Ion-exchange Studies of Zeolite For Selective Removal of Transition Metal Ions From Mix Solutions

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Abstract

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M.Phil Degree

Ion-exchange

Ion-exchange Studies of zeolites for selective

Removal of transition metal ions from mix solutions.

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The work presented in this study details the removal of radioactive isotopes from nuclear chemical wastes, which contain high concentration of magnesium cations, using zeolites, which are stable in acidic media. Following four types of zeolites were used in this work:

1- Zeolite A
2- ZK-4
3- Zeolite Alpha
4- Clinoptilolite

First three zeolites were synthesized and characterized by using the X-ray diffraction, scanning electron microscope and thermogravitational analysis.

Ion-exchange batch process was used to remove the radioactive cations from the nuclear chemical wastes. All the practical work was done at room temperature.
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CHAPTER ONE
INTRODUCTION

1.1 Introduction
Zeolites, both naturally occurring and synthetic, are crystalline hydrated aluminosilicates. Structurally, zeolites are built up of a three-dimensional network of SiO$_4$ and AlO$_4$ units linked through their corners by oxygen atoms [1]. The structural formula of a zeolite can be represented as [2]:

$$M_{x/n} [(AlO_2)_x (SiO_2)_y] \cdot wH_2O$$

Where M is a cation of valence n and w is the number of water molecules. The ratio y/x always varies between 1 and $\infty$ depending upon the structure. The sum (x + y) is the total number of tetrahedra in the unit cell, and the portion represented by the square brackets represents the framework composition. Their framework structures contain channels and cavities occupied by the cations and water molecules. The zeolites can easily be dehydrated by heating and hydrated in air without significant changes in the framework. These cations are responsible for the ion-exchange properties of the zeolites.

Zeolites were first recognised by Freiherr Axel Fredrick Cronstedt in his discovery of stilbite in 1756. He found a new group of minerals consisting of hydrated aluminosilicates of the alkali and alkaline earth cations. As the mineral exhibited intumescence when heated in a blow-pipe flame, he called that mineral ‘zeolite’. The name comes from two Greek words “to boil” and “a stone” [3].

1.2 The structure of zeolites
The basic building units of zeolites are SiO$_4$ and AlO$_4$ tetrahedra. These tetrahedra are linked with each other via oxygen atoms from their corners to form interconnected cages and channels as shown in figure (1.1) [4]. In order to simplify the understanding of the structure of zeolites the term “primary building units” and “secondary building units” are used, which are based on the framework topology of the zeolites. The tetrahedra SiO$_4$ and AlO$_4$ are called primary building units. When these primary building units connect with each other in different ways, they produce Secondary Building Units (SBUs).
Each aluminium $\text{Al}^{3+}$ substitution for silicon ($\text{Si}^{4+}$) in the zeolite framework generates one negative charge on the framework. The greater the aluminium atom substitution, the higher the negative charge on the framework [5]. This negative charge is compensated by the cations such as $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ present in the synthesis and held in the interstices of the structure on crystallization. The water molecules are also present in these voids or channels. The extent and location of the water molecules both depend upon the structure of the zeolite, size and shape of the voids and channels, and the number of cations present in the structure.

Figure 1.1: Structure of zeolite A
Figure 1.2: The secondary building units (SBU) in zeolite structures.
The chemical properties of zeolites dependant on the Si/Al ratio. The sum of the Si and Al is the total number of the tetrahedra in the unit cell. The Si/Al ratio of zeolite A is one, which is the lowest possible ratio. According to Lowenstein’s rule aluminate tetrahedra cannot be neighbours in the framework so that Al-O-Al linkages are forbidden. When Al is incorporated in the zeolite structure there are two main effects: firstly there is an increase in the net negative charge, which means the framework requires a compensating cationic charge to keep the overall framework neutral, and secondly, the material becomes hydrophilic.

1.2.1: Zeolite type A

Syntheses of zeolite type A were first time reported in 1958. Zeolite A has the double 4-ring (D4R) as a common SBU unit in its framework structure.

The composition of the zeolite A is

\[ \text{Na}_{12} \left[ \text{AlO}_2 \right]_{12} \left( \text{SiO}_2 \right)_{12} \] 27 H₂O

The Si/Al ratio in zeolite A is 1:1. The primary unit of zeolite A is made up of simple arrangement of polyhedra, each polyhedron being a three-dimensional array of (Si, Al) O₄ tetrahedra in a different geometric form. In zeolite A, twenty-four of these tetrahedra are joined to form a polyhedron which is called a sodalite cage [6]. The sodalite cage is often called a \( \beta \) cage. The sodalite unit has two types of faces, the square face and the hexagonal face. The square face consists of four oxygen atoms and has a mean free diameter, which is smaller than normal atomic dimensions. The hexagonal face consists of six oxygen atoms with a mean free diameter of 2.2 Å, which allow small molecules and ions to pass into the sodalite cage. The sodalite cages, in a primitive cubic arrangement, are joined via oxygen bridges to form double 4-ring (D4R) rather than sharing a single 4-ring. The central larger cavity, cubo-octahedron or a Type I 26-hedron, is called an \( \alpha \) cage with a diameter of 11 Å as shown in figure 1.3. Each central cavity is bounded by a ring of eight atoms with a free diameter of 4.2 Å. A framework structure
is formed by these two polyhedral; they share all their faces with each other. Figure 1.4 shows the linkage of these polyhedrals. This is called a space filling structure [1].

The unit cell in zeolite A is not a full unit cell and is often called ‘pseudo-unit cell’. The hydrated sodium form of Zeolite A contains 12 sodium ions per pseudo-unit cell. Out of these 12 sodium ions, 8 occupy Site I adjacent to the S6R openings to the β cages, 3 occupy Site II near the centre of the S8R openings to the large α cage and 1 is sited in the centre of the large cavity (α cage). Twenty seven water molecules are present in each pseudo-unit cell and 20 of these form a pentagonal dodecahedron, which lines the α cage. The same type of arrangement of water molecules is present in some clathrates. The remaining water molecules are in the β cages (~4) or held loosely inside clathrates with the help of the Na⁺ ions at the centre of the α cage [1].

Figure 1.3:  (a) α-cage (48 T-atoms)  
(b) β-cage or sodalite cage (24 T-atoms)
Figure 1.4: Building up zeolite structure
1.3 Zeolite Syntheses

The first synthetic zeolite levyne (levynite) was synthesised by Deville in 1862 by heating potassium silicate with sodium aluminate. Unfortunately, these experiments were fairly unreliable, until the work of Professor R. M. Barrer and co-workers in 1940. The first synthesis was reliably characterized by chemical analysis, optical properties and X-ray diffraction by Barrer.

Zeolites can be synthesised under a wide range of experimental conditions. Typically, they are prepared in Teflon-lined steel autoclaves under hydrothermal conditions with temperature ranging from 30° C to 250° C, and autogenous pressure of 30-910 bars. The variables, which affect the formation of a specific zeolite phase, are batch composition, Si/Al sources, Si/Al ratio, alkalinity, water content, inorganic cations, organic templates, solvent, temperature, aging, stirring and seeding. These variables are outlined below

1.3.1 Batch Composition

The batch composition of the reaction mixture is very important to determine the zeolite product formed. Breck’s work showed the effects of batch composition on the resulting phases [7]. In Na₂O-Al₂O₃-SiO₂-H₂O system the water contents were 90-98% at 100 °C. Zeolite A, X, Y and B were produced at different phases. If the water content was reduced to 60-85%, while maintaining the other conditions the same as above, the only zeolite HS (SOD) phase was obtained.

1.3.2 Si/Al Sources

In the synthesis of zeolites, mostly, soluble silicates and their hydrates, silica sols (30% by weight SiO₂), and commercial products such as Syton, Ludox are used to provide the silicon for the reaction mixture. Other less frequently materials used are volcanic stuff, sands, clays, silica gels, glasses and quartz.

Mostly, metal aluminates are used as a source of aluminium. Alternatively used sources for aluminium are freshly prepared Al(OH)₃, Al₂O₃ and AlO(OH) .
1.3.3 Si/Al Ratio

The structure and the composition of the zeolite depend upon the Si/Al ratio of the reaction mixture. A reaction mixture having low Si/Al ratio and strong alkalinity is used in the synthesis of zeolite A (LTA) and other zeolites with low Si/Al ratio (Si/Al \leq 5), whereas a gel of high Si/Al ratio and weak alkalinity or neutral medium is used for the preparation of high-silica zeolites (Si/Al >5). Typically, zeolite LTA is prepared with framework Si/Al ratio of 1. The Si/Al ratio of LTA could be increased up to 3 by using tetramethylammonium cations (TMA⁺).

1.3.4 Sources of Cations:

Alkali-metal hydroxides are commonly used as the alkali source in the synthesis of Al-rich zeolites under basic conditions. In 1961, tetramethylammonium (TMA) was first used by Barrer and Denny as an organic cation. The type of the cation plays an important role in the crystallization of zeolites [8]. Flanigen briefly explained the relationship between the relative sizes of the polyhedral cages and the related specific cations [9]. Besides, she also suggested two roles of alkali-metal cations in the preparation of zeolites. First, as the source of hydroxide ions, which are required for dissolution of silicate and aluminate species; and secondly as a limited structure-directing role.

1.3.5 Other Variables:

The important variables affecting the synthesis of zeolites are solvents, water contents, order of addition of reactant materials, small amount of salts and impurities, pressure, temperature of reaction, reaction time, aging, nature of mixing, stirring and seeding [10-14].

A microwave-assisted hydrothermal synthetic route can also be used as a substitute to a classical hydrothermal synthesis. This route is generally much faster, cleaner and more energy efficient than the other conventional methods. In 1988, microwave- synthesis of NaA (LTA) and ZSM-5 (MFI) was carried out by Mobil Oil Corp. [15]. The crystallisation was found to be significantly accelerated, when the gel was exposed to the microwave radiations. So far, a number of zeolites has been synthesised by using this route [16-20], such as zeolite A (LTA), faujasite (FAU), sodalite (SOD), analcime (ANA), beta (BEA) and ZSM-5 (MFI) etc.
1.4 Applications of Zeolites

The zeolites are the most generally used microporous material in industry due to the thermal stability, natural abundance and commercial values. The main applications of zeolites can be divided into three categories, catalysis, separation and ion-exchange.

1.4.1 - Catalysis

Catalysis is the major area of application for microporous materials, consisting mainly of the use of aluminosilicates zeolites for acid catalysis in the oil refining and petrochemical industries. The catalytic property of the zeolites is based on the formation of Bronsted and Lewis acid sites. In zeolite structure, Bronsted acid sites arise from the creation of hydroxyl group. The hydroxyls are produced by either ammonium or polyvalent cation exchange followed by calcination as the following equation shows:

\[ \text{NaZ}_\text{(s)} + \text{NH}_4^+ \text{(aq)} \rightarrow \text{NH}_4\text{Z}_\text{(s)} + \text{Na}_\text{(aq)} \]

\[ \text{NH}_4\text{Z}_\text{(s)} \rightarrow \text{NH}_3\text{(g)} + \text{HZ}_\text{(s)} \]

The major employment and massive spread of zeolite in industry is accounted by the association between the zeolites properties and their catalytic functionality, for instance the variable pore size within a certain framework produce selected products as shown in figure.

![Figure 1.5: Shape selectivity of zeolites [21]](image-url)
1.4.2 - Adsorption

The voids in the zeolite contain water molecules and cations. After the removal of these water molecules, void space is created which can be taken by other molecules. These voids are of defined molecular dimension that allow the access of specific molecules on the basis of polarity and shape. Adsorption is controlled by the aperture size of the pore entrance. The dimension of the entrance depends on the number of tetrahedrally coordinated atoms and linking oxygen atoms making the ring i.e 6, 8 and 10 membered rings. Si/Al ratio in zeolites can vary from 1 to infinity. In zeolite high aluminium shows hydrophilic tendency while high silica zeolites tend to be hydrophobic. Hence, the sorption properties are influenced by the polarity of the zeolites. The negative charge of the framework and the compensating positive charge of the extra-framework cation in the cavities create strong electrostatic field with in the pore system, which interact the molecules having permanent dipole or local dipole moment. These molecules with dipole moment will be sorbed more energetically compared to the similar molecules of the same size without a dipole moment. Thus, zeolites are very effective in gas-solid chromatography. Zeolites are also used in liquid phase separation, gas chromatography and as water absorbent.

