

**JAERI-Research  
98-058**



**DEVELOPMENT OF PARTITIONING METHOD:  
ADSORPTION OF CESIUM WITH MORDENITE IN ACIDIC MEDIA**

**October 1998**

**Louis DONNET\*, Yasuji MORITA,  
Isao YAMAGISHI and Masumitsu KUBOTA**

**日本原子力研究所  
Japan Atomic Energy Research Institute**

本レポートは、日本原子力研究所が不定期に公刊している研究報告書です。

入手の間合わせは、日本原子力研究所研究情報部研究情報課（〒319-1195 茨城県那珂郡東海村）あて、お申し越してください。なお、このほかに財団法人原子力弘済会資料センター（〒319-1195 茨城県那珂郡東海村日本原子力研究所内）で複写による実費領布をおこなっております。

This report is issued irregularly.

Inquiries about availability of the reports should be addressed to Research Information Division, Department of Intellectual Resources, Japan Atomic Energy Research Institute, Tokai-mura, Naka-gun, Ibaraki-ken, 319-1195, Japan.

© Japan Atomic Energy Research Institute, 1998

編集兼発行 日本原子力研究所

## Development of Partitioning Method : Adsorption of Cesium with Mordenite in Acidic Media

Louis DONNET\*, Yasuji MORITA, Isao YAMAGISHI and Masumitsu KUBOTA

Department of Materials Science  
Tokai Research Establishment  
Japan Atomic Energy Research Institute  
Tokai-mura, Naka-gun, Ibaraki-ken

(Received September 9, 1998)

Adsorption of cesium with mordenite from a acidic solution, typically from a 0.5 mol/L nitric acid solution, was studied to examine the possibility to design a new separation scheme for partitioning of high-level liquid waste. Batch adsorption experiments showed that three mordenites examined (natural mordenite and two synthetic mordenites Zeolon 900Na and 900H) have very close behavior with the parameters of adsorption kinetics, the saturation capacity by Langmuir equation, the distribution coefficient of Cs and adsorption of other elements. In the Cs adsorption with the natural mordenite at 0.5 mol/L nitric acid, distribution coefficient was 1150 ml/g and the saturation capacity was 0.64 mmol/g.

In the adsorption of Cs on column using the natural mordenite, the flow rate of the Cs solution modified only the 5% breakthrough point and gave no influence on the total capacity of Cs. Column experiments with a mixed solution of Cs, Rb, Na, Ba, Sr, Cr, Ni, Ru, Rh and Pd showed that cesium was adsorbed very selectively. Only about 4% of rubidium in a molar ratio were retained in the column. The total quantity of Cs and Rb adsorbed was 0.51 mmol/g at 0.5 mol/L nitric acid.

Elution of Cs (and Rb) with 4 mol/L nitric acid was performed against the column of the loaded natural mordenite. The adsorbed Cs and Rb were well eluted, and a good mass balance was obtained between the adsorbed quantity by breakthrough curves and the quantity found in the eluate.

Keywords : Cesium, Mordenite, Adsorption, Nitric Acid, Distribution Coefficient, Adsorption Capacity  
Separation Factor, Column Adsorption, Elution, Partitioning Process, High-level Waste

---

\* CEA/DCC/DRDD/SPHA France

## 群分離法の開発：モルデナイトによる酸性溶液からの セシウムの吸着

日本原子力研究所東海研究所物質科学研究部

Louis DONNET\*・森田 泰治・山岸 功・久保田益充

(1998年9月9日受理)

高レベル廃液の群分離における新分離スキームの可能性を探るため、モルデナイトによる0.5mol/L硝酸等の酸性溶液からのセシウムの吸着分離について研究した。バッチ吸着実験において、調べた3種のモルデナイト(天然モルデナイト及びZeolon 900Na, 900Hの合成モルデナイト)は、吸着速度、吸着容量、Csの分配係数、他の元素の吸着等の点でほぼ同様の挙動を示した。天然モルデナイトによる0.5 mol/L硝酸からのCsの吸着では、分配係数1150 ml/g、飽和吸着量0.64 mmol/gが得られた。天然モルデナイトを用いたカラム吸着実験では、給液速度は、5%破過点に影響するものの、Csの全吸着量には影響しないことがわかった。元素混合溶液(Cs, Rb, Na, Ba, Sr, Cr, Ni, Ru, Rh及びPd)によるカラム実験で、Csは選択的に吸着されることが示され、Cs以外ではモル比で約4%のRbがカラム中に残るのみであった。Cs及びRbの全吸着量は、0.5 mol/L硝酸からの吸着で、0.51mmol/gであった。4mol/L硝酸による溶離についても検討し、吸着されたCs及びRbはカラムよりよく溶離されることを明らかにした。吸着時の破過曲線から求めた吸着量と溶離液中に観測された溶離量とはよく一致し、よいマスバランスが得られた。

## Contents

1. Introduction .....	1
2. Cesium Adsorption on Three Mordenite .....	3
2.1 Introduction .....	3
2.2 Experimental .....	3
2.2.1 Zeolite Preparation .....	3
2.2.2 Adsorption Procedure .....	3
2.3 Results .....	4
2.3.1 Adsorption Rate .....	4
2.3.2 Distribution Coefficient .....	4
2.3.3 Adsorption Isotherms .....	5
2.4 Conclusion .....	6
3. Adsorption of other Elements .....	18
3.1 Introduction .....	18
3.2 Experimental .....	18
3.3 Results .....	18
3.3.1 Adsorption of Sodium .....	18
3.3.2 Adsorption of Rubidium .....	20
3.3.3 Adsorption of Barium and Strontium .....	20
3.3.4 Adsorption of Nickel, Chromium and PGM .....	20
3.3.5 Comparison with Cs .....	20
3.4 Conclusion .....	20
4. Influence of the other Alkaline Elements on Cesium Adsorption .....	28
4.1 Introduction .....	28
4.2 Experimental .....	28
4.3 Results .....	29
4.3.1 Cesium Adsorption in the Presence of Sodium .....	29
4.3.2 Cesium Adsorption in the Presence of Rubidium .....	29
4.4 Conclusion .....	30
5. Column Adsorption .....	39
5.1 Introduction .....	39
5.2 Experimental .....	39
5.3 Results .....	40
5.3.1 Influence of Flow Rate on the Breakthrough Curve of Cesium .....	40
5.3.2 Influence of other Elements on the Cesium Adsorption on Column .....	41

