.75
HSnO	0.61	0.30	0.92	0.37	1.23	0.60	0.35	0.16	—	—

4.42 Elution

Once 100% breakthrough had been achieved, the feed solution was turned off and replaced by an appropriate eluant. In preliminary tests distilled water and various strengths of nitric acid were tried as suitable eluants. Eventually it was decided to use 0.5M HNO_3 as this was more effective an eluant than dilute acid, which was too slow, and strong acid which literally destroyed the ion exchange sites and rendered the material with no further ion exchange capacity. It was noticed that with repeated elutions the material slowly degraded. Typical elution curve for a Sr loaded $\text{HTiO}:\text{HSiO}$ is given in figure 4.10b.

Figures 4.11a,b,c show the reloading of an eluted column with the same feed solution. A qualitative measure of the reversibility of the exchangers can be taken from the comparison of the value of bedvolumes to 100% breakthrough in curves given in figures 4.11a,b,c (compare with figure 4.10a). These curves also give a quantitative visualisation of the regenerative ability of the hydrous oxide exchangers. The values (≈ 10.3 , 8.5 and 6.8 respectively) merely illustrate the gradual reduction in capacity on success reloadings. This may have resulted from either, incomplete elution or chemical degradation of the the exchanger. The number of cycles to fully exhaust the exchanger were not determined however, it was found that up to 5 successive elutions the exchanger still exhibited substantial capacity.

Figure 4.10b A typical elution curve for HTiO:HSiO loaded with Sr

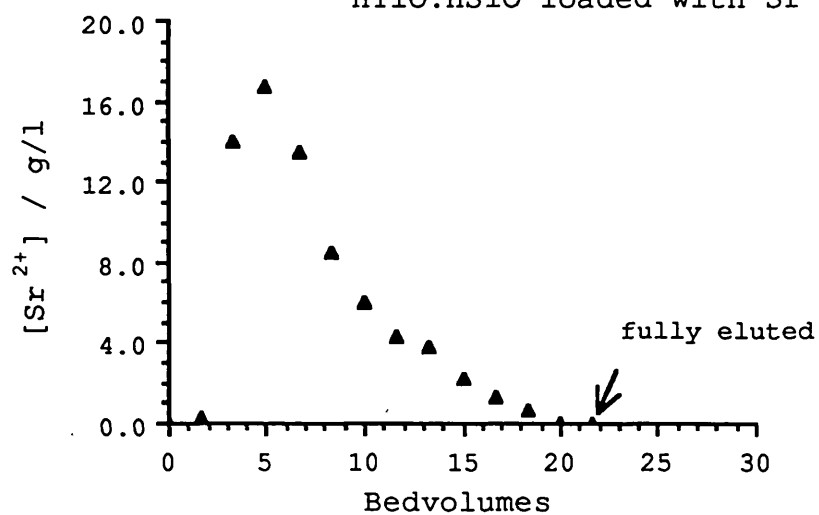


Figure 4.11a First reloading Sr uptake on HTiO

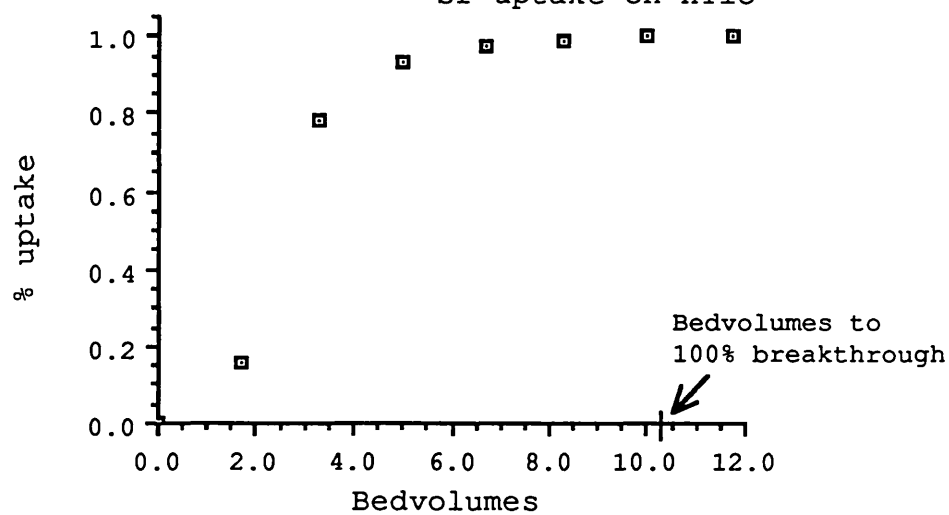


Figure 4.11b Second reloading
Sr uptake on HTiO

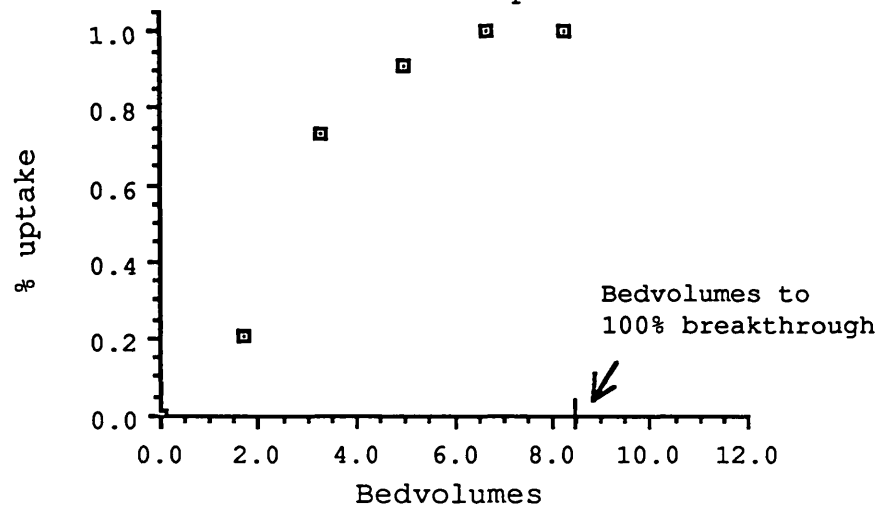
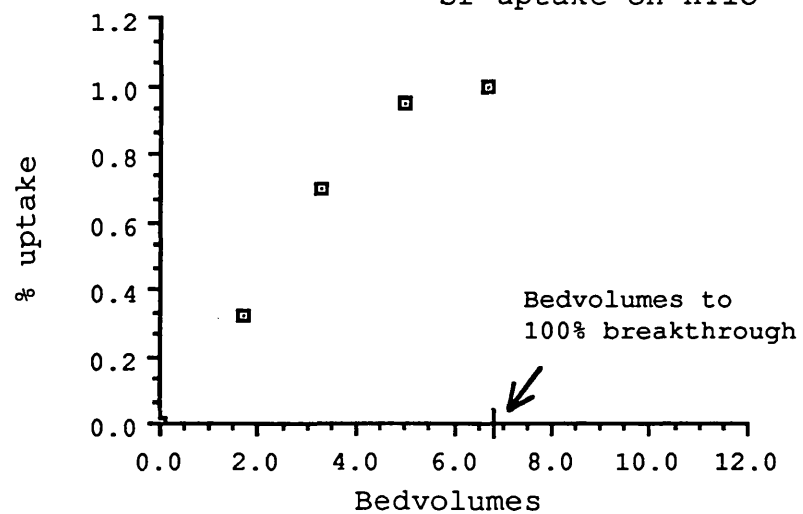


Figure 4.11c Third reloading
Sr uptake on HTiO



4.5 Selectivities

In an ion exchange system, consisting of an exchanger and a solution containing two exchangeable ions, the ions will exchange with the counterions in the exchanger in stoichiometric quantities in order to maintain overall electroneutrality. Also if an exchanger is in contact with this solution, after equilibrium between the two phases has been reached, the amounts of the two ions in the solution phase may not be equal, ie. one of these ions may be "preferred" to the other. A proper definition of selectivity is given in reference¹⁴ and by mathematical modelling it is possible to quote quantitatively the selectivity quotient¹⁴ of one ion over the other. For a system with more than two ions the mathematics becomes complicated. The work presented here, however, only deals with the selectivity series for the radioactive isotopes of interest at different pH values, in a qualitative manner. This is useful when decontaminating waste streams containing a particularly toxic isotope which needs to be selectively extracted under a given chemical environment (pH etc.). The selectivity tests were carried out as follows: A solution ('modsol') was made containing 10^{-4}M Cs^+ , Sr^{2+} , Co^{2+} , Am^{3+} , Eu^{3+} and UO_2^{2+} in equal total equivalence. The Cs, Sr, Co and Eu solutions were made up using their respective nitrate salts as carriers and then spiked with $1.88\mu\text{Ci}$ of Cs^{134} and Sr^{85} , $1.76\mu\text{Ci}$ of Co^{60} and $5.85\mu\text{Ci}$ of Eu^{152} respectively. The UO_2^{2+} contribution was made entirely from 93% enriched $\text{UO}_2(\text{NO}_3)_2$ (in 5M HCl). The total final activity of U^{235} was $0.2\mu\text{Ci}$. The americium

component in the solution was $\ll 10^{-4}\text{M}$ and was merely a spike equivalent to $0.82\mu\text{Ci}$ of activity. The solution pH was 2.5 without any adjustments. All materials were same batch as those used in the capacity tests. HSnO was omitted from these tests due to generally low uptake observed earlier.

Accurately weighed 0.1g portions of exchangers in mesh size 420-210 μm wet sieved, were placed in 60ml plastic bottles. To these bottles were added 25ml aliquots of the modsol solution and the bottles were sealed and placed on a rotary mixer overnight. Next day the pH of the samples were adjusted using nitric acid and sodium hydroxide solutions of various strengths. It was found very difficult to replicate an exact pH value for all the materials. To avoid the precipitation of the element onto the exchangers the upper pH values were chosen so that all the elements existed as soluble cationic species in solution. These limits given in Pourbaix diagrams are discussed by White et.al.¹⁵³ and were extrapolated from the appropriate Pourbaix potential-pH equilibrium diagrams. The selectivity series (and the respective distribution coefficient values) are given in tables 4.2 to 4.5.

The selectivity series for HTiO remained almost similar over the pH range except for U and Eu switching places. The comparative difference in the distribution coefficients are not so significant as to give weighting to any theoretical explanation. However, the distribution coefficients increase with increasing pH which agree with findings discussed in section 4.3. The optimum pH seems to

be 6.7 and pH variations cannot be utilized to alter the selectivity series. HTiO:HSiO composite exchanger also exhibited almost similar selectivity series throughout the pH range with a notable increase in the Cs uptake due to the presence of HSiO. The distribution coefficients for both the Ti(IV) based materials suggest that as pH is lowered the mono- and divalent species are eluted and therefore the process is reversible. However, with Am and Eu the decrease in distribution coefficients from a high pH (6.7) to the lower (2.8) one is not so much as to suggest reversibility, but change may be due to small amounts of chemical precipitation. At the lowest value (1.9) the elution process is apparent. The Ti(IV) based oxides are therefore most suitable for Cs¹³⁴ from 'modsol' type waste streams.

The Mn(IV) based exchangers show reversed trends at lower pH values; they seem to show affinity for ions with greater charge. The high selectivity for Co²⁺ is apparent in both cases. A pH of 2.5 tends to be a favourable working pH with the highest distribution coefficients. The series observed here are in conjunction with the capacity values reported earlier. The HSiO contribution in the Mn(IV) based oxides tend to be suitable for heavy element separation from the 'modsol' type of waste streams.

Table 4.2 Selectivity series for HTiO
Feed concentrations 10^{-4} M for all species in
HNO₃ media

pH	Selectivity series (K_d values)					
6.7	Cs (1357)	> Am (680)	> Eu (506)	> Sr (250)	> U (189)	> Co (51)
2.9	Cs (723)	> Am (591)	> Eu (388)	> Sr (290)	> U (90)	> Co (45)
1.9	Cs (208)	> Am (51)	> U (40)	> Sr (34)	> Eu (19)	> Co (12)

Table 4.3 Selectivity series for HTiO:HSiO
Feed concentration 10^{-4} M for all species in
HNO₃ media

pH	Selectivity series (K_d values)					
5.7	Cs (6300)	>> Am (251)	> Eu (152)	> U (83)	> Sr (39)	> Co (10)
2.8	Cs (942)	> Am (301)	> Eu (186)	> Sr (166)	> U (59)	> Co (30)
1.8	Cs (152)	> Am (49)	~ U (48)	> Sr (36)	> Eu (16)	> Co (6)

Table 4.4 Selectivity series for HMnO
Feed concentration 10^{-4} M for all species in
 HNO_3 media

pH	Selectivity series (K_d values)					
6.7	Eu (654)	> (253)	Cs ~ (254)	Am > (183)	U > (42)	Sr > (14)
2.8	Am (∞)	> (3204)	Eu > (1452)	Sr > (820)	Cs > (285)	Co > (10)
1.8	Am (1876)	> (613)	Cs > (420)	Eu > (198)	Sr > (140)	Co > (45)

Table 4.5 Selectivity series for HMnO:HSiO
Feed concentration 10^{-4} M for all species in
 HNO_3 media

pH	Selectivity series (K_d values)					
6.7	Cs (780)	> (249)	Am > (163)	Eu > (149)	Sr > (82)	U > (72)
2.5	Am (∞)	> (22000)	Eu > (11000)	Co > (1211)	Sr > (964)	U > (673)
1.7	Eu (15000)	> (8509)	Co > (3152)	Am > (534)	Cs > (356)	Sr ~ (355)

4.6 Ion exchange tests with various simulant feeds

A large number of ion exchange tests were carried out on the hydrous oxides with variation in the specifications of simulated BNF plc waste effluent streams. The contacting solutions are listed in appendix I, as solutions A to L and THORPZ. The solutions A to L are, in their isotopic content, the same with varying proportions of 'SDG' and 'JANNITOL' (degreasing reagents used by BNF plc in their fuel reprocessing plants). The pH and the quantity of the reagents of the base solutions A, B and C were altered to determine the most suitable working composition of the waste streams to give maximum uptake by HSnO , HTiO and HTiO:HSiO exchangers. The performances of pure HMnO , HTiO and their composites were also compared using THORPZ. THORPZ only contained Cs^{134} and Co^{60} and the interest here was focussed on the Co^{60} uptake by the Mn(IV) based exchangers. The results are presented in tables 4.6 to 4.18.

The removal of 1% Jannitol from solution A to give solution B, has meant the exchangers losing almost all ion exchange properties, see tables 4.6 and 4.7. Table 4.8 shows that the removal of both SDG and Jannitol has little affect on ion exchange. The pH value of these solutions was very low which also attributed to the almost zero extraction. Table 4.9 shows that the addition of 2M NaNO_3 to 1% SDG and 1% Jannitol gives better extraction. The uptake lowers for solution F, which is only 2M NaNO_3 plus spike and reduces further for solution E which is 2M NaNO_3 , 1% SDG plus spike.

The results in table 4.12 to 4.17 show results of ion exchange tests with various starting and final pH values. Solutions J, K, and L show that high starting pH values are alone not sufficient to enhance extraction and that other factors, like types and amounts of constituents, are also governing factors. Solution I showed the best overall results and should be adopted as the working solution for the extraction of the radionuclides considered using HSnO, HTiO and HTiO:HSiO.

The results in table 4.18 show that all the hydrous oxides are very similar in extracting Am²⁴¹, but HMnO has superior extraction capabilities for Co²⁺ removal over the other exchangers. The loss of Co²⁺ extraction by HMnO:HSiO can only be explained in terms of possible changes in the crystal structure. The results are reasonably consistent with the distribution coefficient values determined in an earlier section.

Table 4.6 : Ion Exchange performances of Hydrous oxides
with contacting Solution A

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	0.5	1.5	1.6	0	1.0	10.2	-0.27
HTiO	2.0	2.6	3.1	0	3.1	2.5	-0.27
HTiO :HSiO	3.0	3.4	2.7	1.1	2.4	3.8	-0.27

Table 4.7 : Ion Exchange performances of Hydrous oxides
with contacting Solution B

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	0	0	1.9	0	0	0	-0.02
HTiO	0	0	1.2	0	0	0	-0.14
HTiO :HSiO	0	0.5	3.5	0	2.3	2.7	-0.02

Table 4.8 : Ion Exchange performances of Hydrous oxides
with contacting Solution C

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	0	2.4	1.6	0	0	1.2	-0.20
HTiO	0	1.2	2.0	0	0	0.1	-0.20
HTiO :HSiO	0	0	0	6.4	2.3	0	-0.13

Table 4.9 : Ion Exchange performances of Hydrous oxides
with contacting Solution D

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	64.7	2.6	1.4	66.4	0	7.5	1.54
HTiO	1.1	0	28.1	1.0	7.1	0	3.50
HTiO :HSiO	23.7	0.8	36.0	20.2	7.8	43.9	2.85

Table 4.10 : Ion Exchange performances of Hydrous oxides
with contacting Solution E

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	15.2	0	0	9.8	0	10.9	1.42
HTiO	0	0	28.2	0	2.6	0	3.22
HTiO :HSiO	26.0	2.0	34.6	17.8	2.3	42.1	2.54

Table 4.11 : Ion Exchange performances of Hydrous oxides
with contacting Solution F

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	12.1	6.0	0	5.5	0.2	12.4	1.15
HTiO	15.1	11.5	31.8	13.7	0	13.7	3.48
HTiO :HSiO	76.5	8.7	34.8	58.0	5.0	84.4	2.47

Table 4.12 : Ion Exchange performances of Hydrous oxides
with contacting Solution G (pH =2.68)

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	4.5	0	0	2.2	5.9	0	2.84
HTiO	2.5	0	18.6	0	52.1	0	5.01
HTiO :HSiO	6.9	0.2	32.9	0.3	47.0	13.6	4.77

Table 4.13 : Ion Exchange performances of Hydrous oxides
with contacting Solution H (pH =2.45)

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	0.8	2.0	1.3	0.6	2.1	6.5	2.61
HTiO	0	0	20.4	0	53.0	0	4.96
HTiO :HSiO	0	0	38.2	0.6	43.2	18.7	4.65

Table 4.14 : Ion Exchange performances of Hydrus oxides
with contacting Solution I (pH =2.17)

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	69.7	56.5	0.6	59.0	0.1	45.9	2.41
HTiO	15.7	49.0	7.3	16.6	94.0	3.2	7.45
HTiO :HSiO	74.6	89.5	25.3	80.2	95.5	67.9	7.54

Table 4.15 : Ion Exchange performances of Hydrus oxides
with contacting Solution J (pH =5.49)

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	48.2	62.7	0	43.9	14.1	47.4	3.99
HTiO	0	3.8	10.9	0	82.1	4.7	9.22
HTiO :HSiO	30.7	30.8	37.1	45.0	95.9	74.3	9.15

Table 4.16 : Ion Exchange performances of Hydrous oxides
with contacting Solution K (pH =7.49)

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	0.3	0	0.5	0	74.0	0	5.67
HTiO	0	0.9	12.6	0	6.6	0.7	8.91
HTiO :HSiO	0	0	35.9	0	9.8	56.1	9.07

Table 4.17 : Ion Exchange performances of Hydrous oxides
with contacting Solution L (pH =7.31)

Sample	Am ²⁴¹	Co ⁶⁰	Cs ¹³⁴	Eu ¹⁵²	Sr ⁸⁵	U ²³⁵	pH
	% ext.	% ext.	% ext.	% ext.	% ext.	% ext.	
HSnO	0	0	0	0	72.2	1.3	5.73
HTiO	0	0	13.6	1.4	8.7	4.2	8.94
HTiO :HSiO	0	0	31.6	2.2	9.2	49.6	8.93

Table 4.18 : Ion Exchange performances of Hydrous oxides
with contacting solution THORPZ (pH =6.86)

Sample	Am ²⁴¹	Co ⁶⁰	pH
	% ext.	% ext.	
HTiO	85.94	44.67	11.50
HTiO:HSiO	98.33	60.48	11.24
HMnO	88.85	79.14	11.70
HMnO:HSiO	91.95	3.67	11.44

Chapter 5

Physical Properties

5.1 Introduction 5.2 Density Measurements 5.3 Surface

Area Determinations 5.4 Structural Analyses 5.5

Physical Strength Determination 5.6 Irradiation Stabilities

5.1 Introduction

This chapter consists of work done on the physical classification and properties of the exchanger materials. Densities of the exchangers are reported. The specific surface area was determined by two independent methods, by methylene blue adsorption (MBA) and nitrogen adsorption (BET), and as expected, showed a slight variation in values, the ratios of which were taken to be the measure of the microporosity of the materials. Thermogravimetric analyses together with infrared spectrometric studies were carried out in an attempt to reveal water content and type of bonding. High temperature X-ray powder diffraction (XRPD) was pursued after XRPD at room temperature proved inconclusive in elucidating the structural form of the materials. The physical strength of the materials was determined by diamond indentation, a technique widely used in the field of engineering ceramics. Irradiation stability studies showed the materials to be stable under high doses of γ -radiation. All materials used were prepared by the capillary reactor method adopted throughout this study.

5.2 Density measurements

Densities were determined by the density bottle method with distilled water. The density of the hydrous oxide ion exchangers , ρ_{ex} at 20°C is given by:

$$\rho_{\text{ex}} = \frac{\text{mass}}{\text{volume}} = \frac{(w_2 - w_1)}{(w_4 - w_1) - (w_3 - w_2)} \cdot \rho_w \quad (5.1)$$

where

w_1 weight of empty bottle,

w_2 weight of bottle with sample,

w_3 weight of bottle with sample plus water (to the mark),

w_4 weight of bottle with water only, and

ρ_w density of distilled water at 20°C.

The exchangers were 'soaked' in water for over 3 hours before the bottles were filled up to the mark, this was to ensure that there were no air trapped in them. The experiments were carried out independently with two sizes of bottles, 25ml and 50ml. The results are presented in table 5.1.

Table 5.1 also gives the densities of the naturally occurring forms of the oxides. The densities of the hydrous oxides were expected to be lower than the more dense natural structures. The silica addition has led to no apparent compaction of the materials as the composites are less dense than their pure counterparts.

Table 5.1 : Densities of inorganic hydrous oxides

Material	density g/cm ³	
	of ion exchangers	of naturally occurring oxides
HTiO	2.494	rutile, 4.26 Anastase, 3.84
HTiO:HSiO	2.170	-
HMnO	3.015	Pyrolusite, 5.03
HMnO:HSiO	2.919	-
HSnO	3.699	Cassiterite, 6.95
HSiO	2.083	-

5.3 Surface area determinations

The specific surface area determinations were done by two independent methods, very similar in principle. The principle of measuring the total surface area of a solid by the physisorption (non-selective adsorption) with gas or a liquid consists of determining the number of gas molecules required to cover the surface of the solid with a monolayer of the adsorbate. So if the area covered by one molecule is known, the surface area of the solid can be calculated from the number of absorbed molecules measured volumetrically, gravimetrically or by other means of measuring the concentration of the adsorbate. The first of the two methods was adsorption of multilayers of nitrogen^{117,119} on to the surface of the exchanger and the second was adsorption of a multilayer of methylene blue^{118,119} dye. The surface areas occupied by nitrogen and MB molecule are 0.16 and 1.3nm² respectively. In contrast to the MB the N₂ molecule is able to enter small pores with diameter > 0.4nm. Therefore the comparison of specific surface areas determined by BET and by MBA is a measure of the microporosity with micropores between 0.4 and 1.3nm.

5.31 Nitrogen adsorption method for specific surface area determination

The experiments were performed using apparatus and experimental procedure given by Chadwick¹²⁰. The method utilizes the classic 'BET isotherm' proposed by Brauner et.al.¹¹⁷

$$\frac{P}{V_{ads} \cdot (P_o - P)} = \frac{C - 1}{V_m \cdot C} \frac{P}{P_o} + \frac{1}{V_m \cdot C} \quad (5.2)$$

Experimentally V_{ads} is measured and from a graphical (straight line plot) expression of data, using equation (5.2) V_m was determined. Once this is known, the total surface area of sample can be determined knowing the effective area covered by a single molecule. The results for the BET tests carried with 0.1g of each material, in mesh size 210-105 μ m are given in table 5.2.

Table 5.2 : Specific surface area - BET method

Sample	Specific surface area, m ² /g
HTiO	0.35
HTiO:HSiO	0.73
HMnO	≤ 0.20
HMnO:HSiO	0.29

The specific area value for HMnO was approximated to 0.20m²/g owing to the problems encountered in obtaining a straight line plot from the experimental data. The results show that the respective composites have greater specific surface areas than the pure exchanger materials. This must

be due to the silica present in a high surface area structural form.

5.32 Methylene blue method for specific area determination

Measurement of surface area from liquid phase sorption can be more complex to interpret because of the interaction between the surface material, the solvent and the attaching molecules. There is the possibility of the two phases undergoing adsorption, absorption, chemisorption, ion exchange or a combination of these or other phenomena. With ion exchange the solution pH could have an effect on the final concentration of the solvent. The use of methylene blue dye has been reported by Greiling and Lieser¹¹⁸.

The experimental procedure was less cumbersome than the BET method. BDH methylene blue dye, 85% dye, molecular weight 355.86, was used to make up the adsorbate solution. An absorbance/concentration calibration line was determined by spectrophotometry at 310nm for various concentrations of methylene blue using a 'Cecil C292' digital spectrophotometer. After some preliminary tests with different starting concentration, a $4.8 \times 10^{-3}\text{M}$ solution of the dye was used. 0.2g portions of exchangers in the 210-420 μm size were contacted with 50ml of solution in 60ml plastic bottles with screw tops. The samples were placed on a rotary mixer for 24 hours after which the solution, less intense in colour, were analysed on the spectrophotometer. The differences in the final to initial

concentrations were used to calculate the total surface area of the samples. The results are presented in table 5.3.

Table 5.3 : Specific surface area - MBA method

Sample	Specific surface area, m ² /g
HTiO	0.24
HTiO:HSiO	0.30
HMnO	0.43
HMnO:HSiO	0.38

The value for the specific areas are of the same order of magnitude as for those in table 5.2. However, the trend is no longer similar to the BET method. This shows the different structure and pore size distributions present. As the N₂ molecule is the smaller of the two molecules, the BET results may be taken as a closer representation of the true specific surface area of the exchangers. The calculations for both the methods assume a monolayer covering the surface, which may not be true, so that the methods are more suitable to comparative studies. However, the ratio of the specific surface areas A(BET) to A(MBA) can be taken as an indication of the degree of the microporosity of the materials with micropores between 0.4

and 1.3nm. The extent of microporosity of the hydrous oxides are given in table 5.4.

The results in table 5.4 show that the addition of silica to HTiO and HMnO increases the porosity of the pure

Table 5.4 : Degree of microporosity of hydrous oxides

Sample	A (BET) /A (MBA)
HTiO	1.46
HTiO:HSiO	2.43
HMnO	≤ 0.47
HMnO:HSiO	0.76

materials. These pores may have resulted from a net-type structure of the surface -OH groups. This may also be a contributory factor towards the enhancement of the ion exchange capacities of the composites over their pure counterparts.

5.4 Structural analyses

Throughout the course of this study the ion exchangers have been abbreviated as HTiO, HMnO etc and have been regarded as hydrous oxides. However, the objective in the present study on structural analyses was to elucidate the possible structure and chemical form of the materials.

5.41 Infrared spectrometry

Infrared studies on the hydrous oxides were carried out by the standard alkali halide disk technique¹⁵⁷. Less than 0.1g of materials in mesh size 420-600 μ m were finely ground with potassium bromide and the powder was pressed under 5-10 tons of pressure for approximately 5 minute. The analysis on the diskettes was carried out on a 'Perkin-Elmer 783' infrared spectrophotometer in the transmission mode with the following settings: slit setting 1, scan time of 3 minutes, noise filter setting at 2 and a chart expansion of 0.5. The analysis was carried out almost immediately to prevent any chances of anion exchange between the exchanger and the KBr¹⁵⁷. The qualitative results are presented in figure 5.1 and show that all the spectra show broad bands at 3400cm⁻¹ associated with interstitial water. The peaks observed at around 1625cm⁻¹ are due to the bending mode of water and any other peaks below 1000cm⁻¹ are characteristic of the metal-O bond. No other noticeable absorption were observed.

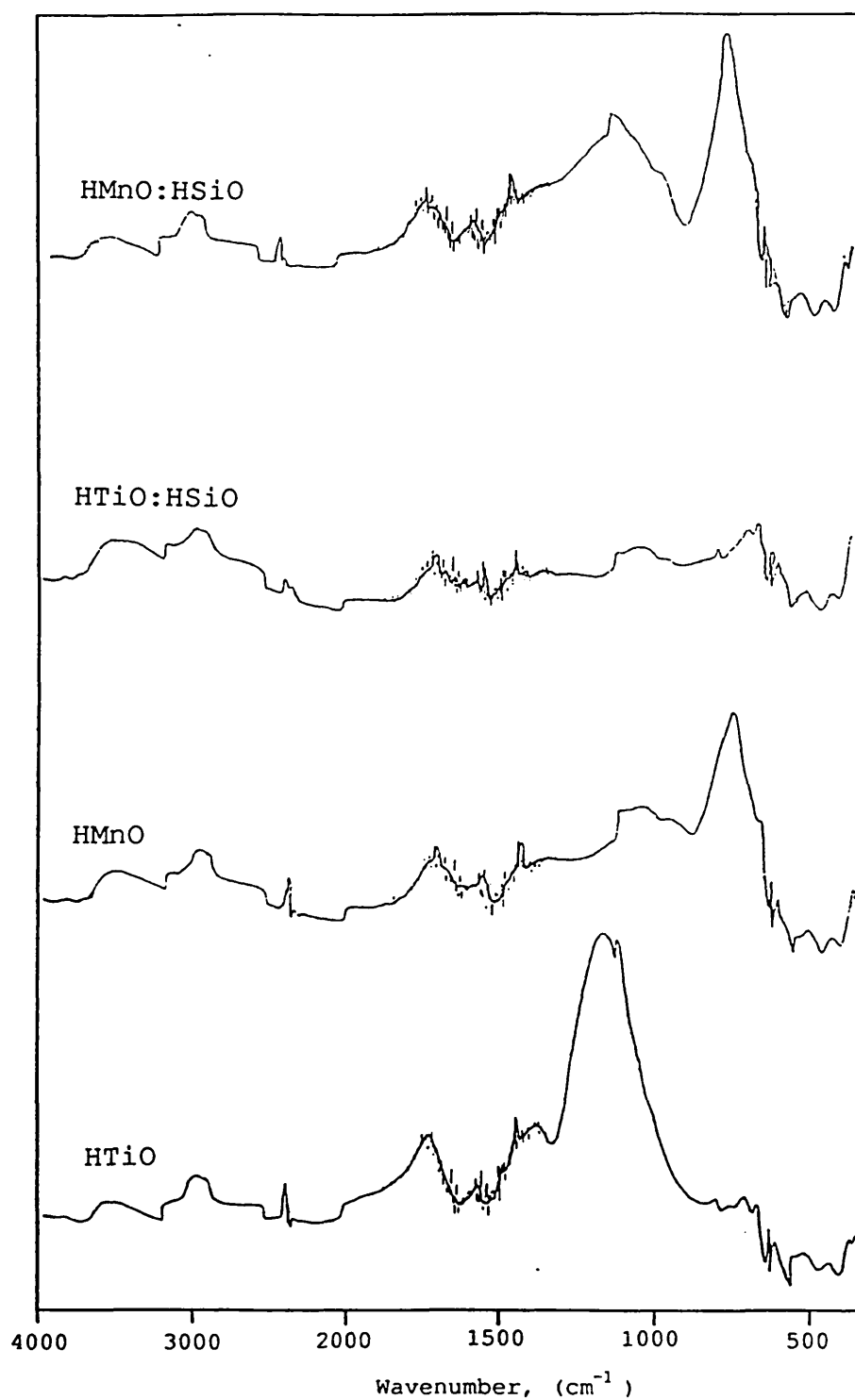


Figure 5.1

Infrared spectra of hydrous oxide ion exchangers

5.42 Thermogravimetric studies

Thermogravimetric studies were carried out to provide information on the synonymous processes of dehydration and dehydroxylation of the hydrous oxides. The dehydration process may be divided into four categories¹²¹, (i) the loss of constitutional water, (ii) the loss of water of crystallization, (iii) the loss of water extraneous to the lattice, and (iv) dehydration accompanied by hydrolysis. These are studied extensively in various text books on the subject^{122,123}. It was also the intention to determine the value of 'n' in the general formulae of the hydrous oxides, eg. $\text{TiO}_2 \cdot n\text{H}_2\text{O}$ (or $\text{Ti}(\text{OH})_4 \cdot n\text{H}_2\text{O}$), and to observe if any, transformations in the lattice arrangement or chemical composition. This was done by the combination of 'thermogravimetric' TG and 'differential thermal analysis', DTA. The detailed theory and standard procedure for the thermogravimetric analysis, with modern equipment of the type utilized in the present work, are given by Pope and Judd¹²². The heating rate, a compromise between peak resolution and experimental time, was 10°C per minute. The mass of the material, maximum and minimum temperatures, and the heating atmosphere are given on the individual plots. A 'Stanton Redcroft STA-780' machine with platinum crucibles was used. After each run the crucibles were washed in hot, concentrated hydrochloric acid to dissolve the exchangers.

The TG and DTA curves for HTiO are given in figures 5.2a and 5.2b respectively, the curves for other materials are given in appendix III.

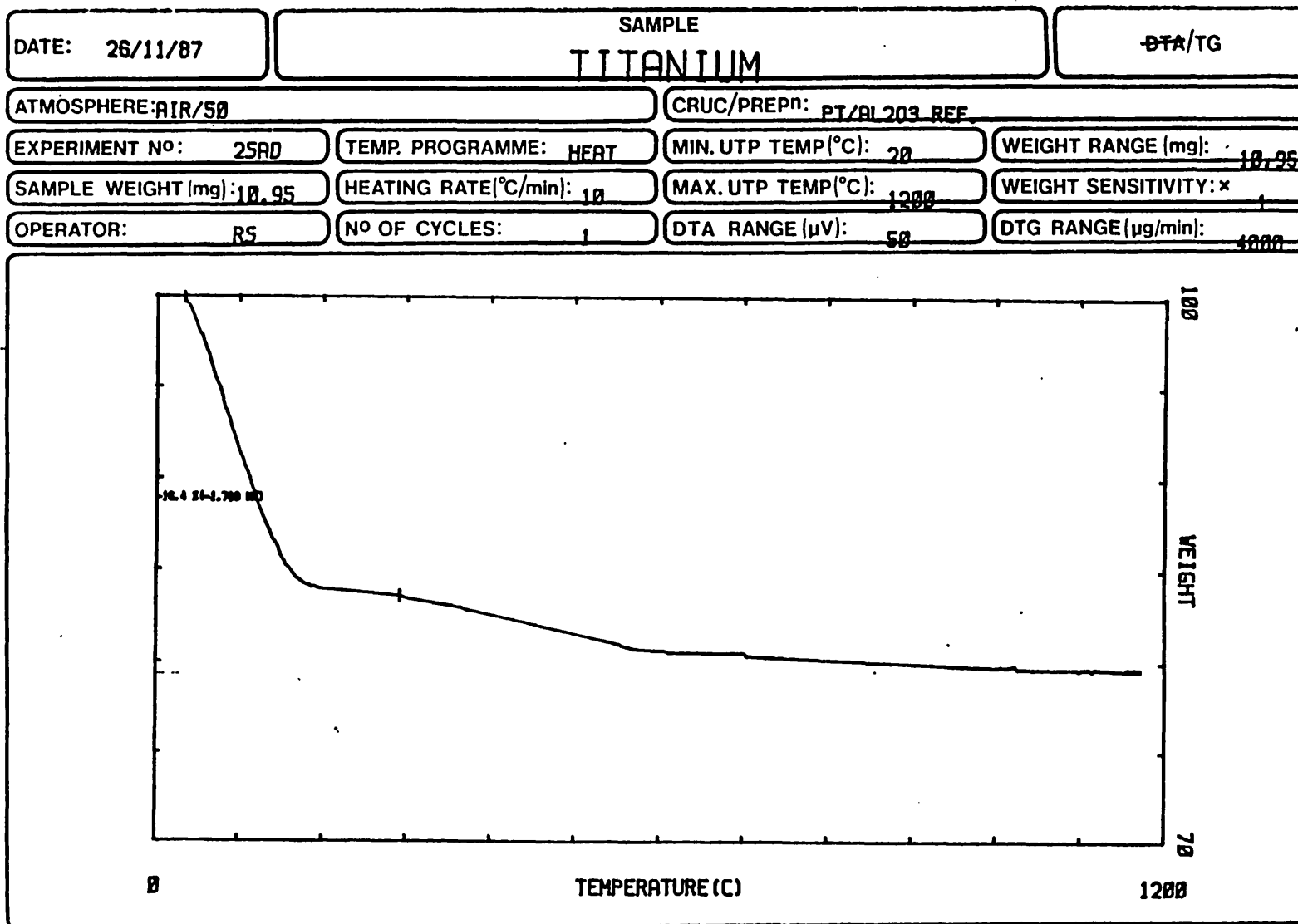


Figure 5.2a TG curve for HT10 ion exchanger.