1.4.3 Ion-exchange in zeolites

Ion-exchange occurs by the replacement of extra-framework cations present in a microporous material for cations present in external solutions or melts the microporous material is immersed. In 1858, Eichorn showed the reversible cation-exchange in the natural zeolites chabazite and natrolite, which was the first property, scientifically studied in zeolites [22]. In the nineteenth century, Gans synthesised aluminosilicate materials capable of water softening [23]. He called them “Permutits” and these materials were used as industrial and domestic water softeners. They were also used for many years in the nuclear industry for the treatment of the nuclear chemical waste.

Zeolites are crystalline by the definition and are composed of tetrahedral \([\text{SiO}_4]^4\) and \([\text{AlO}_4]^3\) connected to the neighbouring tetrahedral with oxygen atom. This generates a net negative charge on the framework; hence each \(\text{Al}^{3+}\) cation in the framework requires a compensating cationic charge to ensure neutrality. The compensating charges usually originate from extra-framework cations within the structure to keep the overall
framework neutral. In 1930s Barrer did detailed studies of zeolites. In 1950s he and his co-worker established the fundamentals of equilibrium and kinetic thermodynamic interpretations of zeolite cation exchange properties [24]. In 1968 the first conference on ion-exchange was held in London. In this conference the only paper was presented by Sherry on cation equilibria in “zeolite T” [25]. There were, however, three papers on zeolite cation exchange kinetics. These were presented by Rees and Brooke on chabazite, Hoinkis and Levi on zeolite FAU and LTA and Dyer and Gettins also on LTA and FAU zeolite [26, 27, 28]. The zeolite study became more interesting after the realization that these materials were much better for cation exchange than organic resin exchangers because they maintained their framework structure on contact with water. Studies showed that zeolites also have the ability to selectively remove the specific cations from the mixtures even when the competing cations are present at higher concentrations. This property of zeolites enhances the interest in natural zeolites for water treatment and environmental cleanup.

1.4.1 Ion-Exchange equilibria

**Introduction to the theory**

The following theoretical approach assumes that:

(a) The system is in a true state of equilibrium:

(b) The exchange process is fully reversible (one representing the forward exchange and another reverse exchange) that needs to be examined separately. The process must have different standard Gibbs energies also, in the reversible case; the forward and reverse reactions have different Gibbs energies although the difference is only in sign. The following theory is a rigorous thermodynamic approach and is, by its nature, exact and can be applied to all cation exchanger [29,30].

**The binary ion exchange process**

The exchange between $\text{A}^{Z_A}$, initially in the solution (the ingoing ion) and $\text{B}^{Z_B}$, initially in the zeolite (the outgoing or counter ion) can be written as:

$$Z_B^{-}A^{Z_A} + Z_A^{-}B^{Z_B} \leftrightarrow Z_B^{-}A^{Z_A} + Z_A^{-}B^{Z_B}$$
Where $Z_{A,B}$ are the valencies of the ions and the characters with a bar relate to a cation inside the zeolite crystal. Simple examples are:

For a univalent exchange

$$Na^+ + \overline{K}^+ \leftrightarrow \overline{Na}^+ + K^+$$

For a divalent exchange

$$2Na^+ + \overline{Ca}^{2+} \leftrightarrow 2\overline{Na}^+ + Ca^{2+}$$

These stoichiometric reactions can be explained by an ion exchange isotherm. This is a pictorial representation of the equilibrium concentrations of cations in solution and zeolite phase. It should ensure that ion exchange equilibrium has been reached. It can be checked by performing some simple kinetics measurements. In zeolites having low framework densities, it takes about a week to establish equilibrium in uni-univalent exchanges. After the confirmation of equilibrium time the isotherm can be plotted as follows. Known amount of zeolite is put in a container with solutions of both the cations (\(A^{ZA}\) ingoing cations and \(B^{ZB}\) outgoing cations). These solutions contain different proportion of cations. Although having different amount of cations but should be a total constant normality (N). Ratio between solution and zeolite should not be less than 20. The detailed experimental methodology has been fully described by Dyer [31] and Townsend [32].

Isotherm can be plotted which records the equivalent fractions (\(A_S\)) of the ingoing cation in solution against its equivalent fraction in zeolite (\(A_Z\)).

The equivalent fraction (\(A_S\)) of \(A^{ZA}\) in solution can be defined as:

$$A_S = \frac{Z_A m_A}{Z_A m_A + Z_B m_B}$$

Where \(m_{A,B}\) are the concentrations (mole/dm³) of the cations in the solution.

The equivalent fraction in the zeolite is:

$$A_Z = \frac{Z_A M_A}{Z_A M_A + Z_B M_B}$$

Where \(M_{A,B}\) are the concentrations of the ions in the solid phase.
Idealised isotherm shapes are shown in Figure 1.6. They give pictorial indications of the relative preferences of the cations for the solid and solution phases. If zeolite has equal affinity for both cations then isotherm would be a straight line (dotted line in figure 1.6). Isotherm (2) is showing that A remains in the solution. It means that A is unable to displace cation B from the zeolite at the conditions of temperature and pressure of the experiment. Isotherm (3) shape is adopted when A replaces B from the zeolite.

The selectivity of the zeolite for an ion can be expressed quantitatively as a separation factor ($\alpha$) where

$$\alpha = \frac{A_Z m_B}{B_Z m_A}$$

Where, by definition,

$$B_Z = 1 - A_Z$$

The value of $\alpha$ can be calculated for isotherm 1 (Figure 1.6), dividing area (a) by area (b). Zeolite will be selective for $A_Z$, when $\alpha > Z_A / Z_B$, when $\alpha = Z_A / Z_B$ zeolite show no preference and when $\alpha < Z_A / Z_B$ zeolite is selective for $B^ZB$ [1].
Distribution coefficient \((K_d)\):

The solid solution distribution coefficient is a relation between adsorbed metal concentration and those present in the solution. Distribution coefficient is defined as the concentration of the radionuclide per unit weight of solid divided by the concentration of a radionuclide per unit volume in the solution per unit volume.

Distribution coefficient can be written as

\[
K_d = \frac{[A_i - A_t]}{[A_t \cdot V/M]}
\]

Where \(A_i\) = initial concentration of solution, \(A_t\) = concentration of solution at equilibrium,

\(V\) = volume of solution \(M\) = weight of zeolite.

1.5 Nuclear Decommissioning Authority (NDA)

Nuclear decommissioning authority is a non-departmental public body established under the energy act 2004. The responsibilities of NDA are decommissioning and clean up of the civil public sector nuclear sites in the United Kingdom. Department for Energy and Climate Change (DECC) which is a Government department, is sponsoring NDA while in Scotland they are responsible to Scottish Ministers [33].

1.5.1 Strategic Objectives of NDA

Strategic themes of NDA have been broken into a number of strategic objectives. Following are the medium term objectives

i. Site Restoration

ii. Integrated waste management

iii. Manage nuclear materials

iv. Reprocessing spent fuels

v. Business optimisation

vi. Critical enablers
i- **Site Restoration**

Site restoration includes remediate hazardous materials from the legacy of early defence programmes, first generation reprocessing, waste handling at Sellafield, maintaining essential infrastructure, capability across the site to ensure ongoing safe and effective performance, the decommission of redundant facilities at Sellafield, to sustain operations of key supporting plants and services at Sellafield plant, To place Magnox reactors into care and maintenance and deliver Dounreay site to an interim end state.

ii- **Integrated Waste Management**

Including implement storage and disposal arrangements. The following are included in integrated waste management.

To provide a physical and geographical discarding site (Geological Disposal Facility (GDF)), manage Low Level Waste (LLW), manage Intermediate Level Waste (ILW) and manage High Level Waste (HLW)

iii- **Managing Nuclear Materials**

Managing nuclear materials, deals with plutonium and uranium in a safe and secure way. This includes the management of plutonium and uranium stocks and optimise value realisation.

iv- **Reprocessing spent fuels**

Spent fuel is reprocessed and managed in a safe and secure way. In Magnox power plants spent Magnox fuel handled and disposed, optimise the management of oxide fuels, finally, manage and ultimately dispose of non-standard, exotic fuels.

v- **Business optimisation**

Business optimisation deals with how to maximise commercial values, determine commercial future of Springfield and Capenhurst and dispose of NDA assets that are no longer required.
vi- Critical enablers

The main aims of critical enablers are to build an effective industry, optimise capability within the NDA and the supply chain to deliver our mission, build and maintain the confidence of the stakeholders and provide national nuclear infrastructure.

1.4.2 Site Licence Companies (SLCs)

NDA does not directly manage these sites. They have the contract with licensed operators; Site Licence companies (SLCs). These companies are responsible to manage the sites that include preparing site plans, performing and sub-contracting work. Parent Body Organisations (PBOs) have shares in SLCs for the duration of their contract with the NDA. The PBO is accountable for managing the delivery of site programmes. Following seven Site Licence Companies (SLCs)

<table>
<thead>
<tr>
<th>Companies</th>
<th>Parent Body Organisation (PBOs)</th>
<th>Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Sellafield Limited</td>
<td>Nuclear Management Partners Limited (NMP, which is a consortium comprising URS, AMEC and AREVA</td>
<td>Sellafield Calder Windscale Capenhurst</td>
</tr>
<tr>
<td>2. Magnox North Limited</td>
<td>Reactor Sites Management Company Limited, which is owned by Energy Solutions Inc.</td>
<td>Magnox North Support Office Chapelcross Hunterston A Oldbury Trawsfynydd Wylfa</td>
</tr>
<tr>
<td>Companies</td>
<td>Parent Body Organisation (PBOs)</td>
<td>Sites</td>
</tr>
<tr>
<td>-------------------------------</td>
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<td>--------------------------------------------</td>
</tr>
<tr>
<td>3. Magnox South Limited</td>
<td>Reactor Sites Management Company Limited, which is owned by Energy Solutions Inc</td>
<td>Magnox South Support Office Berkeley Bradwell Dungeness A Hinkley Point A Sizewell A</td>
</tr>
<tr>
<td>4. Dounreay Site Restoration Limited</td>
<td>UKAEA limited, which is owned by Babcock International Group Plc</td>
<td>Dounreay</td>
</tr>
<tr>
<td>5. Research Sites Restoration Limited</td>
<td>UKAEA limited, which is owned by Babcock International Group Plc</td>
<td>Harwell Winfrith</td>
</tr>
<tr>
<td>6. Low Level Waste Repository Limited</td>
<td>UK Nuclear Waste Management Limited, which is a consortium led by URS Washington Division and including Studsvick, AREVA and Serco Assurance</td>
<td>LLW Repository</td>
</tr>
<tr>
<td>7. Springfields Fuels Limited</td>
<td>Westinghouse Electric UK Limited, which is part of the Toshiba Group</td>
<td>Springfields</td>
</tr>
</tbody>
</table>

**Table 1.1 Site Licence Companies (SCLs)**
1.6 Magnox Nuclear Power Reactor

Magnox is an old type of nuclear power reactor in the world. It is a British designed reactor and two of them were exported abroad, one to Japan and one to Italy. The first reactor was built at Calder Hall, and opened by the Queen on 17th October 1956. They were originally designed to run for 20 to 25 years they are now 30 and 45 years old and still running in United Kingdom.

The Magnox reactor was named after the magnesium alloy used to encase the fuel, which is natural uranium metal. Fuel elements consisting of fuel rods encased in Magnox cans are loaded into vertical channels in a core constructed of graphite blocks. Further vertical channels contain control rods which can be inserted or withdrawn from the core to adjust the rate of the fission process and, therefore, the heat outputs. The whole assembly is cooled by blowing carbon dioxide gas past the fuel cans, which are specially designed to enhance heat transfer. The hot gas then converts water to steam in a steam generator. Early designs used a steel pressure vessel, which was surrounded by a thick concrete radiation shield. In later designs, a dual-purpose concrete pressure vessel and radiation shield was used.

In order to improve the cost effectiveness of this type of reactor, it was necessary to go to higher temperatures to achieve higher thermal efficiencies and higher power densities to reduce capital costs. This entailed increase in cooling gas pressure and changing from Magnox to stainless steel cladding and from uranium metal to uranium dioxide fuel. This in turn led to the need for an increase in the proportion of $\text{U}_{235}$ in the fuel. The resulting design, known as the Advanced Gas-Cooled Reactor, or AGR, still uses graphite as the moderator and, as in the later Magnox designs; the steam generators and gas circulators are placed within a combined concrete pressure vessel or radiation shield.

There are four other types of reactors PWR, BWR, CANDU and RBMK. PWR and BWR uses light water as moderator, RBMK uses graphite like the first two reactors (Magnox and AGR) and CANDU is the only design of heavy water moderator reactor in commercial use. This reactor was designed in Canada and subsequently exported to several countries.
Figure 1.5: Magnox reactor schematic diagram [34]
<table>
<thead>
<tr>
<th>Stations</th>
<th>Location</th>
<th>Licensee</th>
<th>Current Status</th>
<th>Start of Generation</th>
<th>Cessation of Generation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berkeley</td>
<td>Gloucestershire</td>
<td>Magnox South Ltd</td>
<td>Decommissioning</td>
<td>1962</td>
<td>1989</td>
</tr>
<tr>
<td>Bradwell</td>
<td>Essex</td>
<td>Magnox South Ltd</td>
<td>Decommissioning</td>
<td>1962</td>
<td>2002</td>
</tr>
<tr>
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<td>Cumbria</td>
<td>Sellafield Ltd</td>
<td>Decommissioning</td>
<td>1956</td>
<td>2003</td>
</tr>
<tr>
<td>Chapelcross</td>
<td>Dumfrieshire</td>
<td>Magnox North Ltd</td>
<td>Decommissioning</td>
<td>1959</td>
<td>2004</td>
</tr>
<tr>
<td>Dungeness A</td>
<td>Kent</td>
<td>Magnox South Ltd</td>
<td>Decommissioning</td>
<td>1965</td>
<td>2006</td>
</tr>
<tr>
<td>Hinkley Point A</td>
<td>Somerset</td>
<td>Magnox South Ltd</td>
<td>Shutdown</td>
<td>1965</td>
<td>2000</td>
</tr>
<tr>
<td>Hunterston A</td>
<td>Strathclyde</td>
<td>Magnox North Ltd</td>
<td>Decommissioning</td>
<td>1965</td>
<td>1989</td>
</tr>
<tr>
<td>Sizewell A</td>
<td>Suffolk</td>
<td>Magnox South Ltd</td>
<td>Defuelling</td>
<td>1966</td>
<td>2006</td>
</tr>
<tr>
<td>Trawsfynydd</td>
<td>Gwynedd</td>
<td>Magnox North Ltd</td>
<td>Decommissioning</td>
<td>1965</td>
<td>1991</td>
</tr>
<tr>
<td>Oldbury</td>
<td>South Glous-</td>
<td>Magnox North Ltd</td>
<td>operating</td>
<td>1968</td>
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<tr>
<td>Wylfa</td>
<td>Gwynedd</td>
<td>Magnox North Ltd</td>
<td>operating</td>
<td>1971</td>
<td>----</td>
</tr>
</tbody>
</table>

Table 1.2 Magnox power stations constructed in the UK
1.7 Radioactive Wastes

Radioactive waste is a waste product containing radioactive material. Radioactive waste consists of different types of materials, which is produced by the nuclear industry. According to the amount and types of radioactivity, they are classified as following

- Low level wastes
- Medium level wastes
- High level wastes

Radioactivity reduces over the time, so in waste management time is another factor. This depends on the kinds of radioactive isotopes present in them and half lives of each of those isotopes. The half life is the time takes for a given radioactive isotope to lose half of its radioactivity. The various radioactive isotopes have half lives ranging from hours to thousands of years for high level wastes from nuclear power plants and nuclear weapons reprocessing. The rate of decay of an isotope is inversely proportional to its half life; a short half life means its decays rapidly [35].

i. Low Level Wastes (LLW)

This type of waste is generated from industry, hospitals, laboratories and the nuclear fuel cycle. Low level waste consists of clothing, papers, tools filters and rags etc. LLW contains small amount of short-lived radioactive isotopes. It is not difficult to handle but must be disposed of more carefully than normal garbage. It is packed or incinerated (in a closed container) before disposal and then buried in shallow landfill sites. LLW comprises 90% of the volume but only 1% of the radioactivity of all radioactive waste.

ii. Intermediate Level Waste (ILW)

ILW contains higher amounts of radioactivity and may require special shielding. It typically contains chemical sludge resins and reactor components, as well as contaminated materials from reactor decommissioning. ILW makes up 7% of the volume and has 4% of the radioactivity of all radioactive waste. It is solidified in concrete or
bitumen before disposal. Usually short lived waste (mainly from reactor) is buried and long lived waste (from reprocessing nuclear fuel) will be disposed of deep underground.

iii. High-level Waste (HLW)

HLW is a type of nuclear waste produced by the reprocessing of spent nuclear fuel. It contains many of the fission products and transuranic elements, generated in the reactor core and is the highest activity type of nuclear waste. A 1000-MWe nuclear power plant produces about 27 tonnes of spent nuclear fuel every year. HLW holds 95% of the total radioactivity produced in the nuclear power process. It produces a considerable amount of heat and requires cooling, as well as special shielding required before handling and transport. During the reprocessing of the fuel, the separated waste is vitrified by incorporating it into borosilicate glass which is packed inside stainless steel canisters for eventually disposal deep underground.

On the other hand, if the used reactor fuel is not reprocessed, then all the highly-radioactive isotopes remain in it, and the whole fuel assemblies are treated as high level waste. This used fuel comprises about nine times the volume of equivalent vitrified high-level waste which results from reprocessing and which is encapsulated before disposal.

Every year nuclear power generation produces about 200,000 m$^3$ of low and intermediate level radioactive waste, and about 10,000 m$^3$ of high-level wastes including used fuel. A typical 1000MWe light water reactor will generate (directly or indirectly) 200-350 m$^3$ low and intermediate level waste per year. It will also generates about 20 m$^3$ (27 tonnes) of used fuel per year, which relate to a 75 m$^3$ disposal volume following encapsulation if it is treated as waste. If used fuel is reprocessed, only 3 m$^3$ of vitrified waste is produced, which is equivalent to a 28m$^3$ disposal volume following placement in a disposal canister [36].
1.8 – Project Aims

The main focus of this work is to remove the cobalt ions by using zeolites from the nuclear chemical waste, which contains higher concentration of magnesium cations as compared to the cobalt. The stability of the zeolites in acidic media was also studied. For this purpose following zeolites were synthesised and characterised by using different techniques.

i) Zeolite A
ii) ZK-4
iii) Zeolite Alpha
iv) Clinoptilolite

The main reason to choose these above first three zeolites was low Si/Al ratio and higher ratio of extra-framework cations. Clinoptilolite is widely used in nuclear waste treatment so it was also included in this work.
CHAPTER TWO

CHARACTERISATION TECHNIQUES

The following techniques were used to characterise the samples

1. X-ray Diffraction
2. Solid State Nuclear Magnetic Resonance Spectroscopy
3. Scanning Electron Microscope (S.E.M)
4. Inductively Coupled Plasma Spectrometer (I.C.P. Spectrometer)

2.1 X-ray Diffraction

Zeolite materials, being crystalline solids have a characteristic diffraction pattern that can be used to identify their exact structure and to determine their degree of crystallinity. The diffractions of X-rays from zeolite crystallites produce a scattering pattern which is specific of the periodic arrangement of regular arrays of atoms or ions located within the zeolite structure. Each zeolite has its own specific pattern that can be used as reference for the determination of solid crystal phase and it is used as fingerprint for every zeolite. This technique can also show whether the solid sample is amorphous or crystalline phase. The purity of the solid crystal will be measured by comparing the X-ray diffractogram pattern of the sample with X-ray diffractogram pattern of the standard sample.

The principal equation used in the analysis of an X-ray powder pattern is the Bragg law which states that:

\[ n\lambda = 2d_{hkl} \sin \theta_{hkl} \]

where \( n \) is the order of diffraction (\( n = 1, 2, \ldots \)), \( \lambda \) is the wavelength of the incident X-ray beam (\( \lambda = 1.54178 \ \text{Å} \) for Cu K\( \alpha \)), \( \theta_{hkl} \) is the Bragg angle between the incident X-ray beam and the crystal planes and \( d_{hkl} \) is the interplanar distance on a set of planes (Figure 2.1).
A powder diffractometer is an instrument for studying crystalline materials by measuring the way in which they diffract X-ray of known wavelength. In the diffractometer, the intensity of a diffracted beam is measured directly by an electronic counter, which counts the number of pulses per unit time. This number is directly proportional to the intensity of the diffracted X-ray beam entering the counter. In the diffractometer, a monochromatic or filtered radiation is used and the X-ray detector is placed on the circumference of a circle centered on the powdered specimen as depicted in figure 2.2. A powder sample "C" in the form of flat plate is supported on a table "H", which can be rotated about an axis "O" perpendicular to the plane of the drawing. The X-ray source "S" is the line focal spot on the target "T" of the X-ray tube. It is also normal to the plane of the drawing and, therefore, parallel to the diffractometer axis "O". X-rays diverge from the source and are diffracted by the sample to form a convergent diffracted beam which comes to focus at the slit "F" and then enters the counter "G". "A" and "B" are special slits which define and collimate the incident and diffracted beams, respectively. A filter is usually placed in a special holder in the path of the diffracted rather than the incident beam. This filter not only suppresses the K\(\beta\) radiation but also decreases the background radiation originating in the specimen.

**Figure (2.2):** Schematic of X-ray powder diffractometer [36].
The receiving slits and counter are supported on the carriage "E", which is rotated about the axis "O". The supports "E" and "H" are mechanically coupled so that a rotation of the counter through an angle $2\theta^\circ$ is automatically accompanied by rotation of the sample through an angle $\theta^\circ$. This coupling ensures, that the angles of incidence on and reflection from the flat sample will always be equal to one another and equal to half the total angle of diffraction, an arrangement is necessary to preserve focusing conditions. The counter may be power driven at a constant angular velocity about the diffractometer axis (a continuous mode) or in step scanning mode.

Powder sample is placed in a holder of a glass or plastic plate (amorphous material), then compacting it under sufficient pressure to cause cohesion without use of binder and smoothing off the surface. The powder should be grounded extremely fine to size of about 10 $\mu$ or less. If the surface of the sample is rough and the linear absorption coefficient is high, then the intensities of low-angle reflections will be low because of the absorption of the diffracted beams in each projecting portion of the surface. The only way to avoid that is by using a flat surfaced compact of very fine powders or a sample with a polished surface.

The powder X-ray diffraction patterns of the samples were recorded on a Philips X’pert Pro PW3719 X-ray powder diffractometer fitted with an Anton Paar XRK 900 furnace as shown in figure (2.3). A $2\theta$ interval between 2° to 60° was used with a step size of 0.0167° and a step time of 64 seconds. The diffractometer was equipped with Ni-filtered Cu Kα radiation source (8978 eV or $\lambda = 1.5418$ Å). The X-ray source was operated at 30 mA and 40 kV. Sample preparation for the X-ray analysis involved gentle grinding of the solid into a fine powder and packing of approximately 0.3 - 0.5 g of the sample into an aluminium sample holder with light compression to make it flat and tight. The X-ray diffraction patterns of the sample were then recorded on a PC computer with X’pert HighScore Plus software and saved in XRDML text format for further manipulation and processing. A search and match phase was conducted with the Atlas of Zeolite Structure Types [36].
2.2 Solid State Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) is a spectroscopic tool based on the interaction between radio frequency (rf) electromagnetic radiation and the nuclear spin energy levels of nuclei placed in large magnetic fields according to the Bohr frequency condition:

\[ \Delta E = h \nu \]

where \( \Delta E \) is the difference in energy between two quantized states, \( h \) is Planck’s constant and \( \nu \) is the frequency of the light.

From its modest beginnings in 1945, through the discovery of the chemical shift effect in 1949, NMR is now every bit as useful to the modern day chemist as the older-established techniques of infra-red (IR) and ultraviolet (UV). Furthermore, it is complementary to diffraction methods, since it gives information on local environments and mobility that are not available from X-ray diffraction, which yields only the space and time-averaged positions of atoms.
High-resolution solid state NMR spectra can provide the same type of information that is available from corresponding solution NMR spectra, but a number of special techniques and equipment are needed, including magic-angle spinning (MAS), cross polarisation (CP), special 2D experiments and enhanced probe electronics, etc. These can be described quantum mechanically by appropriate Hamiltonians. The total Hamiltonian \( H \) for calculating the NMR spectra of a diamagnetic non-conducting solid is given by:

\[
H = H_Z + H_{CSA} + H_D + H_Q + H_J
\]

Where components represent different interactions (their relative strength is also presented):

- \( H_Z \) Zeeman Splitting \( 10^6-10^9 \)
- \( H_{CSA} \) Chemical Shift Anisotropy \( 0-10^5 \)
- \( H_D \) Dipolar Interactions \( 0-10^6 \)
- \( H_Q \) Quadrupolar interactions \( 0-10^5 \)
- \( H_J \) Spin-spin coupling \( 0-10^4 \)

Both CSA and heteronuclear dipolar interactions can be averaged out by rotating the polycrystalline sample around the axis inclined at 54.74º with respect to the static magnetic field. This technique is known as magic-angle spinning (MAS). This can be explained by the presence of the geometric part in the respective Hamiltonians: \((3\cos^2 \theta-1)\). This term is zero when \( \theta = 54.74^\circ \). So, in theory, if a solid sample is made to spin rapidly at 54°44’ to the field \( B_0 \), the majority of all anisotropic broadenings can be removed. See figure (2.4).