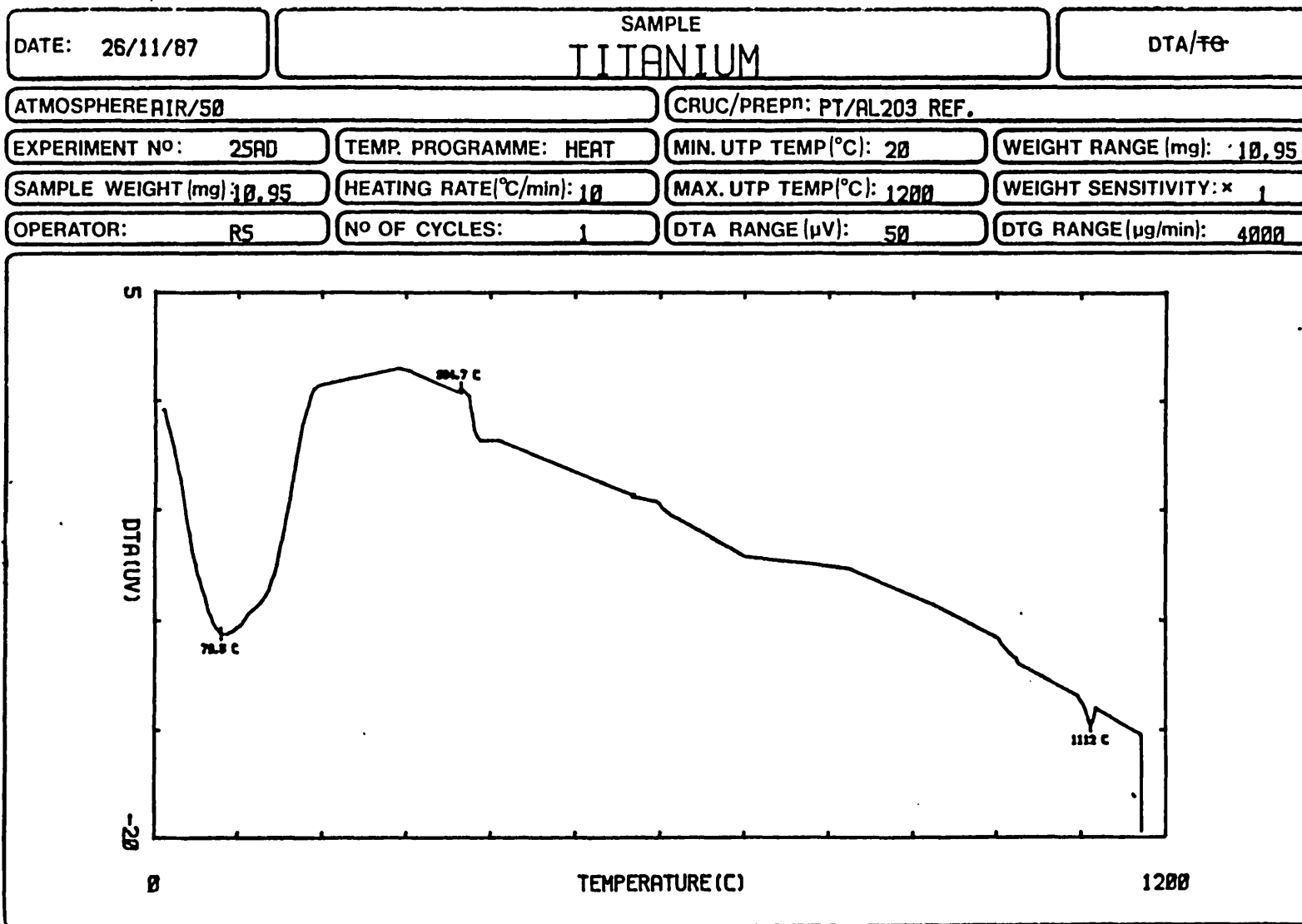


Figure 5.2b DTA curve for HTiO ion exchanger.

All the TG curves show a characteristic loss of water, with almost all the weight loss completed by 200-250°C. There were no unexpected drops in the weight corresponding to a group of water molecules evaporating from the exchangers, as observed by Nancollas and Paterson¹⁵⁹. This would have been illustrative of all the four categories of dehydration mentioned earlier.

All the DTA curves show large drops in the DTA value to a minimum and steady rise followed by a gradual asymptotic profile as temperature tends to 1200°C. The former is characteristic of loss of constitutional water, loss of -OH groups and partially due to the loss of water of crystallization. The temperatures corresponding to the minimum DTA value were below 100°C for Ti and Ti composite and greater than 100°C for all other exchangers. These lower values can be attributed to the existence of constitutional water in large amounts. The narrow troughs are only due to loss of constitutional water, whereas the broader ones may incorporate superimposed peaks corresponding to one or a combination of the above mentioned categories. The predominant category being the loosely bound water. The exothermic transitions on the DTA plots observed immediately after the initial dehydration endotherms were only apparent with Ti and Ti composite at approximately 300°C. Normally these exothermic peaks result from recrystallization of amorphous materials with water loss. All the other exchangers exhibit very broad exotherms with DTA values decreasing with increasing temperature -

indicative of a slow transformation which may also be time dependent¹³⁸. On the other hand such broad exotherms may just be due the loss of interstitial water of crystallization without a significant transformation of crystal structure at relatively low temperatures. This behaviour is exhibited by HMnO and HSnO with no distinctive peaks throughout the temperature range. The Ti composite exhibits an exothermic peak at 666°C, most likely a transformation from one state to a more stable state; anastase to rutile¹²⁵. Mn composite undergoes three endothermic changes at ≈891, 1007 and 1151°C, these can be related to the different forms of MnO₂ that can exist¹²⁵. All these transformations occur at very high temperatures and can be related to phase diagrams, but are of no importance insofar as the ion exchange properties of the materials are concerned.

The peak area in a DTA plot can be calculated¹²² and is a measure of the total enthalpy change. This property is normally used to identify materials when there is a phase change. However, in the case of hydrous oxides it was decided to extrapolate the temperature which corresponded to the end of the (dehydration) endotherm on the DTA plot and used this temperature value on the TG plot to determine exactly the amount (percentage) of water lost. The completion of the endotherm for all the materials was approximately at 200°C except for HSnO. To standardise the results for direct comparison a 200°C value was adopted, as the percentage weight loss between the temperature

corresponding to the completion of the endotherm and 200°C is negligible, even for HSnO. Table 5.5 below shows the percentage water loss at 200°C.

Table 5.5 : % weight loss up to 200°C
(extrapolated from TG-curves)

Sample	% weight loss
HTiO	16.33
HTiO:HSiO	22.01
HMnO	10.36
HMnO:HSiO	5.98
HSnO	9.61

The number of moles of water associated with the exchanger was evaluated using the following equation¹²⁶,

$$\frac{n \times MW_{H_2O}}{MW_{ex} - (n \times MW_{H_2O})} \times 100 = \% \text{ water loss (at } 200^{\circ}\text{C)} \quad (5.3)$$

Table 5.6 gives the n values for all the materials as hydrous dioxides and hydroxides, as yet the structure is not known and is the subject of the section on high temperature X-ray diffraction.

The results show that the number of moles of associated water are the highest for the Ti(IV) based exchangers and,

in general, are in agreement to the values reported in literature⁴⁷. The results indicate that the materials with the high water content are also the ones with the highest microporosity. The HMnO:HSiO had a low water content. The

Table 5.6 : Number of moles of associated water for hydrous oxide exchangers

Sample	Moles of associated water	
	dioxide -O ₂	hydroxide -(OH) ₄
HTiO	0.866	1.257
HTiO:HSiO	1.163	1.724
HMnO	0.507	0.717
HMnO:HSiO	0.291	0.418
HSnO	0.891	1.103

drying temperature of 110°C seems to have driven off the water in HMnO:HSiO composite and therefore it can be said that the contribution of the high degree of water in the Ti based exchangers must be due to the interstitial water in TiO₂ and not from SiO₂. This also implies that the Ti⁴⁺ ion has a greater affinity for H₂O, -OH groups than Mn⁴⁺ and Si⁴⁺.

Differential thermal gravimetric (DTG) analysis technique

is normally used to determine the kinetics of weight loss as a function of temperature or time. As the temperature changes likely to occur in a typical ion exchange process are minor, such studies were deemed unnecessary. The kinetics of ion exchange as a function of temperature and various other factors are covered in the chapter on ion exchange kinetics.

5.43 High temperature X-ray diffraction

Every crystalline material has a specific geometrical form and it is made from repetitive unit cells^{138,139}. X-ray (powder) diffraction techniques can produce patterns which are the material 'finger prints' and can therefore be used to identify unknown materials from their structure, lattice spacings and relative intensities etc. However, X-rays cannot be diffracted off non-crystalline amorphous materials, as they are absorbed, and therefore one can only achieve the diffraction by removing the water by application of heat. The extraction of water may reveal the fundamental structure of the material or allow it to crystallize into a thermally stable form.

The inorganic ion exchange materials and hydrous oxides in particular are amorphous. The amount of associated water and hydroxyl groups, as the active functionalities in the ion exchange process, depend on the central metal ion. X-ray powder diffraction analysis at room temperature together with the thermogravimetric analysis substantiate the amorphous nature of the hydrous oxides.

Throughout this study the Ti(IV), Mn(IV) and Sn(IV) based materials have been referred to as hydrous oxides, it was the aim of high temperature X-ray powder diffraction studies to elucidate the possible structural and subsequently the chemical form of these materials.

The high temperature X-ray powder diffraction facility utilized at Birkbeck College has the following instruments: a Siemens D500 diffractometer with a K710 generator

operated at a voltage of 40kV and a current of 30mA, which produces CuK α radiation with wavelength $\lambda = 1.5418 \times 10^{-10}\text{m}$. The detector receiving slit has an angle of 0.150 degree with a fixed divergence aperture of 1.0 degree. The entire system is linked up to a 'Digital Professional' computer with data analysis software and a computer library containing over 80,000 crystalline patterns.

Preliminary runs at room temperature were carried out with materials ground and sieved through a 38 μm sieve. The smaller the particle size the better were the counting statistics for the system. Less than 0.1g of powder was sprinkled on an 18/8Ti stainless steel 'GTP' sample holder greased with silicone vacuum gel. The scans were carried from 15° to 75° with a step width of 0.100°. The room temperature diffractograms obtained from these runs are given in figure 5.3 for Ti and Ti composite, figure 5.4 for Sn, figure 5.5 for Mn at room temperature (and higher temperatures) and figure 5.6 for Mn composite hydrous oxide ion exchangers. Figures 5.5 and 5.6 for Mn and Mn composite gave absolutely no indication of any structural arrangements and there were no 'best fits' to the diffractograms from the powder diffraction files¹⁴⁰ stored in the computer. On first glance the diffractograms for Ti and Ti composite are identical and by comparing the Ti diffractogram with two naturally existing phases of TiO₂, given in figure 5.7, there were early indications of the possible presence of anastase (PDF no.21-1276)¹⁴⁰ and rutile (PDF no.21-1272)¹⁴⁰ or a combination of both structures. The

room temperature diffractogram of Sn was quite conclusive with nearly all the peaks corresponding to the naturally occurring cassiterite SnO_2 form (PDF no.21-1250)¹⁴⁰, with all the defined interplanar spacing (d-values) matching those reported by Inoue et. al.⁷⁴ for their sample. It was therefore decided to pursue with high temperature X-ray powder diffraction only with Ti and Mn based exchangers.

Earlier attempts at high temperature X-ray powder diffraction with uncompact powder in $\approx 22\text{mm}$ square x 3mm deep brass holder yielded very low statistics from the diffracted X-ray beam as the surface of the sample disintegrated resulting in an uneven surface for the X-rays to diffract. To achieve high diffractive counts, the samples were prepared into 32mm diameter x 3mm depth diskettes from very fine powder of the material.

Sample preparation :

The exchanger materials were ground in a pestle and mortar and sieved through $38\mu\text{m}$ sieve. Approximately 4 to 7g of powder ($\sim 2.4\text{cm}^3$ depending on material density) were placed on the bottom plate of a 32mm diameter 'Specvac' die. The thrust bar was placed on top and a weight of 15-20 tons was applied for about 10 minute using a Specvac hydraulic press. The diskettes were carefully removed and shaped with a sharp razor to be accommodated into the brass holder.

The Ti temperature profiles adopted for Ti were as

follows : after the initial scan at room temperature, the sample was heated at 5°C per minute to 140°C and then at 2°C per minute to 150°C. The temperature was monitored independently by a thermocouple and a chart recorder, and the X-ray scan was initiated only when both the sources registered the desired temperature. The scans were carried out from an angle of 20° to 70° with a step width of 0.100°. The process was repeated for temperatures of 225°C and 300°C. The diffractograms for the four temperatures are given in figure 5.8. It was observed that there was no gradual progression to the final diffractogram, which relates to the anastase form of TiO₂. The recrystallization takes place only when a specific amount energy is absorbed by the material. Figure 5.9 shows the diffractogram of Ti at 300°C to correspond with the anastase powder diffraction file. This is an interesting result as the rutile is known to be more stable than the anastase crystalline form of TiO₂. The recrystallization temperature of 300°C corresponds exactly to the exothermic peak on the DTA plot given in figure 5.2b.

Similarly, the Mn diskette was scanned from 20° to 70° with a step width of 0.167°. However in this case with a higher step width the scans were carried out whilst the material was being heated, the rate of temperature rise was set to 5°C per minute. Figure 5.5 shows the diffractograms at room temperature, from 97-120°C, 237-251°C and at 300°C. The diffractograms show absolutely no structural rearrangement, even at 300°C. No attempts could be made at

fitting any known forms of MnO_2 , $\text{Mn}(\text{OH})_4$ etc. as the diffractograms are totally random and have no significance in X-ray diffraction analysis. By referring to the Mn-O phase diagram¹²⁵ and the DTA peaks on the DTA-plots one can suspect the HMnO to be as a $\text{Mn}(\text{OH})_4$ based material and not MnO_2 , as MnO_2 readily undergoes phase changes (from β to γ to δ with increasing temperature).

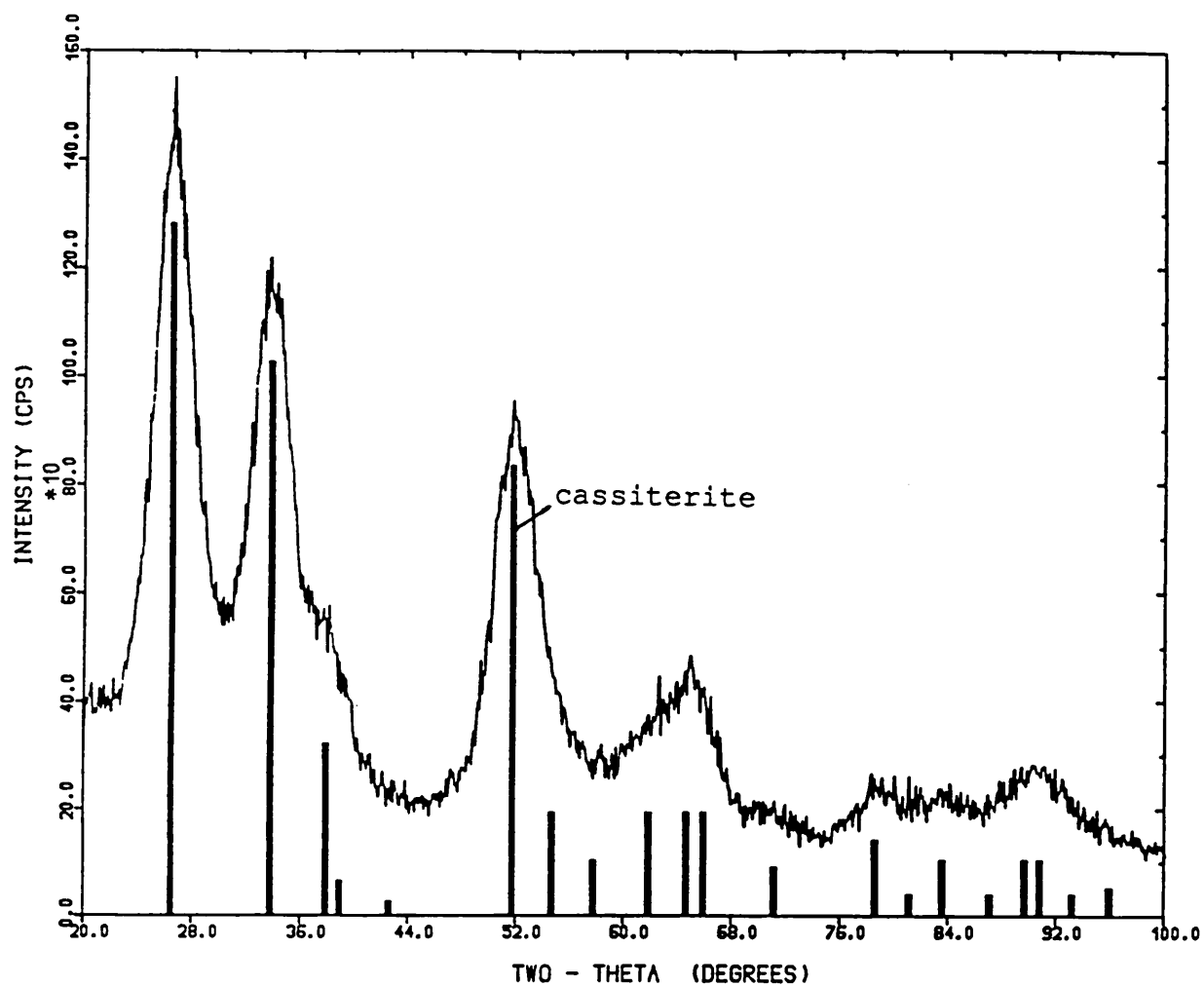


Figure 5.4 XRPD diffractogram for HSnO at room temperature compared with cassiterite.

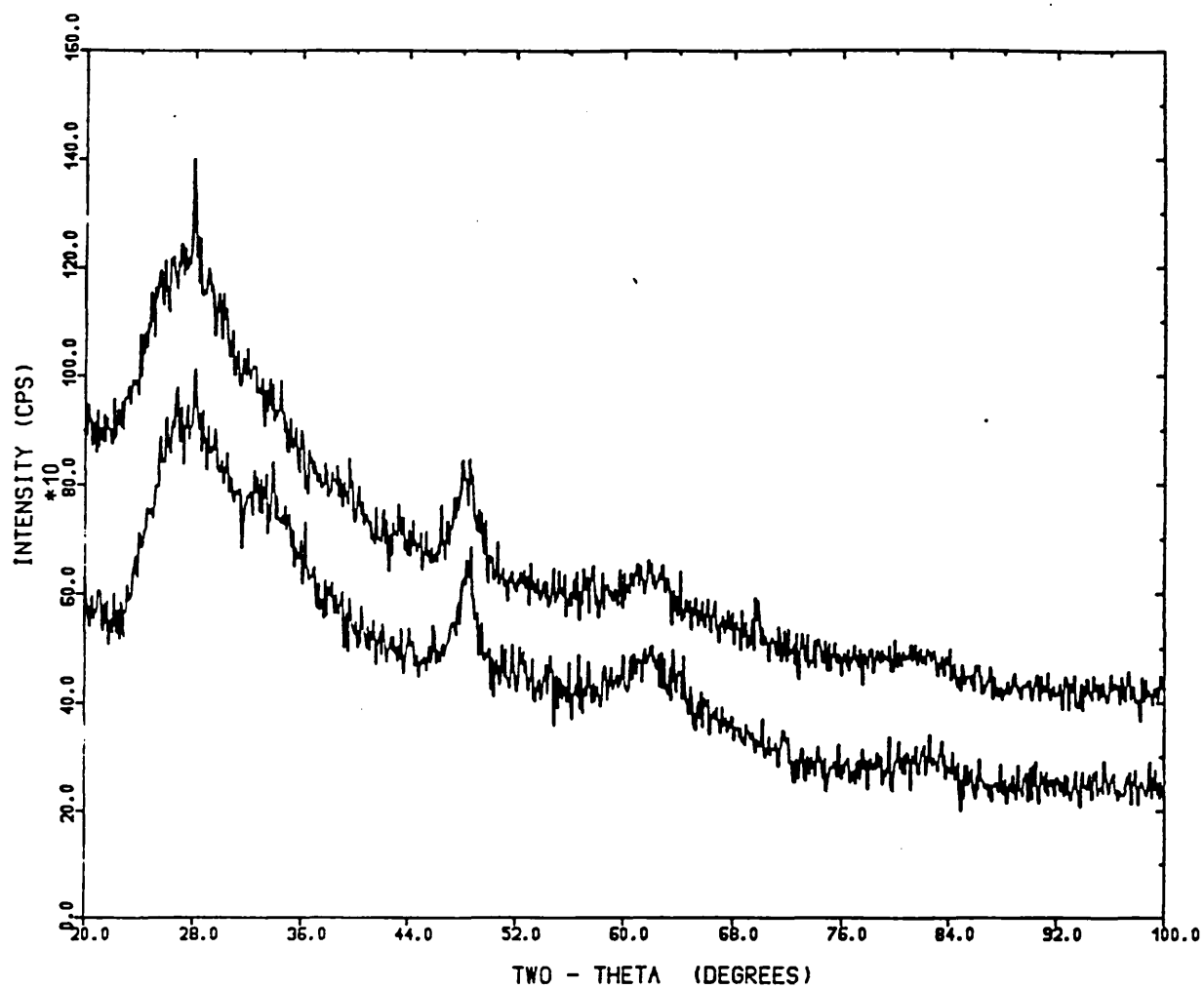


Figure 5.3 XRPD diffractograms for HTiO and HTiO:HSiO at room temperature.

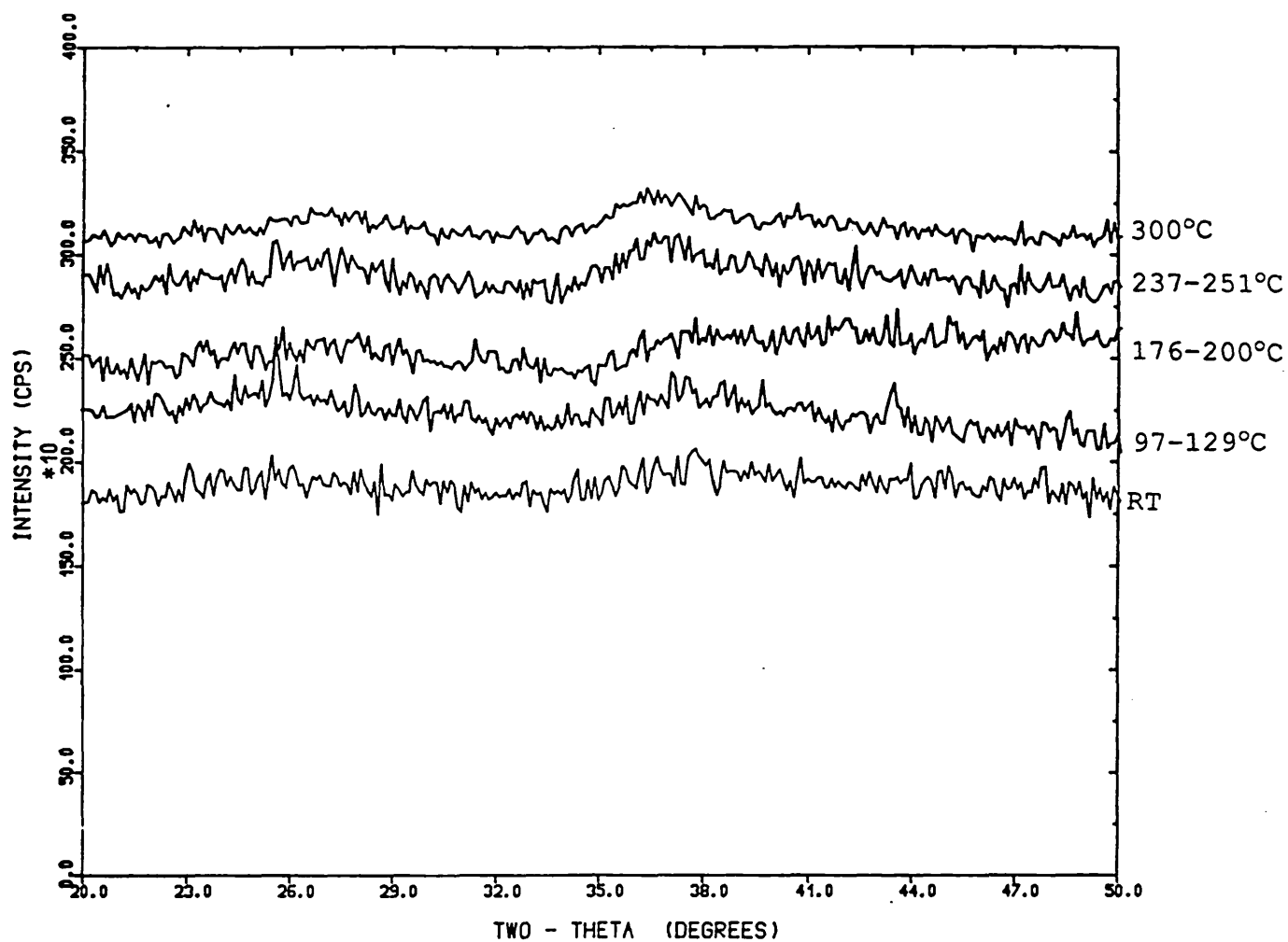


Figure 5.5 XRPD diffractogram for HMnO at room temperature and whilst heating to 300°C.

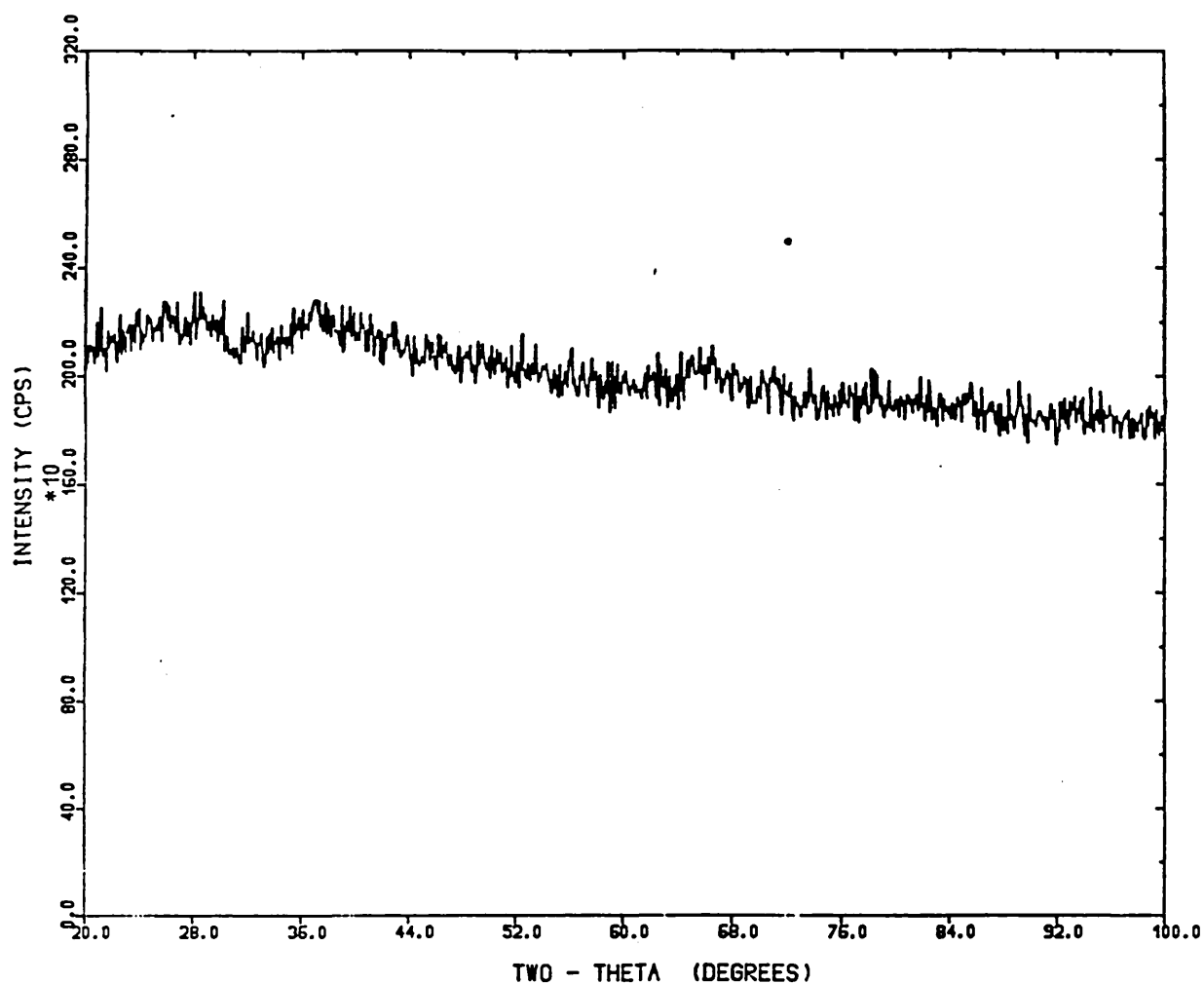


Figure 5.6 XRPD diffractogram for HMnO:HSiO at ,
room temperature.

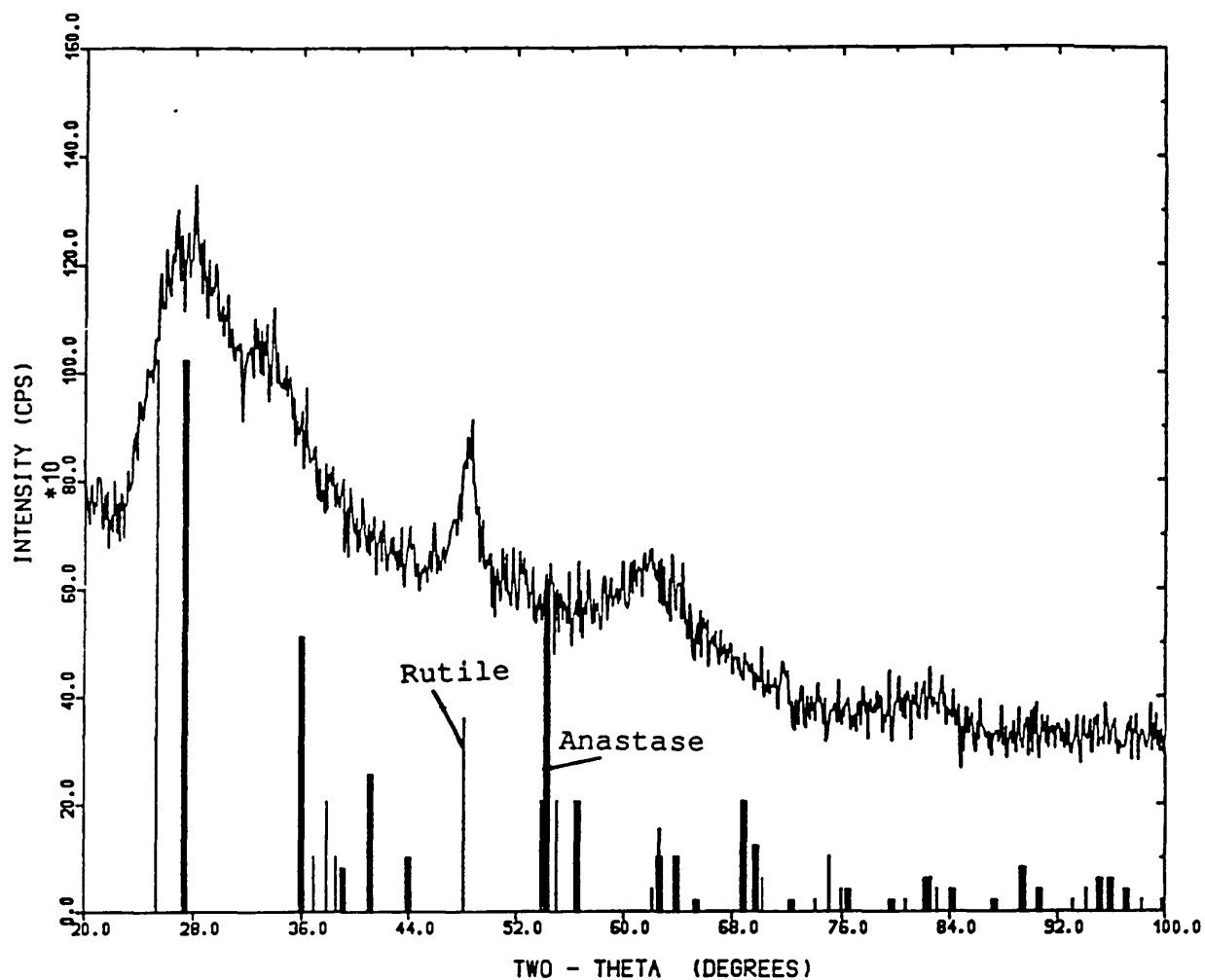


Figure 5.7 XRPD diffractogram for HTiO at room temperature compared with rutile and anatase.

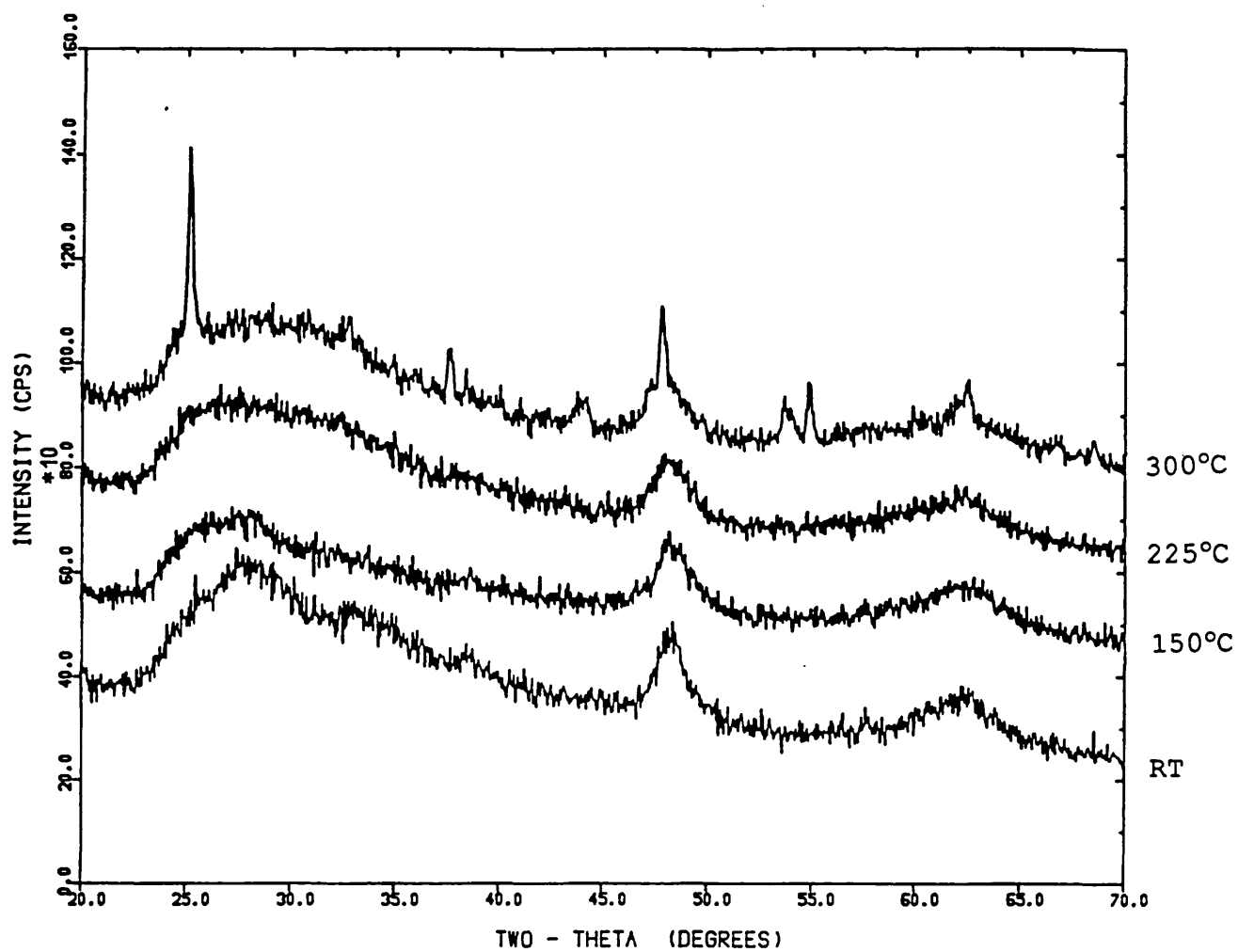


Figure 5.8 XRPD diffractograms for HTiO at four different temperatures.

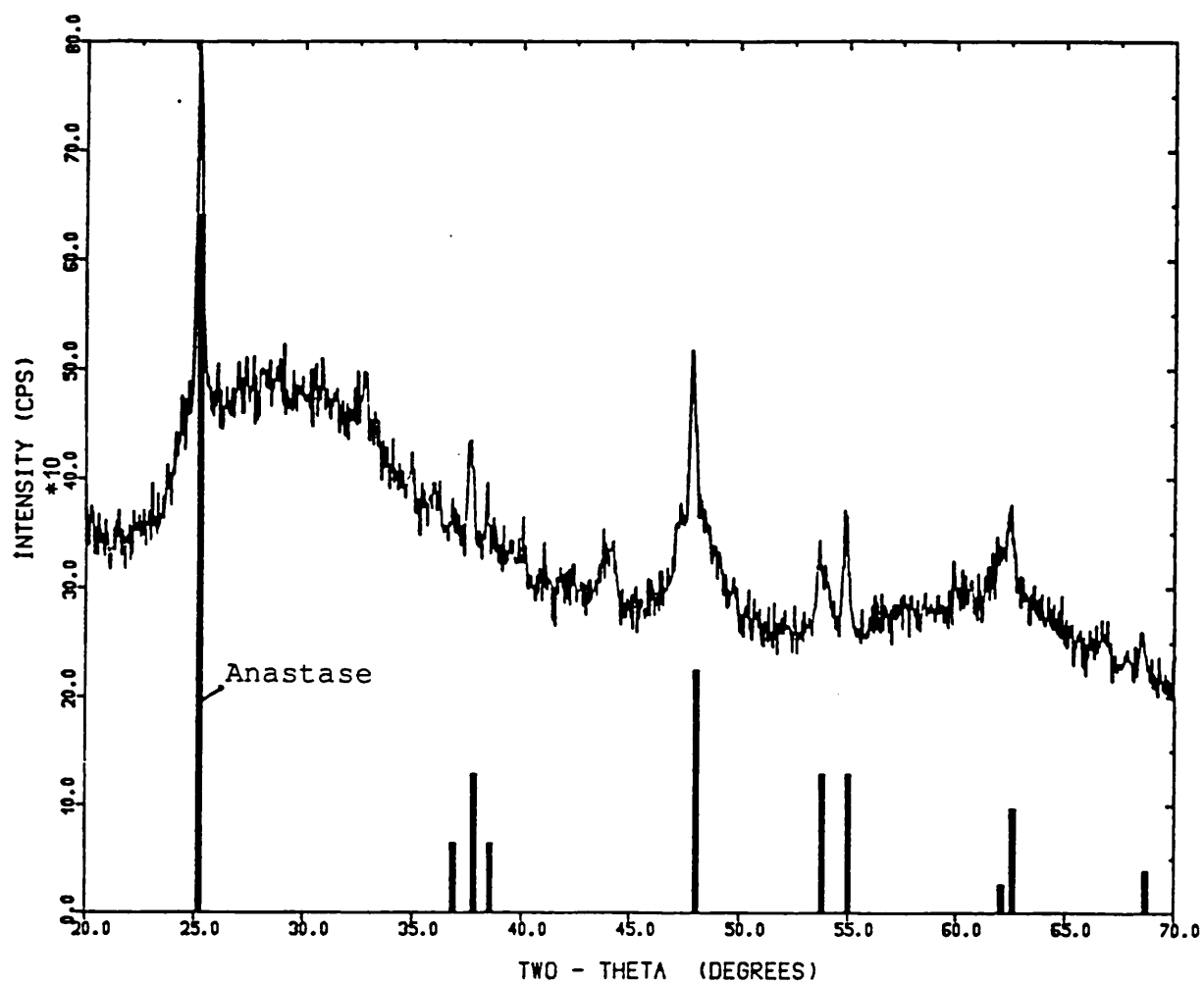


Figure 5.9 XRPD diffractogram for HTiO at 300°C compared with anastase.

5.5 Physical strength determination

Inorganic ion exchangers have been studied extensively, with an emphasis on the chemical and ion exchange characteristics of the materials. In a practical application, it would be necessary to use these ion exchangers in a packed column of a fairly large size. For this reason a measure of the strength of these materials is needed. This would allow a comparison with similar products such as ceramic or glass packing to ascertain the suitability of the inorganic exchanger for its application on a large scale. Unfortunately, a number of these exchangers may have desirable sorption properties but have no physical strength and, with the consistency of fine powder, are of no use in any large scale application in a packed bed.

The physical strength of inorganic ion exchangers has not been studied extensively in the literature. However, Newit and Coway-Jones¹²⁸ have investigated in detail, the physical strength of agglomerates of spherical sand particles in detail and propose a relationship relating maximum load to material parameters. In a similar study Golden and Irving¹²⁹ developed an apparatus enabling them to compare the relative strengths of organic ion exchange resins in spherical geometry. Recently, Skriba and Kunin¹²⁷ developed an apparatus to determine the resin performance under mechanically induced stresses and effects of osmotic forces. However, no concise method for measuring the inherent physical strength of inorganic ion exchange

materials has yet been published.

In this study the the Vickers indentation technique, widely used in the field of engineering ceramics, has been used to determine the critical fracture toughness (K_{1c}) of inorganic hydrous oxides.

5.51 The Diamond Indentation Technique as a method for measuring material strength

The indentation technique for measuring the critical stress intensity factor or fracture toughness (K_{1c}), can be applied to hydrous oxides by two well attested methods. The direct crack measurement method¹³⁰ is utilised here as opposed to the strength method¹³¹. In comparison with more conventional testing techniques, the Vickers indentation method which uses a standard Vickers hardness diamond indenter of fixed geometry, offers simplicity and economy in the test procedure.

As will be seen later, the determination of K_{1c} by the indentation fracture of small specimens requires a knowledge of the hardness to Young's modulus ratio, H/E , for the specimen material. The hardness of a material is a property which is not uniquely defined¹³² since a number of different tests have been claimed to measure hardness. Indentation hardness measures resistance to plastic flow or permanent deformation under static loading (also referred to as static indentation hardness). The Vickers and Knoop hardness tests are widely used in materials science. Both use a diamond pyramidal indenter, with corresponding

symbols H_v and H_k respectively. The Vickers test is used much more frequently, and unless stated otherwise hardness data for ceramics usually refers to Vickers hardness data and H without a subscript refers to H_v . For a full treatment of hardness see Tabor¹³³ and Dieter¹³⁴.

A simple method for determining H/E has been developed by Marshall, Noma Tatsuo and Evans¹³⁵ and is summarised here

$$\frac{b'}{a'} \approx \frac{b'}{a} = \frac{b}{a} - \frac{\partial H_v}{E} \quad (5.3)$$

where a and b are the long and short diagonal dimensions of the Knoop indenter respectively, and are in the ratio of 1:7.11 respectively. a' and b' are the 'recovered' lengths of the diagonals of an indented sample. ∂ is the gradient. Marshall, Noma, Tatsuo and Evans¹³⁵ have verified equation (5.3) for a number of ceramic materials and show that the intercept $b'/a' = b/a = 1/7.11$ and the gradient $\partial = 0.45$. Chanikul et.al.¹³⁰ have shown that the critical stress intensity factor, K_{1c} can be related to H/E ratio, peak load P and the crack length c_o associated with a Vickers hardness as follows

$$K_{1c} = 0.016 \left[\left(\frac{E}{H} \right)^{\frac{1}{2}} \cdot \left(\frac{P}{\sqrt{c_o^3}} \right) \right] \quad (5.4)$$

Equation (5.4) is the basic equation for evaluating the material toughness; the first expression $\sqrt{(E/H)}$ is evaluated from the Knoop and Vickers hardness tests and the

second $(P/\sqrt{c_o^3})$ from the Vickers hardness test. The expression relating H_K and H_V to load, diagonal lengths and crack lengths are derived in references^{133,134} and are as follows:

$$H_K = 14.229 \frac{P}{d_K^2} \left[\frac{\text{kg}}{\text{m}^2} \right] \quad (5.5)$$

$$H_V = 1.8544 \frac{P}{d^2} \left[\frac{\text{kg}}{\text{m}^2} \right] \quad (5.6)$$

P = applied load [kg]

d_K = Knoop indent mean long diagonal length [m]

d = Vickers indent mean diagonal length [m].

5.52 Experimental procedure

Hydrous oxide materials in the size range 600-420 μm were allowed to set in resin overnight. Less than 0.25g of each material was used, enough to give a reasonable number of particles spread evenly across a 3cm² resin area. The hardened resin blocks were mechanically polished with the various grades of diamond paste; ultimately to 0.25 micron, to produce an optical finish. The HMnO and the HMnO:HSiO composite materials required extensive polishing to produce black shining surfaces under the optical microscope. High quality polishing enhances the physical appearance of the cracks and exposes any irregularities in the material surface under test.

A Leitz micro-hardness tester was used to carry out both

the Knoop and Vickers hardness tests. Exploratory tests were carried out on each material to determine the correct load to give clearly visible and reasonable crack lengths. It has been demonstrated by Rawlings¹³⁶ that the hardness variation with load is small and within experimental scatter. A scanning electron micrograph of the radial cracks from a Vickers indent is given in figure 5.10. If the load is excessive the crack propagates too far meeting up with an irregularity in the material, while with a small load the cracks are not clearly visible. Several indents may be carried on a single particle thus rendering a high statistical accuracy in the results.

HSnO and HMnO posed some difficulties in obtaining suitably visible cracks. HMnO was found to be an extremely 'soft' material; the variation of load with crack lengths was outside experimental scatter as the material tended to fragment on application of load. The results quoted for HSnO were achieved after many tests at different sites. There were no difficulties encountered in the crack visibility of HTiO, HTiO:HSiO and HMnO:HSiO, however the bright silvery lustrous appearance of amorphous HSnO made it difficult to see the entire crack as the crack 'disappeared' at bright spots. The problem of crack visibility can be overcome by vacuum depositing¹³⁷ a thin gold film on the optically polished surface. By doing this the cracks appear as bright reflections under the optical microscope.

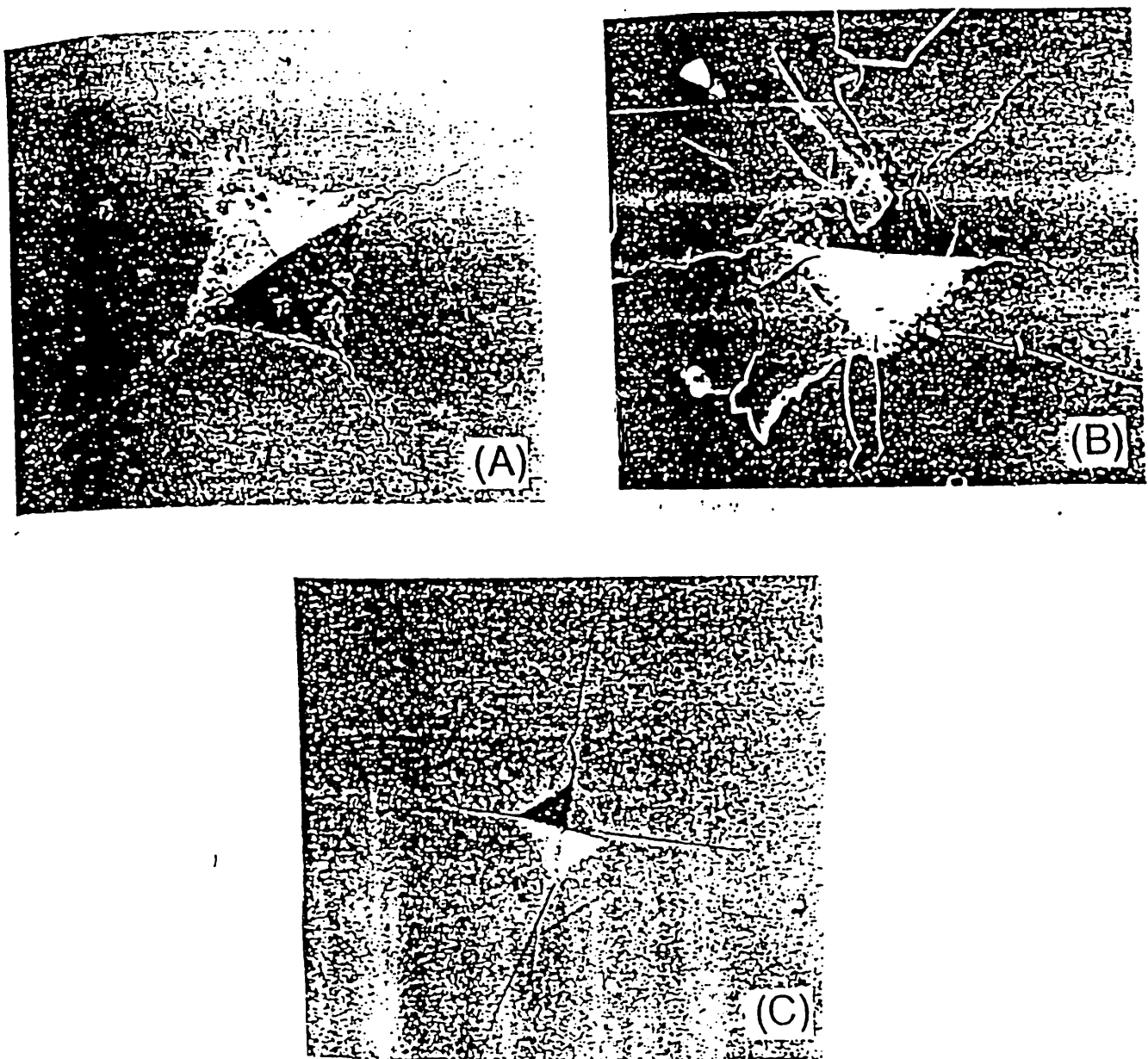


Figure 5.10 Scanning electron micographs of radial cracks from a Vickers indent.

(A) Small load, cracks observed with difficulty.

(B) High load, cracks meeting up with irregularities in material.

(C) Ideal load.

(from reference 130)

5.53 Results

The number of indentations carried out for each material was decided by the scatter in results. Several indents were made for each of the the Knoop and Vickers test results. The difficulty with the Vickers test was in deciding where a crack finished, as the intensity of the crack under the microscope diminished considerably towards the end. Any suspect crack length values were discarded to avoid large inaccuracies in the final data. The mean of Knoop and Vickers hardness values for each material are presented in Table 5.7 and Table 5.8, respectively. The Knoop hardness test was carried out to determine the b'/a' ratio, the value for the Knoop hardness is merely tabulated for comparison with the Vickers hardness. A sample calculation showing the derivation of values given in tables 5.7, 5.8, and 5.9 is given in appendix IV.

The Young's modulus and fracture toughness values for the hydrous oxides are given in Table 5.9. For comparison known data for some materials is given appendix IV.

The results presented in Table 5.9 for hydrous oxides can be compared directly with the data for well attested ceramic materials (appendix IV). The validity of the technique applied to inorganic hydrous oxides is apparent from the values obtained for H_k , H_v and K_{1c} ; all the results fall within the order of magnitude of reference materials, some of which are also amorphous. The advantage of this technique is that practical values of the material strength have been put forward. $HTiO$ was expected to be the tougher

material, the addition of silica to HTiO reduced its hardness. Conversely the addition of silica to the HMnO has considerably enhanced the hardness of the composite material. The addition of silica to HMnO and HTiO have yielded K_{1c} values in the category of polycrystalline materials. The relatively low value of $0.16 \text{ MPa.m}^{1/2}$ for HSnO can be attributed to the difficulties described earlier.

Table 5.7 : Knoop Hardness Tests

Material	Load, P/kg	Mean long diagonal length, $d_k/\mu\text{m}$	Mean short diagonal length, $a_1/\mu\text{m}$	Knoop Hardness $H_k, \text{kg/m}^2$
HTiO	0.50	62.90 ± 5.02	8.03 ± 0.78	17.98×10^9
HTiO:HSiO	0.30	65.01 ± 2.99	8.17 ± 0.85	10.10×10^9
HMnO	0.10	34.44 ± 3.93	3.10 ± 0.30	12.00×10^9
HMnO:HSiO	0.50	64.40 ± 1.48	6.61 ± 0.15	17.15×10^9
HSnO	0.30	60.44 ± 2.84	6.69 ± 0.63	11.69×10^9

Table 5.8 : Vickers Hardness Tests

Material	Load, P/kg	Mean crack length, $c_o/\mu\text{m}$	Mean diagonal length, $d/\mu\text{m}$	Vickers Hardness $H_v, \text{kg/m}^2$
HTiO	0.50	17.69 ± 3.63	21.38 ± 2.17	2.02×10^9
HTiO:HSiO	0.20	63.16 ± 5.52	20.50 ± 1.00	0.88×10^9
HMnO	0.025	8.93 ± 0.93	8.80 ± 0.21	5.99×10^9
HMnO:HSiO	0.50	7.55 ± 1.49	16.85 ± 0.80	3.25×10^9
HSnO	0.10	54.75 ± 8.57	10.22 ± 0.15	1.78×10^9

Table 5.9 : Fracture Toughness Values for
Hydrous Oxide exchangers

Material	Material Characterization	Young's Modulus, E (GPa)	Vickers Hardness $H_v, (\text{GPa})$	Fracture Toughness K_{1c} (MPa.m ^{1/2})
HTiO	Amorphous	689.35	19.89	6.20
HTiO:HSiO	Amorphous	259.95	8.65	0.34
HMnO	Amorphous	52.17	5.87	0.44
HMnO:HSiO	Amorphous	376.98	31.84	12.88
HSnO	Amorphous	312.45	17.47	0.16

5.6 Irradiation stabilities

When ionic species, removed by an ion exchanger, include radioactive nuclides, the energies of the radioactive decay process imparted to the ion exchanger material and its environment make the system more susceptible to rapid deterioration. This phenomena is not generally well understood, although there is growing recognition of the potential problems associated with the radiolytic effects in ion exchange matrices. Under normal operating conditions of the ion exchange systems, radiation effects can be identified as due to direct radiolytic reaction on the ion exchange matrix and indirect attack on the ion exchanger by the radiolysis products of solvents and solutes present in the system. The radiolytic effects on the ion exchangers can manifest in a variety of ways, most of them often undesirable to process operations, it is therefore important to recognise the consequences of radiation effects on ion exchangers and their environment to carry out safe and reliable operation of ion exchange systems.

Radiation stability of some thermally stable heteropolyacid type inorganic ion exchangers have been reported by Janardanan et. al.¹⁴¹ and Varshney et. al.¹⁴². Howard¹⁴³ has reported studies carried out on clinoptolite and cyanoferrates of Na and K. Work on organic and inorganic materials has been summarised in a comprehensive review paper by Pillay¹⁴⁴. Pillay¹⁴⁵ in a separate study and Streat¹⁵⁸ have presented extensive data on the effects of ionizing radiation on organic resins.

In this study the effects of ionizing radiation were measured in terms of ion exchange capacity and chemical stability. 'Dry' and 'wet' samples were irradiated using the Co⁶⁰ γ -irradiation source at Imperial college to doses of up to 1000 Mrads (10 MGy). Ion exchange tests were carried out on both the dry and wet samples, chemical stability was measured by the dissolution of the exchangers in the wet medium and infra-red analysis were carried out on the dry samples. Unlike the studies mentioned earlier^{141,142} the ion exchange tests were carried out with a multi-component 'MODSOL' solution (as used with selectivity tests) and to higher doses.

Experimental :

All the hydrous oxides were prepared using the capillary reactor, as described in chapter 3. HSnO was not considered in this study due to its low overall ion exchange performance. The Co⁶⁰ irradiation source was calibrated in the usual manner¹⁵² and was rated at 0.67 Mrad per hour (6.7 kGy/h). All the samples, wet and dry, were placed in a tin can approximately 25cm high placed at the centre of the γ -source. The dose rate was assumed uniform over the entire can at 0.67 Mrad/h.

For irradiation tests with the dry samples, approximately 0.2g of each exchanger in mesh size 105-53 μ m were placed in a small narrow glass vials with plastic tops. Four batches, each containing the four exchanger materials, were wrapped separately to be irradiated to four different periods of

time. The four batches were retrieved at ≈ 200 , ≈ 400 , ≈ 800 and ≈ 1600 hours. After the given irradiation doses the ion exchange tests were carried out in the usual manner with accurately weighed 0.1g portions of the irradiated samples contacted with 30ml of the MODSOL solution. The modsol solution was of the same specification as used in the selectivity studies and required a Sr^{85} spike. The pH of the contacting solution after 24 hours of mixing was measured and required adjustments in some cases to standardise to pH 2.0 ± 0.2 . The remaining portion of the dry irradiated samples were retained for infra-red studies.

In the wet irradiation tests the wetting agent was distilled water treated with nitric acid to pH 3. Accurately weighed 0.1g portions of each exchanger material, mesh size 105-53 μm were contacted with 15ml of treated water in a 20ml glass vials with plastic tops. The batches were arranged as before and irradiated simultaneously for identical doses. After irradiation the water above the exchanger was drawn off very carefully using a pasteur pipette, filtered through a 0.22 μm millipore filter paper to remove any fines and the pH values recorded. These filtered solutions were later analysed for dissolution of the exchanger metal ions. The Mn^{4+} in HMnO and Mn-composite was analysed by atomic absorption¹¹², the Ti^{4+} in HTiO and Ti-composite was determined spectrophotometrically^{111,112}. The ion exchange tests with the wet irradiated exchangers were carried out in the usual manner. The pH of the contacting solution were

adjusted as before for direct comparison.

The distribution coefficient values for the various radioisotopes for the four hyrous oxides are given in figures 5.11-5.14 for dry and figures 5.15-5.18 for wet irradiated samples. The pH values of the supernatant solution of the wet samples immediately after the irradiation are presented in table 5.10. The chemical stability test results are tabulated in table 5.11. Figure 5.19 gives the infra-red spectra for all the samples irradiated to 1068 Mrads. Figure 5.20 gives the IR spectra for HTiO:HSiO samples irradiated at various doses.

On removal of dry samples from the radiation source it was noticed that Mn(IV) based materials were moist for doses greater than 500 Mrads and no change in physical appearance was noticed. The Ti(IV) based materials underwent a colour change from white to 'charred' yellow, but remained dry.

From the ion exchange results in figures 5.11 and 5.18 the following general points were noted :

(i) that the trends for almost all ion exchanger/isotope combinations were generally identical. These observations may be linked to earlier ion exchange tests, ie. Am, Eu and Co uptakes with Mn(IV) based exchangers were still relatively high and overall U uptake is low for all the exchangers,

(ii) except for a few cases, the distribution coefficient values gradually drop with increasing doses; however, despite the high levels of irradiation the changes are less

than an order of magnitude for almost all the cases,

(iii) with the exception of Cs^+ uptake by Ti composite (wet irradiated), all the Ti and Ti composite samples (wet and dry irradiated), show a marked increase in uptake with a gradual drop thereafter,

(iv) in several cases large increases are observed at around the 500 Mrad dose of irradiation, these occurrences are most noticeable with the Am and Eu uptakes,

(v) there are no significant differences between the respective wet and dry irradiated samples.

The effect of direct radiolysis on the amorphous metal oxide structure might be expected to disrupt the metal-oxygen bonds. This could have a two-fold affect (a) liberation of metal into solution, very unlikely and not observed as the results have shown in table 5.11 or (b) giving a change to the oxidation states of the metal. The oxidation states of the metals (Ti, Mn and Si) are at the most stable state in the oxides. Any radiation induced change might be expected to revert rapidly by reaction with the environment (the interstitial water of hydration) to the states in the oxides prior to radiolysis. It is unlikely that any persistent change in oxidation state could be brought about by radiolysis in these chemically simple systems.

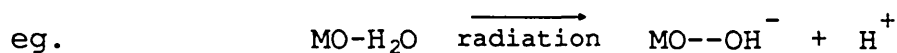
With regards to the moistening exhibited by the Mn(IV) hydrous oxide exchangers it is possible that some change in the associated hydration shell could be brought about by radiation providing cation capacity with strong anion

groups and releasing H^+ into the associated solution. The yield per 100eV of radiation is given by the G-value equation:

$$G = \frac{10^{-9} \text{ mol cm}^{-3} (\text{pH } 6) \times 6.02 \times 10^{23} (N_A) \times 100}{200 \times 10^6 (\text{dose in rads}) \times 6.24 \times 10^{13} (\text{rads to eV})}$$

$$= 4.82 \times 10^{-8} \text{ per 100eV}$$

The pH values in table 5.10 show that after an initial drop in pH the changes thereafter are not necessarily so significant. The initial decrease may be due to the release of H^+ ions in the radiolytic hydrolysis of interstitial water as illustrated by the above equation. A typical pH change equivalent to $10^{-6}M$ H^+ ion concentration corresponds to a very inefficient radiolytic process.



Any radiation induced change in the water of hydration would not however be expected to be more than transient.

It seems then that these materials are very radiation stable and a very logical systematic interpretation of the apparent changes of K_d cannot be made.

The chemical stability tests given in table 5.11 are very conclusive in that they show no loss of the materials even at high irradiation doses. The atomic absorption results were close to the limits of detection of the apparatus and therefore should not be regarded as absolute values,

however they are indicative of the high thermal and irradiational stabilities of the exchangers.

The IR spectra in figure 5.19 are given to show that radiolytic hydrolysis effects are not so evident for the hydrous oxide ion exchangers. Figure 5.20 shows the IR spectra over the duration of the experiment. These figures clearly show the all the characteristic peaks for the hydrous oxides, as shown in figure 5.1. The figures reassert the transient nature of the radiation induced changes.

All the results indicate that the radiation has no major long term change of capacity affect on all the hydrous oxides tested and that the intermediate points merely represent experimental scatter.

Table 5.10 : pH values of 'wet' irradiated hydrous oxides

Material	pH at various doses/Mrads				
	0	144	253	561	1068
HTiO	10.3	8.7	7.6	6.9	6.3
HTiO:HSiO	10.1	8.3	7.6	6.8	6.1
HMnO	10.3	8.5	7.4	6.8	6.2
HMnO:HSiO	10.2	8.3	8.1	7.7	7.4

Table 5.11 : Chemical stability test results for 'wet' irradiated hydrous oxides

Dose / Mrads	[metal ion]/ppm in solution			
	Ti ⁴⁺		Mn ⁴⁺	
	HTiO	HTiO:HSiO	HMnO	HMnO:HSiO
0	-	-	-	-
144	-	-	-	-
253	-	-	2.0	1.0
561	-	5.0	4.0	1.0
1068	1.3	5.75	5.0	2.0

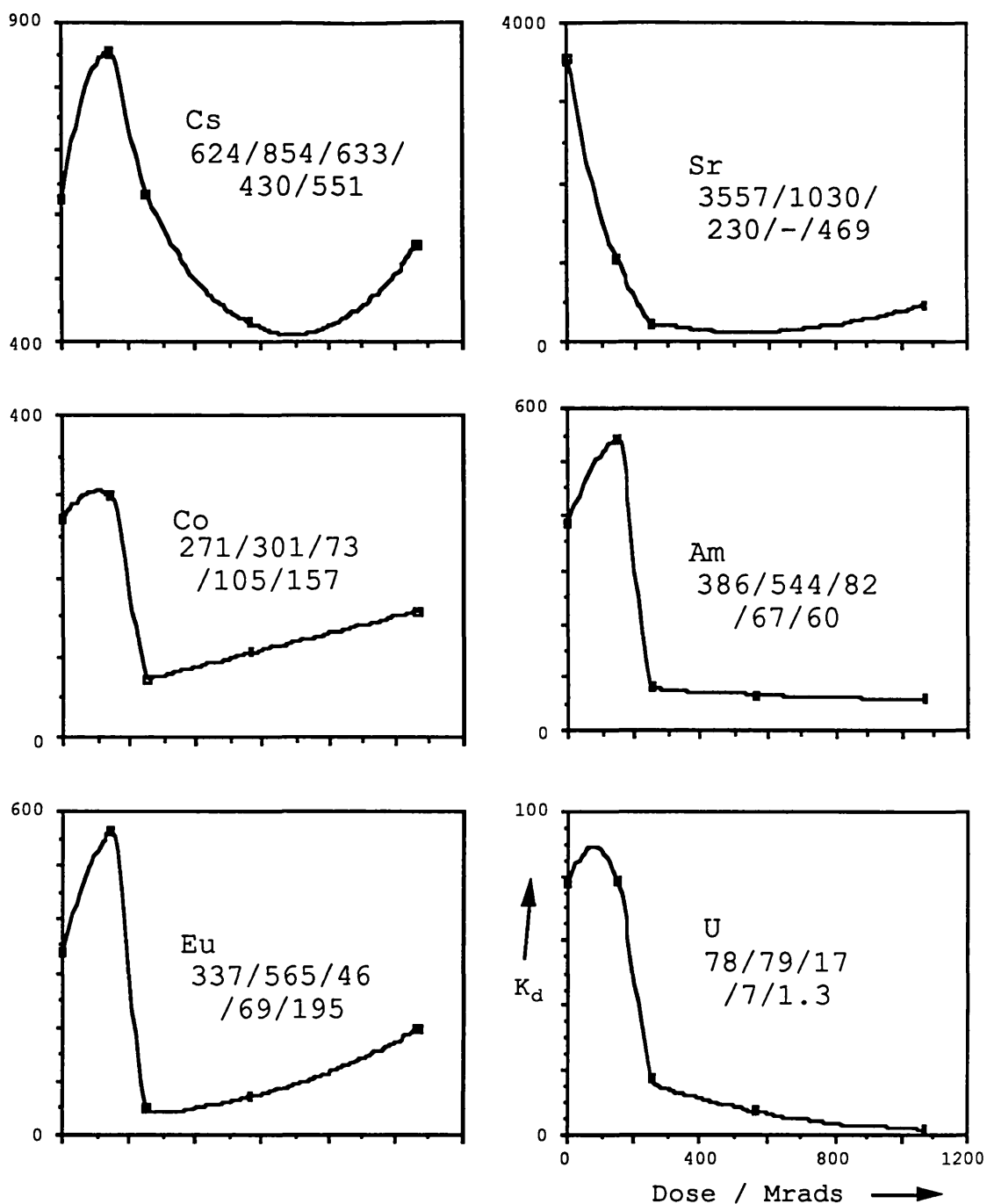


Figure 5.11 Effects of ionizing radiation on ion exchange properties of HTiO, irradiated dry (K_d values given below chemical symbols)

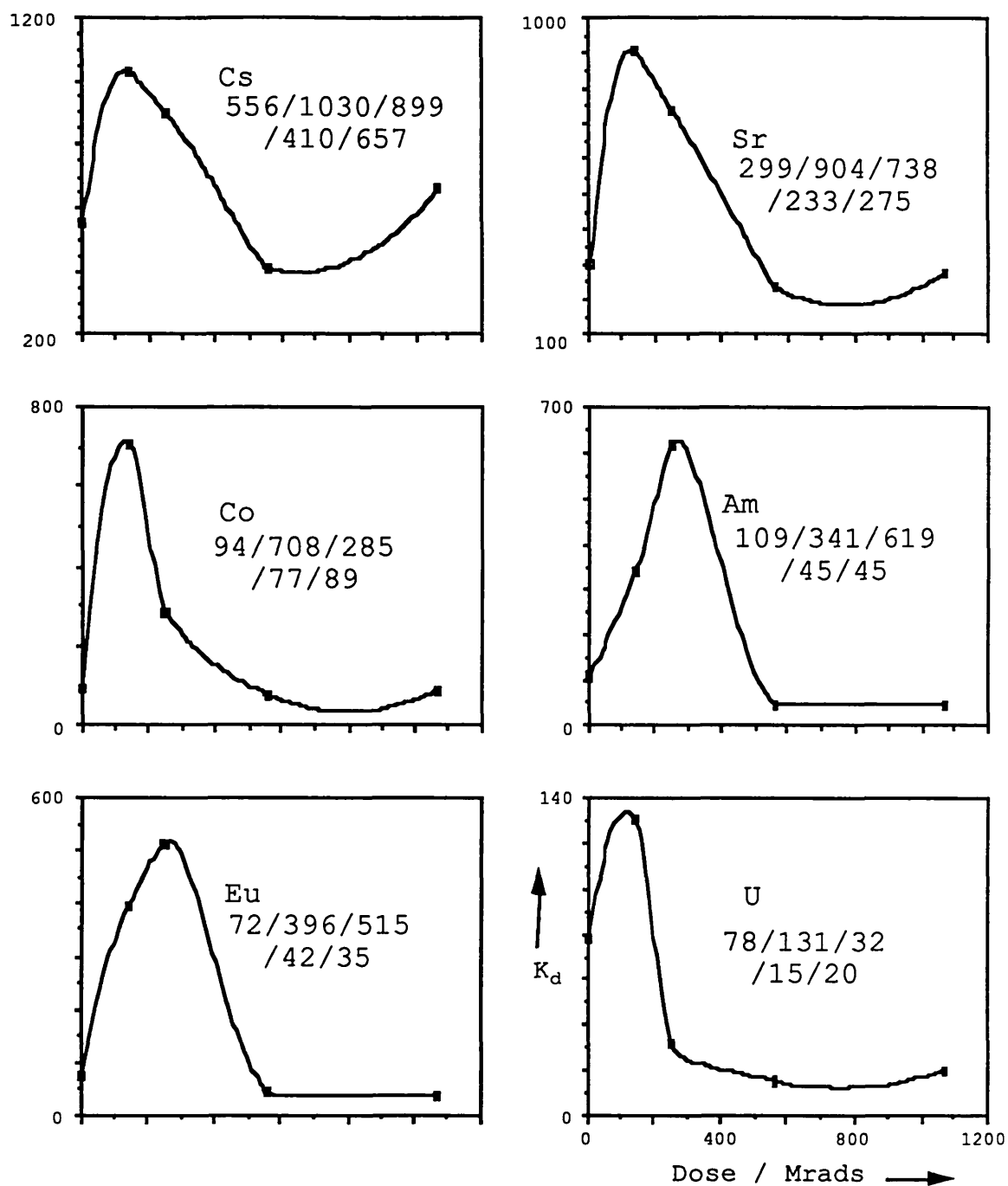


Figure 5.12 Effects of ionizing radiation on ion exchange properties of HTiO:HSiO, irradiated dry (K_d values given below chemical symbols)

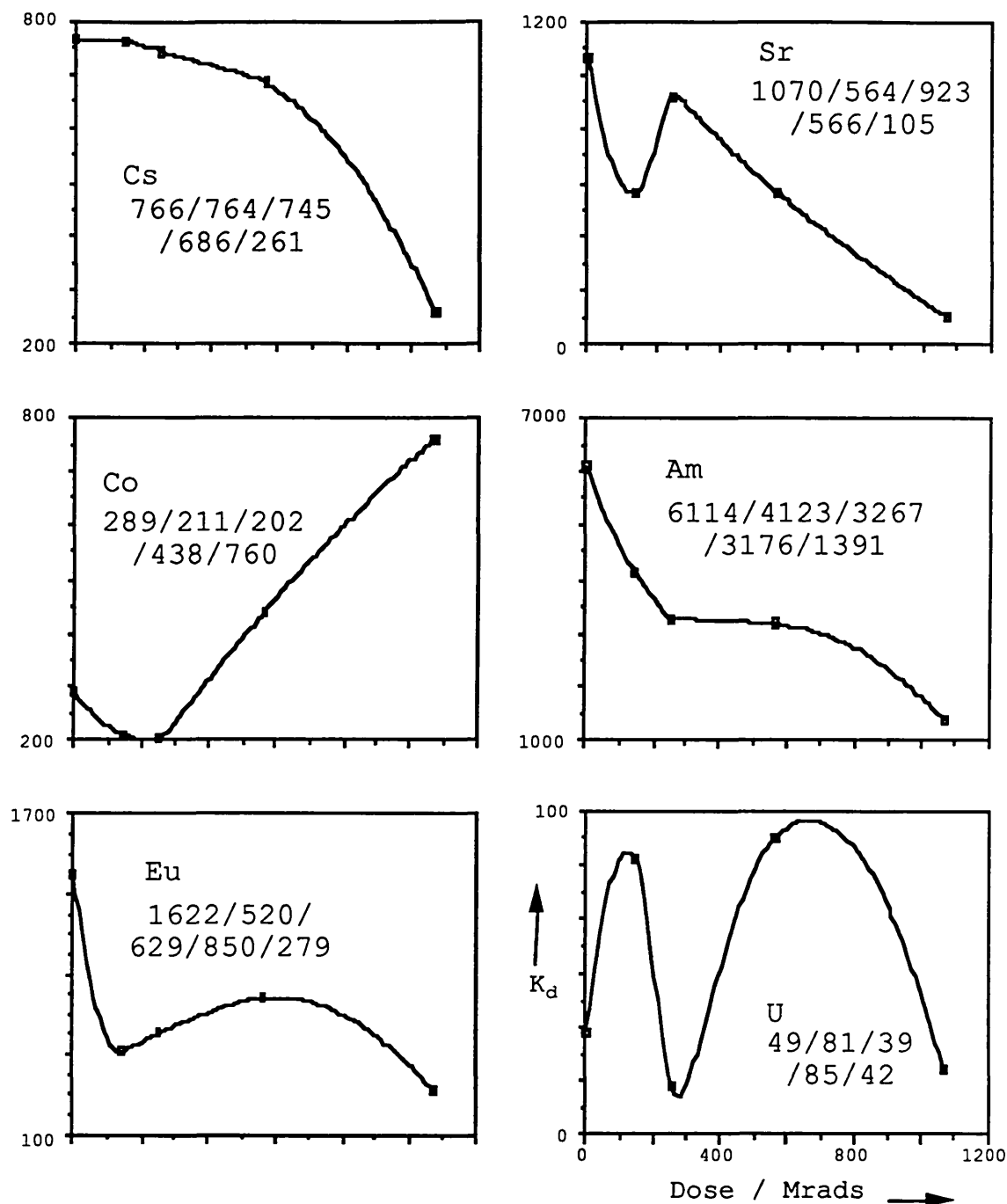


Figure 5.13 Effects of ionizing radiation on ion exchange properties of HMnO, irradiated dry (K_d values given below chemical symbols)

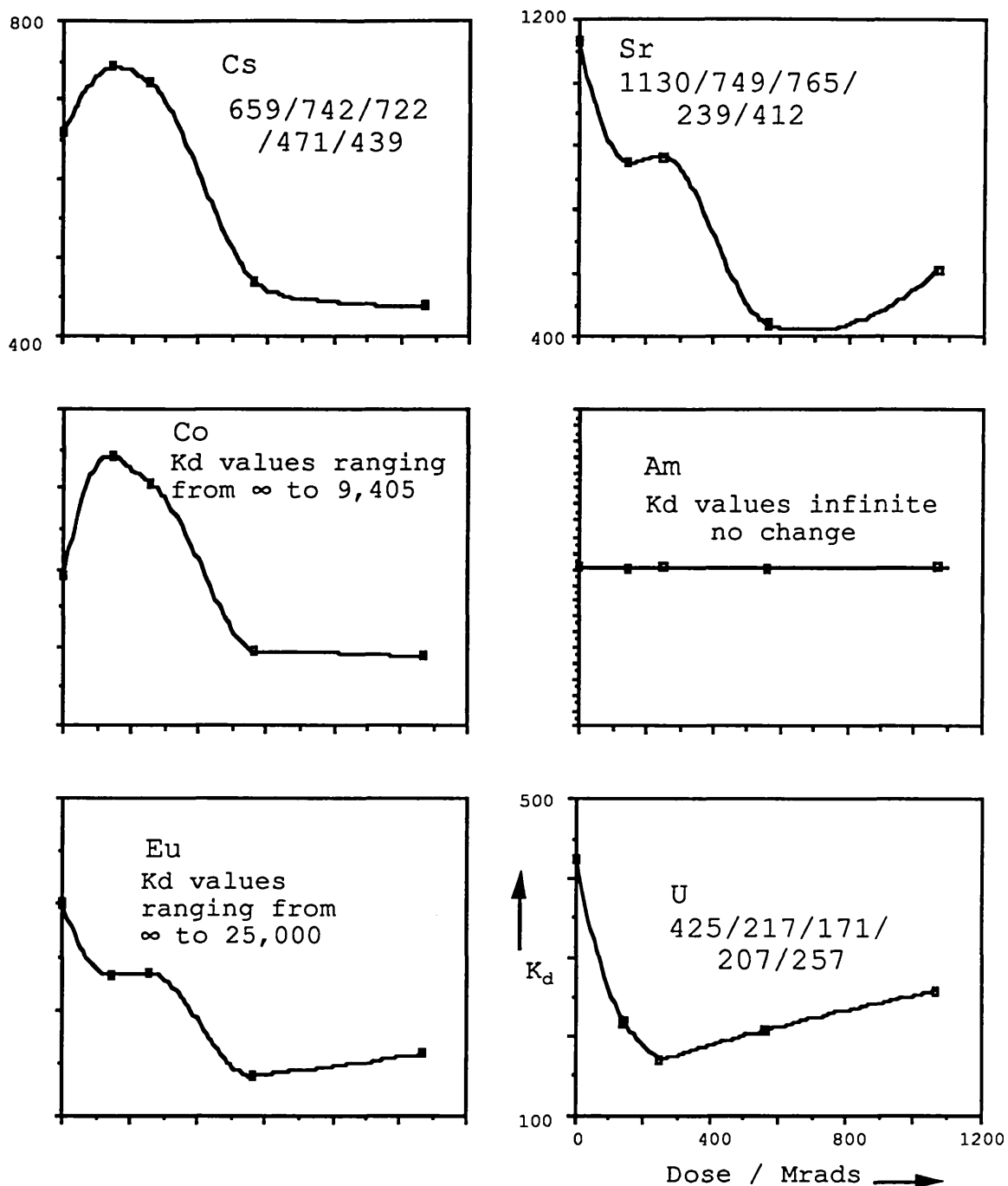


Figure 5.14 Effects of ionizing radiation on ion exchange properties of $\text{HMnO}:\text{HSiO}$, irradiated dry (K_d values given below chemical symbols)