Figure (2.4): MAS in solid state NMR.

Oxygen, silicon and aluminium are the basic constitute of aluminosilicate framework and the NMR measurements are carried out via the naturally occurring isotopes, \(^{17}\text{O}, \ ^{29}\text{Si} \) and \(^{27}\text{Al} \). However, \(^{17}\text{O} \) has a very low natural abundance of only 0.037% and a quadrupole moment giving rise to line broadening which makes the application of \(^{17}\text{O} \) NMR even more difficult. In contrast to \(^{17}\text{O} \), the \(^{27}\text{Al} \) isotope is 100% abundant but also has a low quadrupole moment. \(^{29}\text{Si} \) is 4.7% abundant and has a nuclear spin of \( I = \frac{1}{2} \) and thus gives rise to relatively narrow
resonance lines. So, Magic angle spinning (MAS) technique is carried out in these experiments which removes the line broadening and produce highly resolved NMR spectra, providing a large number of structural information.

The individual peaks of $^{29}$Si NMR spectrum are characterized by three main parameters, which can be readily extracted from the highly resolved spectrum: the chemical shift, the intensity and linewidth. The most informative parameter is the chemical shift which reflects the immediate structural surroundings of silicon atoms and is determined by the number of Si and Al atoms attached to the SiO$_4$ unit being considered. Replacement of Si with Al results in low-field shifts. The peak intensity provides direct information on the quantitative proportions of the different Si sites. The linewidth is mainly affected by dispersion of chemical shift due to structural disorder, but paramagnetic impurities may also cause line broadening. In general, narrow peaks are observed for well ordered systems while disordered systems are characterized by large linewidths.

$^{29}$Si MAS NMR spectrum may consist one or five possibilities signal that correspond to five possible silicon environments in the zeolite framework SiO$_4$ [nSi, (4-n)Al], (n = 0-4). With increasing number of Al atoms in the first tetrahedral coordination sphere of the silicon atom, the peaks are systematically shifted to low field. Silicon in zeolite framework can be classified into five environments depending on the total silicon and aluminium that coordinated to tetrahedral SiO$_4$ i.e, Si(0Al) represents Si(OSi)$_4$, Si(1Al) represents Si(OSi)$_3$(OAl), Si(2Al) represents Si(OSi)$_2$(OAl)$_2$, Si(3Al) represents Si(OSi)(OAl)$_3$ and Si(4Al) represents for Si(OAl)$_4$. See figure (2.5).

Provided that the $^{29}$Si NMR spectrum is correctly interpreted in terms of Si(nAl) units and no Al-O-Al linkages are present in the zeolite studied due to Loewenstein’s rule, the quantitative ratio of tetrahedral Si and Al in the zeolite framework can be directly calculated from five peak intensities according to the following equation:

$$\text{Si/Al} = \frac{I_4 + I_3 + I_2 + I_1 + I_0}{I_4 + \frac{1}{4} I_3 + \frac{1}{2} I_2 + \frac{3}{4} I_1}$$

Where $I$ is the peak intensity of the NMR signal referred to Si(nAl) units, and $n$ indicates the number of coordinated Al atoms in the first coordinated SiO$_2$ sphere for the given peak.
Figure (2.5): $^{29}\text{Si}$ Solid state-NMR signals for Zeolite sample.

Figure (2.6) shows the ranges of $^{29}\text{Si}$ chemical shift for each of the five $Q^4(n\text{Al})$; $\text{SiO}_4[n\text{Si},(4-n)\text{Al}]$ in solid aluminosilicate. The replacement of one or more Si atoms by Al atoms in coordination sphere results in significant low-field shift, i.e. give less negative $\delta$ value. Besides, the increasing of Si/Al ratio will increase the signal intensity to higher field. In General, each substitution Si-O-Si by Si-O-Al brings about a deshielding of ca 5 ppm for the central silicon atom. A detailed knowledge of the types and quantitative distribution of the various $Q^n(m\text{Al})$ structural groups provide an important basis for obtaining further information on the aluminosilicate structure, especially on the composition (Si/Al ratio) and silicon aluminium ordering of the framework [37, 38].

Figure (2.6): Range of $^{29}\text{Si}$ chemical shifts of $Q^4(n\text{Al})$ units in aluminosilicates [37, 38].
There are two features which make $^{27}$Al a very favourable nucleus for NMR investigations: the 100% natural abundance and the fast relaxation generally observed for quadrupolar nuclei. The quadrupole interaction parameters may provide information on the local charge distribution around the $^{27}$Al, on coordination number and symmetry of the AlO$_n$ polyhedra in aluminosilicates. $^{27}$Al NMR studies of zeolites have also been carried out extensively, because it is the incorporation of aluminium in tetrahedral framework sites that determine the catalytic activity and hydrothermal stability. The quadrupolar character of the $^{27}$Al nucleus ($I = 5/2$) results in broader peaks than those obtained for $^{29}$Si, but because aluminium atoms can exist in very different environment (four-, five- and six-fold coordination to oxygen) these resonances appear separated in the spectra. Typical approximate chemical shifts in zeolites are: tetrahedral framework aluminium at 50-60 ppm, five-fold coordinated non-framework aluminium species at 30 ppm and octahedral framework aluminium species at 0 ppm [37, 39, 40].

![Diagram](image)

**Figure (2.7):** Range of $^{28}$Al chemical shifts in aluminosilicates.

The NMR spectra were obtained at 9.4 Tesla on a Bruker Avance III-400 spectrometer using 4mm ZrO$_2$ rotors at room temperature. The spectrometer consists of the following subunits: Operator console including the host computer, monitor, keyboard, and BSMS keyboard, console containing the electronic hardware, and magnet system including the shim system,
preamplifiers (HPPR) and probe. All aspects of the spectrometer operation are controlled from the operator console. The design and implementation of experiments as well as the analysis of data are controlled by commands entered by the operator at the console. The host computer runs the Topspin program (version 2.1) and handles all the data analysis and storage. All operations relevant to data acquisition are controlled by a second computing system called the Acquisition Control System (AQS) housed within the console itself [39]. Figures (2.8, 9 and 10) and table (2.1) show the main parts of NMR spectrometer, NMR spectrometer which was used, and the experimental conditions used for $^{27}$Al and $^{29}$Si MAS-NMR respectively.

*Figure (2.8):* Photo of Magnet, Shim System, Probe and HPPR [41]
Figure (2.9): The main parts of NMR spectrometer [42].
2.3 Scanning Electron Microscopy

Scanning electron microscope is very helpful to see the fine details of the interior structure of the specimens which requires high magnifications. In contrast to optical microscopes, scanning electron microscope (SEM) is able to achieve magnification of 80,000, which make it the perfect tool to analyze and study the surface of specimens over a wide range of magnifications. It can provide topographical, compositional and crystallographic information. The basic theory of any SEM is based on the focused beam of electrons, being either scanned across the surface of a specimen to form an image, or stopped on a fixed location to perform an analytical function. The interaction of the electron beam gives secondary electrons, backscattered electrons, Auger electrons, characteristic X-rays, and photons of various energies. The backscattered and secondary electrons observed by their respective detectors, are amplified and are responsible for imaging. Secondary electrons mainly provide surface
topographic imaging. Information comes from the surface and the portion of the specimen close to the surface.

Energy dispersive X-ray spectroscopy (EDX) is an analytical tool, usually attached to the SEM used for chemical characterization. The specimen contains unexcited electrons around the nucleus. The incident beam, however, excites an electron in an inner shell, prompting its ejection. An electron from the outer, higher energy shell fills the gap, and the excess energy of that electron is released in the form of an X-ray. The released X-ray creates spectral lines that are highly specific to individual elements [43].

Figure 2.11 Scanning electron microscope Quanta™ 250 [44]
2.4 Inductively Coupled Plasma Spectrometer (I.C.P. Spectrometer)

Inductively coupled plasma atomic emission spectroscopy also referred to as inductively coupled plasma optical emission spectroscopy, is an analytical technique used for the detection of trace metals. This technique uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission depends upon the concentration of the sample.

The ICP-AES consists of two parts, first called ICP and the second is optical spectrometer. The ICP torch composed of three concentric quartz glass tubes. The output or work coil of the radio frequency generator surrounds part of this torch. Argon gas is mostly used to create plasma.

When the torch is switched on, an intense electromagnetic field is produced within the coil by the high power radio frequency signal flowing in the coil. This RF signal is produced by the RF generator which is effectively a high power radio transmitter driving the work coil. The argon gas flowing through the torch is ignited to start the ionization process. The argon gas is ionized in the intense electromagnetic field and flows toward the magnetic field of the RF coil. A stable, high temperature plasma is generated due to the inelastic collisions between the neutral argon atoms and the charged particles. A peristaltic pump delivers an aqueous sample into a nebulizer. This sample is atomized and introduced inside the plasma flame. This sample collides with the electrons and charged ions in the plasma and broken down into charged ions. The various molecules break up into their respective atoms which then lose electrons and recombine repeatedly in the plasma, giving off radiation at the characteristics wavelengths of the elements involved. After the light is separated into different wavelengths the light intensity is measured with a photomultiplier tube. The intensity of each line is then compared to previously measured intensities of known concentrations of the elements, and their concentrations are then computed by interpolation along the calibration lines [45].
Figure 2.12: ICP spectrometer [46]
CHAPTER THREE
EXPERIMENTAL WORK

Following four types of zeolites were prepared for ion-exchange

1. Zeolite A
2. ZK-4
3. Zeolite Alpha
4. Clinoptilolite (Natural zeolite)

3.1 Synthesis of Zeolite A:

The synthetic type A zeolite was prepared as the sodium form by the crystallization of sodium aluminate gels [47]. For the synthesis of zeolite A 0.723g NaOH was completely dissolved in 80.0042 grams deionised water (solution A) and divided into two equal volumes. In the one-half of the solution A, 8.258g sodium aluminate was completely mixed and a clear mixture obtained. I mixed 15.49 grams sodium metasilicate in the second half of the solution A. Then silicate solution was quickly mixed into aluminate solution and a homogeneous thick gel formed. Finally this mixture is placed at 100 °C for 4 hours. For crystallization the gel was removed from the heat source and cooled below 30 °C, filtered and washed with deionised water until pH of the filtrate was below 9. The final product was placed in a watch glass and kept at 80 °C overnight.

For the purpose of characterization of the product XRD, TGA and elemental analysis were done. The following formula was derived after the above analysis

$$\text{Na}_{0.833}\text{H}_{0.167}[\text{AlSiO}_4] \times 1.79\text{H}_2\text{O}$$
Figure 3.1: XRD pattern of Zeolite A

Figure 3.2: TGA of zeolite A

Figure 3.3: ESEM picture of Zeolite A
3.1.2 Cations selectivity of Zeolite A:

Zeolite A was treated with different solutions having different concentrations of cations. Six types of solutions were prepared in deionised water to check the competition between cobalt and magnesium. In each experiment 0.05 grams of zeolite A was used and number of moles of sodium in that amount of zeolite is $2.44 \times 10^{-4}$ moles. In experiments A and B single solutions of cobalt and magnesium was used respectively. In the next four experiments (C-F) 5 ml of each solution of cobalt and magnesium and 0.05 grams of zeolite were in a propylene bottle and stirred for 48 hours at room temperature. The ratio between the cobalt and magnesium solutions was 1:1, 1:10, 1:20 and 1:50 in experiments C-F respectively. After 48 hours the mixture was filtered by using syringe filtration technique. The elemental analysis of the zeolite was done and the concentration of the cations in the filtrate was calculated by ICP spectroscopy.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Conc. of Co solutions</th>
<th>Conc. of Mg solutions</th>
<th>Initial pH of mixture</th>
<th>pH after 48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>925 ppm</td>
<td>-----</td>
<td>7.36</td>
<td>5.56</td>
</tr>
<tr>
<td>B</td>
<td>-----</td>
<td>438 ppm</td>
<td>9.75</td>
<td>8.51</td>
</tr>
<tr>
<td>C</td>
<td>1851 ppm</td>
<td>976 ppm</td>
<td>7.71</td>
<td>7.01</td>
</tr>
<tr>
<td>D</td>
<td>1851 ppm</td>
<td>7192 ppm</td>
<td>8.07</td>
<td>7.07</td>
</tr>
<tr>
<td>E</td>
<td>1851 ppm</td>
<td>14384 ppm</td>
<td>8.10</td>
<td>6.81</td>
</tr>
<tr>
<td>F</td>
<td>1851 ppm</td>
<td>35960 ppm</td>
<td>7.98</td>
<td>6.60</td>
</tr>
</tbody>
</table>

Table 3.1: concentrations of cobalt and magnesium solutions
3.2 Synthesis of ZK-4

ZK-4 was prepared by G.T. Kerr’s method [48]. In the synthesis of ZK-4 sodium hydroxide (3.001 grams) and sodium aluminate (10.7503 grams) were mixed in distilled water (145.006 grams). Silica solution (28.505 grams) was mixed into Tetramethylammonium hydroxide solution (146.034 grams) and stirred approximately 30 minutes in a separate propylene bottle. Then the first mixture was put into the second mixture having silica solution and stirred vigorously. Finally the mixture was heated in a oven at 100 °C for 48 hours. Then filtered and washed with 1L distilled water and finally dried at 80 °C for 15 hours. The characterization was done by elemental analysis, TGA, and XRD.

For sodium enrichment ZK-4 was refluxed with 0.2M NH₄Cl at 60 °C four times. After that same sample was refluxed with 2M NaCl solution at 80 °C overnight. Finally that sodium enriched ZK-4 was again characterized by XRD, elemental analysis and TGA.

The following formula derived by elemental analysis and TGA,

\[ \text{Na}_{0.483}\text{H}_{0.203}(\text{TMA})_{0.1235}[\text{Al}_{0.8}\text{Si}_{1.2}\text{O}_{4}] \times 1.33\text{H}_{2}\text{O} \]

![Figure 3.4: ESEM picture of ZK-4](image-url)
Figure 3.5: XRD pattern of ZK-4

Figure 3.6: TGA of ZK-4
3.2.1 Cations selectivity of ZK-4:

ZK-4 was treated with different solutions having different concentrations of cations. Cobalt chloride and magnesium chloride were used to prepare different types of solutions in deionised water to check the competition between cobalt and magnesium cations. In each experiment 0.05 grams of ZK-4 was used and number of moles of sodium in that amount of zeolite is $1.476 \times 10^{-4}$ moles. In first two experiments single solution of cobalt and magnesium was used respectively. In the next four experiments (C-F) 5 ml of each solution of cobalt and magnesium and 0.05 grams of zeolite were put in a propylene bottle and stirred for 48 hours at room temperature. The ratio between the cobalt and magnesium solutions was 1:1, 1:10, 1:20 and 1:50 in experiments C-F respectively. After 48 hours the mixture was filtered by using syringe filtration technique. The elemental analysis of the zeolite was done and the concentration of the cations in the filtrate was calculated by ICP spectroscopy.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Conc. of Co solutions</th>
<th>Conc. of Mg solutions</th>
<th>Initial pH of mixture</th>
<th>pH after 48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>435.42 ppm</td>
<td>-----</td>
<td>7.97</td>
<td>7.23</td>
</tr>
<tr>
<td>B</td>
<td>-----</td>
<td>179.35 ppm</td>
<td>9.31</td>
<td>8.38</td>
</tr>
<tr>
<td>C</td>
<td>870.84 ppm</td>
<td>358.7 ppm</td>
<td>8.10</td>
<td>7.22</td>
</tr>
<tr>
<td>D</td>
<td>870.84 ppm</td>
<td>3781.5 ppm</td>
<td>8.27</td>
<td>6.95</td>
</tr>
<tr>
<td>E</td>
<td>870.84 ppm</td>
<td>7563 ppm</td>
<td>8.29</td>
<td>6.93</td>
</tr>
<tr>
<td>F</td>
<td>870.84 ppm</td>
<td>18414 ppm</td>
<td>8.29</td>
<td>6.92</td>
</tr>
</tbody>
</table>

Table 3.2: concentrations of cobalt and magnesium solutions
### 3.2.2 Calcination of ZK-4

ZK-4 was synthesized using TMA$^+$ ions as template and 500 °C temperatures is required to thermally decompose them. TMA$^+$ ions present in the supercage can be removed at low temperature but TMA$^+$ ions present in the sodalite cages required comparatively high temperature.

The calcination of ZK-4 was done by heating for 17 hours at 500 °C in air [38]. For the purpose of sodium enrichment calcined ZK-4 was refluxed with 0.2M NH$_4$Cl at 60 °C four times. After that ZK-4 was refluxed with 2M NaCl at 80 °C four times. Finally the sample was washed with deionised water and dried at 100 °C for 15 hours.

Characterization was done by XRD, TGA and SEM. The empirical formula derived from TGA and elemental analysis done by SEM is following

\[ \text{Na}_{0.512} \text{H}_{0.338} [\text{Al}_{0.85} \text{Si}_{1.14} \text{O}_4] 1.74 \text{H}_2\text{O} \]

![ESEM picture of calcined ZK-4](image)

**Figure 3.7:** ESEM picture of calcined ZK-4
Figure 3.8: XRD pattern of calcined ZK-4
3.2.3 Cations Selectivity of Calcined ZK-4:
Calcined ZK-4 was treated with different solutions having different concentrations of cations. Same method was followed for ion-exchange as in zeolite A & ZK-4. Solutions of cations were prepared in deionised water to check the competition between cobalt and magnesium cations. In each experiment 0.05 grams of calcined ZK-4 was used and number of moles of sodium in that amount of zeolite is $1.577\times10^{-4}$ moles. In first two experiments single solution of cobalt and magnesium was used respectively. In the next four experiments (C-F) 5 ml of each solution of cobalt and magnesium and 0.05 grams of zeolite were put in a propylene bottle and stirred for 48 hours at room temperature. The ratio between the cobalt and magnesium solutions was 1:1, 1:10, 1:20 and 1:50 in experiments C-F respectively. After 48 hours the mixture was filtered by using syringe filtration technique. The elemental analysis of the zeolite was done and the concentration of the cations in the filtrate was calculated by ICP spectroscopy.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Conc. of Co solutions</th>
<th>Conc. of Mg solutions</th>
<th>Initial pH of mixture</th>
<th>pH after 48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>465.5 ppm</td>
<td>-----</td>
<td>7.52</td>
<td>6.88</td>
</tr>
<tr>
<td>B</td>
<td>-----</td>
<td>191.75 ppm</td>
<td>8.77</td>
<td>7.80</td>
</tr>
<tr>
<td>C</td>
<td>931 ppm</td>
<td>397 ppm</td>
<td>7.56</td>
<td>6.87</td>
</tr>
<tr>
<td>D</td>
<td>931 ppm</td>
<td>3863 ppm</td>
<td>7.73</td>
<td>6.69</td>
</tr>
<tr>
<td>E</td>
<td>931 ppm</td>
<td>7848 ppm</td>
<td>7.83</td>
<td>6.41</td>
</tr>
<tr>
<td>F</td>
<td>931 ppm</td>
<td>19175 ppm</td>
<td>7.86</td>
<td>6.47</td>
</tr>
</tbody>
</table>

*Table 3.3*: concentrations of cobalt and magnesium solutions
3.3 Synthesis and characterization of Zeolite Alpha

Zeolite alpha was prepared by GH Kuhl’s method [49].

Reagents used

Following reagents were used for the preparation of the zeolite alpha,

- Distilled water
- Tetramethylammonium hydroxide (25% TMAOH)
- Sodium aluminate (28% Na₂O 42.75% Al₂O₃)
- Precipitated Silica (Hi-Sil 233, 88% SiO₂)

Preparation

Sodium aluminate (15.601 grams) was added in distilled water (46.404 grams) and stirred the mixture to dissolve it completely. Tetramethylammonium hydroxide solution (111.707 grams) was added in sodium aluminate solution. Precipitated silica (44.506 grams) was added in the above mixture with constant stirring. This mixture was incubated for 48 hours at room temperature and then kept in oven for 30 hours at 90 °C. Finally filter the mixture by decantation, washed with water and dried at 100 °C for 15 hours. Yield of the product was 38 grams. The product was characterized by XRD, TGA and elemental analysis.

Sodium Enrichment

Zeolite alpha was refluxed with 0.2M NH₄Cl four times. After that it was refluxed with 2M NaCl solution at 80 °C overnight. This process was repeated four times and finally the sodium enriched zeolite was washed with water, dried and characterized again by XRD, TGA and elemental analysis (ESEM).

Following formula of zeolite alpha was derived after the characterization,

\[
\text{Na}_{0.201} \text{H} (\text{TMA})_{0.171} [\text{Al}_{0.49} \text{Si}_{1.51} \text{O}_4] \times 1.129\text{H}_2\text{O}
\]
Figure 3.9: XRD pattern of zeolite alpha

Figure 3.10: ESEM picture of zeolite alpha

Figure 3.11: TGA of zeolite alpha
3.3.1 Cations selectivity of zeolite alpha

Ion-exchange method was same as explained in zeolite A and ZK-4. The amount of zeolite in each experiment was 0.05 grams and number of moles of sodium in that amount of zeolite is $6.357 \times 10^{-5}$ moles. In first two experiments single solution of cobalt and magnesium was used respectively. In the next four experiments (C-F) 5 ml of each solution of cobalt and magnesium and 0.05 grams of zeolite were put in a propylene bottle and stirred for 48 hours at room temperature. The ratio between the cobalt and magnesium solutions was 1:1, 1:10, 1:20 and 1:50 in experiments C-F respectively. After 48 hours the mixture was filtered by using syringe filtration technique. The elemental analysis of the zeolite was done and the concentration of the cations in the filtrate was calculated by ICP spectroscopy.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Conc. of Co. solutions</th>
<th>Conc. of Mg. solutions</th>
<th>Initial pH of mixture</th>
<th>pH after 48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>187.52 ppm</td>
<td>-----</td>
<td>6.67</td>
<td>7.67</td>
</tr>
<tr>
<td>B</td>
<td>----</td>
<td>77.233 ppm</td>
<td>6.72</td>
<td>7.38</td>
</tr>
<tr>
<td>C</td>
<td>375 ppm</td>
<td>154.466 ppm</td>
<td>7.02</td>
<td>7.25</td>
</tr>
<tr>
<td>D</td>
<td>375 ppm</td>
<td>1544.66 ppm</td>
<td>6.84</td>
<td>7.02</td>
</tr>
<tr>
<td>E</td>
<td>375 ppm</td>
<td>3089.32 ppm</td>
<td>6.84</td>
<td>7.12</td>
</tr>
<tr>
<td>F</td>
<td>375 ppm</td>
<td>7723.3 ppm</td>
<td>6.90</td>
<td>7.22</td>
</tr>
</tbody>
</table>

**Table 3.4:** Concentration of cobalt and magnesium solutions used for ion-exchange in zeolite alpha and pH of the mixtures before and after 48 hours.
3.3.2 Calcination of Zeolite Alpha

Calcination and sodium enrichment of zeolite alpha was done by following the same method as explained in the calcination of ZK-4. Characterization of zeolite alpha was done by XRD, TGA and SEM. The empirical formula derived from TGA and elemental analysis done by SEM is following

Na$_{0.28}$ H$_{0.25}$ [Al$_{0.53}$Si$_{1.47}$ O$_4$] 1.39 H$_2$O

3.3.3 Cations Selectivity of Calcined Zeolite Alpha

Ion-exchange method was same as explained in zeolite A and ZK-4. The amount of zeolite in each experiment was 0.05 grams and number of moles of sodium in that amount of zeolite is 9.26×10$^{-5}$ moles. The volumes and concentration ratios between the cobalt and magnesium solution was also the same as mentioned in the above zeolites. The elemental analysis of the zeolite was done and the concentration of the cations in the filtrate was calculated by ICP spectroscopy.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Conc. of Co. solutions</th>
<th>Conc. of Mg. solutions</th>
<th>Initial pH of mixture</th>
<th>pH after 48 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>273.17 ppm</td>
<td>-----</td>
<td>6.33</td>
<td>6.10</td>
</tr>
<tr>
<td>B</td>
<td>-----</td>
<td>112.5 ppm</td>
<td>6.89</td>
<td>6.38</td>
</tr>
<tr>
<td>C</td>
<td>546.34 ppm</td>
<td>225 ppm</td>
<td>6.60</td>
<td>5.78</td>
</tr>
<tr>
<td>D</td>
<td>546.34 ppm</td>
<td>2250 ppm</td>
<td>6.51</td>
<td>5.53</td>
</tr>
<tr>
<td>E</td>
<td>546.34 ppm</td>
<td>4500 ppm</td>
<td>6.63</td>
<td>5.24</td>
</tr>
<tr>
<td>F</td>
<td>546.34 ppm</td>
<td>11250 ppm</td>
<td>6.61</td>
<td>5.30</td>
</tr>
</tbody>
</table>

Table 3.5: Concentration of cobalt and magnesium solutions used for ion-exchange in zeolite alpha and pH of the mixtures before and after 48 hours.
Figure 3.12: ESEM picture of Calcined Zeolite Alpha

Figure 3.13: XRD pattern of Calcined Zeolite Alpha
3.4 Clinoptilolite (Natural Zeolite).