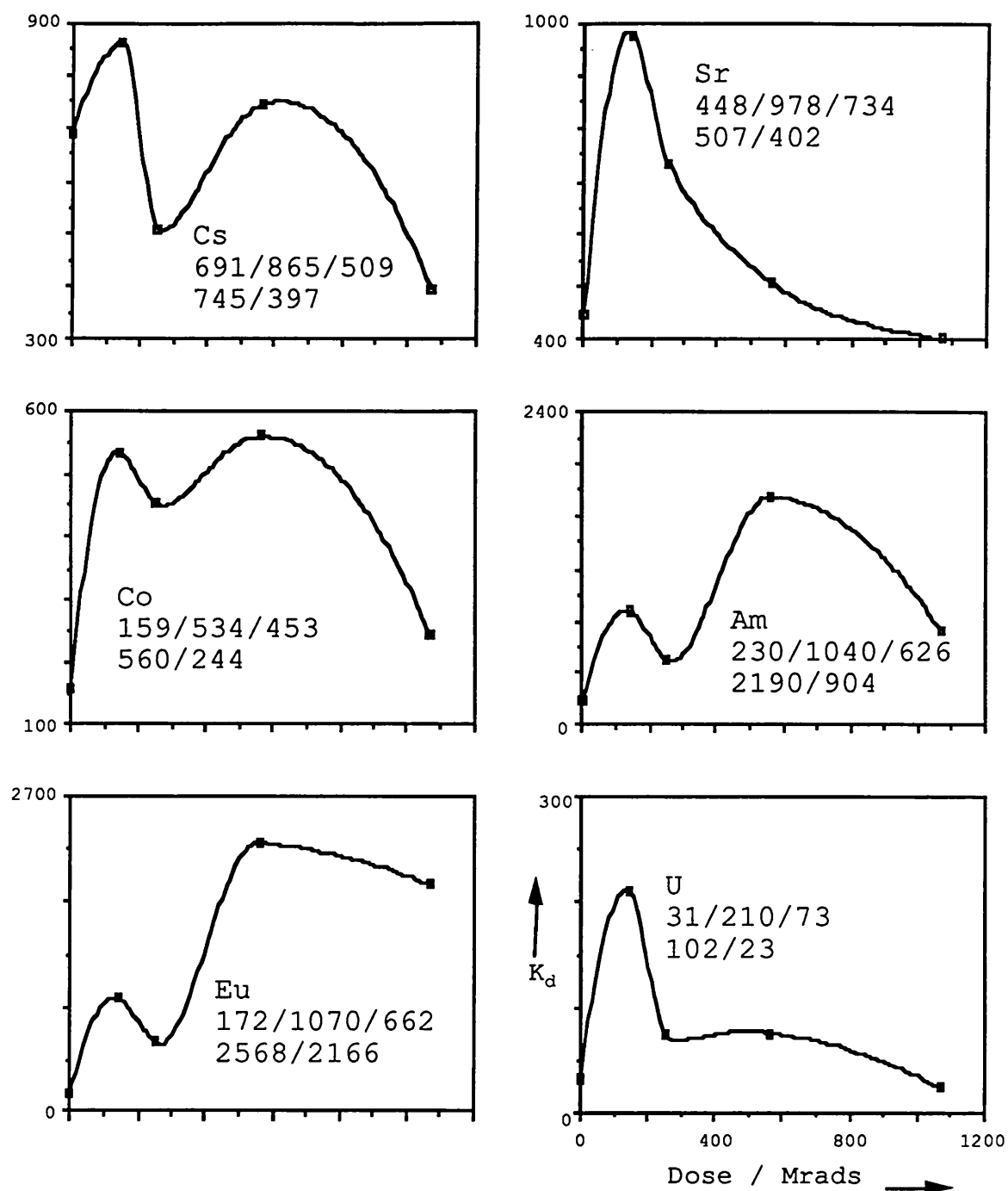


Figure 5.15 Effects of ionizing radiation on ion exchange properties of HTiO, irradiated wet
(K_d values given below chemical symbols)

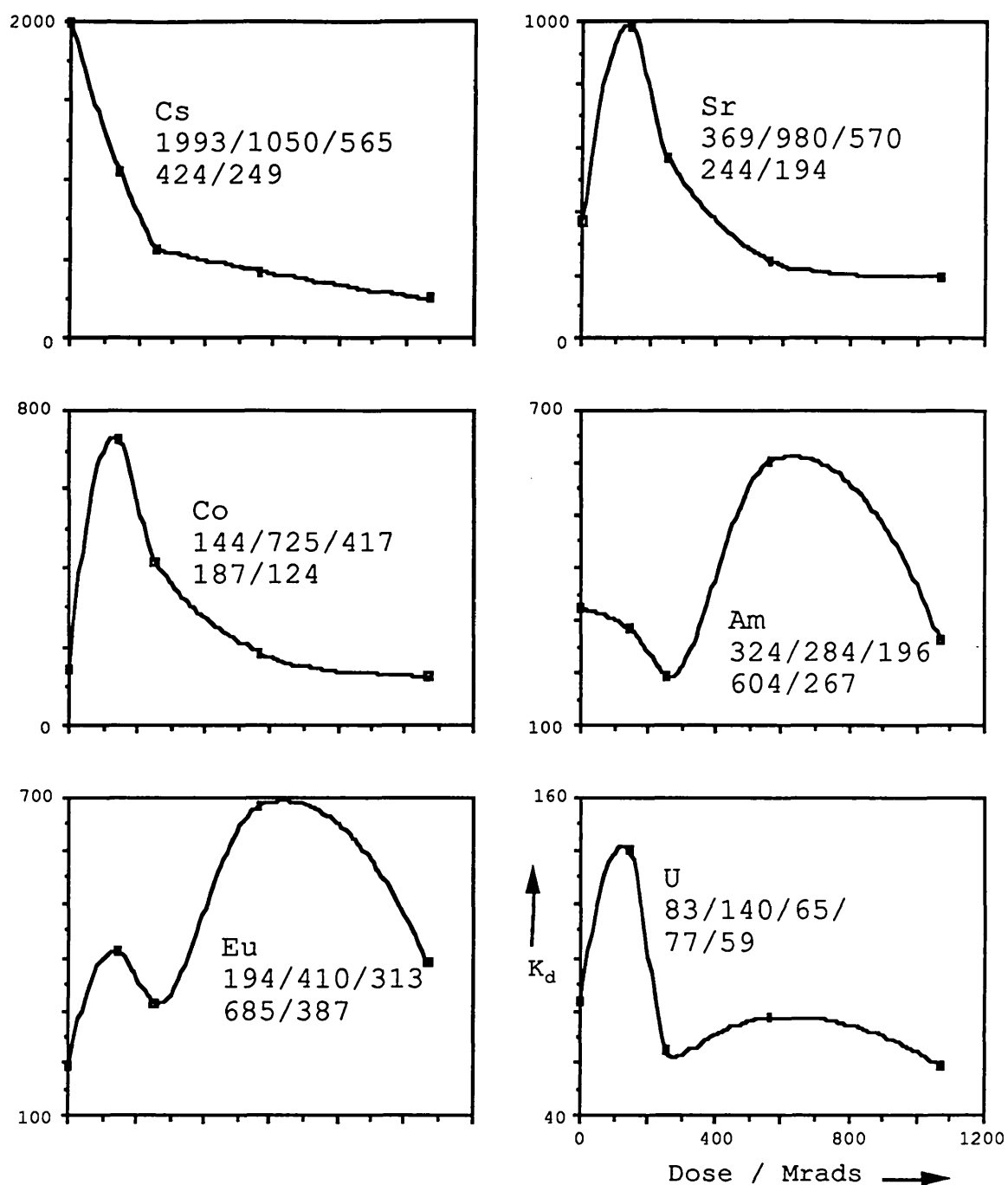


Figure 5.16 Effects of ionizing radiation on ion exchange properties of HTiO:HSiO, irradiated wet (K_d values given below chemical symbols)

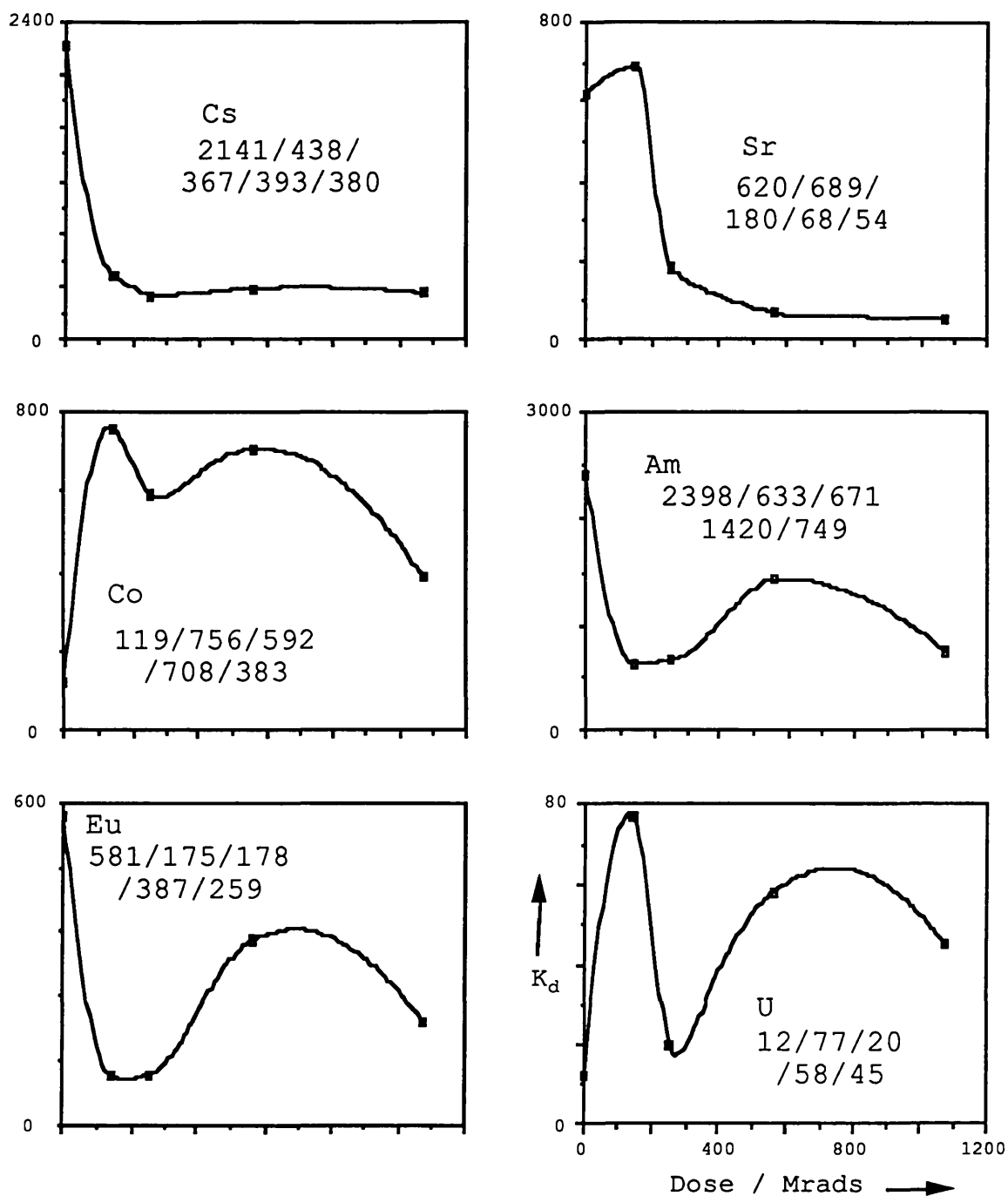


Figure 5.17 Effects of ionizing radiation on ion exchange properties of HMnO, irradiated wet
(K_d values given below chemical symbols)

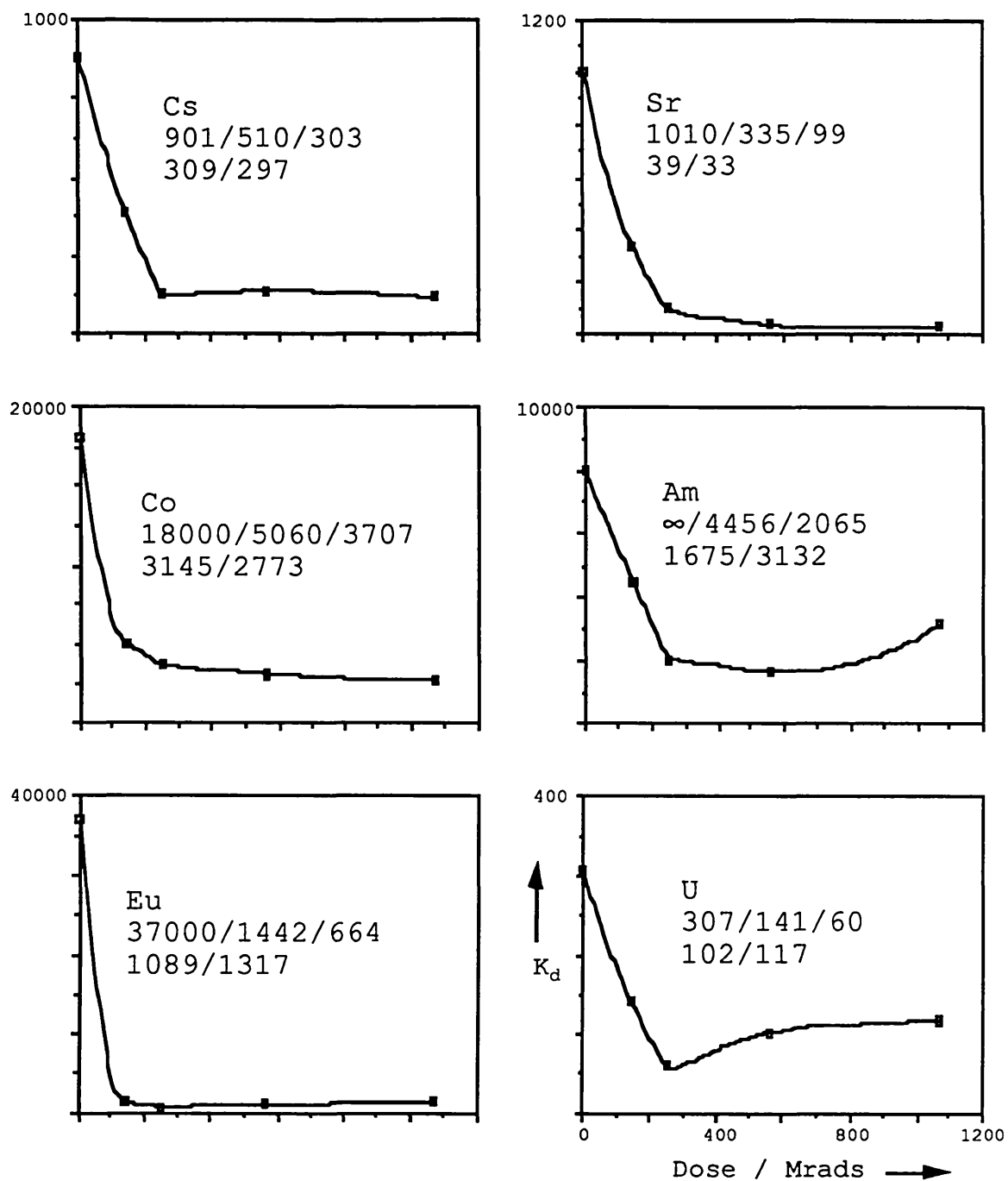


Figure 5.18 Effects of ionizing radiation on ion exchange properties of HMnO:HSiO, irradiated wet (K_d values given below chemical symbols)

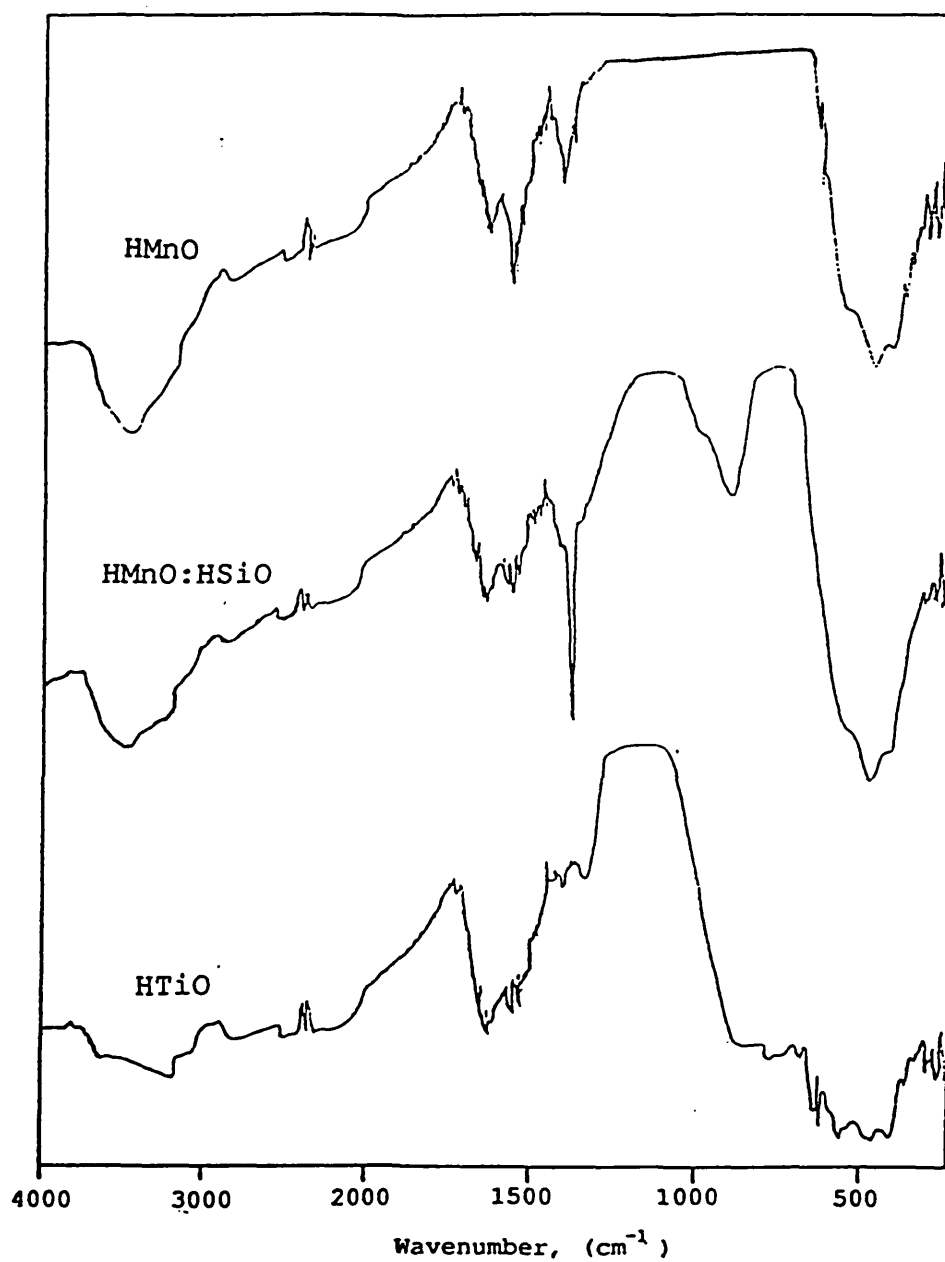


Figure 5.19

Infrared Spectra of irradiated hydrous oxide ion exchangers
(~1068Mrads)

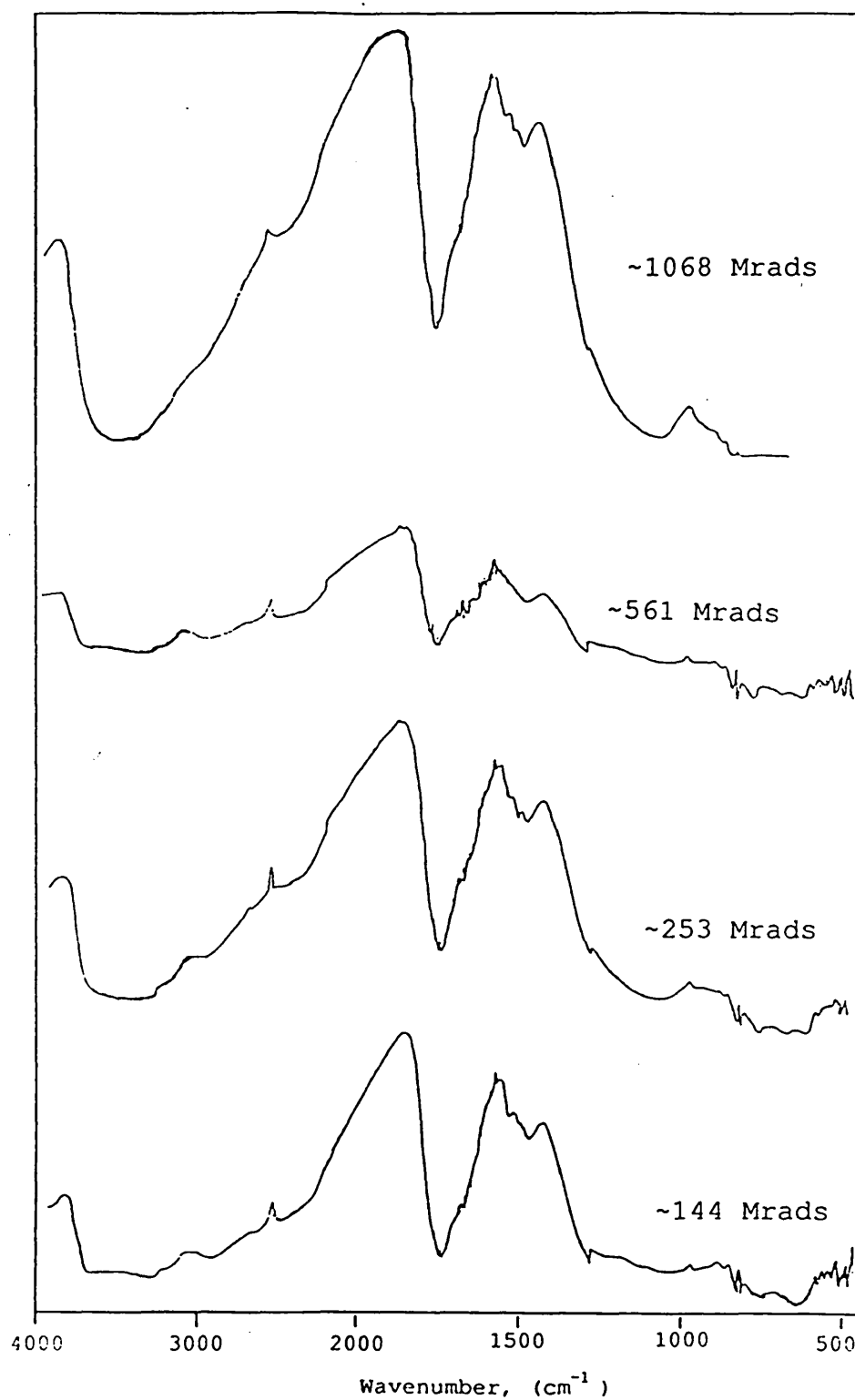


Figure 5.20

Infrared spectra of irradiated HTiO:HSiO at Various doses

Chapter 6

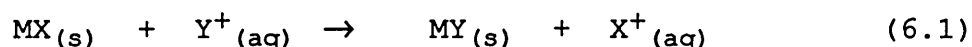
Kinetics

*6.1 Introduction 6.2 Rate Equations 6.3 Experimental 6.4
Results and Discussion 6.5 Conclusions and Future work.*

6.1 Ion exchange kinetics - an introduction

In designing an ion exchange column it is useful to know the time it takes to saturate an ion exchanger. It is important, therefore to understand the kinetics of ion exchange and be able to predict theoretical values of such parameters and establish theory to support experimental data.

A typical cation exchange reaction such as :-



may be regarded as taking place through a number of steps:

(i) film diffusion of Y^{+} ions through the solution up to the surface of the exchanger particle,

(ii) diffusion of Y^{+} ions to an ion exchange site MX within the particle,

(iii) chemical exchange between Y^{+} and MX,

(iv) diffusion of X^{+} in the solid to the surface (reverse of step (ii)), and

(v) film diffusion of X^{+} ions through the solution away from the particle (reverse of step (i)).

Conway et.al.¹⁵⁰ have shown that if (i) and (v) were rate controlling, the rate of exchange would be dependent upon stirring characteristics and upon concentration of Y^{+} ion in solution. For particle diffusion (ii) and (iv) on the other hand, the rate should be independent of these factors but vary with particle size. A chemically controlled process would have a rate independent of particle size.

A large variety of tests on the kinetics of ion exchange

were carried out between the four hydrous oxide exchangers and solutions of varying strengths of Cs^+ solutions. Two diffusional mechanisms^{146,151}, one where the rate is controlled by diffusion of ions within the particle (pdc) and the other whereby the process is controlled by diffusion of ions across a finite liquid film (fdc), were sought for. Attempts at distinguishing between the two different diffusion processes were made by (i) by the variation of stirring speed^{26,149}, and (ii) by interruption tests^{147,148}. The values for diffusion coefficients were determined in certain cases. The activation energy for the ion exchange process was also determined.

6.2 Rate Equations

Film and particle diffusion are sequential steps, the slower of the two is rate controlling. A quantitative criterion has been derived¹⁴⁶ whereby the rate controlling step can be predicted theoretically, for given values of the ion exchange capacity, solution concentration, particle size, film thickness, diffusion coefficient and separation factor :

$$\frac{C'D'\delta}{CDr_o} \left(5 + 2\alpha_y^x \right) \ll 1 \quad \text{particle diffusion control} \quad (6.2)$$

$$\frac{C'D'\delta}{CDr_o} \left(5 + 2\alpha_y^x \right) \gg 1 \quad \text{film diffusion control} \quad (6.3)$$

It was not possible to fit the experimental data of the present study to the above criteria as the separation factor

value $\alpha_{H^+}^{Cs^+}$ was not known.

6.21 Film diffusion control

The following rate equation derivations are chiefly based on studies by Boyd et.al.¹⁶, detailed derivations may be found in the literature.

Figure 6.1 illustrates the model considered: a spherical adsorbent particle of radius r_o is surrounded by an aqueous liquid film of thickness δ , where $\delta = r_o' - r_o$ and that there exists a concentration gradient in the liquid film. Let C be the concentration in bulk of the solution at any time

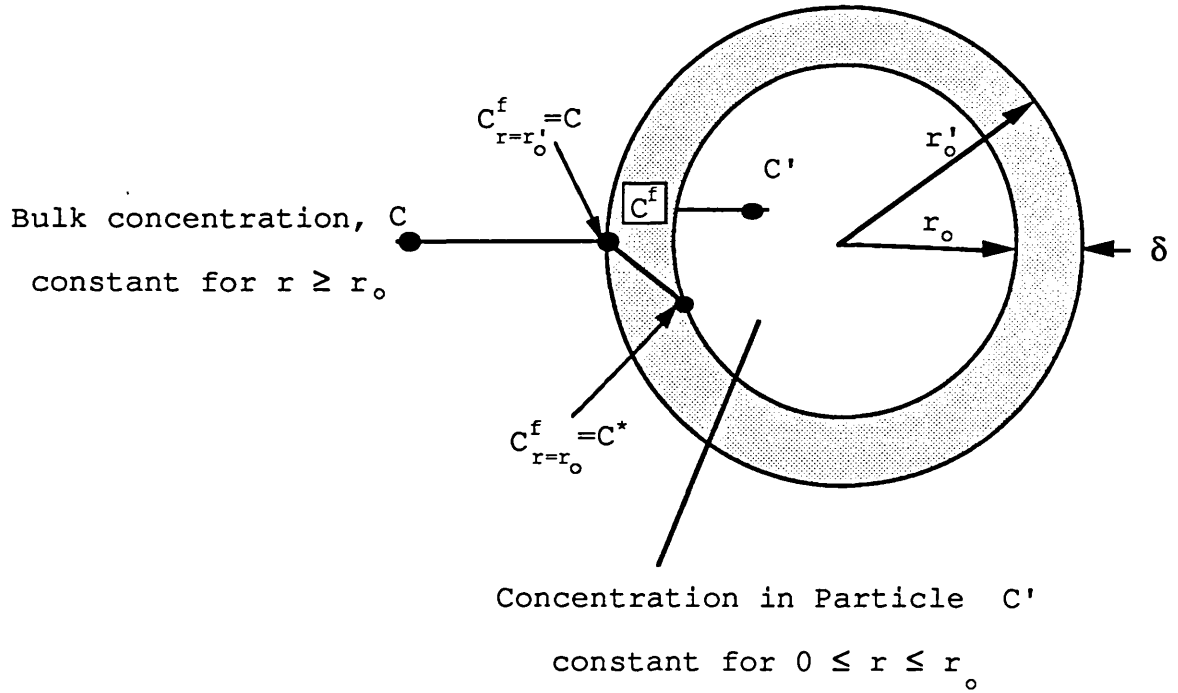


Figure 6.1 Ion exchange kinetics model

and considered constant for $r \geq r_o'$; and C^f the concentration in the film taken to vary linearly from $C^f_{r=r_o'} = C$ to $C^f_{r=r_o} = C^*$, the concentration in the solution adjacent and in equilibrium with the solid. The concentration within the particle C' , is assumed constant in the region $0 \leq r \leq r_o$. By denoting the equilibrium concentrations in the solid and liquid by C_e' and C_e respectively the distribution coefficient (assumed independent of concentration) may be defined as $C_e' = K_d C_e$. This assumption will only apply exactly to solution infinitely dilute in species being adsorbed.

The concentration at the surface of the particle is

assumed to be in equilibrium with the concentration in the solid throughout the experiment so that for $r = r_o$

$$C_{r=r_o}^f = \frac{C'}{K_d} = \frac{Q}{\frac{4}{3}\pi r_o^3 K_d} \quad (6.4)$$

where Q = total amount of adsorbate per particle
 = (volume) x (concentration) of particle,

$$= \frac{4}{3}\pi r_o^3 C'$$

If the diffusion through the film is rate controlling, then the rate of permeation, P (related to diffusion through the film) is given by,

$$P = -D \left(\frac{\partial C^f}{\partial r} \right)_{r=r'_o} \quad (6.5)$$

The total rate of flow of adsorbate across the the film dQ/dt is given by,

$$\frac{dQ}{dt} = 4\pi r_o^2 \cdot D \left(\frac{\partial C^f}{\partial r} \right)_{r=r'_o} \quad (6.6)$$

For a linear concentration gradient in the film, the gradient expression in equation (6.6) may be written as,

$$\left(\frac{\partial C^f}{\partial r} \right) = \frac{(C - C_{r=r_o}^f)}{\delta} \quad (6.7)$$

Substituting equation (6.7) into (6.6) gives it the following form,

$$\begin{aligned}\frac{dQ}{dt} &= \frac{4\pi r_o^2 \cdot D}{\delta} \left(C - C_{r=r_o}^f \right) \\ &= \frac{3 D}{\delta r_o K_d} \left(\frac{4\pi r_o^3 \cdot C K_d}{3} - Q \right)\end{aligned}\quad (6.8)$$

For a given system $3D/\delta r_o K_d$ is constant, therefore let $R = 3D/\delta r_o K_d$. In a infinite volume solution (IVS), the total amount adsorbed at equilibrium, Q_∞ may be defined as $4\pi r_o^3 C K_d/3$, since for a large volume C is assumed constant. By substituting Q_∞ and R , equation (6.8) may be rewritten as;

$$\frac{dQ}{dt} = R(Q_\infty - Q) \quad (6.9)$$

and integration, with the boundary condition that $Q=0$ when $t=0$, equation (6.9) becomes,

$$Q = Q_\infty (1 - \exp(-Rt)) \quad (6.10)$$

Defining the extent of reaction¹⁵⁰, F as

$$F = \frac{\text{the amount of exchange at time, } t}{\text{the amount of exchange at time, } t_\infty} \quad (6.11)$$

Hence equation (6.9) may be written as,

$$\ln(1-F) = -Rt \quad (6.12)$$

$$\text{or} \quad F = 1 - \exp(-Rt) \quad (6.12a)$$

The extent of reaction, F depends only on the dimensionless time parameter $D/\delta r_o K_d$ (or $DC/\delta r_o C'$). The half time of ion exchange ($t=t_{1/2}$ at $F=0.5$) is defined as,

$$t_{\frac{1}{2}} = 0.23 \frac{\delta r_o C'}{D.C} \quad (6.13)$$

In a finite solution volume (FSV), it may be shown that¹⁷,

$$F = 1 - \exp\left(\frac{-3D(V'C' + VC)}{\delta r_o C'V} t\right) \quad (6.14)$$

All the experiments carried out in this study were assumed to be of infinite solution volume.

6.22 Particle diffusion

It is assumed in the following derivation that the initial and final solution concentrations are constant in an infinite solution volume system. The internal diffusion coefficient D' is also assumed constant. The diffusion equation for a spherical particle, from Fick's Law, may be written in the form,

$$\frac{\partial u}{\partial t} = D' \left(\frac{\partial^2 u}{\partial x^2} \right) \quad (6.15)$$

where u is defined as $u = C'r$, the boundary conditions for the required solution of equation (6.15) for C' are as follows:

$$\begin{aligned} u &= 0 \quad \text{at } r = 0 \quad \text{for } t \geq 0, \\ u &= rK_dC \quad \text{at } r = r_0 \quad \text{for } t \geq 0, \\ u &= rC' \quad \text{at } t = 0 \quad \text{for } 0 < r < r_0 \end{aligned}$$

and the solution is given elsewhere¹⁶.

The amount of solute entering a particle per unit area in a given time, t is

$$q = \int_0^t P \, dt = -\int_0^t D' \left(\frac{\partial C'}{\partial r} \right)_{r=r_0} dt \quad (6.16)$$

By substituting the solution for C' , and knowing that $Q=4\pi r_0^2 \cdot q$, the above equation (6.16) may be written as,

$$Q = \frac{4\pi r_0^3 K_d C}{3} \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D' \pi^2 n^2 t}{r_0^2} \right) \right] \quad (6.17)$$

Similarly as before writing this in terms of F ,

$$F = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D' \pi^2 n^2 t}{r_0^2} \right) \quad (6.18a)$$

For small values of n equation (6.18a) can be approximated to a more convenient form as,

$$F \approx \left[1 - \exp\left(\frac{-D' \pi^2 t}{r_o^2}\right) \right]^{\frac{1}{2}} \quad (6.18b)$$

Equation (6.18b) can further be expressed in a familiar form (as for fdc),

$$\ln(1-F^2) = -Bt \quad (6.18c)$$

where $B = D'\pi^2/r_o^2$.

The half time of ion exchange for particle diffusion control is given by,

$$t_{\frac{1}{2}} = 0.03 \frac{r_o^2}{D'} \quad (6.19)$$

For a small value of the dimensionless constant $D'\pi^2 t/r_o^2$ the following approximation can be shown¹⁶ to be applicable,

$$F = 1.08 \sqrt{Bt} \quad (6.20)$$

Theoretical curves for F against Bt for particle diffusion control, equation (6.20), and film diffusion control, equation (6.12a) are plotted in figure 6.2. The tabulated form of function (6.18) is given elsewhere¹⁷.

If the kinetic experimental data shows particle diffusion control, then the plots of $\ln(1-F^2)$ against t should be straight lines. The values for B should be constant, thus

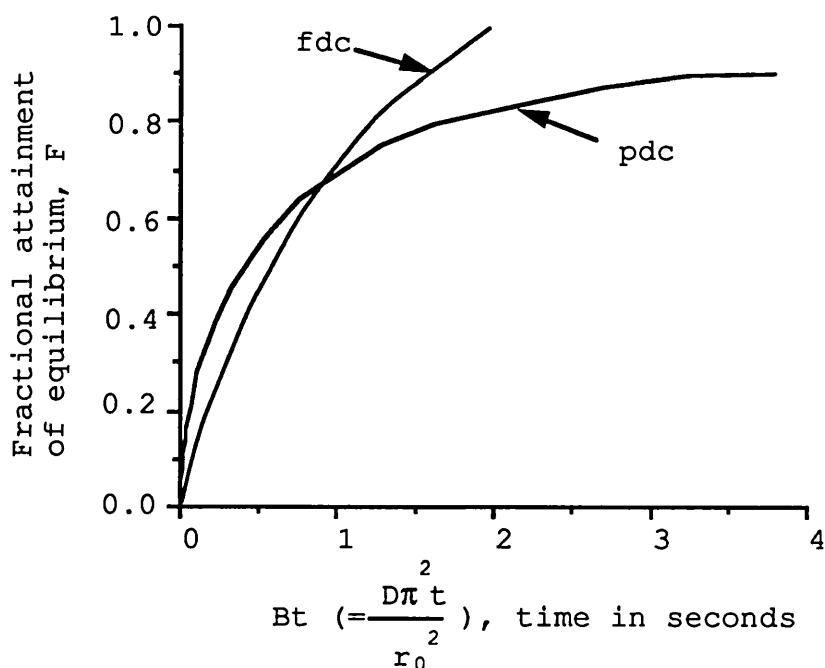


Figure 6.2 Theoretical curves of F against Bt for particle and film diffusion control

knowing the particle size (r_0) an average value of the particle diffusion coefficient D' can be determined. In the case of film diffusion control, a plot of $\ln(1-F)$ against time should be a straight line with a gradient $-R$. Knowing the particle size, K_d and assuming a value for δ (reference 16 and 106), the diffusion coefficient in the liquid film can be determined.

Adsorption kinetics based on chemical phenomenon^{16,17} and other effects^{17,106} that may be superimposed on ordinary diffusion mechanisms have not been covered in this study.

Kinetic profiles at various temperatures can be analysed using the Arrhenius equation (6.21) to obtain a value for the activation energy.

$$D = D_o \exp \left(-\frac{E_{act}}{RT} \right) \quad (6.21)$$

or

$$\ln D = \left(\frac{-E_{act}}{R} \right) \cdot \left(\frac{1}{T} \right) + \ln D_o \quad (6.21a)$$

The magnitude of the activation energy is useful in determining the prevailing mechanism of sorption.

6.3 Experimental

Attempts at showing the different kinetic phenomena have been illustrated using HTiO and HTiO:HSiO exchangers with a monovalent cationic solution of CsNO₃. The kinetics of uptake of the four hydrous oxides were compared using the CsNO₃ solution. The kinetics of the hydrous oxides with di- and trivalent (radioactive) cationic species (Sr²⁺ and Eu³⁺) were evaluated on a comparative basis. The influence of temperature on the rates of exchange were investigated to determine the prevailing ion exchange mechanism(s) (diffusion or others) for a given system.

All the hydrous oxide ion exchangers were prepared as described in chapter 3. The materials were wet sieved into four sizes. Particle sizes were measured under a microscope on a calibrated grid and are given in Table 6.1. All the test solutions were made from the nitrate salts of the metal cation and spiked with the respective radioisotope. γ -spectrometry measurements using the standard radioactive isotope tracer techniques, are described in the literature^{105,106,107}. γ -scintillation counting was carried out using a 'Phillips PW4800' machine incorporating a NaI detector with a microcomputer controlled automatic sample changer.