Clinoptilolite is a natural zeolite and mostly used in nuclear waste treatment. This zeolite was bought from R.S. Minerals Guisborough, UK. The characterisation was done by XRD, TGA and elemental analysis (ESEM).

For sodium enrichment clinoptilolite was refluxed four times with 2M NaCl at 80 °C overnight. Then washed with deionised water, dried in oven at 80 °C. Finally, sodium enriched clinoptilolite was characterised again by XRD, TGA and elemental analysis.

Following is the empirical formula of clinoptilolite which was derived from elemental analysis and TGA,

\[ \text{Na}_{0.19} \text{Fe}_{0.022} \text{H}_{0.117} [\text{Al}_{0.49} \text{Si}_{1.51} \text{O}_4] \times 0.936\text{H}_2\text{O} \]

![Figure 3.14: ESEM picture of clinoptilolite (Natural Zeolite)](image-url)
Figure 3.15: XRD Pattern of Clinoptilolite

Figure 3.16: TGA of Clinoptilolite
3.1.4.1 Cations selectivity of Clinoptilolite

Ion-exchange method was same as explained in zeolite A and ZK-4. The amount of zeolite in each experiment was 0.05 grams and number of moles of sodium in that amount of zeolite was $6.685 \times 10^{-5}$ moles. In first two experiments single solution of cobalt and magnesium was used respectively. In the next four experiments (C-F) 5 ml of each solution of cobalt and magnesium and 0.05 grams of zeolite were put in a propylene bottle and stirred for 48 hours at room temperature. The ratio between the cobalt and magnesium solutions was $1:1$, $1:10$, $1:20$ and $1:50$ in experiments C-F respectively. After 48 hours the mixture was filtered by using syringe filtration technique. The elemental analysis of the zeolite was done and the concentration of the cations in the filtrate was calculated by ICP spectroscopy.

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Conc. Of Co. Solutions</th>
<th>Conc. of Mg. solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>197 ppm</td>
<td>-----</td>
</tr>
<tr>
<td>B</td>
<td>----</td>
<td>81.223 ppm</td>
</tr>
<tr>
<td>C</td>
<td>394 ppm</td>
<td>162.44 ppm</td>
</tr>
<tr>
<td>D</td>
<td>394 ppm</td>
<td>1624.46 ppm</td>
</tr>
<tr>
<td>E</td>
<td>394 ppm</td>
<td>3248.92 ppm</td>
</tr>
<tr>
<td>F</td>
<td>394 ppm</td>
<td>8122.3 ppm</td>
</tr>
</tbody>
</table>

Table 3.6: Concentrations of cobalt and magnesium solutions used for ion-exchange in clinoptilolite.
3.5 Stability of Zeolites in Acids:

Stability of the zeolite A, ZK-4, zeolite alpha and clinoptilolite was noted by treating the zeolites with HNO₃ solution of different concentrations. Four solutions of HNO₃ having concentrations 0.05M, 0.1M, 0.3M and 0.5M were prepared in deionized water. Clinoptilolite was treated with 2M, 4M, 6M and 8M HNO₃. Four experiments were done for each zeolite to check the stability. In each experiment 0.5 grams zeolite was stirred with 10 ml HNO₃ solution in propylene bottle. After 48 hours zeolite was filtered and washed with deionized water and dried. The characterization of zeolite was done by X-ray differection to check the stability and crystallinity of each zeolite.
CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Sorption of Zeolite A:

Ion-exchange equilibrium for zeolite A was calculated by treating the sample with cationic solutions. The zeolite was treated for 1, 2, 3 and 4 days. The maximum uptake of cations by zeolite A was obtained after 2 days. So 48 hours were given to each sample for cation exchange. $K_d$ values given in table 4.2 were calculated from liquid analysis obtained from ICP spectroscopy. Distribution coefficients for cobalt cations were much higher than magnesium cations at room temperature and pH range was 6-8 shown in table 3.1. In one to one ratio between cobalt and magnesium cations the $K_d$ value for cobalt was 283 g/mL much higher than magnesium which was only 9.57 g/mL as shown in table 4.2. As we increased the concentration of the magnesium cations up to 50 times the decrease in $K_d$ value of cobalt took place. This decrease in $K_d$ for cobalt was 39% and showed in graph 4.1. According to figure 4.2 zeolite having Cobalt cations had more intense peaks as compared to the initial zeolite. The diffractograms obtained in these experiments did not show any new peaks.
<table>
<thead>
<tr>
<th>No. of Exp.</th>
<th>No. of moles of Na in Zeolite (0.05g)</th>
<th>No. of moles of Cobalt in Solution</th>
<th>No. of moles of Magnesium in Solution</th>
<th>No. of moles of Cobalt in Zeolite</th>
<th>No. of moles of Magnesium in Zeolite</th>
<th>Total No. of moles (Co+Mg) in Zeolite</th>
<th>Chemical formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.44×10^{-4}</td>
<td>1.5678×10^{-4}</td>
<td>------</td>
<td>9.8983×10^{-5}</td>
<td>------</td>
<td>9.8983×10^{-5}</td>
<td>Na_{0.22}Co_{0.21}H_{0.36}[Al Si O_{4}]</td>
</tr>
<tr>
<td>2</td>
<td>2.44×10^{-4}</td>
<td>------</td>
<td>1.8025×10^{-4}</td>
<td>------</td>
<td>9.0535×10^{-5}</td>
<td>9.0535×10^{-5}</td>
<td>Na_{0.32}Mg_{0.19}H_{0.29}4[Al Si O_{4}]</td>
</tr>
<tr>
<td>3</td>
<td>2.44×10^{-4}</td>
<td>1.5678×10^{-4}</td>
<td>1.8025×10^{-4}</td>
<td>9.186×10^{-5}</td>
<td>8.23×10^{-6}</td>
<td>1.0009×10^{-4}</td>
<td>Na_{0.25}Mg_{0.18}Co_{0.19}H_{0.31}9[Al Si O_{4}]</td>
</tr>
<tr>
<td>4</td>
<td>2.44×10^{-4}</td>
<td>1.5678×10^{-4}</td>
<td>1.4798×10^{-3}</td>
<td>7.3220×10^{-5}</td>
<td>2.9218×10^{-5}</td>
<td>1.02438×10^{-4}</td>
<td>Na_{0.25}Mg_{0.06}Co_{0.15}H_{0.31}5[Al Si O_{4}]</td>
</tr>
<tr>
<td>5</td>
<td>2.44×10^{-4}</td>
<td>1.5678×10^{-4}</td>
<td>2.9597×10^{-3}</td>
<td>6.4746×10^{-5}</td>
<td>4.5267×10^{-5}</td>
<td>1.10013×10^{-4}</td>
<td>Na_{0.25}Mg_{0.09}Co_{0.13}H_{0.27}9[Al Si O_{4}]</td>
</tr>
<tr>
<td>6</td>
<td>2.44×10^{-4}</td>
<td>1.5678×10^{-4}</td>
<td>7.3992×10^{-3}</td>
<td>5.5932×10^{-5}</td>
<td>1.0823×10^{-4}</td>
<td>1.6416×10^{-4}</td>
<td>Na_{0.29}Mg_{0.23}Co_{0.11}H_{0.01}[Al Si O_{4}]</td>
</tr>
</tbody>
</table>

**Table 4.1:** Number of moles of cations before and after the ion-exchange in zeolite A (Na_{0.83}H_{0.16} [Al Si O_{4}] × 1.79H_{2}O)
<table>
<thead>
<tr>
<th>Cobalt: Magnesium</th>
<th>$K_d$ of Cobalt</th>
<th>$K_d$ of Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>283.00</td>
<td>9.57</td>
</tr>
<tr>
<td>1:10</td>
<td>175.25</td>
<td>4.028</td>
</tr>
<tr>
<td>1:20</td>
<td>140.70</td>
<td>3.10</td>
</tr>
<tr>
<td>1:50</td>
<td>110.90</td>
<td>2.97</td>
</tr>
</tbody>
</table>

**Table 4.2:** $K_d$ values of cobalt and magnesium at different concentration ratios in zeolite A

**Figure 4.1:** Graph between $K_d$ values of cobalt and concentrations of Mg cations in zeolite A
Figure 4.2: XRD patterns of zeolite A with cobalt and magnesium cations. 1B039 with cobalt, 1B042 with magnesium, 1B044 with Co$^{2+}$ and Mg$^{2+}$ (1:1), 1B083 with Co$^{2+}$ and Mg$^{2+}$ (1:10), 1B086 with Co$^{2+}$ and Mg$^{2+}$ (1:20) and 1B089 with Co$^{2+}$ and Mg$^{2+}$ (1:50)
4.1.1 Stability of Zeolite A

Figure 4.3 shows the stability of the zeolite A. zeolite A was stable 0.1M acidic solution and completely decomposed in 0.3M HNO₃.
Figure 4.3 Comparison of different patterns of zeolite A after the treatment with HNO₃. First pattern of zeolite A is without acid treatment. Second, third, fourth and fifth pattern were obtained after the treatment with 0.05M, 0.1M, 0.3M and 0.5M HNO₃ solutions respectively.
4.2 Sorption of ZK-4

Ion-exchange equilibrium for ZK-4 and for the other zeolites used in this work was calculated by the method as explained in sorption of zeolite A. Ion-exchange of ZK-4 was studied at room temperature and pH range between 7 and 9 as showed in table 3.2. In ZK-4 $K_d$ values rapidly changed by increasing the concentration of the magnesium cations. According to table 4.4 in 1:1 ratios, distribution coefficient for cobalt cations $K_d$ was high (688.61 g/mL) and suddenly decreased to (194.04) when this ratio was changed to 1:20. A graph was plotted between $K_d$ values for cobalt and the concentrations of the magnesium. Figure 4.3 showed the (80.6%) decrease took place by increasing the concentration of magnesium cations in the external solution from 1:1 ratio to 1:50. This decrease was much higher as compared to zeolite A (39%). For the characterization of the zeolite XRD were take and the diffractograms shown in figure 4.4. It was noticed that the zeolite loaded with cobalt cations showed more intense peaks as compared to the initial zeolite.
**Figure 4.3:** Number of moles of cations before and after ion-exchange in zeolite ZK-4

\((Na_{0.483}H_{0.203} \text{ (TMA) } 0.1235[Al_{0.8}Si_{1.2}O_4] \times 1.33H_2O)\)

<table>
<thead>
<tr>
<th>NO. of Exp.</th>
<th>No. of moles of Na in Zeolite (0.05g)</th>
<th>No. of moles of Cobalt in Solution</th>
<th>No. of moles of Magnesium in Solution</th>
<th>No. of moles of Cobalt in Zeolite</th>
<th>No. of moles of Magnesium in Zeolite</th>
<th>Total No. of moles (Co+Mg) in Zeolite</th>
<th>Chemical formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.476×10⁻⁴</td>
<td>7.38×10⁵</td>
<td>----</td>
<td>6.21×10⁵</td>
<td>6.21×10⁵</td>
<td>Na_{0.25}Co_{0.203}H_{0.174} [Al_{0.83}Si_{1.17}O_4]</td>
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<td>2</td>
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<td>----</td>
<td>7.38×10⁵</td>
<td>4.25×10⁵</td>
<td>4.25×10⁵</td>
<td>Na_{0.344}Mg_{0.139}H_{0.238} [Al_{0.86}Si_{1.14}O_4]</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>1.476×10⁻⁴</td>
<td>7.38×10⁵</td>
<td>7.38×10⁵</td>
<td>5.719×10⁵</td>
<td>6.317×10⁵</td>
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<td>7.78×10⁴</td>
<td>4.19×10⁵</td>
<td>3.57×10⁵</td>
<td>Na_{0.206}Mg_{0.117}Co_{0.137}H_{0.146} [Al_{0.86}Si_{1.14}O_4]</td>
<td></td>
</tr>
<tr>
<td>5</td>
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<td>7.38×10⁵</td>
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<td>3.634×10⁵</td>
<td>4.506×10⁵</td>
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</tr>
<tr>
<td>6</td>
<td>1.476×10⁻⁴</td>
<td>7.38×10⁵</td>
<td>3.789×10⁻³</td>
<td>2.956×10⁵</td>
<td>4.1×10⁴</td>
<td>Na_{0.22}Mg_{1.34}Co_{0.097} [Al_{0.85}Si_{1.15}O_4]</td>
<td></td>
</tr>
</tbody>
</table>

\(Al_{0.8}Si_{1.2}O_4\)
<table>
<thead>
<tr>
<th>Cobalt: Magnesium</th>
<th>$K_d$ of Cobalt</th>
<th>$K_d$ of Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>688.61</td>
<td>18.72</td>
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<td>1:10</td>
<td>663.21</td>
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<td>1:20</td>
<td>194.04</td>
<td>5.96</td>
</tr>
<tr>
<td>1:50</td>
<td>133.65</td>
<td>0.89</td>
</tr>
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</table>

**Table 4.4:** $K_d$ values of Co$^{2+}$ and Mg$^{2+}$ at different concentration ratios in ZK-zeolite

**Figure 4.4:** Graph between $K_d$ values of cobalt in Zk-4 and concentrations of Mg cations in external solution.
**Figure 4.5:** XRD patterns of ZK-4 with cobalt and magnesium cations. 1B174 with cobalt, 1B176 with magnesium, 1B178 with Co\(^{2+}\) and Mg\(^{2+}\) (1:1), 1B180 with Co\(^{2+}\) and Mg\(^{2+}\) (1:10), 1B182 with Co\(^{2+}\) and Mg\(^{2+}\) (1:20) and 1B184 with Co\(^{2+}\) and Mg\(^{2+}\) (1:50)
4.2.1 Stability of ZK-4

ZK-4 shows the crystalline characteristics in 0.1M acidic solution and when it is treated with 0.3M HNO₃ solution, no sharp peak was obtained. It means ZK-4 is no more crystalline in 0.3M HNO₃ solution. It means that zeolite ZK-4 can maintain its crystallinity in 0.1M HNO₃ solution.
Figure 4.6 Comparison of different patterns of ZK-4 after the treatment with HNO₃. First pattern of ZK-4 is without acid treatment. Second, third, fourth and fifth pattern were obtained after the treatment with 0.05M, 0.1M, 0.3M and 0.5M HNO₃ solutions respectively.
4.3 Sorption of ZK-4 (Calcined)

The method to check the equilibrium time and conditions of the experiments were the same as used in the zeolite A and ZK-4. It was observed that calcined ZK-4 was more selective for cobalt cations as compared to ZK-4 without calcination. In the cationic solution with ratio 1:1 $K_d$ values for cobalt was (826g/mL) which was high than ZK-4 without calcination (688.61g/mL). For Co-Na exchange in ZK-4 calcined, the selectivity decrease took place drastically with the increase of magnesium concentration as shown in table 4.6. This change in $K_d$ values for cobalt was 87.53% and can be calculated from the table 4.5 and 4.6. In figure 4.5 this change showed in the form of graph. It is cleared that calcined, sodium enriched ZK-4 was more selective for cobalt as compared to ZK-4 without calcination.

<table>
<thead>
<tr>
<th>NO. of Exp.</th>
<th>No. of moles of Na in Zeolite (0.05g)</th>
<th>No. of moles of Cobalt in Solution</th>
<th>No. of moles of Magnesium in Solution</th>
<th>No. of moles of Cobalt in Zeolite</th>
<th>No. of moles of Magnesium in Zeolite</th>
<th>Total No. of moles (Co+Mg) in Zeolite</th>
<th>Chemical formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$1.577 \times 10^4$</td>
<td>$7.89 \times 10^{-5}$</td>
<td>$7.008 \times 10^{-5}$</td>
<td>$7.008 \times 10^{-5}$</td>
<td>$7.008 \times 10^{-5}$</td>
<td>$7.008 \times 10^{-5}$</td>
<td>$\text{Co}<em>{0.228}\text{H}</em>{0.434}[\text{Al}<em>{0.85}\text{Si}</em>{1.14}\text{O}_4]$</td>
</tr>
<tr>
<td>2</td>
<td>$1.577 \times 10^4$</td>
<td>$8.17 \times 10^{-5}$</td>
<td>$6.204 \times 10^{-5}$</td>
<td>$6.204 \times 10^{-5}$</td>
<td>$6.204 \times 10^{-5}$</td>
<td>$6.204 \times 10^{-5}$</td>
<td>$\text{Mg}<em>{0.20}\text{H}</em>{0.49}[\text{Al}<em>{0.85}\text{Si}</em>{1.14}\text{O}_4]$</td>
</tr>
<tr>
<td>3</td>
<td>$1.577 \times 10^4$</td>
<td>$8.17 \times 10^{-5}$</td>
<td>$6.263 \times 10^{-5}$</td>
<td>$1.33 \times 10^{-5}$</td>
<td>$7.39 \times 10^{-5}$</td>
<td>$7.39 \times 10^{-5}$</td>
<td>$\text{Mg}<em>{0.037}\text{Co}</em>{0.203}\text{H}<em>{0.41}[\text{Al}</em>{0.85}\text{Si}_{1.14}\text{O}_4]$</td>
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<tr>
<td>4</td>
<td>$1.577 \times 10^4$</td>
<td>$7.95 \times 10^{-4}$</td>
<td>$4.415 \times 10^{-5}$</td>
<td>$3.97 \times 10^{-5}$</td>
<td>$8.385 \times 10^{-5}$</td>
<td>$8.385 \times 10^{-5}$</td>
<td>$\text{Mg}<em>{0.13}\text{Co}</em>{0.143}\text{H}<em>{0.344}[\text{Al}</em>{0.85}\text{Si}_{1.14}\text{O}_4]$</td>
</tr>
<tr>
<td>5</td>
<td>$1.577 \times 10^4$</td>
<td>$1.58 \times 10^{-3}$</td>
<td>$3.57 \times 10^{-3}$</td>
<td>$5.06 \times 10^{-5}$</td>
<td>$8.63 \times 10^{-5}$</td>
<td>$8.63 \times 10^{-5}$</td>
<td>$\text{Mg}<em>{0.164}\text{Co}</em>{0.116}\text{H}<em>{0.33}[\text{Al}</em>{0.85}\text{Si}_{1.14}\text{O}_4]$</td>
</tr>
<tr>
<td>6</td>
<td>$1.577 \times 10^4$</td>
<td>$3.98 \times 10^{-3}$</td>
<td>$2.09 \times 10^{-5}$</td>
<td>$5.89 \times 10^{-5}$</td>
<td>$7.98 \times 10^{-5}$</td>
<td>$7.98 \times 10^{-5}$</td>
<td>$\text{Mg}<em>{0.191}\text{Co}</em>{0.068}\text{H}<em>{0.372}[\text{Al}</em>{0.85}\text{Si}_{1.14}\text{O}_4]$</td>
</tr>
</tbody>
</table>

Figure 4.5: Number of moles of cations before and after ion-exchange in zeolite

ZK-4 calcined Na$_{0.512}$H$_{0.338}$[Al$_{0.85}$Si$_{1.14}$O$_4$] $\times$ 1.74H$_2$O
<table>
<thead>
<tr>
<th>Cobalt: Magnesium</th>
<th>$K_d$ of Cobalt</th>
<th>$K_d$ of Magnesium</th>
</tr>
</thead>
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<td>826</td>
<td>32.16</td>
</tr>
<tr>
<td>1:10</td>
<td>254</td>
<td>10.52</td>
</tr>
<tr>
<td>1:20</td>
<td>165.1</td>
<td>6.63</td>
</tr>
<tr>
<td>1:50</td>
<td>103</td>
<td>0.743</td>
</tr>
</tbody>
</table>

Table 4.6: $K_d$ values of Co$^{+2}$ and Mg$^{+2}$ at different concentration ratios in ZK-4(Calcined).

**Figure 4.7:** Graph between $K_d$ values of cobalt in Calcined ZK-4 and concentrations of Mg cations in external solution.
4.4 Sorption of Zeolite Alpha

$K_d$ values showed in table 4.4 that zeolite alpha is more selective to magnesium cations as compared to ZK-4 and zeolite A. A similar decrease of selectivity was observed in zeolite alpha for cobalt and magnesium cations. In 1:1 ratio between cobalt and magnesium cations, $K_d$ value for cobalt was 457.89 g/mL. This $K_d$ value decreased to 90.7 g mL$^{-1}$ when the concentration of the Mg$^{2+}$ increased up to fifty times as compared to cobalt cations. According to data available in table 4.8 the decrease in $K_d$ was 88.3% due to 50 times high concentration of Mg$^{2+}$ cations. This decrease can be observed from the graph available in figure 4.6. These samples were characterized by XRD. Crystalline characteristics of zeolite alpha can be observed from diffractograms shown in figure 4.7.

<table>
<thead>
<tr>
<th>NO. of Exp.</th>
<th>No. of moles of Na in Zeolite (0.05g)</th>
<th>No. of moles of Cobalt in Solution</th>
<th>No. of moles of Magnesium in Solution</th>
<th>No. of moles of Cobalt in Zeolite</th>
<th>No. of moles of Magnesium in Zeolite</th>
<th>Total No. of moles (Co+Mg) in Zeolite</th>
<th>Chemical formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.357×10$^{-5}$</td>
<td>3.178×10$^{-5}$</td>
<td>---</td>
<td>2.856×10$^{-5}$</td>
<td>---</td>
<td>2.856×10$^{-5}$</td>
<td>Na$<em>{0.106}$Co$</em>{0.089}$H$<em>{0.264}$[Al$</em>{0.544}$Si$_{1.455}$O$_4$]</td>
</tr>
<tr>
<td>2</td>
<td>6.357×10$^{-5}$</td>
<td>---</td>
<td>3.178×10$^{-5}$</td>
<td>---</td>
<td>2.684×10$^{-5}$</td>
<td>2.684×10$^{-5}$</td>
<td>Na$<em>{0.161}$Mg$</em>{0.084}$H$<em>{0.237}$[Al$</em>{0.55}$Si$_{1.446}$O$_4$]</td>
</tr>
<tr>
<td>3</td>
<td>6.357×10$^{-5}$</td>
<td>3.178×10$^{-5}$</td>
<td>3.178×10$^{-5}$</td>
<td>2.21×10$^{-5}$</td>
<td>1.326×10$^{-5}$</td>
<td>3.536×10$^{-5}$</td>
<td>Na$<em>{0.107}$Mg$</em>{0.042}$Co$<em>{0.069}$H$</em>{0.224}$[Al$<em>{0.549}$Si$</em>{1.45}$O$_4$]</td>
</tr>
<tr>
<td>4</td>
<td>6.357×10$^{-5}$</td>
<td>3.178×10$^{-5}$</td>
<td>3.178×10$^{-4}$</td>
<td>1.246×10$^{-5}$</td>
<td>3.635×10$^{-5}$</td>
<td>4.881×10$^{-5}$</td>
<td>Na$<em>{0.055}$Mg$</em>{0.114}$Co$<em>{0.039}$H$</em>{0.23}$[Al$<em>{0.593}$Si$</em>{1.409}$O$_4$]</td>
</tr>
<tr>
<td>5</td>
<td>6.357×10$^{-5}$</td>
<td>3.178×10$^{-5}$</td>
<td>6.357×10$^{-4}$</td>
<td>9.915×10$^{-6}$</td>
<td>4.021×10$^{-5}$</td>
<td>5.012×10$^{-5}$</td>
<td>Na$<em>{0.088}$Mg$</em>{0.126}$Co$<em>{0.031}$H$</em>{0.138}$[Al$<em>{0.536}$Si$</em>{1.463}$O$_4$]</td>
</tr>
<tr>
<td>6</td>
<td>6.357×10$^{-5}$</td>
<td>3.178×10$^{-5}$</td>
<td>1.589×10$^{-3}$</td>
<td>6.695×10$^{-6}$</td>
<td>6.214×10$^{-5}$</td>
<td>6.883×10$^{-5}$</td>
<td>Na$<em>{0.06}$Mg$</em>{0.195}$Co$<em>{0.021}$H$</em>{0.028}$[Al$<em>{0.52}$Si$</em>{1.48}$O$_4$]</td>
</tr>
</tbody>
</table>

Table 4.7: Number of moles of cations before and after ion-exchange in zeolite alpha Na$_{0.203}$H (TMA)$_{0.171}$[Al$_{0.49}$Si$_{1.51}$O$_4$] × 1.129H$_2$O
Table 4.8: $K_d$ values of Co$^{+2}$ and Mg$^{+2}$ at different concentration ratios in zeolite alpha

<table>
<thead>
<tr>
<th>Ratio</th>
<th>$K_d$ of Cobalt</th>
<th>$K_d$ of Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>457.89</td>
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<tr>
<td>1:10</td>
<td>128.95</td>
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<tr>
<td>1:20</td>
<td>90.7</td>
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</tr>
<tr>
<td>1:50</td>
<td>53.38</td>
<td>8.14</td>
</tr>
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</table>