All the experiments were carried out using the same experimental setup as given in figure 6.3. A 500ml three necked round bottom flask was clamped in the water bath such that the necks were easily accessible above the

Table 6.1 Mean diameter measurements of various mesh sizes used in kinetic tests

Size code	BS mesh sizes / μm	Mean diameter / mm
Size 1	850 - 420	0.967 ± 0.033
Size 2	420 - 210	0.399 ± 0.011
Size 3	210 - 105	0.212 ± 0.014
Size 4	105 - 53	0.105 ± 0.009

polystyrene insulation spheres. The temperatures of the test solution and the water bath were measured using two identical thermometers, one placed directly in the water bath and the other in the test solution. The temperature readings were accurate to $\pm 0.5^\circ\text{C}$. The central neck was used to accommodate the stirrer connected to a variable speed 'Citenco' motor. The speed of the motor was measured using a mechanical tachometer, with an accuracy of $\pm 25\text{rpm}$ in the range of 500-5000 rpm. Before commencing the tests the motor was allowed a warm-up period to reach steady speed. Special stirrers were made, from 6mm diameter stainless steel rod with glass stirring head

1. Variable speed motor
2. Stainless steel strengthened impellor
3. Thermometer
4. Constant temperature water bath
5. Syringe for sample collection
6. Sample collection tube (no.4 sinter)
7. Polystyrene balls
8. Test solution

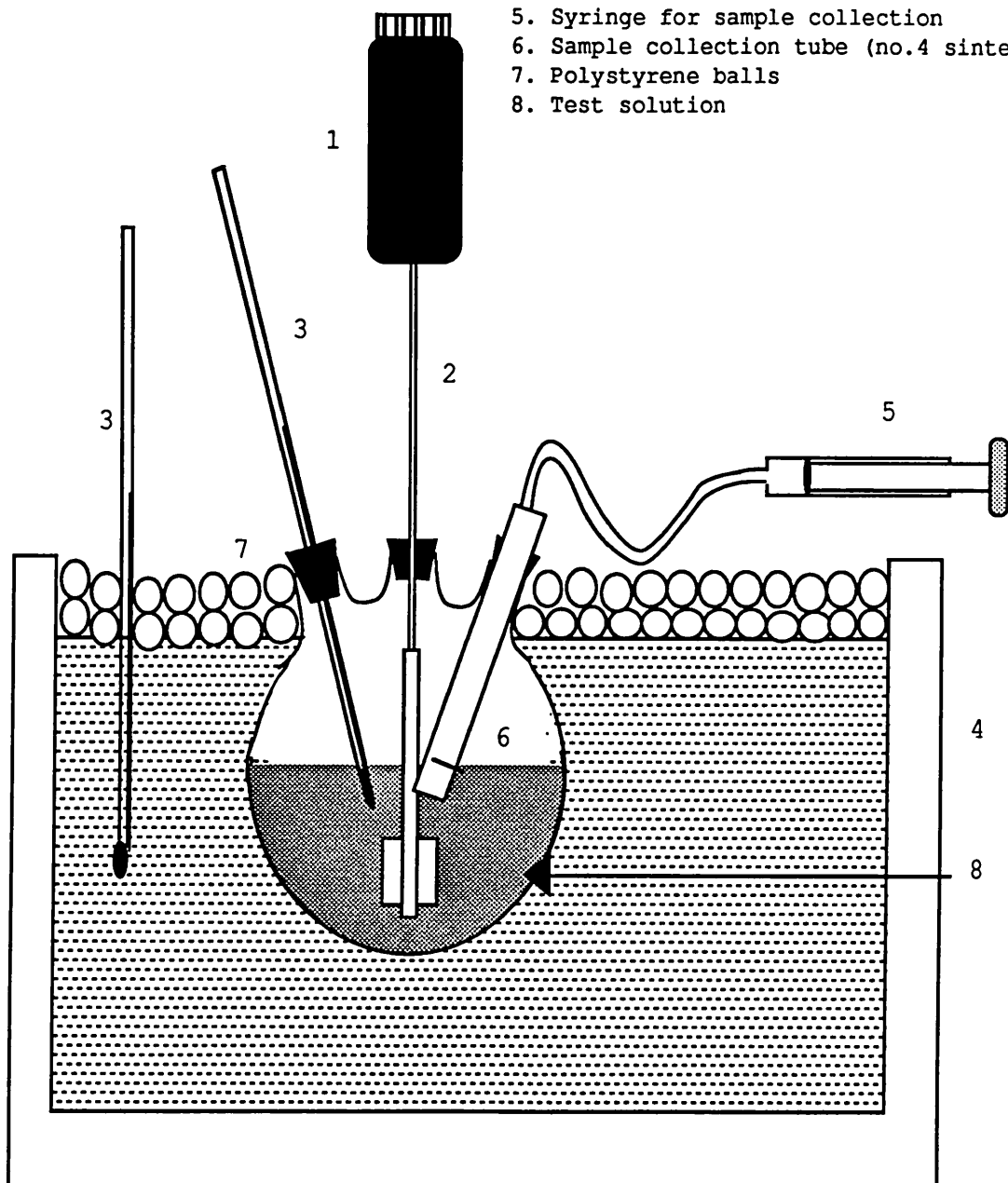


Figure 6.3 Apparatus used for kinetics tests

covered with plastic tubing, to avoid vibrations at high speeds. A sintered glass filter (number 4) at the end of a glass tube was placed in the third neck to extract samples of solution, which are free from fines of the test material, using a 10ml plastic syringe.

The concentration changes in the test solutions were determined by extracting approximately 6ml of test solution at specified times. 5ml were accurately pipetted for γ -spectrometry and 1ml was used to back-flush the sinter. Immediately after the counting period, which varied for different experiments, the sample solution was returned to the flask. In all experiments 250ml of solution were contacted with 0.1g of sample in size 2 (420-210 μ m), to satisfy the infinite solution volume condition. The error due to removal of 5ml sample for counting was assumed negligible as this was only 2% of the total volume. The use of the NaI detector with its high efficiency minimized the counting time which also reduced this error. All tests were carried out at $20^{\circ}\text{C} \pm 0.5^{\circ}\text{C}$, unless stated otherwise.

6.31 Variation of stirrer speed

The variation of stirrer speed experiments were carried out with HTiO:HSiO exchanger using CsNO_3 solution at two concentrations of 10^{-3}M and 10^{-4}M . Prior to adding the exchanger, the motor was allowed to run at 400rpm for the first run, and the speed was checked regularly. 0.1g of

material (size 2) was contacted with 250ml of 10^{-3}M CsNO_3 at time $t=0$. Thereafter, the samples were collected at times $t=15, 55, 145, 240, 360$, and 540 minutes. After some preliminary tests the final time of 540 minutes was considered sufficient for acquiring equilibrium and was adopted as t_∞ throughout the kinetic studies. The same procedure was repeated with identical conditions at speeds of 800, 1200, 1600 and 2000 rpm. The entire experiment was repeated with 10^{-4}M CsNO_3 test solution.

6.32 Interruption tests

There are two types of interruption tests¹⁰⁶ used in kinetic studies to distinguish between particle and film diffusion control; (a) conventional interruption test, and (b) a modified speed interruption test. The speed interruption tests were performed and are reported here to illustrate the presence of film diffusion control as the rate determining step.

0.1g of material was contacted with 250ml of 10^{-4}M CsNO_3 solution, which was spiked with higher Cs^{134} activity for better counting statistics, at time $t=0$. A stopwatch was started, and every 5 minutes a sample was extracted and counted for 90 seconds and immediately returned to the flask. The experiment was started at 500 rpm speed and allowed to continue at this speed for 30 minutes. After this time the speed was suddenly increased to 3500 rpm and samples collected again at 5 minutes intervals. At time,

$t=60$, the speed was decreased again to 500rpm for another 30 minutes, and at the end of this period the experiment was terminated. During the 30 minute periods the motor speed was regularly checked and adjusted when required. This experiment was carried out for the four hydrous oxide materials with 10^{-4}M CsNO_3 solution.

6.33 Variation of concentration

The effect of varying the test solution concentrations on ion exchange profiles were investigated for three CsNO_3 concentrations, 10^{-4}M , 10^{-3}M , and 10^{-2}M on HTiO. 0.1g of exchanger, (size 2), was contacted with 250ml of 10^{-4}M CsNO_3 solution being stirred at a constant speed of 1200 rpm. The samples were extracted at the same times as those in section 6.31 and the experiment was terminated at t_∞ , as before. Similarly, experiments were repeated for 10^{-3}M and 10^{-2}M CsNO_3 solutions.

6.34 Variation of particle size

The variation of particle size was studied on the HTiO at two concentrations of CsNO_3 , 10^{-3} and 10^{-4}M . The ion exchanger was wet sieved and dried at room temperature in a fume cupboard. The particle sizes of various fractional sizes were optically measured over a large number of particles.

For each particle size, a 0.1g portion of exchanger was contacted with 250ml of 10^{-3}M CsNO_3 solution at time, $t=0$.

The stirrer speed was set to a steady speed of 1200 rpm in the usual manner. The samples of test solution were extracted as before, counted and returned to the flask. The procedure was repeated for all the four particle sizes and then in a separate set of tests the experiment was repeated with 10^{-4}M CsNO_3 solution.

6.35 Variation in temperature

The kinetic experiments were carried out at temperatures of 20, 40, 60 and 80°C, in order to determine the activation energy for the sorption process involving Cs^+ ion and HTiO:HSiO exchanger.

Once the temperature of the test solution matched that of the bath at 20°C, a 0.1g portion of HTiO:HSiO in size 2 was contacted with 250ml of 10^{-4}M CsNO_3 solution stirred at a constant speed of 1200 ± 25 rpm. Samples were collected at times, $t=5, 10, 15, 20, 30, 40, 60$ and 120 minutes. The 120 minute sample was assumed to be in equilibrium, (t_{∞} sample). Due to the faster kinetics expected at higher temperatures, the solution was made more active with Cs^{134} spike for better counting statistics and also allowed shorter counting periods. Samples were counted for 90 seconds and then returned to the flask. The tests were repeated for higher temperatures with identical experimental conditions.

The possibility of the test solution evaporating at higher temperatures was investigated by stirring 250ml of

water for 120 minutes. The weight loss was found to be negligible at the highest temperature (80°C). The physical breakdown of exchanger was not visually apparent.

6.38 Comparative kinetic studies of hydrous oxides

The ion exchange kinetics of the four hydrous oxides were compared using a 10^{-4}M CsNO_3 solution. 0.1g portion of an exchanger, (size 2), was contacted with 250ml of test solution, stirred at 1200 rpm. The samples were collected in the usual manner at time, $t=15, 55, 145, 240, 360$ and 540 minutes. Similarly, the experiment was repeated for all the hydrous oxides.

6.39 Comparative kinetic studies with mono, di- and trivalent cations

The kinetic behaviour of four hydrous oxides was investigated with mono, di- and trivalent cationic species in equivalent molar concentrations. Cs^+ , Sr^{2+} and Eu^{3+} species were made to 10^{-4}N using the nitrate salts, and were spiked with Cs^{134} , Sr^{85} and Eu^{152} respectively.

0.1g portion of material (in size 2) was contacted with 250ml of a solution, stirred at 1200rpm and as before the samples were collected at times $t=15, 55, 145, 240, 360$, and 540 minutes.

The tests with the $\text{Eu}(\text{NO}_3)_3$ solution was carried out with the composite hydrous oxides only.

6.4 Results and discussion

The kinetic profiles as a function of stirrer speed for HTiO:HSiO in 10^{-4}M and 10^{-3}M CsNO_3 are given in figures 6.4 and 6.5 respectively. As the stirrer speed increases, the film thickness decreases to a hydrodynamic minimum possible value for the system. Since the rate of sorption of Cs is independent of stirrer speed at both the concentrations it appears that film diffusion control is not the rate determining step. There is however, a significant differences between the sorption profiles at 10^{-4}M and 10^{-3}M CsNO_3 concentration. It can be said that on the basis of these results the sorption process is particle diffusion controlled in both concentrations.

The modified speed interruption tests were carried out to investigate the presence of film diffusion controlled process at the lower of the two concentrations. The interruption test results are presented in figures 6.6 to 6.9 for the four hydrous oxides in 10^{-4}M CsNO_3 solution. The interruptions simulated by the sudden speed changes are marked by the arrows. The graphs are plotted as raw counts against time where the counts are directly proportional to caesium concentration in the solution (and the error in the counts is taken to be $\pm\sqrt{\text{counts}}$). In a film diffusion controlled process the effect of sudden increase in stirrer speed (decrease in the film thickness) is expected to lead to an increase in the diffusion through the liquid film. Consequently this would lead to a drop in the counts

Figure 6.4 Sorption profiles at various stirrer speeds

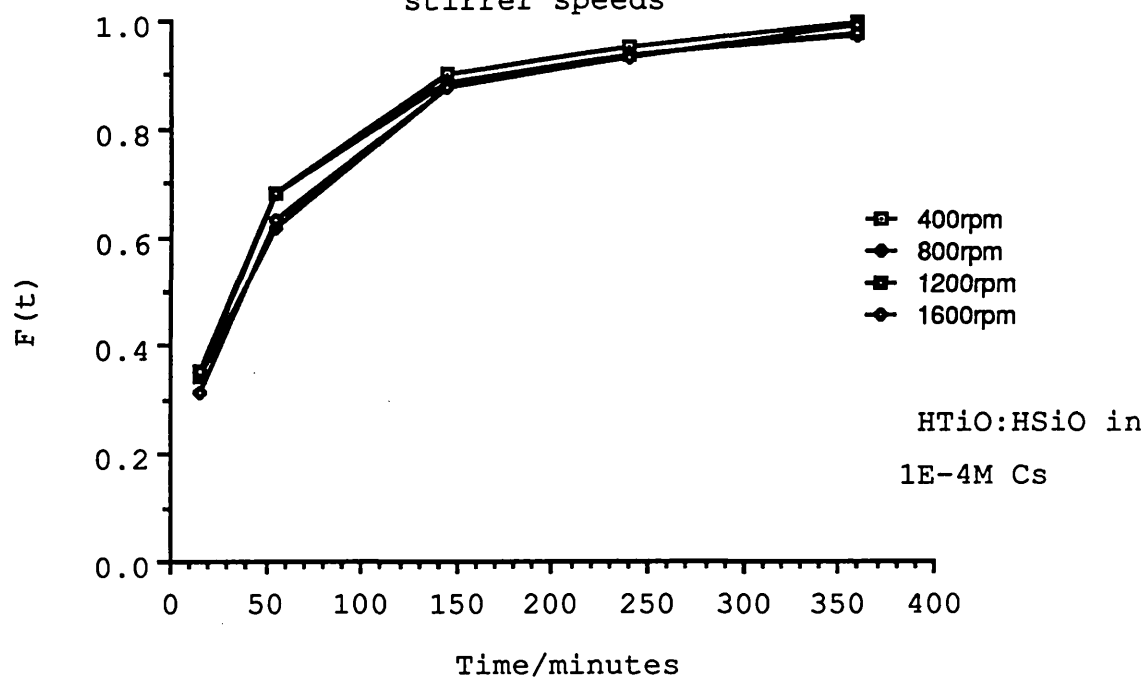


Figure 6.5 Sorption profiles at various stirrer speeds

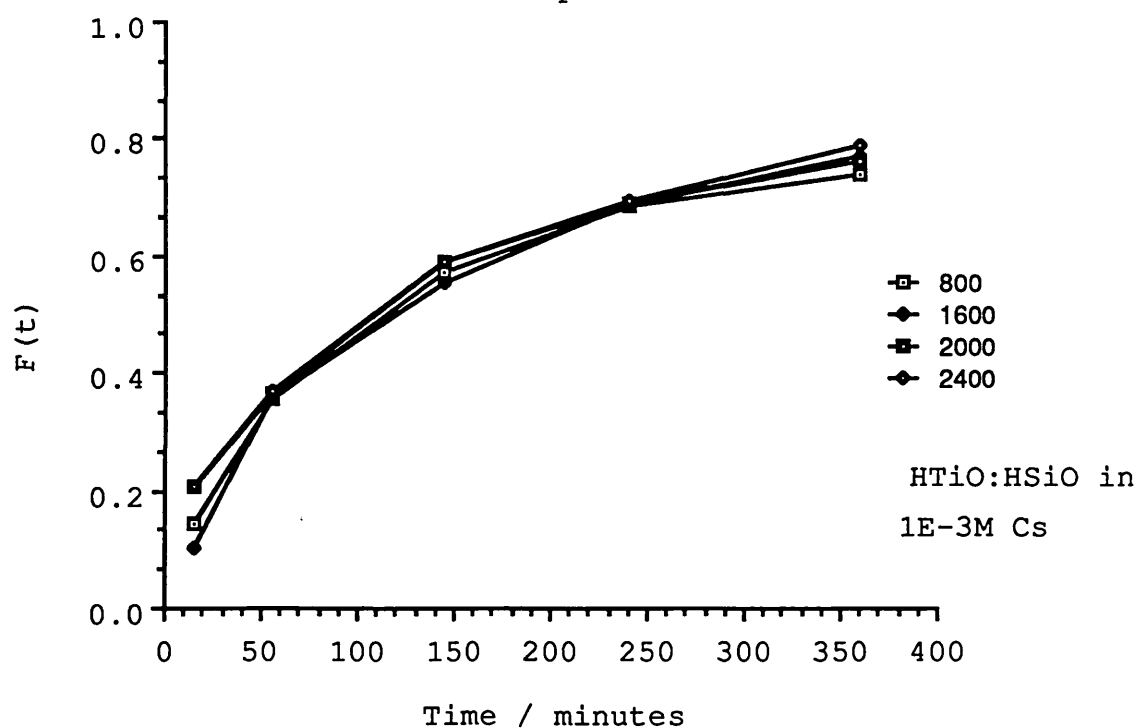


Figure 6.6 Speed interruption tests for
HTiO in 1E-4M Cs

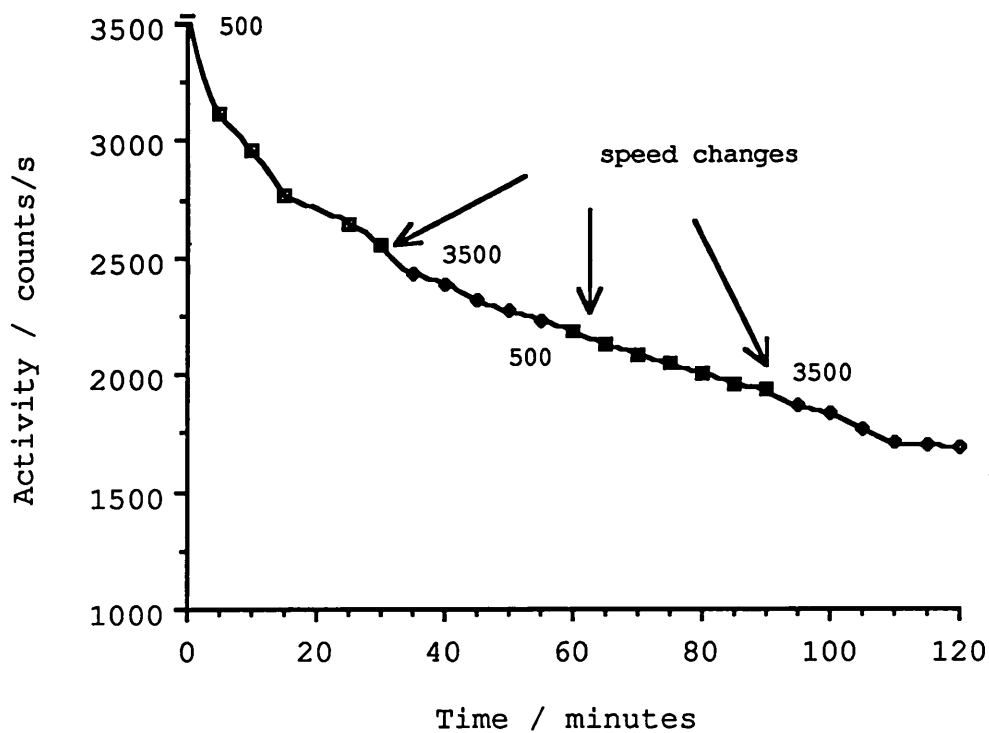


Figure 6.7 Speed interruption tests for
HTiO:HSiO in 1E-4M Cs

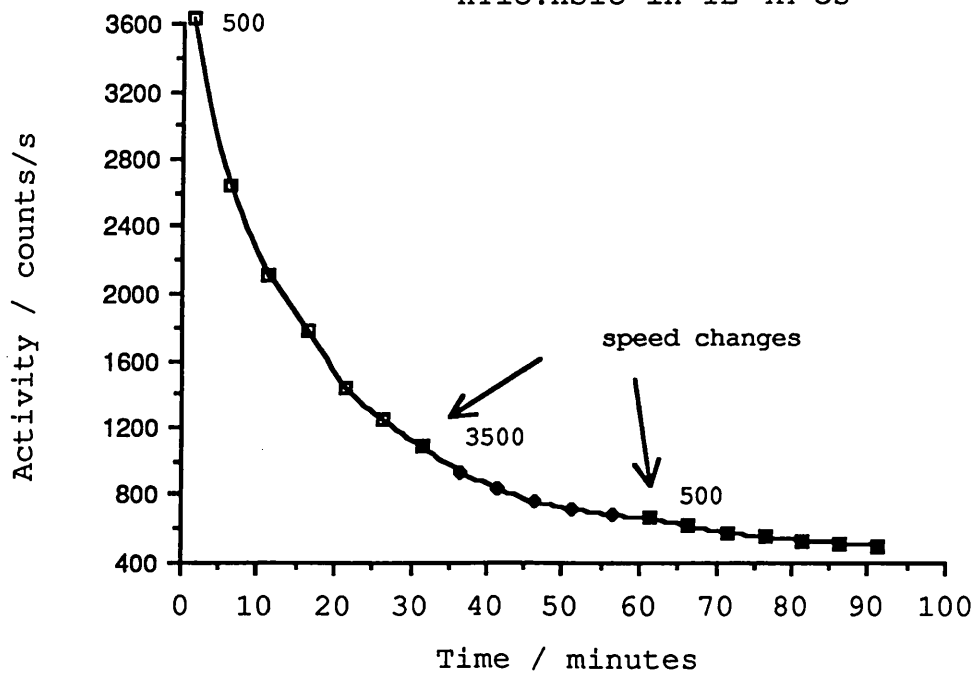


Figure 6.8 Speed interruption tests for
HMnO in 1E-4M Cs

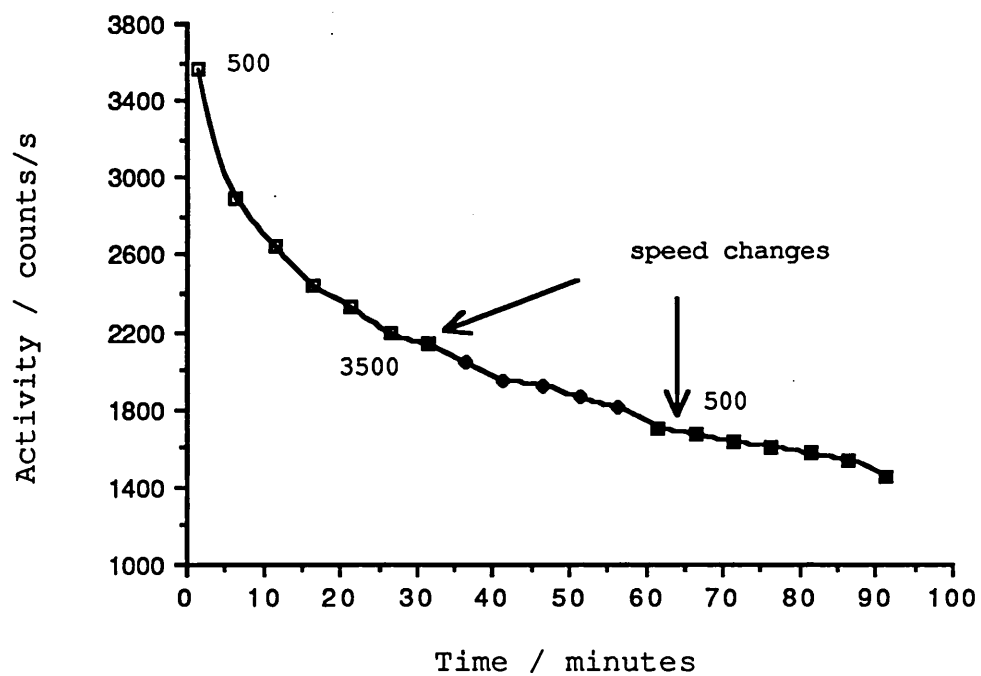
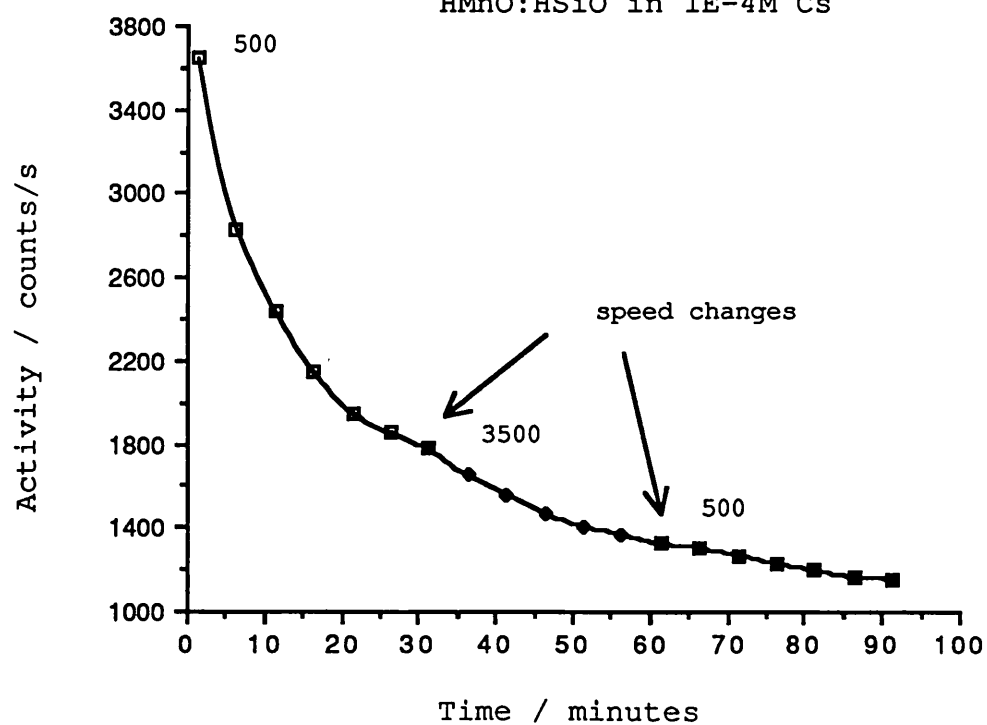


Figure 6.9 Speed interruption tests for
HMnO:HSiO in 1E-4M Cs



immediately after the interruption. The 555 interruptions marked on the graphs are not very clear. The slight apparent interruptions are small and unconvincing to be attributable to a film diffusion process. It is plausible to assume that these irregularities are due to the γ -spectrometry data susceptible to some degree of error. The speed interruption tests have therefore shown that at 10^{-4}M CsNO_3 concentration, the diffusional process is more likely to be particle diffusion controlled as observed earlier.

Figure 6.10 shows the effect of varying solution concentration on the uptake rate. The sorption rates decrease with increasing concentration. Throughout the tests the film thickness was assumed constant as the stirrer speed was maintained at 2000 rpm. If particle diffusion control was the rate determining step at these concentrations then it can be confirmed by determining the particle diffusion coefficients values at these concentrations. The diffusion coefficient values for a particle diffusion controlled process should be independent of the concentration. These values were determined by plotting $\ln(1-F^2)$ versus time and evaluating the slope of the lines. These plots are presented in figure 6.11, the straight lines are indicative of a particle diffusion controlled process. From the values of the slope ($= B = D'\pi^2/r_o^2$) the particle diffusion coefficients were thus calculated and given in table 6.2.

The large discrepancy in the particle diffusion

Figure 6.10 Sorption profiles at various concentrations for HTiO

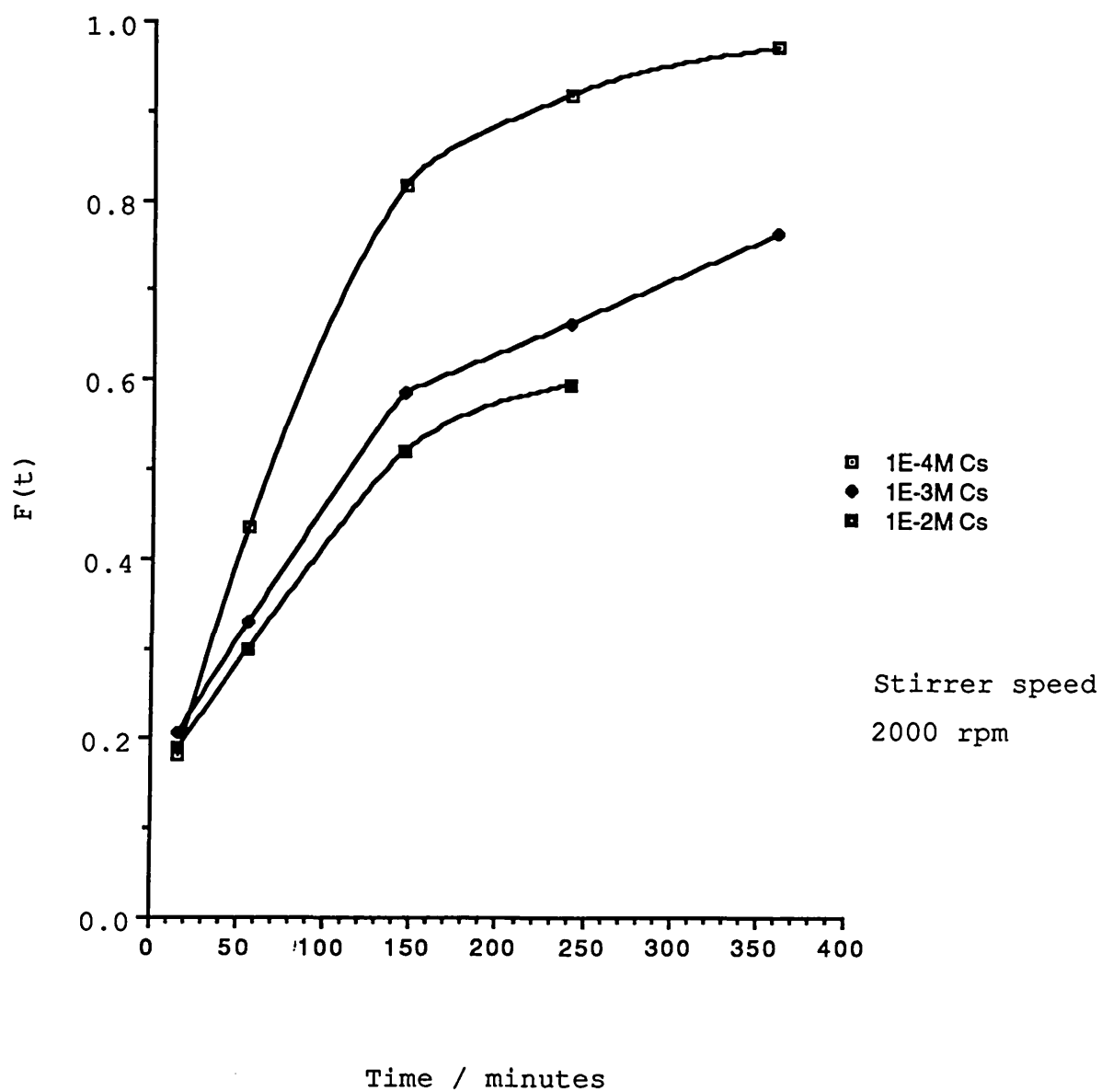


Figure 6.11 $\ln(1-F^2)$ vs time plots at various concentrations sample : HTiO

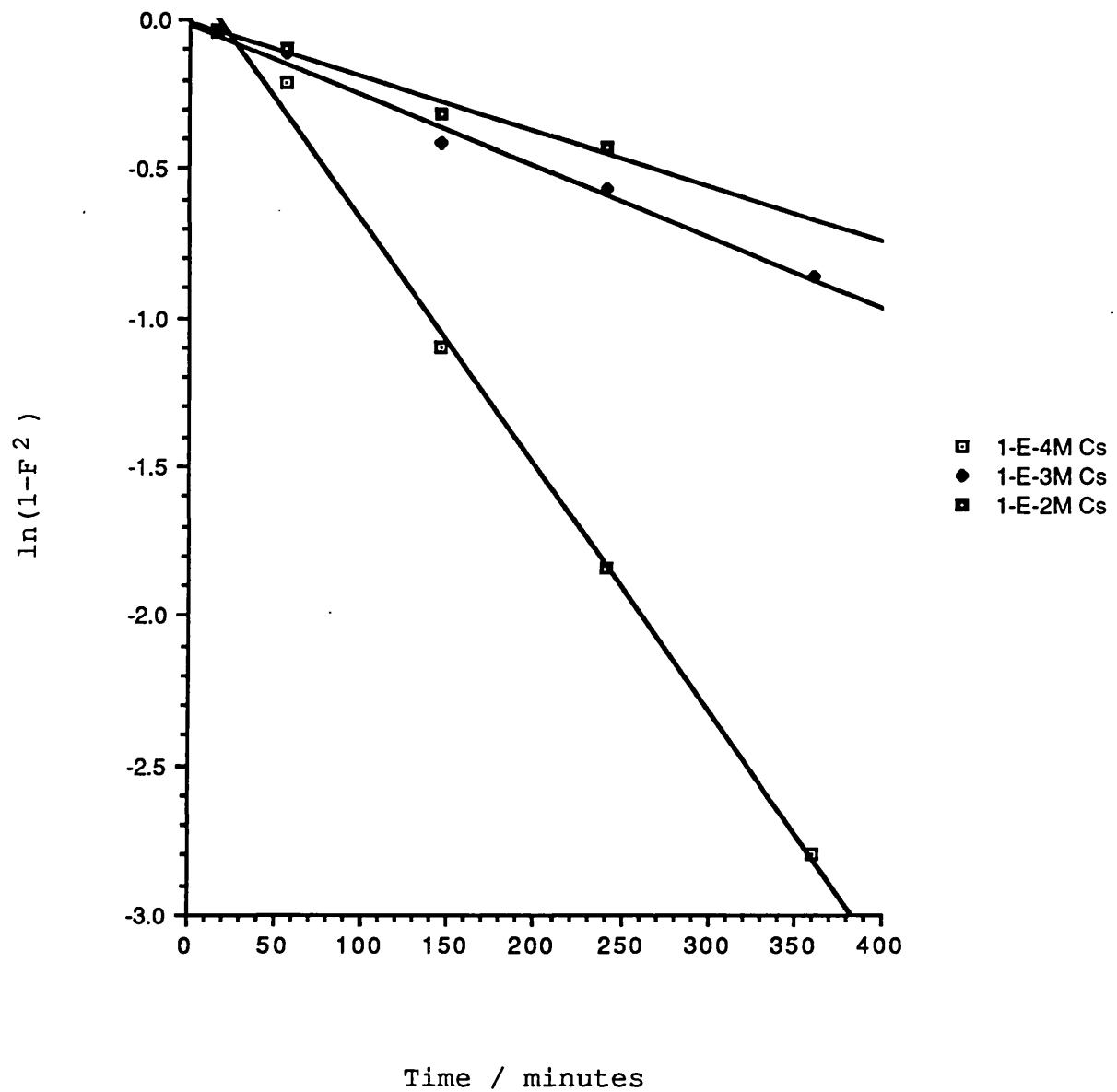


Table 6.2 Particle diffusion coefficient values for HTiO in various concentrations of CsNO₃ (size 2) calculated using equation 6.18b and figure 6.11

concentration M	B x 10 ⁻⁵ /s	D'x 10 ⁻¹³ m ² /s
10 ⁻⁴ M CsNO ₃	13.68	5.517
10 ⁻³ M CsNO ₃	3.98	1.605
10 ⁻² M CsNO ₃	3.07	1.238

coefficient value at 10⁻⁴M CsNO₃ solution concentration suggests the possibility of film diffusion or possibly both mechanisms present.

The results for the variation of particle size for two concentrations are presented in figures 6.12 and 6.13 for 10⁻⁴M and 10⁻³M CsNO₃ solutions respectively contacted with HTiO. The sorption profiles show that as the particle size decreases the half times of uptake are also significantly reduced. In general, the uptake rates are faster for the respective sizes in the lower concentration (10⁻⁴M CsNO₃ solution). Figure 6.14 and 6.15 give the ln(1-F) and ln(1-F²) versus time plots for various sizes of HTiO in 10⁻⁴M CsNO₃. The former is indicative of film and the latter of particle diffusion control. It was found that the experimental data was more suitable to the particle diffusion model. The straight lines in figure 6.14 do not pass through the origin and the points have a greater degree of experimental scatter.

Figure 6.12 Sorption profiles for various sizes

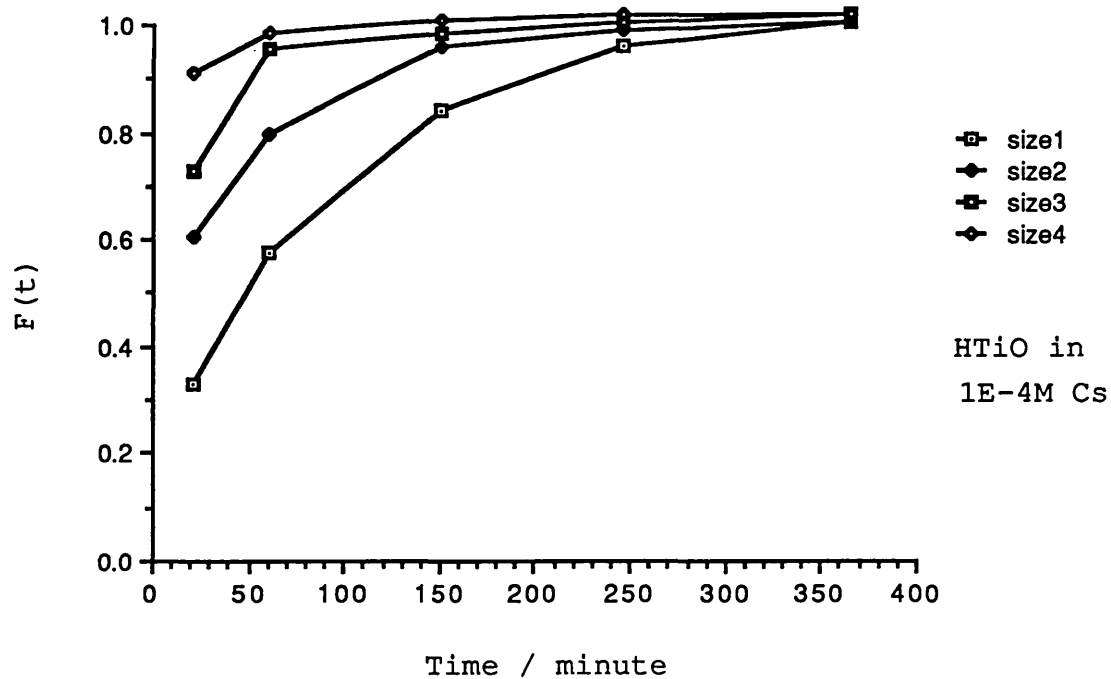


Figure 6.13 Sorption profiles for various sizes

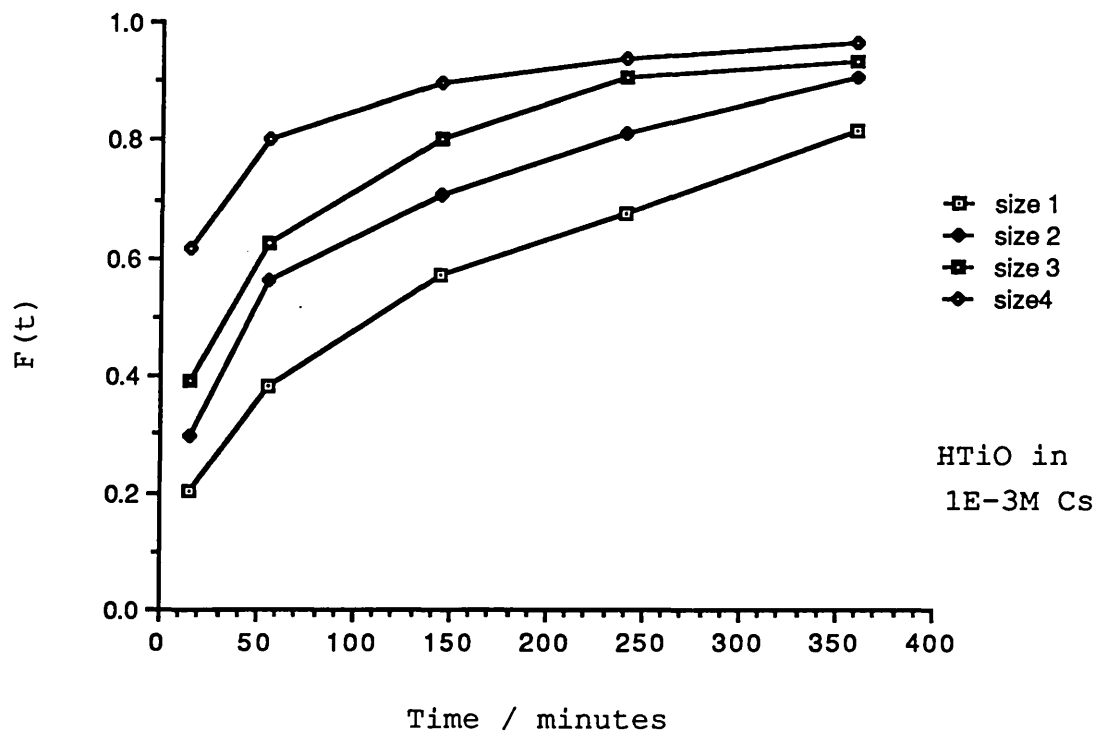


Figure 6.14 $\ln(1-F)$ vs time plots for various sizes of HTiO in $1E-4M$ Cs

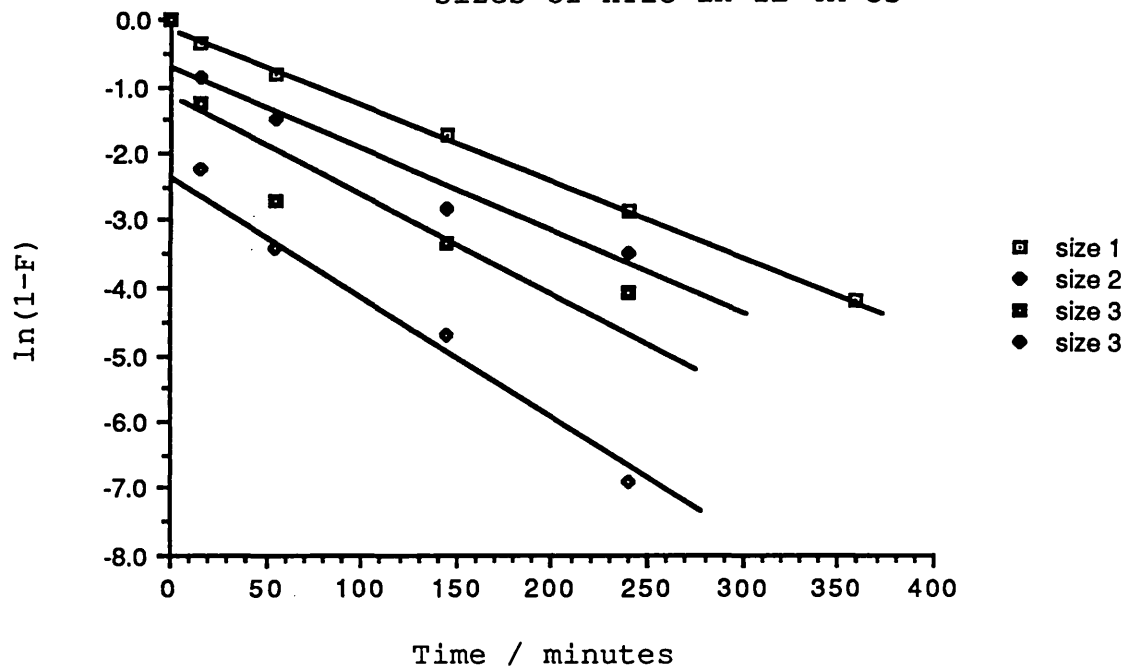


Figure 6.15 $\ln(1-F^2)$ vs time plots for various sizes of HTiO in $1E-4M$ Cs

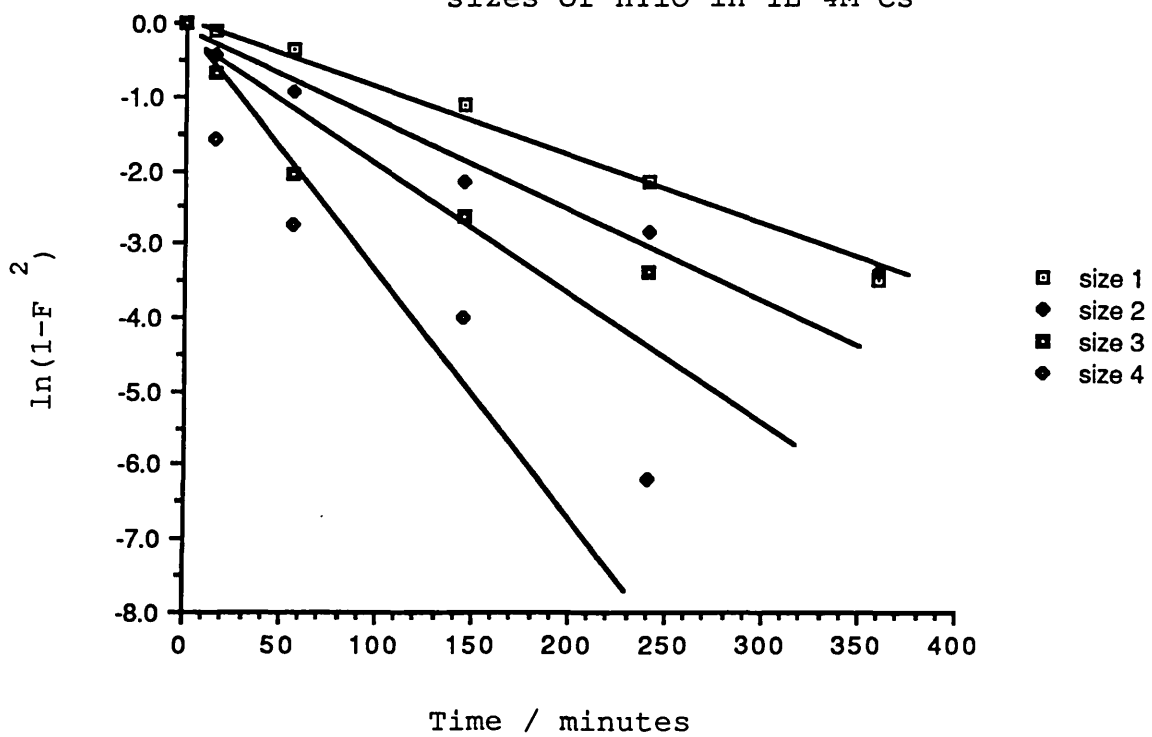
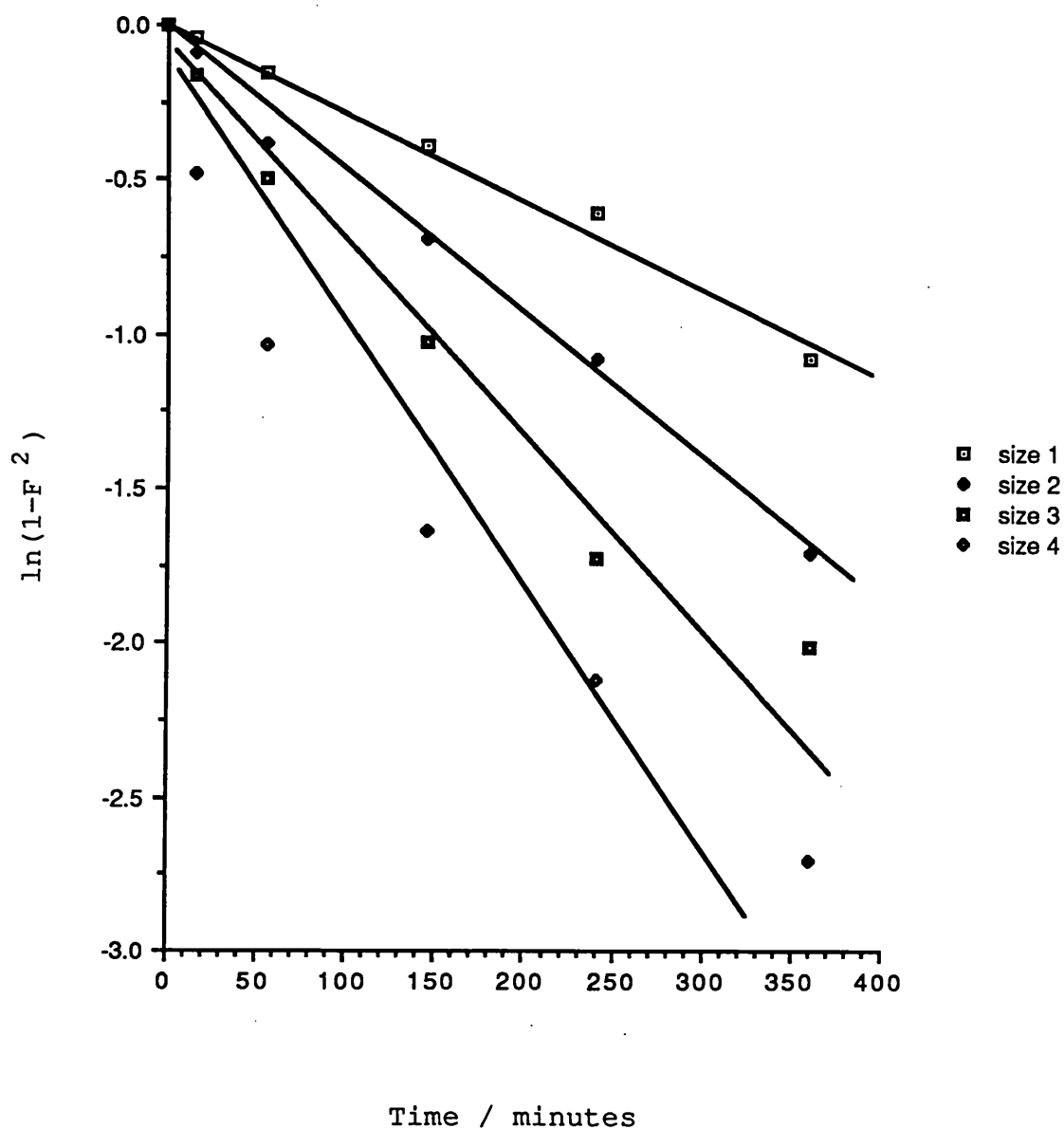


Figure 6.16 $\ln(1-F^2)$ vs time plots for various sizes
 sizes of HTiO in 1E-3M Cs



On analysing the data for 10^{-3}M CsNO_3 concentration it was found to fit the particle diffusion model (figure 6.16). The $\ln(1-F)$ against time plots at 10^{-3}M CsNO_3 concentration were not found to fit a straight line thus confirming particle diffusion control.

The following relationships between the relative rate and particle size may be deduced from the half time of ion exchange equations for film diffusion (6.13) and particle diffusion (6.19) controlled processes:

$$\text{relative rate} \propto \frac{1}{r_0} \quad (\text{film diffusion})$$

$$\text{relative rate} \propto \frac{1}{r_0^2} \quad (\text{particle diffusion})$$

The straight line plots in figure 6.18 show the relative rate (1/half life) to be proportional to $1/r_0^2$, thus reasserting particle diffusion control at 10^{-3}M solution. However figure 6.17 shows the rate to be proportional to $1/r_0$ and $1/r_0^2$. These findings together with a high diffusion coefficient value at 10^{-4}M CsNO_3 (table 6.2) give some weighting to the existence of both processes at 10^{-4}M CsNO_3 concentration.

Using the slopes evaluated in figure 6.16 the particle diffusion coefficient values were determined and are given in table 6.3.

The sorption profiles at different temperatures are

Figure 6.17 Rate as a function of particle size
HTiO in 1E-4M Cs

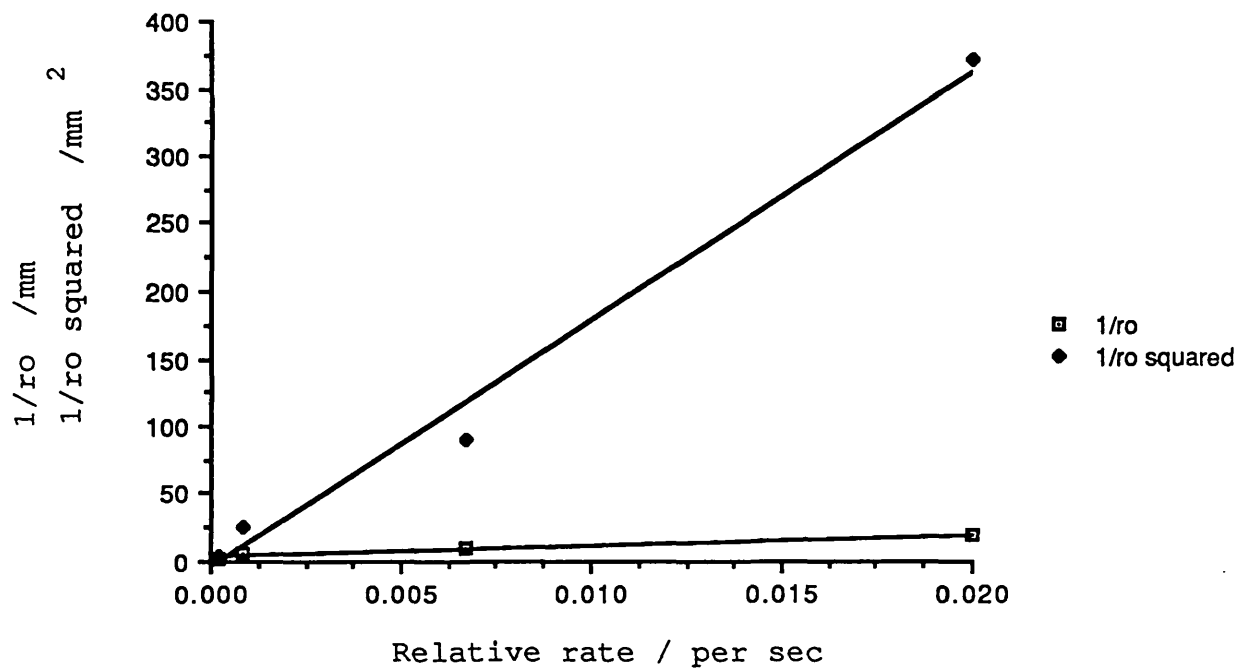


Figure 6.18 Rate as a function of particle size
HTiO in 1E-3M Cs

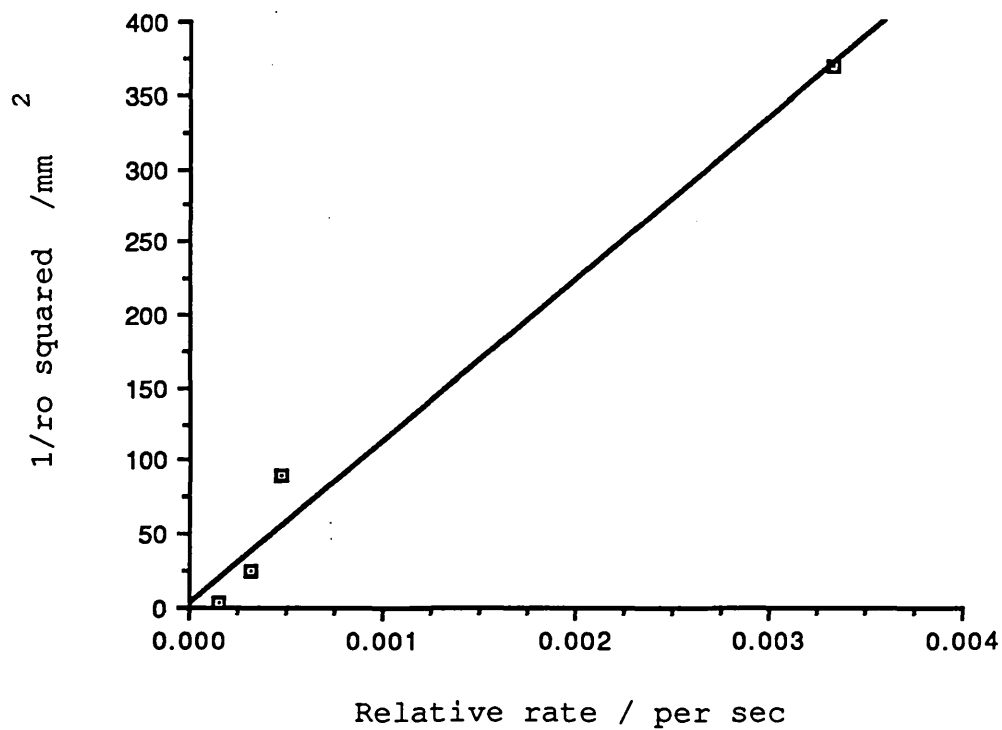


Table 6.3 Particle diffusion coefficient values
for various sizes of HTiO in 10^{-3} M CsNO_3

size	r_o/mm	B $\times 10^{-5}/\text{s}$	$D' \times 10^{-13} \text{ m}^2 / \text{s}$
1	0.4835	4.833	11.447
2	0.1995	7.667	3.092
3	0.1060	9.667	1.100
4	0.0525	15.852	0.446

presented in figure 6.19. The curves show a marked increase in the rate with increasing temperature. It is widely understood that a particle diffusion process is more sensitive to temperature changes than film diffusion. In parallel to this phenomenon the rates of chemical reaction are also very temperature dependent. The magnitude of the activation energy value can be used to distinguish between diffusion and chemical reaction control.

The $\ln(1-F^2)$ versus time plots for the four temperatures are given in figure 6.20. The slopes of the lines were utilized in the usual manner to determine the particle diffusion coefficient values. The Arrhenius plot for the various temperatures, utilizing equation (6.21a), was plotted and is given in figure 6.21. The slope of the straight line plot was used to evaluate the activation energy value. An activation energy value of 8.70

Figure 6.19 Sorption profiles at various
temperatures - HTiO:HSiO in 1E-4M Cs

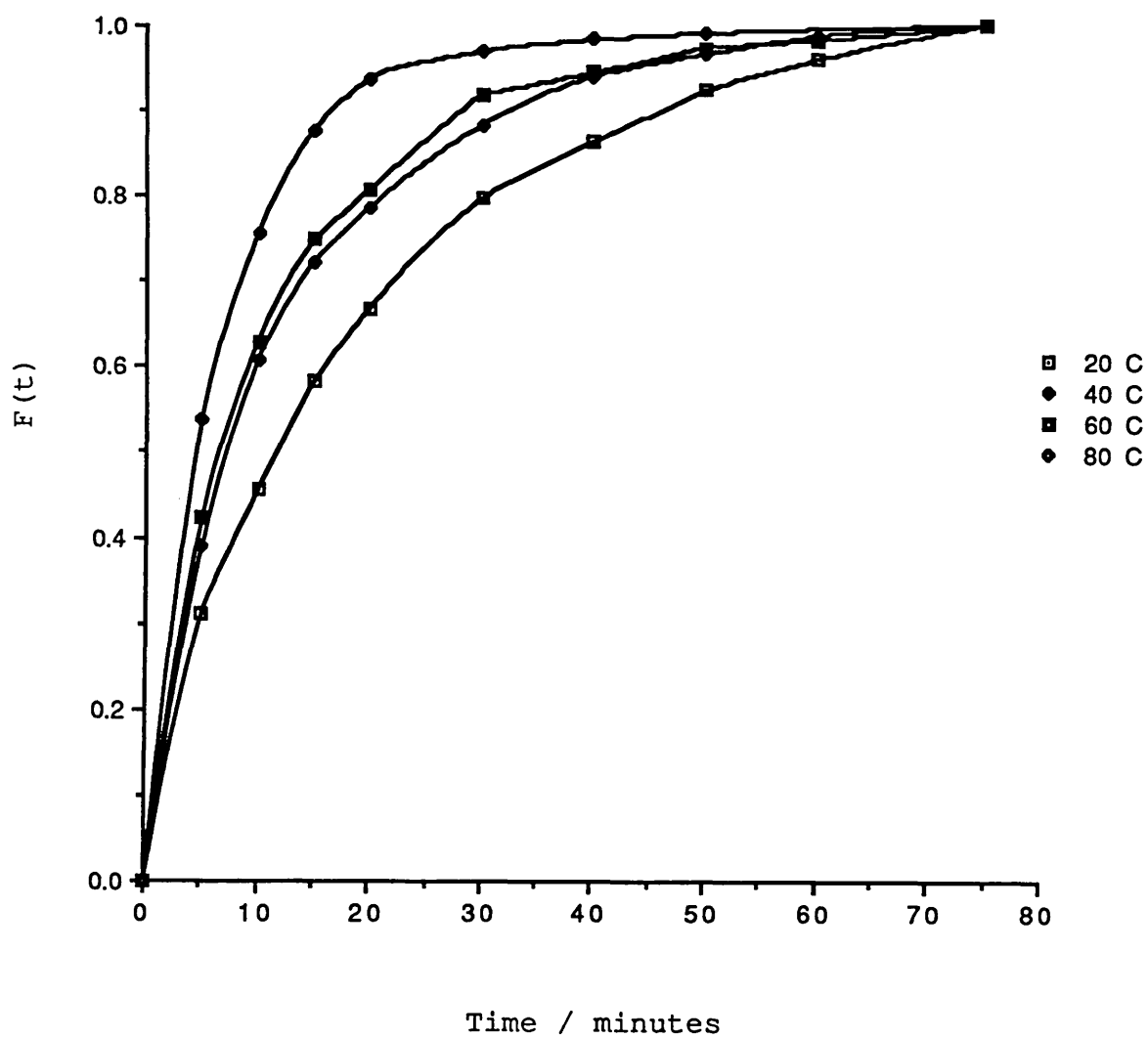


Figure 6.20 $\ln(1-F^2)$ against time plots for
HTiO:HSiO in $1E-4M$ Cs at various temperatures

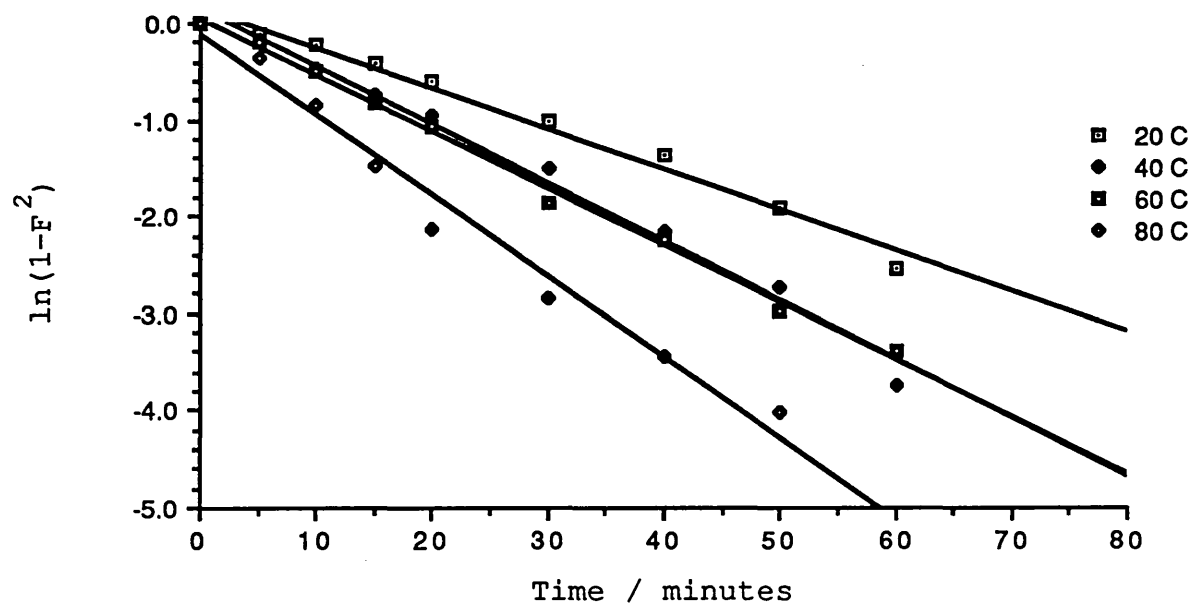
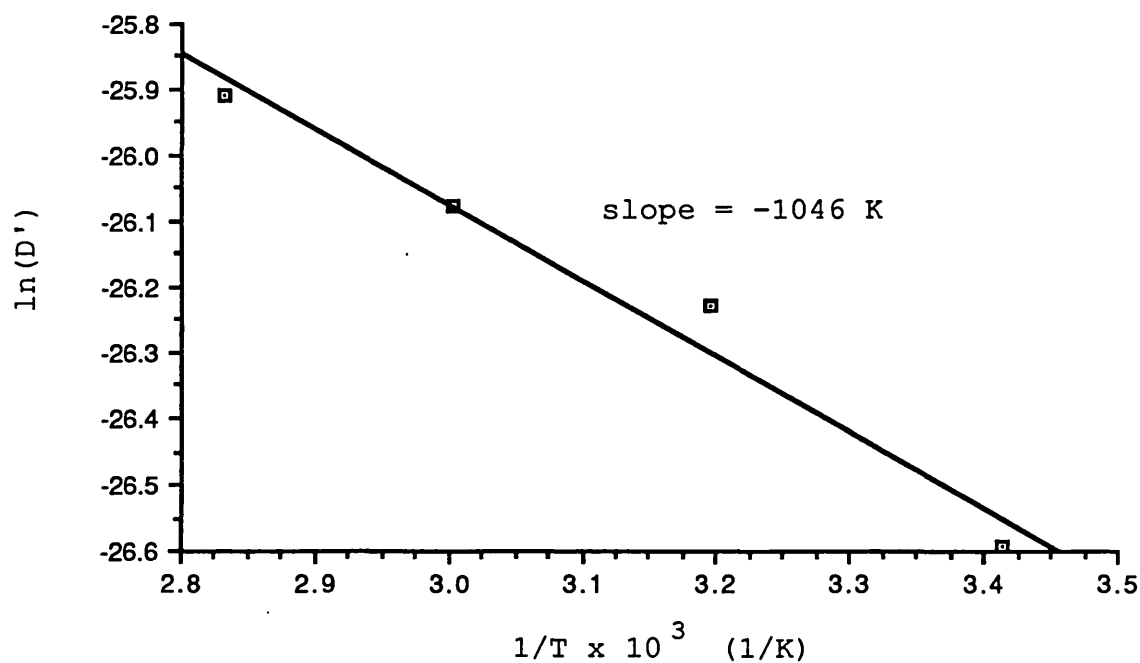


Figure 6.21 Arrhenius plot for a pdc process
(HTiO:HSiO in $1E-4M$ Cs)



kJ/mol was obtained. Boyd and Soldano^{154,155} have reported activation energy values in the ranges 8.4 - 20.9 kJ/mol and 12.6 - 41.9 kJ/mol for film and particle diffusion processes respectively. The activation energy for a chemical reaction is much higher and therefore it can be said that a diffusional process is rate determining with the HTiO:HSiO in 10^{-4}M CsNO_3 solution. The activation energy value is within the film diffusion control range and very close to the range corresponding to particle diffusion. On the grounds of earlier findings and the activation energy value obtained here, it is likely that both particle and film diffusion processes are prevailing at 10^{-4}M concentration.

The sorption profiles of pure and composite hydrous oxides with 10^{-4}N $\text{Cs}(\text{NO}_3)_3$ and $\text{Sr}(\text{NO}_3)_2$ solutions in figure 6.22 and 6.23, show a difference between their rates, with the composites exhibiting faster kinetics of uptake. The trends for Cs^+ uptake can be related to the respective slopes of figures 6.6 to 6.9, the steeper the slope the faster the kinetics. The sorption profiles for the hydrous oxide composites in 10^{-4}N $\text{Eu}(\text{NO}_3)_3$ solution in figure 6.24 show similar trends to those exhibited in figure 6.23. However, the equilibrium times are generally in the order $\text{Cs} < \text{Sr} < \text{Eu}$.

The particle diffusion coefficient values for Sr and Eu solution tests were calculated in the usual manner and are

given below in tables 6.4 and 6.5. The values are of the same order of magnitude except for HMnO with a high diffusion coefficient in the Sr solution and the composite higher still in the Eu solution.

Table 6.4 Particle diffusion coefficient values for the hydrous oxides (size 2) in 10^{-4} N Sr solution

Exchanger	$B \times 10^{-5} / s$	$D' \times 10^{-13} \text{ m}^2 / s$
HTiO	3.833	1.546
HTiO:HSiO	8.167	3.293
HMnO	3.333	1.344
HMnO:HSiO	7.667	3.092

Table 6.5 Particle diffusion coefficient values for composite hydrous oxides (size 2) in 10^{-4} N Eu solution

Exchanger	$B \times 10^{-5} / s$	$D' \times 10^{-13} \text{ m}^2 / s$
HTiO:HSiO	4.500	1.815
HMnO:HSiO	2.667	1.075

Figure 6.22 Sorption profiles of various hydrous oxides in 1E-4M Cs

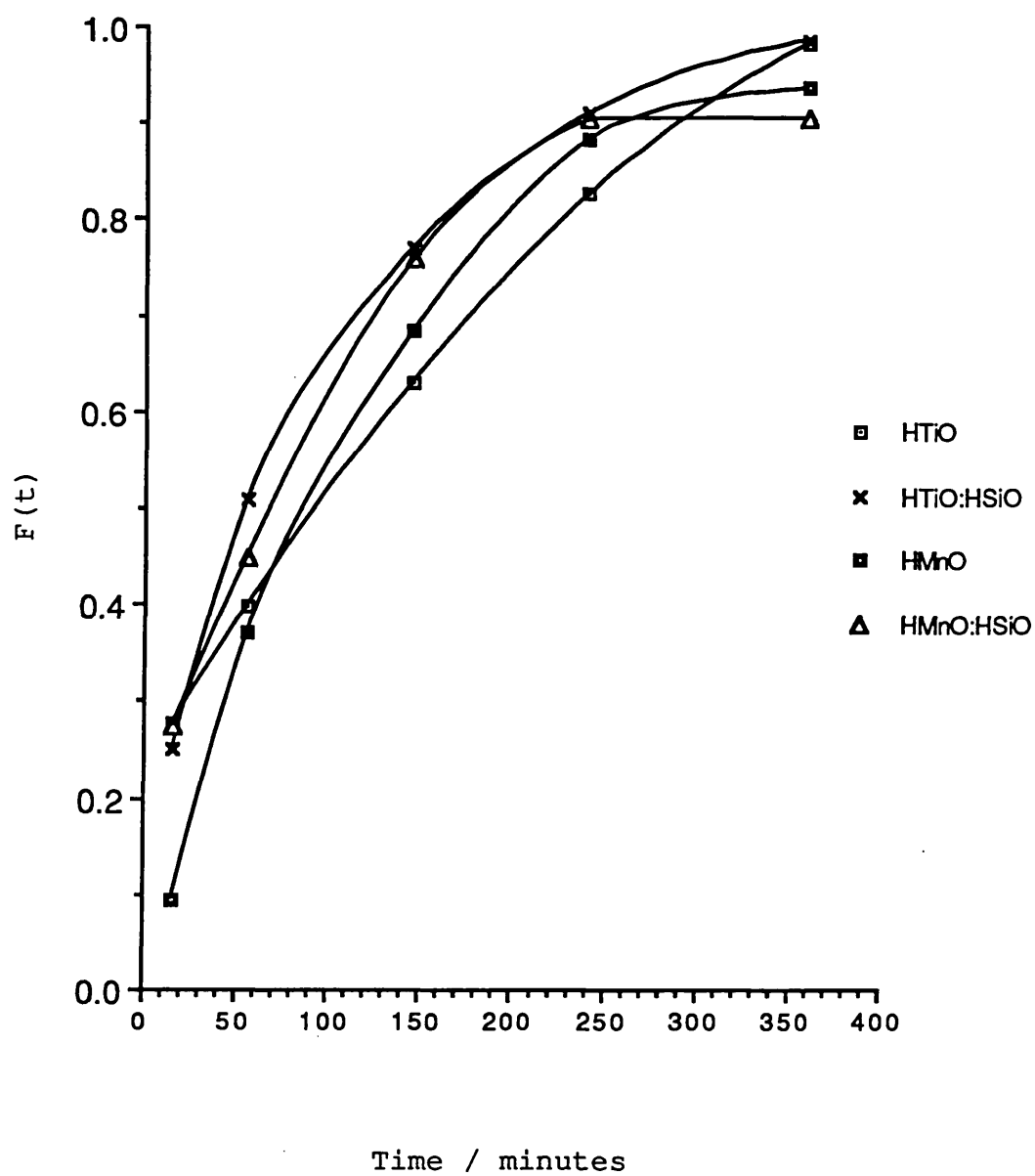


Figure 6.23 Sorption profiles of various
hydrous oxides in $1\text{E-}4\text{N Sr}$

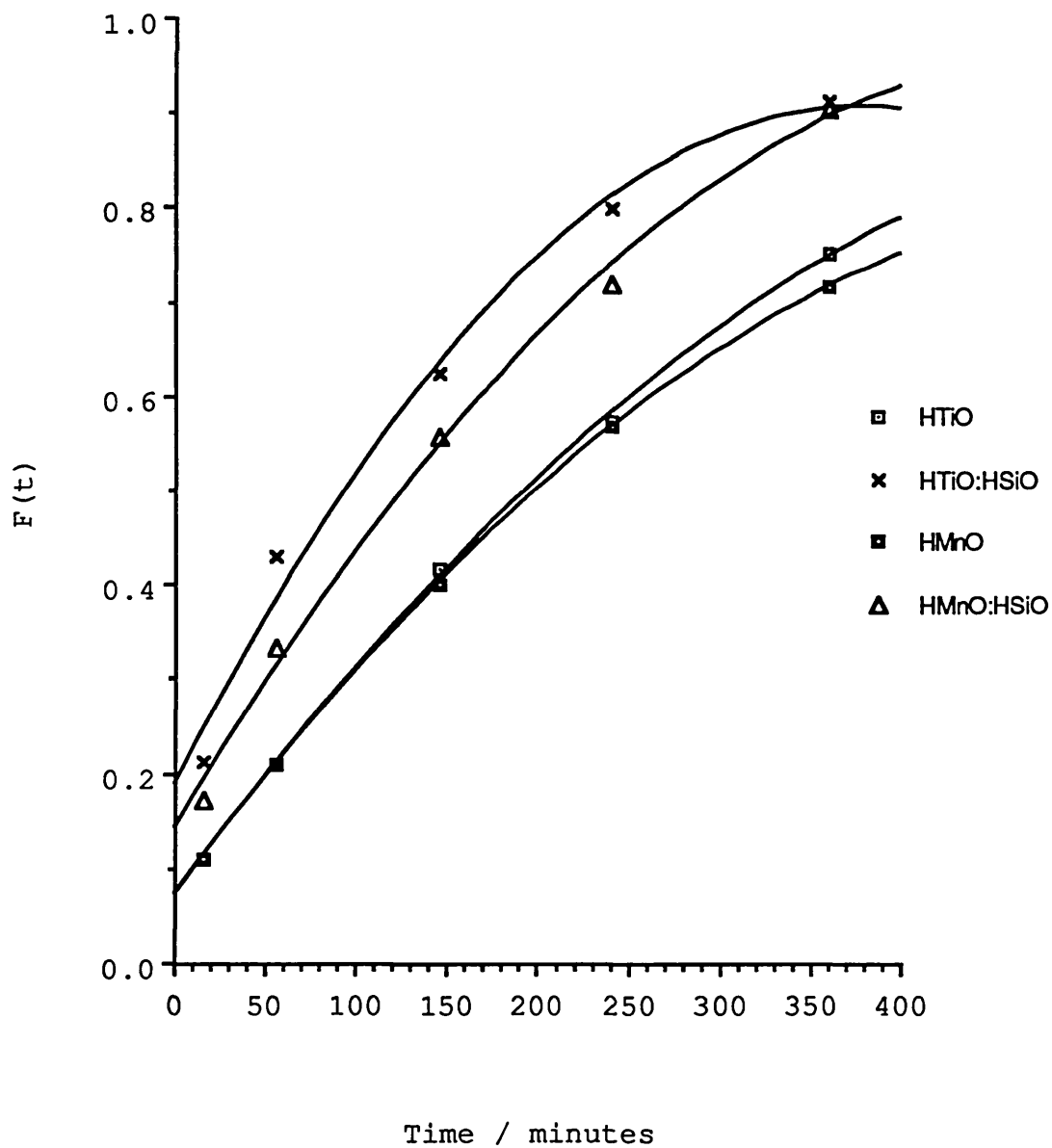
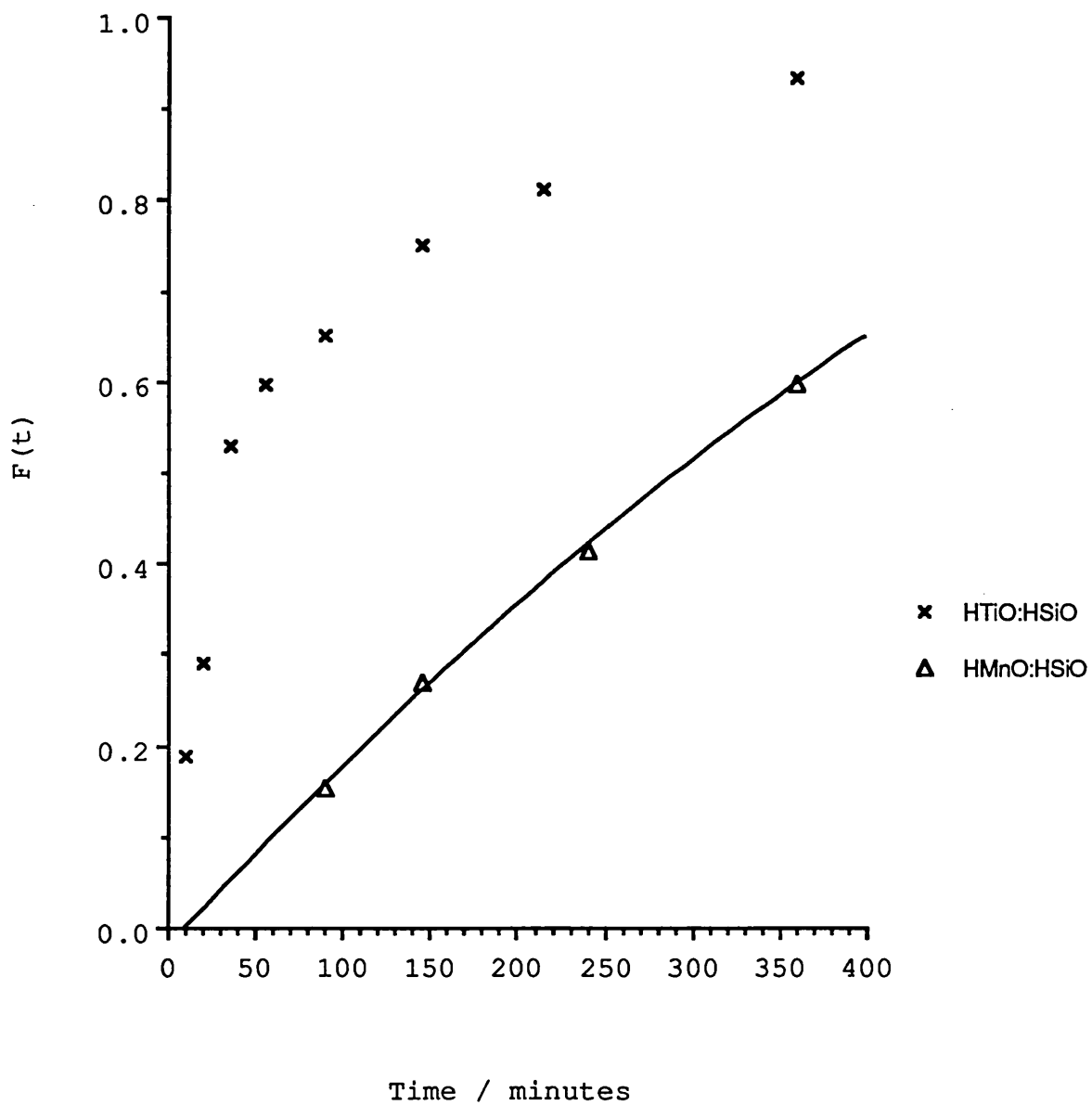


Figure 6.24 Sorption profiles of composite
hydrous oxides in $1\text{E-}4\text{N}$ Eu



6.5 Conclusions and Future work

In summarising the results of the kinetic studies, it is found that the ion exchange mechanisms are dependent upon the solution concentration, agitation rate, particle size and temperature and that the sorption processes are diffusional processes as opposed to chemical reaction. It was suspected that below concentrations of 10^{-3}M film diffusion would be the rate determining step and particle diffusion above this concentration. However 10^{-4}M seems to be a 'border line' concentration for the two diffusional mechanisms. It is suggested that further kinetic tests be carried out at concentrations below 10^{-4}M CsNO_3 (e.g. 10^{-6}M) to conclusively elucidate the film diffusion phenomenon and determine the relevant parameters. The data from the present study should be tried for a model intermediate between film and particle diffusion¹⁷ to confirm it is indeed border line between the two.