Figure 4.8: Graph between $K_d$ values of cobalt in zeolite alpha and concentrations of Mg cations in external solution.
**Figure 4.9:** XRD patterns of zeolite alpha having cobalt and magnesium cations. 1B143 with cobalt, 1B146 with magnesium, 1B149 with Co$^{2+}$ and Mg$^{2+}$ (1:1), 1B152 with Co$^{2+}$ and Mg$^{2+}$ (1:10), 1B155 with Co$^{2+}$ and Mg$^{2+}$ (1:20) and 1B158 with Co$^{2+}$ and Mg$^{2+}$ (1:50)
4.4.1 Acidic Stability of Zeolite Alpha

Zeolite alpha shows crystallinity in 0.3M HNO₃ to some extent and minor peak obtained in pattern fourth as shown in figure 4.10. Crystalline structure of zeolite alpha completely destroyed in 0.5M HNO₃.
Figure 4.10 Comparison of different patterns of zeolite alpha after the treatment with HNO₃. The first pattern shown is without acid treatment. Second, third, fourth and fifth pattern were obtained after the treatment with 0.05M, 0.1M, 0.3M and 0.5M HNO₃ solutions respectively.
4.5 Sorption of Zeolite Alpha (Calcined)

$K_d$ values available in the table 4.10 were calculated from the liquid analysis obtained from ICP spectroscopy shown in table 4.9. In zeolite alpha calcined, decrease of selectivity for cobalt cations was observed due to the high concentration of magnesium cations. $K_d$ values showed that zeolite alpha (calcined) was more selective for cobalt than magnesium cations. This selectivity was badly affected by increasing the concentration of magnesium cations. For Co-Na exchange in zeolite alpha (calcined), 85.86% selectivity decrease took place when the concentration of Mg$^{2+}$ in the outer solution was increased up to fifty times as compared to cobalt cations. Figure 4.8 showed the graph between $K_d$ values of cobalt and the concentration of the magnesium cations.

<table>
<thead>
<tr>
<th>NO. of Exp.</th>
<th>No. of moles of Na in Zeolite (0.05g)</th>
<th>No. of moles of Cobalt in Solution</th>
<th>No. of moles of Magnesium in Solution</th>
<th>No. of moles of Cobalt in Zeolite</th>
<th>No. of moles of Magnesium in Zeolite</th>
<th>Total No. of moles (Co+Mg) in Zeolite</th>
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</tr>
</thead>
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<tr>
<td>1</td>
<td>9.26×10^5</td>
<td>4.63×10^5</td>
<td>4.17×10^5</td>
<td>4.17×10^5</td>
<td>4.17×10^5</td>
<td>Co$<em>{0.126}$H$</em>{0.278}$[Al$<em>{0.53}$Si$</em>{1.47}$O$_4$]</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>9.26×10^5</td>
<td>4.63×10^5</td>
<td>3.68×10^5</td>
<td>3.68×10^5</td>
<td>3.68×10^5</td>
<td>Mg$<em>{0.111}$H$</em>{0.308}$[Al$<em>{0.53}$Si$</em>{1.47}$O$_4$]</td>
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</tr>
<tr>
<td>3</td>
<td>9.26×10^5</td>
<td>4.63×10^5</td>
<td>2.95×10^5</td>
<td>1.42×10^5</td>
<td>4.37×10^5</td>
<td>Mg$<em>{0.043}$Co$</em>{0.09}$H$<em>{1.336}$[Al$</em>{0.53}$Si$_{1.47}$O$_4$]</td>
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</tr>
<tr>
<td>4</td>
<td>9.26×10^5</td>
<td>4.63×10^5</td>
<td>1.66×10^5</td>
<td>4.98×10^5</td>
<td>6.64×10^5</td>
<td>Mg$<em>{0.15}$Co$</em>{0.05}$H$<em>{0.13}$[Al$</em>{0.53}$Si$_{1.47}$O$_4$]</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>9.26×10^5</td>
<td>9.26×10^4</td>
<td>1.34×10^5</td>
<td>6.42×10^5</td>
<td>7.76×10^5</td>
<td>Mg$<em>{0.194}$Co$</em>{0.04}$H$<em>{0.062}$[Al$</em>{0.53}$Si$_{1.47}$O$_4$]</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.26×10^5</td>
<td>2.31×10^3</td>
<td>9.15×10^6</td>
<td>2.88×10^5</td>
<td>3.80×10^5</td>
<td>Mg$<em>{0.087}$Co$</em>{0.028}$H$<em>{0.3}$[Al$</em>{0.53}$Si$_{1.47}$O$_4$]</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 4.9** Number of moles of cations before and after ion-exchange in zeolite alpha calcined Na$_{0.28}$H$_{0.25}$[Al$_{0.53}$Si$_{1.47}$O$_4$] × 1.39H$_2$O
<table>
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<tr>
<th>Cobalt: Magnesium</th>
<th>$K_d$ of Cobalt</th>
<th>$K_d$ of Magnesium</th>
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<td>348.7</td>
<td>88.46</td>
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<tr>
<td>1:10</td>
<td>112</td>
<td>24.10</td>
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<td>1:20</td>
<td>81.44</td>
<td>14.90</td>
</tr>
<tr>
<td>1:50</td>
<td>49.32</td>
<td>2.52</td>
</tr>
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</table>

**Table 4.10:** $K_d$ values of $\text{Co}^{+2}$ and $\text{Mg}^{+2}$ at different concentration ratios in zeolite alpha (Calcined)

**Figure 4.11:** Graph between $K_d$ values of cobalt in calcined zeolite alpha and concentrations of Mg cations in exter
4.6 Sorption of Clinoptilolite

A similar decrease of selectivity for cobalt cations was observed in clinoptilolite due to the high concentration of magnesium cations. In a 1:1 ratio between cobalt and magnesium solution, $K_d$ value for cobalt cations was 161.47 g/mL. $K_d$ value for cobalt decreased to 18.89 g/mL when the concentration of the magnesium cations was increased up to 50 times as compared to the cobalt cations. The total decrease in $K_d$ value of cobalt was 88.301 g/mL due to high concentration of Mg cations. Figure 4.9 showing the graph between $K_d$ values of cobalt and magnesium cations concentration. Figure 4.10 showing the XRD patterns of the clinoptilolite after the cations exchange.

<table>
<thead>
<tr>
<th>NO. of Exp.</th>
<th>No. of moles of Na in Zeolite (0.05g)</th>
<th>No. of moles of Cobalt in Solution</th>
<th>No. of moles of Magnesium in Solution</th>
<th>No. of moles of Cobalt in Zeolite</th>
<th>No. of moles of Magnesium in Zeolite</th>
<th>Total No. of moles (Co+Mg) in Zeolite</th>
<th>Chemical formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.685×10⁵</td>
<td>3.339×10⁵</td>
<td>2.0508×10⁵</td>
<td>2.0508×10⁵</td>
<td>2.0508×10⁵</td>
<td>Na₀.108Fe₀.013³Co₀.058³H₀.123 [Al₀.374Si₁.626O₄]</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>6.685×10⁵</td>
<td>3.3425×10⁵</td>
<td>1.8199×10⁵</td>
<td>1.8199×10⁵</td>
<td>1.8199×10⁵</td>
<td>Na₀.95Fe₀.031³Mg₀.0517H₀.1558 [Al₀.323Si₁.677O₄]</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>6.685×10⁵</td>
<td>3.3425×10⁵</td>
<td>6.1728×10⁶</td>
<td>6.1728×10⁶</td>
<td>2.1088×10⁵</td>
<td>Na₀.099Fe₀.024³Mg₀.0175Co₀.042³H₀.086[Al₀.35Si₁.65O₄]</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>6.685×10⁵</td>
<td>3.3425×10⁵</td>
<td>2.3868×10⁵</td>
<td>2.3868×10⁵</td>
<td>3.0309×10⁵</td>
<td>Na₀.104Fe₀.036³Mg₀.068Co₀.018³H₀.0814 [Al₀.43Si₁.57O₄]</td>
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</tr>
<tr>
<td>5</td>
<td>6.685×10⁵</td>
<td>7.0535×10⁴</td>
<td>3.7449×10⁵</td>
<td>3.7449×10⁵</td>
<td>4.1856×10⁵</td>
<td>Na₀.091³Fe₀.019³Mg₀.106³Co₀.012³ [Al₀.34Si₁.66O₄]</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>6.685×10⁵</td>
<td>1.8117×10⁵</td>
<td>1.1379×10⁴</td>
<td>1.1379×10⁴</td>
<td>1.1667×10⁴</td>
<td>Na₀.092³Fe₀.017³Mg₀.32³Co₀.008² [Al₀.34³Si₁.65³O₄]</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.11 Number of moles of cations before and after ion-exchange in clinoptilolite

\[(Na_{0.19}Fe_{0.022}H_{0.117}[Al_{0.49}Si_{1.51}O_4] \times 0.936H_2O)\]
<table>
<thead>
<tr>
<th>Cobalt: Magnesium</th>
<th>$K_d$ of Cobalt</th>
<th>$K_d$ of Magnesium</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>161.47</td>
<td>46.13</td>
</tr>
<tr>
<td>1:10</td>
<td>47.80</td>
<td>14.50</td>
</tr>
<tr>
<td>1:20</td>
<td>30.41</td>
<td>11.21</td>
</tr>
<tr>
<td>1:50</td>
<td>18.89</td>
<td>13.40</td>
</tr>
</tbody>
</table>

**Table 4.12:** $K_d$ values of Co$^{2+}$ and Mg$^{2+}$ at different concentration ratios in clinoptilolite

**Figure 4.12:** Graph between $K_d$ values of cobalt in clinoptilolite and concentrations of Mg cations in the external solution.
Figure 4.13: XRD patterns of clinoptilolite having cobalt and magnesium cations. 1B117 with cobalt, 1B120 with magnesium, 1B105 with Co\(^{2+}\) and Mg\(^{2+}\) (1:1), 1B108 with Co\(^{2+}\) and Mg\(^{2+}\) (1:10), 1B111 with Co\(^{2+}\) and Mg\(^{2+}\) (1:20) and 1B114 with Co\(^{2+}\) and Mg\(^{2+}\) (1:50).
4.6.1 Acidic Stability of Clinoptilolite

Clinoptilolite is very stable in nitric acid even in 8M solution as shown in the XRD patterns in figure 4.14. The Si/Al ratio of clinoptilolite is 5. Due to high ratio it maintains crystallinity even in highly acidic solution.
Figure 4.14: Comparison of different patterns of clinoptilolite after the treatment with HNO₃. The first pattern shown is without acid treatment. Second, third, fourth and fifth pattern were obtained after the treatment with 2M, 4M, 6M and 8M HNO₃ solutions respectively.
3.12 Conclusions

3.12.1 Ion-exchange in Zeolites

It has been clearly concluded that the decrease in the selectivity in zeolite A is minimum, which is 39% in the presence of excess magnesium cations in the external solution. While the other zeolites show decrease in the selectivity of cobalt more than 80% in the presence of excess magnesium cations. It is very obvious from $K_d$ values giving in table 4.1, 4.2 that zeolite A has the more affinity for cobalt cations. So zeolite A is the perfect zeolite to remove the radioactive cobalt from the nuclear chemical waste which contains the excess amount of the magnesium cations.

3.12.2 Acidic Stability of Zeolites

The powder XRD patterns of all the above zeolites suggest that stability depend upon the Si/Al ratio of the zeolite. Clinoptilolite was the most stable zeolite having Si/Al ration 5 as shown in figure 4.14, XRD pattern of clinoptilolite shows sharp peaks after the treatment with 8M HNO$_3$. XRD pattern in figure 4.3 shows that zeolite A is not stable even in 0.3M HNO$_3$ having Si/Al ratio 1. Si/Al ratio of ZK-4 is about 1.4; it is also not stable in 0.3M HNO$_3$ as shown in Figure 4.6. Zeolite alpha has Si/Al ratio 3, XRD pattern in figure 4.10 shows few peaks in 0.3M HNO$_3$. Final conclusion is that stability is directly proportional to Si/Al ratio. Zeolites having higher Si/Al ratio are more stable and zeolites having low Si/Al ratio are less stable.

4.7 Future work

In this work the main focus was to remove the cobalt cations from the nuclear chemical wastes. Zeolite A can be used to remove the nickel and iron cations from the nuclear chemical wastes, which contains higher concentrations of magnesium cations. Further experiments can be done to check the ion-exchange capacity of zeolite A at different temperatures and at different pH.
CHAPTER 5

References

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49. G. H. Khül, US Patent 4 191 663