The rates were faster at lower concentrations. The agitation rate does not have any affect in high concentrations ($\geq 10^{-4}\text{M}$). The sorption rates have an inverse relationship with particle size. Finally it was shown that the ionic species, particularly the charge, present in the solution also affected the sorption rate - as the charge increases the rate of sorption decreases.

All the above factors need to be understood and customised values for a given system determined before using these hydrous oxides in the design of an ion exchange

bed. The phenomenon of chemical reaction between the sorbed ions and the exchange sites for a heterogeneous system need to be investigated. Theoretical understanding of heterogeneous reaction kinetics may be found in the literature^{17,106}. The model adopted in this study is not truly applicable to amorphous materials and needs to be modified. The modification should also account for the surface perturbations encountered in inorganic hydrous oxide type exchanger 'resins' as these are not exactly spherical as assumed in the present model.

In conclusion this kinetic study of the hydrous oxides has not answered all the mechanistic questions of the ion exchange process nor provided every detail for all the materials. However, basic data has been presented to coherently initiate a more detailed kinetic study for the hydrous oxides. Such data is important for practical use of these materials in a process plant for radioactive waste decontamination.

Chapter 7

Discussion

7.1 Discussion

7.1 Discussion

This work describes a wide range of experiments that have been carried out to develop mixed oxide inorganic ion exchangers for commercial use. Much of the work has followed the standard experimental procedures used by previous workers. The novel aspects of this present work include, however,

1. The development of capillary reactors to produce the flow precipitates with, a) consistency in reproducibility, b) enhanced manufacturing economics for hydrous MnO_2 , and c) the potential to upgrade production to large scale manufacture.

2. The formally quantified washing procedure, that is the use of counter current batch washing and its control using conductivity measurements.

3. The development of the composite inorganic hydrous oxides with properties suitable for radioactive decontamination, and

4. The use of standard hardness measuring techniques to show that the exchangers can be used in large scale plant columns.

There are a number of different types of materials used in the process industries for sorption processes. These materials include activated carbon, molecular sieve-type and a wide range of synthetic organic ion exchangers. Manufacturers of these materials usually offer quite a range of these products for use in industry. In the present case the use of composite ion exchangers thus provides manufacturers with the ability to make a variety of

products simply based on changing the ratio of feed oxides used. In the earlier part of this thesis (section 3.5) some considerations were given to the selection of the types of composites used in later work. Obviously this selection has to be made to reduce the total amount of work required to a reasonable level. Having thus provided a method for producing a variety of exchangers for use in the market, does not mean that the composite hydrous oxides will always be better than pure oxides for a particular application. The mechanisms involved in radioactive sorption processes can be complex and there may be particular reasons why a pure oxide may be best for a given application. These considerations must be left for future work but the process demands of the investigation have meant that the sorption of a wide variety of isotopes should be studied. BNF plc were interested in sorption of transuranic elements for instance. To be able to market mixed oxide exchangers requires that they must be versatile and that they can be 'tailored' to customer requirements.

On balance however this work has shown that mixed oxide exchangers offer quite a number of advantages. These have been mentioned in the text but some of the main ones are, a) the substantial increases in the uptake of transuranic species in low and high pH media by Sn(IV) and Ti(IV) based composites (table 3.6 and 3.7), b) they exhibit marked amphoteric behaviour in some systems, c) can enhance physical strength over pure oxides, and d) irradiation stabilities match those of pure oxides.

The ion exchange tests described in section 3.3 are a

basic simple assessment of ion exchange properties and the evaluated K_d values may be taken as an approximate indication of bedvolumes passed through a column before breakthrough. With the half time to equilibrium approximately an hour the K_d values were assumed to be at equilibrium. The final pH in such tests can be useful in conceptualising the sorption process of ion exchange. The high K_d values for Am^{241} and Pu^{242} with Ti(IV) based exchangers at pH 12 (table 3.7) are indicative of chemical precipitation of the species on to the exchangers. At such concentrations of the species (in Thorp simulant), the precipitation or agglomeration of colloids adhered to surface could be shown by scanning electron microscopy. The resulting final pH 9 for Ti(IV) exchangers in the low pH test solution (Earp) in table 3.6 could be due to exchange of OH^- ions for Am and Pu in forms of anion complexes. This process conforms to the predominantly anion exchange behaviour exhibited by pH curves of HTiO and Ti composite. The Sn(IV) based oxides, however undergo cation exchange with the natural pH of test solutions becoming acidic as a result of H^+ ions released into solution.

The total effective capacity values are comparable to those given for similar hydrous oxides in literature. The values of 1.67 and 1.09 for HTiO are within the overall ranges of 3.9-1.25 meq/g⁵² and 2.35-0.8 meq/g⁴⁸ for Cs^+ and Sr^{2+} respectively. The capacities for Eu^{3+} , UO_2^{2+} and Th^{4+} were also found within the same range and can be appreciated if expressed as mmol per g of exchanger.

The curves in figure 4.11a ,b and c show the regenerative

(or reversibility) of the exchangers. In laboratory applications, the cost of the regenerant material is considered unimportant, however for large scale operations the correct choice of regenerant would need to be determined by further tests. Earlier tests showed that an unnecessarily strong regenerant solution (concentrated HNO_3 acid) should always be avoided. In the sorption of alkalis and alkali earth elements by HTiO (and HSnO), the exchange reversibility depends on the strength of the sorbed species and conditions of competing ions in the system; consequently it depends on sorbate as well as on the sorbent properties.

The results of the composite oxides show that the addition of silica enhances the overall ion exchange capacity and in some cases it has an opposite effect. These can be understood, in general terms, by invoking the concept of point-of-zero change (PZC). At PZC the surface charges on the solid from all sources will be zero. Below the PZC value the surface charge is positive and the hydrous oxide behaves as an anion exchanger; and above the PZC value the charge is negative and the oxide behaves as a cation exchanger. The PZC value of a composite however can be approximated as the weighted average of the two PZC values of the constituent oxides. For example, the PZC value for HTiO is pH 4 (figure 4.2) and therefore exhibits poor cation sorption below this value, while the HSiO PZC value is pH 10 (figure 4.7) and has better cation properties. The PZC of the Ti composite was found to be around 6-8 (figure 4.3). This concept could ideally be

illustrated by comparing anion and cation sorption of a composite hydrous oxide to that of the respective pure hydrous oxide and hydrous silica. An illustration of this, considering only cationic uptake, can be taken from the work on two cationic species in section 4.3. Figures 4.8b and 4.9b show that due to the shift in the PZC the K_d value for Sr^{2+} was improved from 235 to 340 respectively. Occurrences of this type are also noticeable in tables 3.6 and 3.7.

The acid base properties of the exchangers revealed by pH titration investigations reflect the electronic density of OH-groups which act as the exchangeable functionalities. Large ionic potential of the central metal for example Sn in HSnO provide for small electronic density for OH^- groups, this facilitates the release for H^+ ions exchangeable with cations in the solution. In the case of HTiO large electronic density of OH^- groups, due to the smaller ionic potential of the central metal ion, makes the exchanger undergo predominantly anion exchange. The pH titration curves show the changes in the characteristic ion exchange behaviour of the hydrous oxides and also illustrated the respective shifts in the PZC values. The titration curves in the sodium chlorate system were intended to exhibit the overall stability of the

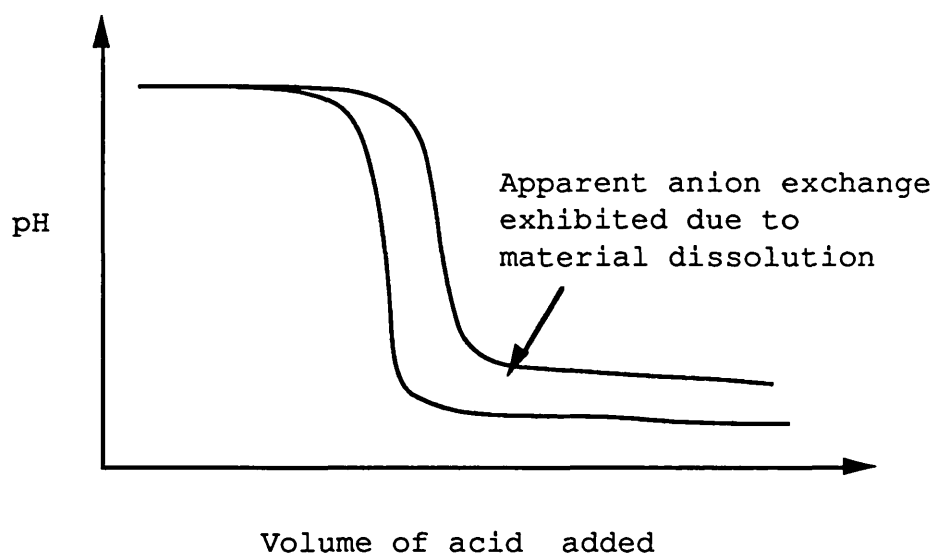


Figure 7.1 pH titration curve for an unstable inorganic ion exchanger

exchangers. The HMnO is produced by a redox reaction and both this and HMnO:HSiO could be affected by the presence of an oxidizing agent. If dissolution of the exchangers was occurring then the titration curve would be above and parallel to the blank showing greater 'anion exchange', as depicted by figure 7.1.

The pH titration curves in the Na^+ system for almost all the exchangers show little or no Na^+ exchange. This is due to the exchangers already being in the Na^+ form. Although the washing of the precipitates is thorough there still remains enough Na^+ in the precipitates to show the effects of ' Na^+ -pretreatment'. So in the systems where cation exchange is exhibited, it can be said that the cation of the system is above Na^+ in the selectivity series for the exchanger concerned.

Contrary to what the pH titration curves show, HTiO and HTiO:HSiO do exhibit significant cation exchange behaviour

at low pH values as illustrated by figures 4.8 and 4.9. These figures show the dependency of the distribution coefficient values of an alkali metal and an alkaline earth metal ion on the pH of solution. The trends given are similar to those reported by Inoune and Tsuji⁵⁶, but show higher K_d values which may be due to differences in the preparatory methods.

The selectivity series presented in this work cannot be compared to any given in literature due to the combination of species present, their respective concentrations, pH of solutions and of course the preparation history. It would also be inconsistent to compare the K_d values to those given in literature as the contacting solutions considered in this work are multicomponent and the effects of competing ions on the K_d values cannot be neglected. The order of magnitude of the K_d values may be considered viable for comparative analyses. Heitner-Wirguin and Albu-Yaron⁴⁸ have reported with HTiO values of 194 and 151 for Cs^+ and Sr^{2+} respectively. These compare with 208 and 34 at pH 1.9. Inoune and Tsuji⁵⁶ reported a Co^{2+} value for HTiO of 87 at pH 3.6 which compares to 45 at pH 2.9.

From the selectivity tests it is important to notice that the selectivity series for Ti(IV) based hydrous oxides differ very little over the pH range considered. The results suggest that the strength of the electrostatic interaction between the hydrated ions and ion exchange sites in the exchanger determine the selectivity of the exchangers.

The greatest degree of reversal in the series was

observed with Mn(IV) based exchangers. Interestingly the K_d values for Am and Eu with Mn(IV) exchangers increased as the solution pH became more acidic. The selectivity of hydrous oxide exchangers is therefore also affected by the charge of the ions. The trends for Mn(IV) based exchangers suggest that the electrostatic interaction between the cations in the solution and the ion exchange sites in the hydrous oxides may be strong enough (ie. greater than ΔG of hydration) to remove the solvated water molecules from the cations. This, the ion hydration theory, seems feasible as HMnO (γ -MnO₂) is known to have ion sieve type properties and the absorptive properties of HMnO is strongly dependent on the crystal and pore structure. The ionic radii of the species are in the order $\text{Co}^{2+} < \text{U}^{6+}$ (as UO_2^{2+}) $< \text{Eu}^{3+} < \text{Am}^{3+} < \text{Sr}^{2+} < \text{Cs}^+$. Since the selectivity series of Mn(IV) based exchangers does not parallel that of ionic radii series implicates the presence of effects other than ion sieve, for example the charge of the ions as mentioned earlier. Although the crystal structure of Mn(IV) based exchangers was not entirely determined, there is a strong probability of more than one form of MnO₂ present. The higher K_d values for uranium with Mn(IV) based exchangers may not entirely be ascribed to ion hydration theory, there may be possibilities of weak bonding between UO_2^{2+} and the exchanger. Owing to a combination of this and ion sieve effects the sorption of the heavy elements has been reported in literature to be an irreversible process. Such considerations are left for future work.

In general terms the selectivity tests show that Ti(IV)

based exchangers are good for alkali metals and actinides and that Mn(IV) based are suitable for heavy elements. Therefore it can be said that in the presence of other species Ti(IV) based exchangers would be poor scavengers for transition elements and Mn(IV) based exchangers poor scavengers for radioactive Cs and Sr.

The ion exchange tests with the BNF plc feed degreasents were carried out merely to determine the best working environment. The results of uptakes of cations are conflicting from one solution to another. A theoretical explanation of the ion exchange behaviour can be established with further detailed studies. For this a knowledge of the organic constituents of the degreasents would also be needed. The reported results do however confirm that, the uptake of (radioactive) cations on hydrous oxides is very much pH dependent. Comparing the results of solution I, which contains no degreasents, to those of solution G suggest that the organic constituents of 'Jannitol' and 'SDG' form stable complexes with the cations in solution thus lowering their uptake.

Repeated studies have shown that the sorption properties of hydrous oxides are very sensitive to the conditions of preparation, heat treatment and ageing etc. With similar argument, the density, surface area and other physical properties of a given batch of precipitate may vary considerably if washed and dried to differing degrees and at different times. Therefore the discrepancies in the ion exchange capacities of the hydrous oxides cannot be readily expressed in terms of a single structural feature of the

exchanger or easily defined properties of particular ions.

The density values given in table 5.1 are in accord with amorphous nature of the exchanger materials - all the exchangers are less dense than the naturally occurring oxides of the respective metal ions. The density of HSnO is comparable within the range $3.06\text{--}3.80\text{ g/cm}^3$ ^{64,65}, however the HMnO value is considerably lower than 4.49 g/cm^3 reported by Hunter⁹¹. The density value reported by Hunter was for lithium bearing $\lambda\text{-MnO}_2$. The value given in this work substantiates the pure and amorphous nature of HMnO . The pH of preparations were > 10 in all the cases, which resulted in the specific area values of $< 1\text{m}^2/\text{g}$. This was not too unexpected as a detailed study by Nelson and Eggertsen⁶⁰ had shown similar behaviour for titania gels prepared at various pH values. The values were thus expected to be low, the ion-sieve type sorption mechanism (of nitrogen) may also be responsible for slightly higher values. This phenomenon is discussed later in relation to cross linking of metal-oxygen bonds. The microporosity of the composite exchangers is high in some cases and may subsequently explain good sorption for some ions by an ion-sieve type process. The microporous nature and low specific surface area values of the hydrous oxides are in keeping with the idea of an increase in the three dimensional network of ion exchangers at a high pH.

The thermogravimetric data show that the hydrous oxides cannot be simply formulated as MO_2 . The room temperature diffractograms together with TGA, DTA curves and infrared spectra all confirm the amorphous nature of the oxides in

general and the homogeneity of the composite materials. It is plausible to assume that in addition to water bound in the form of hydroxyl ions the hydrous oxides contain a vast number of water molecules within the bulk of the solid of which some are present interstitially and some coordinately bound to the metal ions. The TGA results indicate that a higher temperature than 110°C is needed for removal of the chemically bound water (exchangeable hydroxyl ions). This can be correlated to the ion exchange tests for a batch of HSnO dried at various temperatures, ranging from room temperature to 210°C (tables 3.11 and 3.12). This characteristic behaviour of partial dehydration is a norm for most hydrous oxides. It is likely that an increase in the drying temperature to an upper limit causes greater condensation in the structure of the exchanger. Drastic drop in the capacities are reportedly observed²⁸ at drying temperatures > 300°C due to crystallization of the material matrix.

Since all the exchangers are amorphous the structure must be related to the properties of the respective metal ions in solution. It is known that aqueous solutions do not contain simple M^{4+} cations but rather polymers of hydrolysed species or complex ions such as $(-TiO-)^{2n}$. By polymerisation of these hydrolysed species on addition of caustic soda a macromolecular gel (of the ion exchanger) is formed with more or less open structure according to the degree of

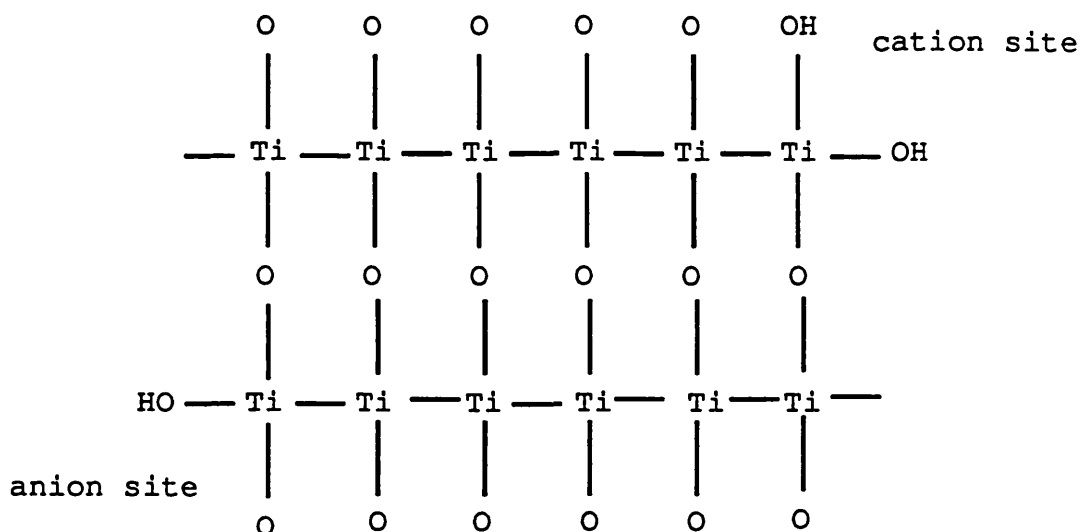


Figure 7.2 HTiO matrix

crosslinking. At a high pH a hydrous oxide exchanger may exhibit molecular sieve effects, due to the high degree of crosslinking. This effect may have occurred in the BET method of determining specific surface area by nitrogen adsorption, thus giving an 'inaccurate' value. However such exchangers can still contain enough OH^- and H^+ ions available for ion exchange. The latter contention may apply for $\text{M} = \text{Ti}, \text{Sn}, \text{Mn},$ and Si , however the crosslinking phenomenon only applies to Ti, Sn and Si . As the XRPD data has shown that the Mn(IV) based exchangers did not undergo any form of crystallization up to 300°C and therefore have rather more complex principle structures.

The cross linking postulate comes to light with XRPD diffractograms at higher temperatures. The HSnO has shown the highest degree of crystallinity at room temperature, which may however, explain its overall low ion exchange capability. Although still containing 9.6 weight percent of

water up to 200°C, HSnO has a principle structure of cassiterite (figure 5.4). The narrower the peaks in a diffractogram the higher is the degree of crystallinity. This was illustrated in the four diffractograms of HTiO at various temperatures (figure 5.8). The HTiO at 300°C was determined to have its principle structure corresponding to anatase. It shows in the case of HTiO (and HSnO if heated) that on heating an ordering is obtained influenced by the diffusion of ions to proper sites in the matrix to form the most thermally stable structure. Usually such processes are at the expense of sorption properties of the exchangers due to excessive water loss. In case of the double-salt type 'composite' exchangers it has been reported that thermal treatment, higher drying temperatures, have led to better sorption³⁰. The diffractograms of Mn(IV) based exchangers show no crystallinity even at 300°C. The DTA plots for the hydrous oxides can be utilized to determine any structural arrangement of an exchanger and subsequently can be used to determine the 'working' temperature region of the exchanger before drastic losses in capacity.

The hardness tests show that compositing the hydrous oxides does not necessarily mean an improvement in the physical strength. The increase in the strength of HMnO:HSiO is very significant and this phenomenon can be explained by the assumption that there exists chemical bonding between the constituent elements. In the case of HTiO:HSiO the silica 'impurity' acts to the detriment of the material's physical integrity.

With the foundations of the indentation technique rooted

in the strength of perfectly homogeneous material, it is essential that the material contains no pre-existing stresses prior to the test. This may explain a lower than expected value of K_{Ic} for HSnO. It seems from the difficulties encountered with HMnO that it is not a well behaved material to an indentation test. So, the technique is limited to materials with a good indentation response or Young's modulus; it must be noted there is no direct correlation between Young's modulus and critical stress factor. Ideally the technique is suited to toughness evaluation on comparative basis. So the materials under question may all be treated, as indeed are the ion exchangers (typically 'H⁺ form'), prior to the test to establish their toughness under 'real' operating conditions.

Hitherto, the indentation technique was a viable method for providing qualitative predictive modelling. It has proved simplistic and economic; the greatest advantage of the technique is the small amount and size (> 100 microns) of material required. The results indicate that HTiO and HMnO:HSiO are most suited for column operation in a large scale plant. However more work needs to be done in the areas of washing and drying to acquire a greater degree of hardness of inorganic hydrous oxides by relieving internal stresses which can build up in the body of the exchanger due to thermal, osmotic stress or inclusion of impurities.

The irradiation studies generally show that the hydrous oxide exchangers have a high resistance to irradiation. The observed overall decreases in the ion exchange capacities

of the four ion exchangers cannot entirely be attributed to the applied radiation doses as the ageing of the exchangers can also lead to natural (ion exchanger) degradation. It should be noted that the experiments were carried out over a period of four months. Comparative studies over a longer period with a lower dose rate need to be carried out to conclusively substantiate the latter possibility. Owing to age related degradation of ion exchangers (also occurring with organic resins) it is a standard practice in the ion exchange industry to use 'fresh' batches of exchangers.

The yellow colouration of the Ti(IV) based exchangers after 1000 Mrads of irradiation is certainly due to Ti chemistry and may specifically be due to titanium ion reacting with radiolytic products of water. The radiolytic hydrolysis of the interstitially bound water was clearly illustrated by the infrared spectra. The IR spectra given in figure 5.20 coincide with the rise in the K_d values at around 200 Mrads. It seems possible that at this dose an amount of bound water is hydrolysed and as a consequence gives rise to additional sites. The rise and fall of K_d value to starting value implies that there exist a finite number of ion exchange sites that are characteristic of an exchanger and are destroyed due to ageing (or irradiation) as mentioned earlier.

The chemical stability test results (table 5.14) for the hydrous oxides irradiated to various doses give weighting to the degradation due to ageing phenomenon. The dissolution concentration values for HTiO (1.3ppm) and HTiO:HSiO (5.75ppm) irradiated to 1068 Mrads can be

directly compared to 'Ti 100%' and 'Ti 70%' samples in table 3.8. If the exchangers were decomposing as a result of irradiation then the metal ion concentrations would have been much higher.

Chapter 8

Conclusions

8.1 Conclusions and Future work.

8.1 Conclusions and future work

The hydrous oxides studied in the present work have been characterized with respect to their ion exchange properties, physical strength and irradiation stabilities. The ion exchange properties, in particular, have been studied in direct relation to the waste management problems faced by British Nuclear Fuels plc.

The hydrous oxides preparation procedure lacks continuity due to the batch wise washing process. Electrolytic precipitation of the metal dioxides, with an appropriate membrane technology, should be investigated as this may bypass the intermediate non-continuous washing step.

The study of the effects of chelating agents such as EDTA and citrates is recommended. The total effective capacities of various elements given in this study were determined by passing single-component feeds through the exchanger columns. Similar type of investigation is suggested with 'modsol' type solutions to evaluate effective decontamination properties of multi-component waste streams. Large scale tests with BNF plc generated streams would yield the materials' performances under working conditions.

Irradiation studies over smaller doses may give better understanding of the radiolytic hydrolysis effects observed with the hydrous oxides. Tests need to be devised to check the validity of the age degradation phenomenon discussed earlier.

The materials developed in this study have shown desirable ion exchange properties and chemical stabilities.

However, it is important at this stage to investigate the compatibilities of these materials with different solidifying matrices, like glass and concrete, if these materials are to be stored over long periods of time in man made radioactive burial sites.

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Appendices

Appendix I Contacting solutions

Appendix II Theory of counter-current washing

Appendix III TG and DTA curves for hydrous oxides

*Appendix IV Sample calculation for determining K_{IC} and
 K_{IC} values for known ceramics*

Appendix I

SPECIFICATION OF CONTACTING SOLUTIONS

EARP simulant feed:

Sodium Nitrate	8.235 g/l
Nitric Acid	0.5 g/l
Am ²⁴¹	196 nCi/l
Cs ¹³⁴	305 nCi/l
Pu ²⁴²	417 nCi/l
Sr ⁸⁵	324 nCi/l

Solution pH 1.29

Thorp simulant feed:

Sodium hydroxide	0.7 g/l
Sodium Nitrate	1.9 g/l
Sodium Nitrite	0.2 g/l

Am ²⁴¹	195 nCi/l
Cs ¹³⁴	225 nCi/l
Pu ²⁴²	396 nCi/l
Sr ⁸⁵	517 nCi/l

Solution pH 12.2

Contacting Solutions A to L:

Solution A

2M HNO₃

1% w/v SDG

1% w/v Jannitol

Am²⁴¹ = 420 nCi/l ; Co⁶⁰ = 1140 nCi/l

Pu²⁴² = 420 nCi/l ; Cs¹³⁴ = 600 nCi/l

U²³⁵ = 350 nCi/l ; Eu¹⁵² = 640 nCi/l

pH = -0.3

Solution B

2M HNO₃

1% SDG

+ similar radiochemical content as solution A

pH = 0.0

Solution C

2M HNO₃

+ similar radiochemical content as solution A

pH = -0.2

Solution D

2M NaNO₃

1% w/v SDG

1% w/v Jannitol

+ similar radiochemical content as solution A
except for:

Co⁶⁰ = 1900 nCi/l ; Cs¹³⁴ = 1077 nCi/l

Eu¹⁵² = 1273 nCi/l ; Sr⁸⁵ = 1777 nCi/l

pH = 1.4

Solution E

2M NaNO₃

1% w/v SDG

+ similar radiochemical content as solution D

pH 1.3

Solution F

2M NaNO₃
+ similar radiochemical content as solution D
pH = 1.1

Solution G

2M NaNO₃
1% w/v SDG
1% w/v Jannitol
+ similar radiochemical content as solution D
except for:
Cs¹³⁴ = 2063 nCi/l
pH = 2.7 (adjusted with NaOH)

Solution H

2M NaNO₃
1% SDG
+ similar radiochemical content as solution G
pH = 2.5 (adjusted with NaOH)

Solution I

2M NaNO₃
+ similar radiochemical content as solution G
pH = 2.2 (adjusted with NaOH)

Solution J

2M NaNO₃
+ similar radiochemical content as solution G
except for:
Am²⁴¹ = 800 nCi/l
pH = 5.5 (adjusted with NaOH)

Solution K

2M NaNO₃
1% w/v SDG
+ similar radiochemical content as solution J
pH = 7.5 (adjusted with NaOH)

Solution L

2M NaNO₃

1% w/v SDG

1% w/v Jannitol

+ similar radiochemical content as solution J

pH = 7.3 (adjusted with NaOH)

Solution ThorpZ

Calcium chloride 5.73 x 10⁻⁴ g/l

Cobalt sulphate 4.76 x 10⁻⁴ g/l

Sodium chloride 2.54 x 10⁻⁴ g/l

Boracic acid 3.17 x 10⁻⁴ g/l

Am²⁴¹ 900 nCi/l

Co⁶⁰ 3600 nCi/l

Appendix II

COUNTER CURRENT WASHING OF ION EXCHANGE

FLOCS-THEORY AND OPTIMISATION

A semicontinuous countercurrent washing theory is formulated and considered with respect to the washing of floc precipitates with ion exchange properties. For a given system the number of stages required for an optimal washing process may be determined by a graph of λ , (degree of washing) versus k , (slurry ion concentration). The volume of wash water per stage and thus total volume required can be determined for the system.

INTRODUCTION

Counter current washing processes have been discussed in a number of papers. Treybal (1) considers leaching processes in his monograph and the use of counter current washing for uranium ores has been considered ((Meritt (2))). In these sort of applications the solid being washed is chemically inert and does not absorb any soluble chemical species. Washing theory applied to this sort of process is therefore quite a simple process. However not all types of slurry are chemically inert. Salts precipitated from solution are frequently very effective sorbtion agents for soluble ionic species. It is obvious that it is more difficult to remove soluble material from slurries made of these sorbtive materials.

One practical process in which this problem is encountered involves the manufacture of inorganic ion exchangers which are being developed for the treatment of radioactive waste. Such an exchanger is hydrous titanium dioxide,, HTiO. It is manufactured by precipitating the hydroxide floc by contacting titanium tetrachloride with caustic soda. Quantities of sodium chloride are produced in this reaction. The floc precipitate has to be washed filtered and dried to produce the ion exchange material.

The removal of NaCl from the hydroxide floc before drying is an important aspect in the manufacture of ion exchange materials. Sodium chloride has to be removed from the floc for a number of reasons. Firstly the inclusion of soluble material in the exchanger would hinder any subsequent ion exchanger process.

Secondly and exchanger dried with soluble salt inclusions has very poor mechanical properties. Distilled water has to be used for the washing process as tap water contains undesirable soluble ions such as Ca^{++} .

In making pilot plant scale batches of ion exchanger cocurrent washing is a simple process. This involves repeated washings with distilled water and the application of this mode of washing has been considered in a previous papers (White (3)). These show that cocurrent washing uses very large quantities of distilled water to wash the floc precipitates. For this reason we are now producing our products by semicontinuous counter current washing. This uses far less distilled water than the co-current processes and will be discussed in this paper.

Counter-current Washing Theory

The basis of the calculation is one cubic metre of product slurry which contains $f \text{ m}^3$ of floc. If the concentration of salt in the water is C_n then the salt sorbed on to the floc is equal to flC_n , where l is the ion exchange distribution constant for the precipitate. So the total amount of salt in 1 m^3 of slurry is given by

$$(1 - f + fl)C_n = kC_n \quad (1)$$

Here k is the total ion capacity per cubic metre of the slurry. In a washing stage, L cubic metres of water is contacted with 1 m^3 of slurry, so a mass balance around stage n gives

$$kC_{n+1} + LC_{n-1} = (L + k)C_n \quad (2)$$

This is a standard finite difference equation for C_n whose general solution is

$$C_n = A\alpha^n + B\beta^n \quad (3)$$

Where A and B are constants and α and β are the roots of the quadratic equation

$$k(C_n)^2 - (k + L)C_n + L = 0$$

The solution of this equation gives $\alpha = L/k$ and $\beta = 1$. Accordingly equation (3) becomes

$$C_n = A \left(\frac{L}{k} \right)^n + B$$

The constants A and B are evaluated from the boundary conditions that $C_0 = 0$ (wash water) and $C_{N+1} = C_f$ (feed concentration). Applying the first boundary condition gives $B = -A$ and the second gives

$$C_{N+1} = A \left(\frac{L}{k} \right)^{N+1} - A = C_f \quad (\text{The feed concentration})$$

The general solution to the finite difference equation is therefore

$$\frac{C_n}{C_f} = \frac{(L/k)^n - 1}{(L/k)^{N+1} - 1} \quad (4)$$

Now C_1 is the concentration of salt in the final stage of washing so, defining $\lambda = C_f/C_1$ as the degree of washing required gives,

$$\begin{aligned} \lambda &= \frac{(L/k)^{N+1} - 1}{(L/k) - 1} \\ &= 1 + (L/k) + (L/k)^2 + \dots + (L/k)^N \end{aligned} \quad (5)$$

Now the overall volume of a plant to wash one cubic metre of slurry is given by $N(1 + L)$. N is the number of stages in the plant and $(1 + L)$ is the total volume of process fluid in any one stage. Washing can be done in any number of stages but for optimum conditions the process should be carried out in as small

a volume as possible. For a given value of λ we need to maximise the function P_N where

$$P_N = \frac{1}{N(1 + L)} \quad (6)$$

To show how the optimisation can be visualised we can take $k = 2$ and plot P against λ for 1, 2 and 3 stage washing plants. For a 1, 2 and 3 stage plant

$$P_1 = \frac{1}{1 + \frac{L}{k}} \quad \lambda = 1 + \left(-\frac{L}{k}\right) \quad (7)$$

$$P_2 = \frac{1}{2\left(1 + \frac{L}{k}\right)} \quad \lambda = 1 + \left(-\frac{L}{k}\right) + \left(-\frac{L}{k}\right)^2 \quad (8)$$

$$P_3 = \frac{1}{3\left(1 + \frac{L}{k}\right)} \quad \lambda = 1 + \left(-\frac{L}{k}\right) + \left(-\frac{L}{k}\right)^2 + \left(-\frac{L}{k}\right)^3 \quad (9)$$

Values for P_1 , P_2 and P_3 can be evaluated given L . This for $k = 2$ and $L = 4$ the expression for the two stage washing plant gives

$$P_2 = 0.1 \quad \text{and} \quad \lambda = 7$$

A whole set of curves for P_1 , P_2 and P_3 as a function of λ can be built up as shown in Fig.2 for the case where $k = 2$. The curve for P_1 lies above that for P_2 and there is a crossover when $\lambda = 5.9$. Thereafter P_2 lies above P_1 and P_3 until $\lambda = 23.0$ when P_3 is the larger of the three functions. The value of λ therefore decides whether one stage, two stage or three stage

washing is the best procedure. The higher the value of degree of washing required the more stages have to be used for optimal usage of plant capacity.

A General Optimisation Procedure

For a crossover between an $(N - 1)$ and an N stage washing process, the functions P_{N-1} and P_N have the same value. This will occur when the wash liquid to slurry volume ratio is L for the $N-1$ stage process and M for the N stage process. Therefore

$$P_{N-1} = \frac{1}{(N-1)(L+1)} = P_N = \frac{1}{N(M+1)}$$

This can be rearranged to give

$$L = \left\{ \frac{N(M+1)}{(N-1)} \right\} - 1 \quad (10)$$

The values of λ are the same for both plants. Thus

$$\lambda = ((L/k)^N - 1) / ((L/k) - 1) \quad (11)$$

and

$$\lambda = ((M/k)^{N+1} - 1) / ((M/k) - 1)$$

The last expression can be rearranged to give the relationship

$$-\frac{M'}{k} = [\lambda \left(-\frac{M}{k} \right) - 1] + 1 \quad (12)$$

A simple iteration procedure can now be used to solve the equations for L, M and λ for given k and N. A guess is made for M and the value of L is calculated using equation (10). Then the estimated value of λ is worked out using relationship (11). Finally a new guess for M (denoted as M') can be calculated using equation (12). With this value a new guess of L is worked out and the process repeated. The iteration procedure usually takes a long time to converge, taking around fifty cycles. However convergence can be speeded up using over relaxation and the process is a stable one. A 'Fortran' programme of thirty statements was written to perform the necessary numerical calculation on a desk top PC.

The results of the calculation are shown in Fig.3 which gives the locus of crossover points for plants with up to six stages as a function of the degree of washing (λ) and the slurry ion capacity (k). The change in λ as k increases is however more marked than appears on the figure as the abscissa has a three decade logarithmic scale. Thus when k = 2.75 and $\lambda = 100$ a four stage washing process is the best to use. The actual value of L to use can be obtained by simple iterative solution using equation (12) for the value of k set at 2.75 and N = 4.

$$L/k = [\lambda((L/k) - 1) + 1]^{\frac{1}{N+1}}$$

Guessing L initially at 8 successive iterations give 3.108, 3.149, 3.158, 3.159, 3.159 for the value of L/k; convergence after 5 cycles. This gives a value for L of 8.69. Thus using four 20 litre containers the amount of slurry that can be

produced in the washing process is $20/(1+L) = 2.06$ litres slurry in each container.

Carrying Out the Washes

For each production line one fresh batch of floc is made each day and the washing process is carried out manually by draining out the settled floc through taps in the bottom of plastic bottles as shown in Fig.4. The bottles are arranged in racks vertically above each other. The method of carrying out one wash cycle for a three stage process is as follows:

1. Fill bottle 1 with fresh distilled water
2. Drain slurry out of bottle 2 as product
3. Drain slurry from bottle 3 into bottle 1
4. Drain slurry from bottle 4 into bottle 2
5. Lift all bottles up one shelf and remove bottle 4, and
6. Place feed slurry produced for the day into bottle 3.

Batch tests using two litre graduated cylinders can be used to obtain working data to specify continuous processes. The concentration of dissolved species in the slurry can be determined by measuring the solution conductivity using a commercially available instrument which is capable of accuracy over several decades. In dilute solutions conductivity is proportional to salt concentration. The floc concentration of the settled slurry can be determined and the slurry ion capacity (k) can be measured directly in the graduated cylinder. Let V_0 = volume of settled slurry which has a conductivity of μ_0

(expressed in micro-Siemens) when mixed with a volume W of water the conductivity becomes μ . Then assuming μ is proportional to the dissolved salt in solution.

$$kV_o\mu_o = (W + kV_o)\mu$$

or

$$k = W\mu / V_o(\mu_o - \mu) \quad (13)$$

The tests using a graduated cylinder and the optimisation scheme outlined in this paper can be used to obtain basic data for pilot plant counter current washing processes.

List of Symbols

f	volume of floc in 1 m ³ slurry
L, M	volume of wash water for 1 m ³ slurry
N	total stages in plant
C_f	dissolved concentration of salt (in feed)
C_o	dissolved concentration of salt (in wash water, =0)
l	ion exchange distribution constant for a given slurry
k	total ion capacity per cubic metre of slurry
λ	degree of washing
p	total production rate
V_o	volume of settled slurry
W	volume of wash water
μ_o	conductivity initial slurry
μ	conductivity of final slurry

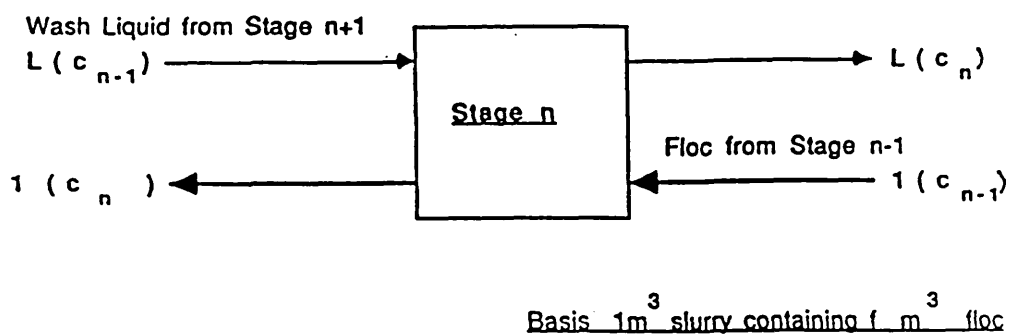


FIG 1 COUNTER-CURRENT WASHING STAGE

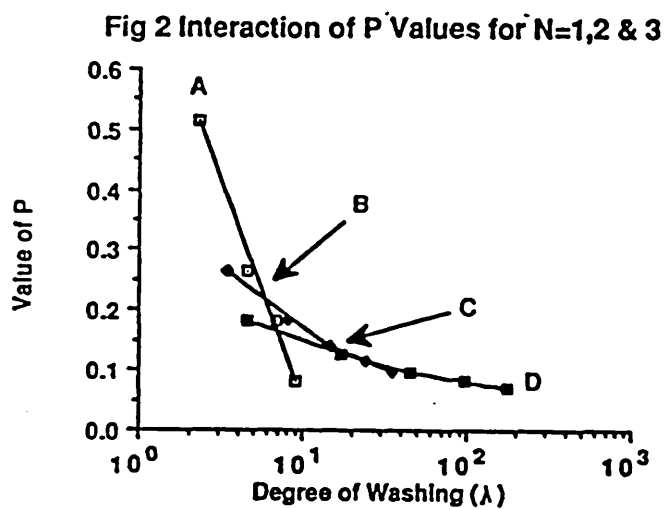


Fig 2 Interaction of P Values for $N=1,2$ & 3

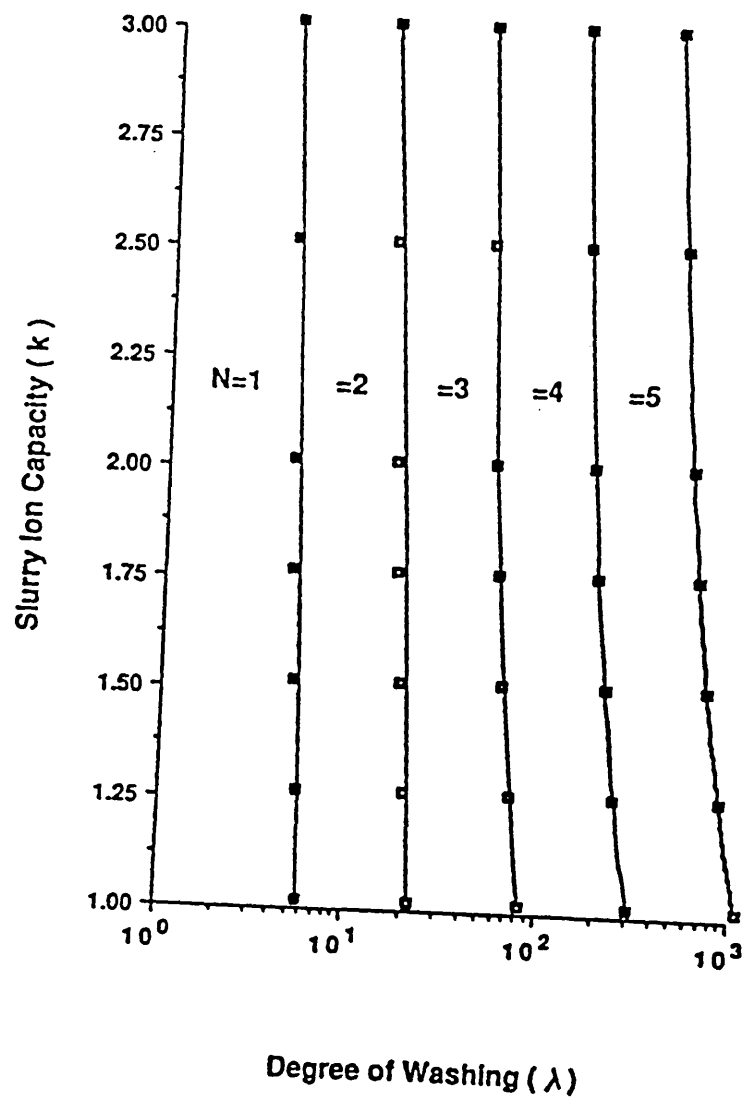


Fig 3 General Optimal Solution

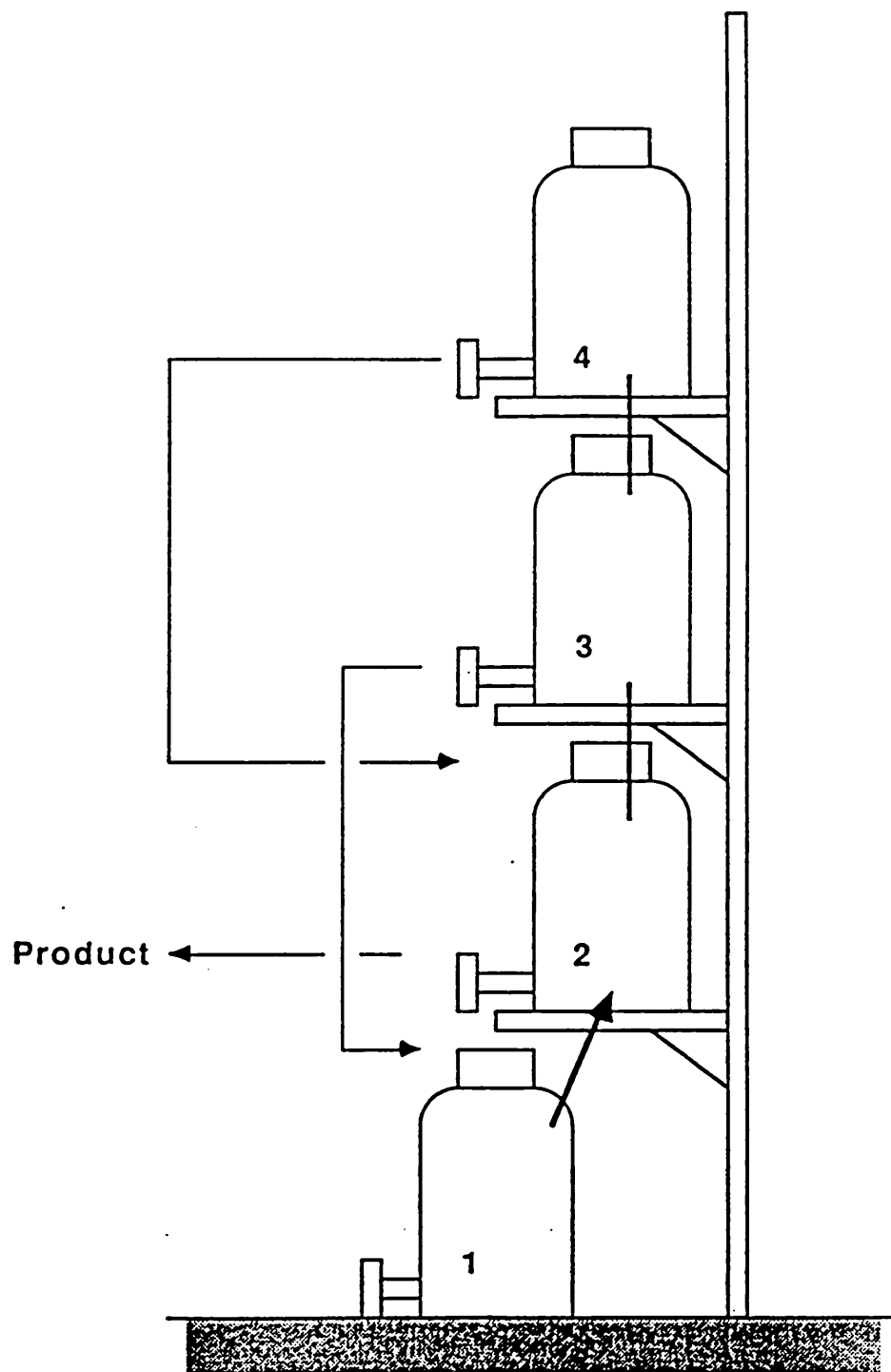


FIG 4 A THREE STAGE WASHING PROCESS

Appendix III

TG AND DTA CURVES FOR HYDROUS OXIDE ION EXCHANGERS

- Figure 1 TG curve for HTiO:HSiO ion exchanger
- Figure 2 DTA curve for HTiO:HSiO ion exchanger
- Figure 3 TG curve for HMnO ion exchanger
- Figure 4 TG curve for HMnO ion exchanger
- Figure 5 TG curve for HMnO:HSiO ion exchanger
- Figure 6 DTA curve for HMnO:HSiO ion exchanger
- Figure 7 TG curve for HSiO ion exchanger
- Figure 8 DTA curve for HSiO ion exchanger
- Figure 9 TG curve for HSnO ion exchanger
- Figure 10 DTA curve for HSnO ion exchanger

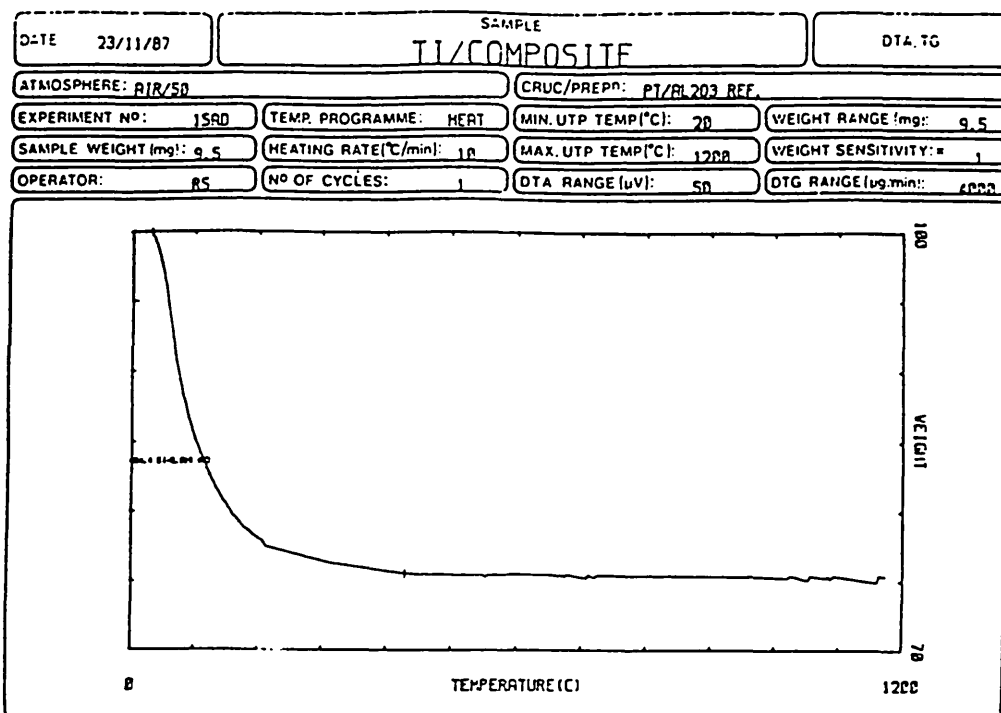


Figure 1 TG curve for HTiO:HSiO ion exchanger.

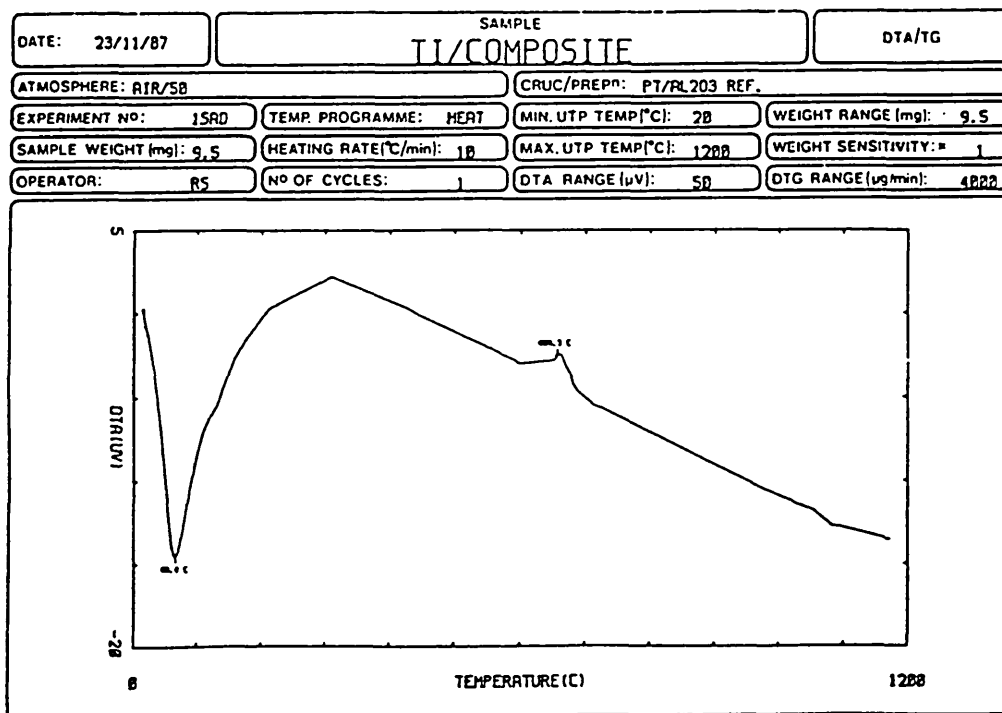


Figure 2 DTA curve for HTiO:HSiO ion exchanger.

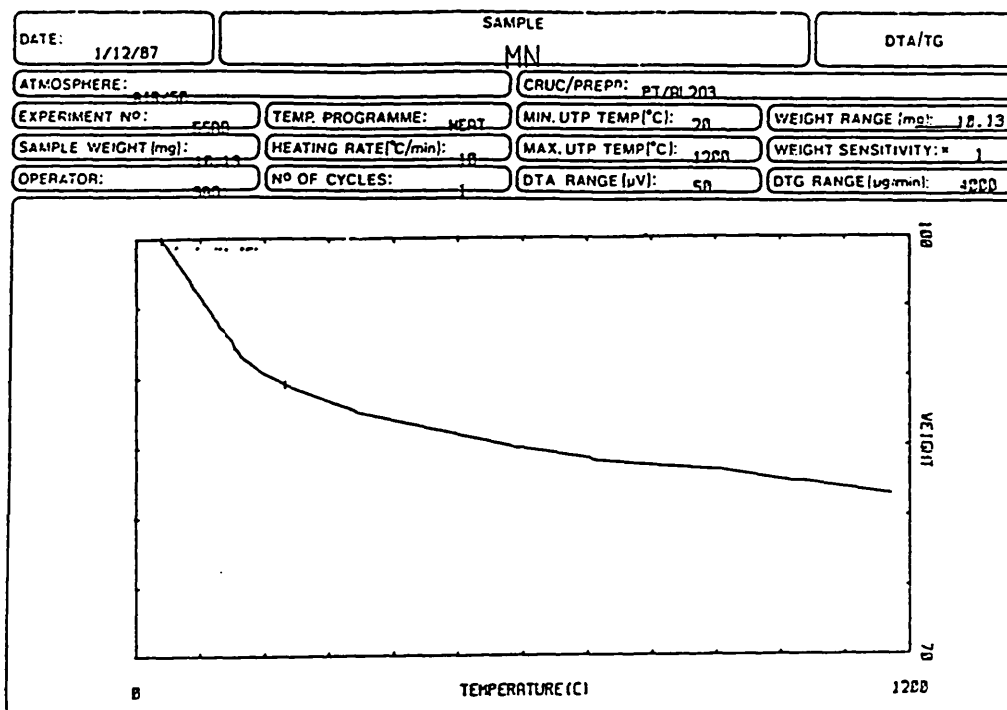


Figure 3 TG curve for HMnO ion exchanger.

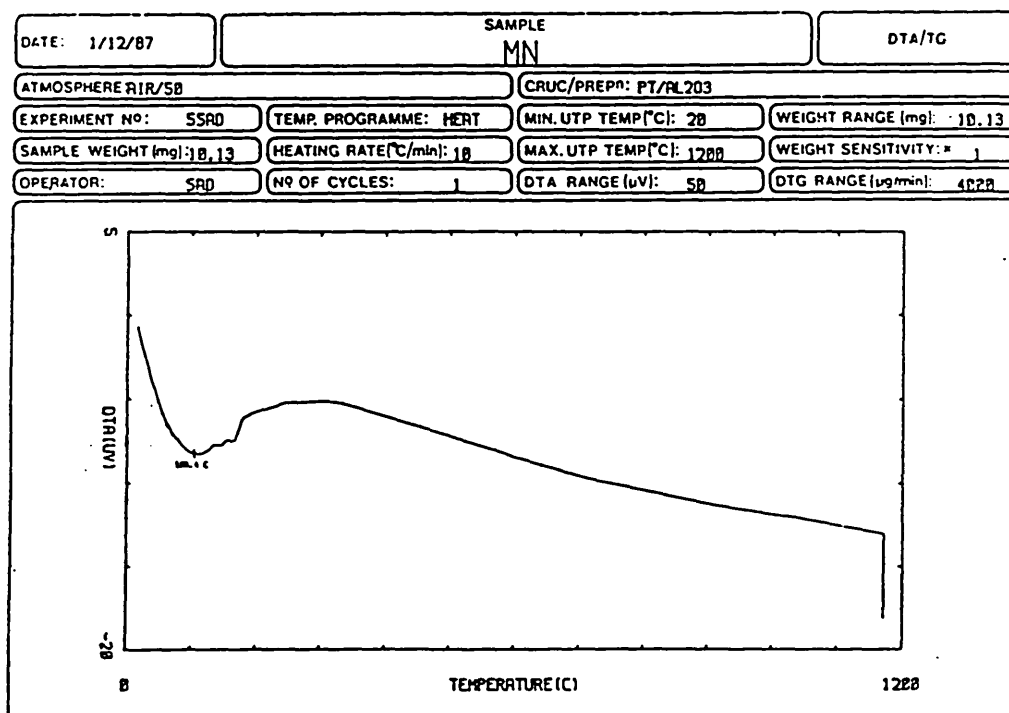


Figure 4 DTA curve for HMnO ion exchanger.

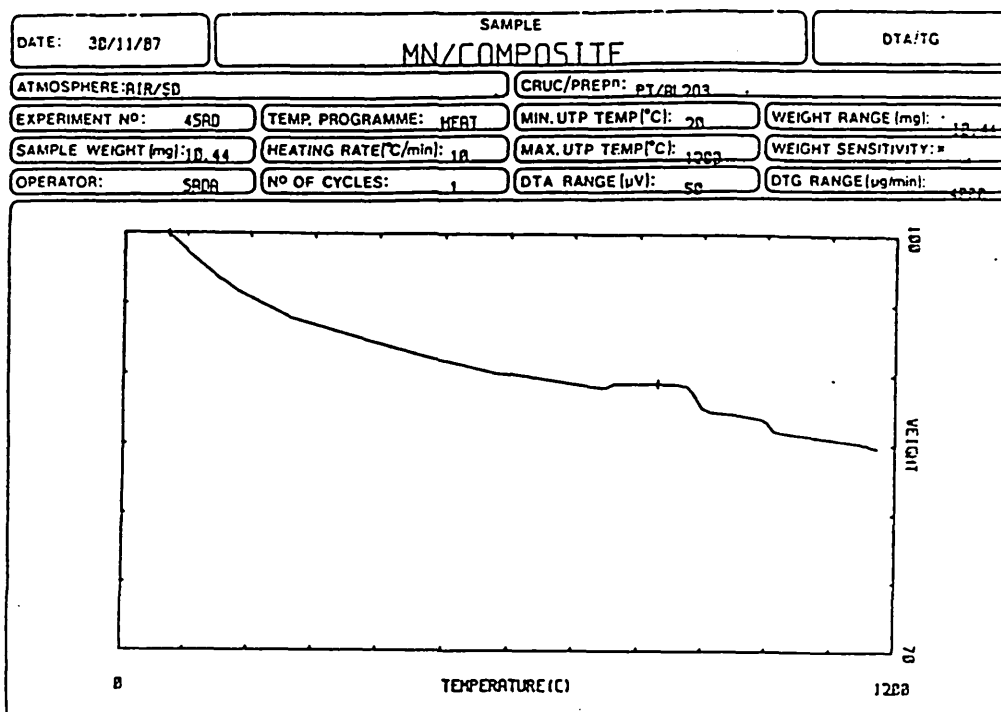


Figure 5 TG curve for HMnO:HSiO ion exchanger.

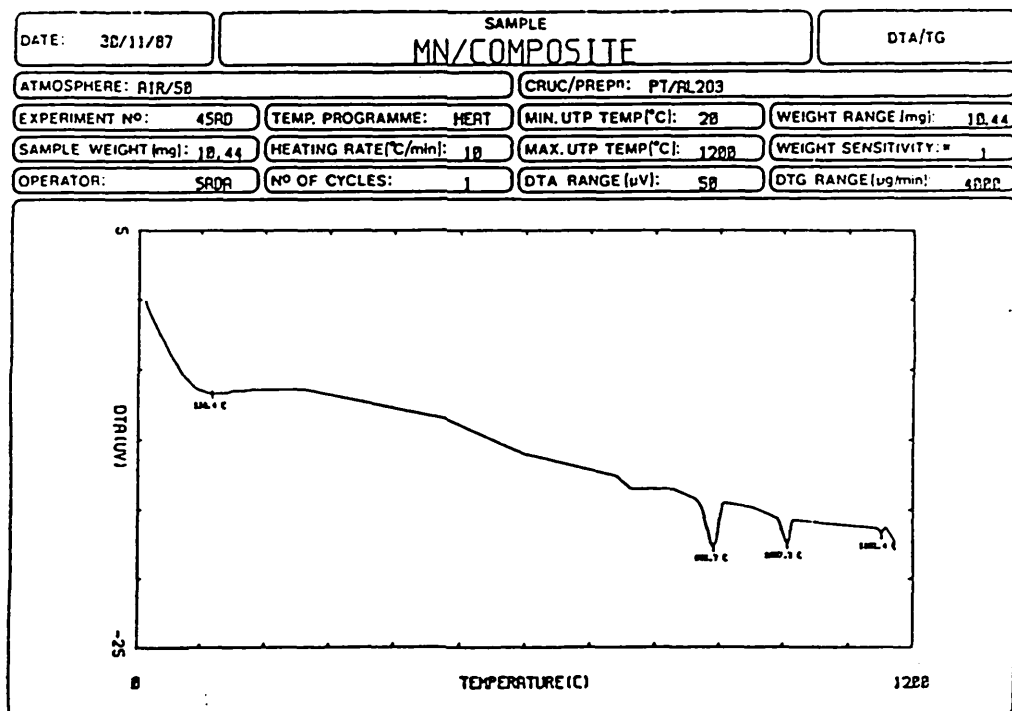


Figure 6 DTA curve for HMnO:HSiO ion exchanger.

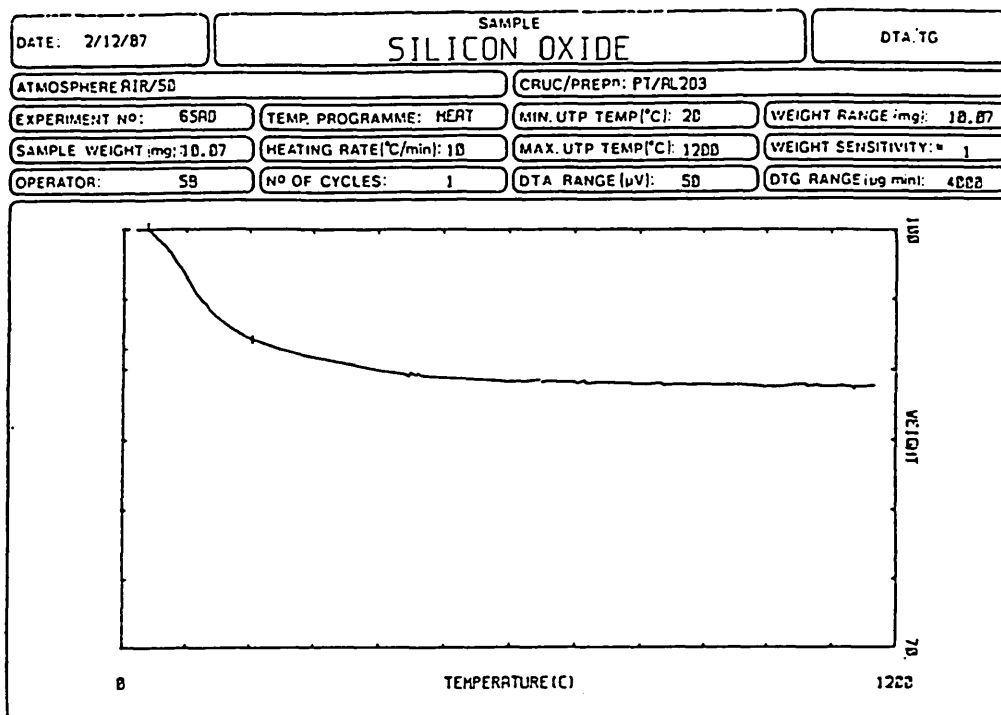


Figure 7 TG curve for HSiO ion exchanger.

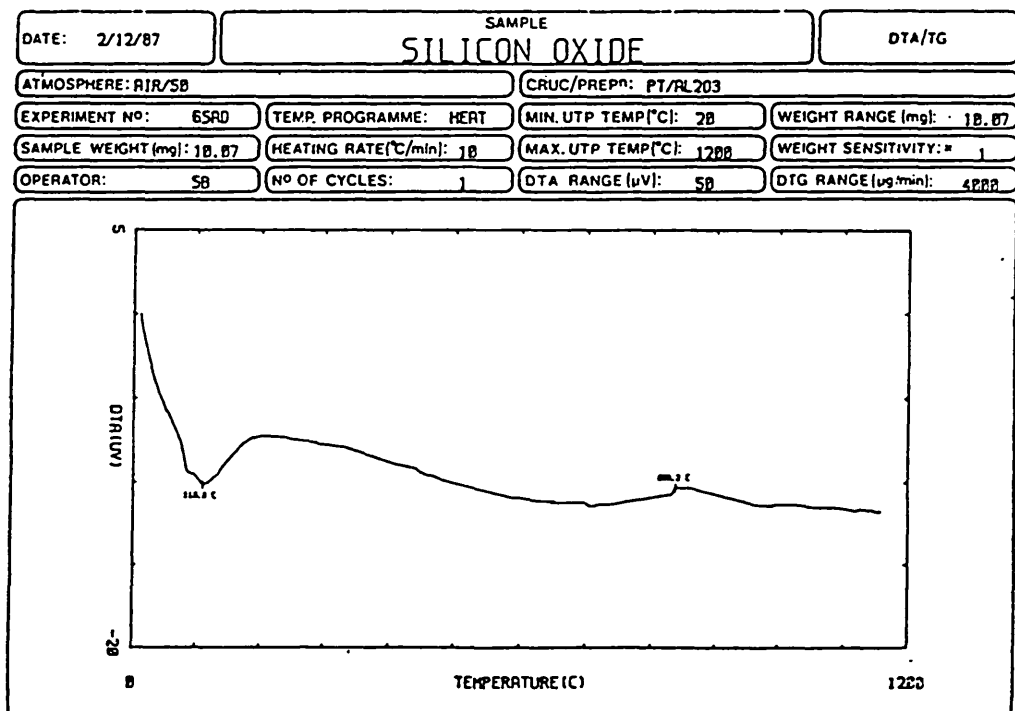


Figure 8 DTA curve for HSiO ion exchanger.

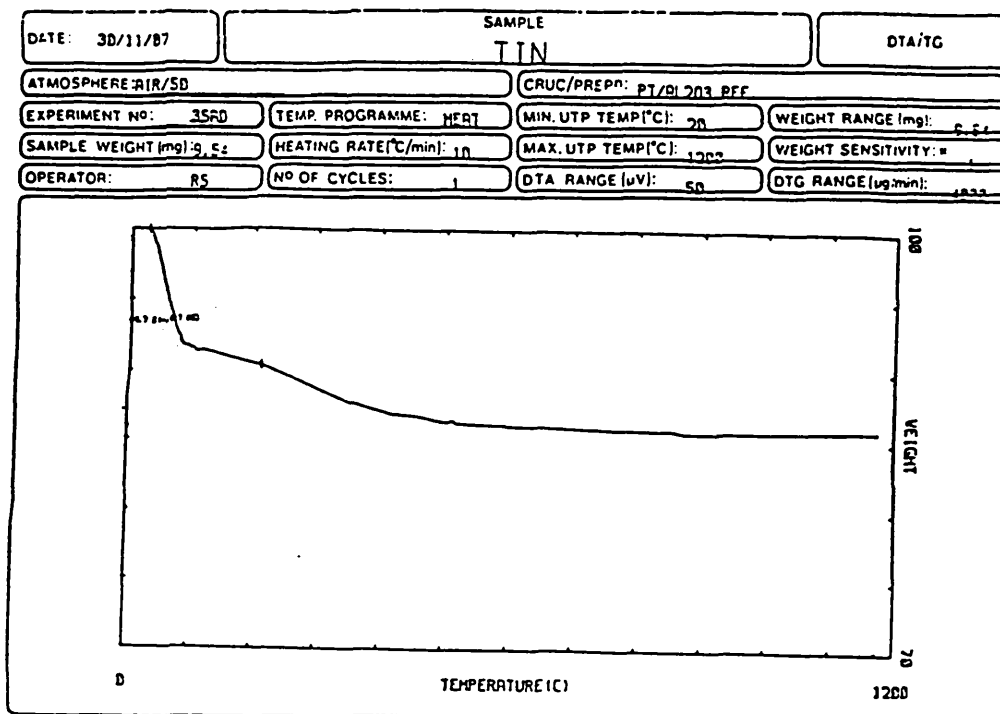


Figure 9 TG curve for HSnO ion exchanger.

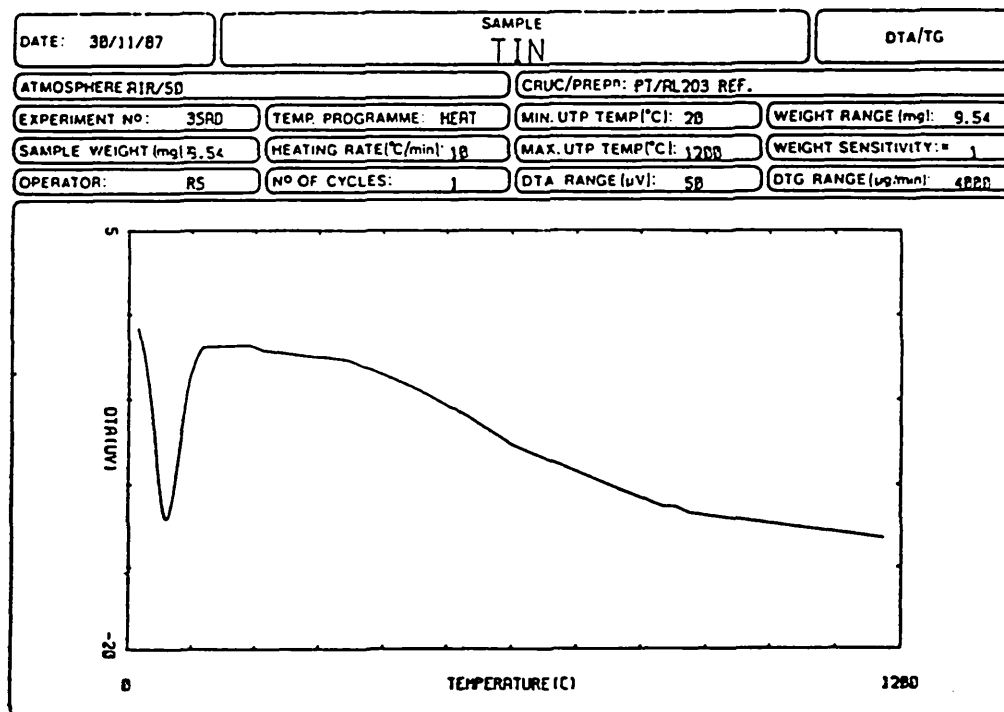


Figure 10 DTA curve for HSnO ion exchanger.

Appendix IV

A sample calculation for determining the critical stress intensity factor, K_{1c} . The value reported for HTiO is taken as an example.

The first step is to calculate the Young's Modulus from the Knoop and Vickers hardness test data. Using the applied load, $P = 0.5$ kg and the long diagonal length, $d_k = 62.9$ μm in equation (5.5) for Knoop Hardness, and multiplying the value by $g = 9.80665$ ms^{-2} gives the Knoop hardness value, $H_k = 17.63$ GPa [$\text{kgm}^{-2} \times \text{ms}^{-2} = \text{Nm}^{-2} = \text{Pa}$]. Similarly from the Vickers hardness test, the applied load, $P = 0.5$ kg and diagonal length, $d = 21.38$ μm substituted into equation (5.6) give $H_v = 19.89$ GPa. Now equation (5.3) may be rearranged for the Young's modulus E , knowing that $b/a = 1/7.11$, $\partial = 0.45$, $b'/a' = a_1/d_k = 8.03/62.90$, and that $H_v = 19.89$ GPa, E is found to be $= 689.35$ GPa. By substituting E , H_v and P and c_o ($= 17.69$ μm) from the Vickers Hardness test into equation (5.4) the value for the critical stress intensity factor, K_{1c} may be determined. The unit for K_{1c} normally adopted in the engineering ceramics field is $\text{MPa.m}^{1/2}$ so therefore it is necessary to multiply the determined value by g , to give $K_{1c} = 6.20$ $\text{MPa.m}^{1/2}$.

Table A K_{1C} values for known ceramics

Material	Characterisation	Young's Modulus, E (GPa)	Hardness, Hv (GPa)	Fracture toughness, K_{1C} (MPa.m ^{1/2})
Soda-lime glass	Amorphous	70	5.5	0.74
Alumino silicate glass	Amorphous	89	6.6	0.91
Lead alkali glass	Amorphous	65	4.9	0.68
Al ₂ O ₃ (AD90)	Polycrystal	390	13.1	2.90
SiC (Ca- stabilized)	Polycrystal	436	24.0	4.0