5.3.3 Influence of Nitric Acid Concentration on the Column Adsorption of Cesium and Alkaline Metals and Comparison of the Capacity Obtained from the Batch Adsorption .....	41
5.4 Conclusion .....	43
6. Conclusion .....	62
Acknowledgement .....	62
References .....	63

## 目 次

1. はじめに .....	1
2. 3種のモルデナイトによるセシウムの吸着 .....	3
2.1 序 .....	3
2.2 実 験 .....	3
2.2.1 モルデナイトの調製 .....	3
2.2.1 吸着実験方法 .....	3
2.3 結 果 .....	4
2.3.1 吸着速度 .....	4
2.3.2 分配係数 .....	4
2.3.3 吸着等温線 .....	5
2.4 結 論 .....	6
3. 他の元素の吸着 .....	18
3.1 序 .....	18
3.2 実 験 .....	18
3.3 結 果 .....	18
3.3.1 ナトリウムの吸着 .....	18
3.3.2 ルビジウムの吸着 .....	20
3.3.3 バリウム及びストロンチウムの吸着 .....	20
3.3.4 ニッケル、クロム及び白金族元素の吸着 .....	20
3.3.5 セシウムとの比較 .....	20
3.4 結 論 .....	20
4. セシウム吸着に及ぼす他のアルカリ金属元素の影響 .....	28
4.1 序 .....	28
4.2 実 験 .....	28
4.3 結 果 .....	29
4.3.1 ナトリウム共存下でのセシウムの吸着 .....	29
4.3.2 ルビジウム共存下でのセシウムの吸着 .....	29
4.4 結 論 .....	30
5. カラム吸着 .....	39
5.1 序 .....	39
5.2 実 験 .....	39

5.3 結 果 .....	40
5.3.1 セシウム の破過曲線に及ぼす流速の影響 .....	40
5.3.2 セシウム のカラム吸着に及ぼす他の元素の影響 .....	41
5.3.3 セシウム及びアルカリ金属のカラム吸着に及ぼす硝酸濃度の影響、 及びバッチ吸着で得た吸着容量との比較 .....	41
5.4 結 論 .....	43
6. 結 論 .....	62
謝 辞 .....	62
参考文献 .....	63



## 1. Introduction

A partitioning process has been studied in Japan Atomic Energy Research Institute (JAERI)<sup>(1-3)</sup> for separating the elements in high-level liquid waste (HLLW) into four groups: transuranium elements (TRU), Tc - platinum group metals (PGM), Sr - Cs and the other elements, as shown in Figure 1.1. In this 4-Group Partitioning Process, HLLW is first denitrated with formic acid to reduce the nitric acid concentration to about 0.5mol/L. Then, TRU and rare earth elements (RE) are separated from the denitrated HLLW by extraction with diisodecylphosphoric acid (DIDPA)<sup>(4)</sup>. The raffinate from the DIDPA extraction process is denitrated to a neutral region as a pH value, which makes it possible to separate Tc and PGM as a precipitate<sup>(5,6)</sup>. Finally, Sr and Cs are separated by adsorption with mixed inorganic ion exchangers, titanitic acid for Sr and zeolite for Cs. The advantage of them is that the exchangers loaded with Sr and Cs can be converted to a very stable form by direct calcination<sup>(7)</sup>. A partitioning test facility was constructed in NUCEF (Nuclear Fuel Cycle Safety Engineering Research Facility) at JAERI, Tokai, in order to demonstrate the 4-Group Partitioning Process with a real HLLW<sup>(8)</sup>. A hot test will be performed soon.

As described above, in the present 4-Group Partitioning Process, Cs is adsorbed with mordenite from the neutral solution, since Sr and Cs are separated simultaneously and Sr adsorption with titanitic acid requires higher pH than 4 or 5. If the Cs adsorption is conducted separately from the Sr adsorption, several choices arise for the separation process, because mordenite has an ability to adsorb Cs from an acidic solution<sup>(9-11)</sup>. For instance, it would be possible to separate Cs by the mordenite adsorption directly from the DIDPA raffinate. The nitric acid concentration in the raffinate is a little higher than 0.5 mol/L. (Extraction of some elements such as RE increases the nitric acid concentration from 0.5 mol/L.) If Cs is separated at an earlier step, the later steps can be operated in much lower radiation field.

In addition, mordenite is known to have a high selectivity toward Cs<sup>(9,12)</sup>, particularly in acidic media. The separation step only for Cs would enable us to isolate Cs. The isolated Cs might be used as a radiation source. One of the purposes of HLLW partitioning is the utilization of valuable elements or nuclides in HLLW<sup>(2,3)</sup>.

For these reasons, the study on the Cs adsorption with mordenite from an acidic solution, typically 0.5 mol/L nitric acid solution, was performed and the results are given and discussed in the present report. The behavior of the other elements contained in the DIDPA raffinate and their effect on the Cs adsorption are also examined.

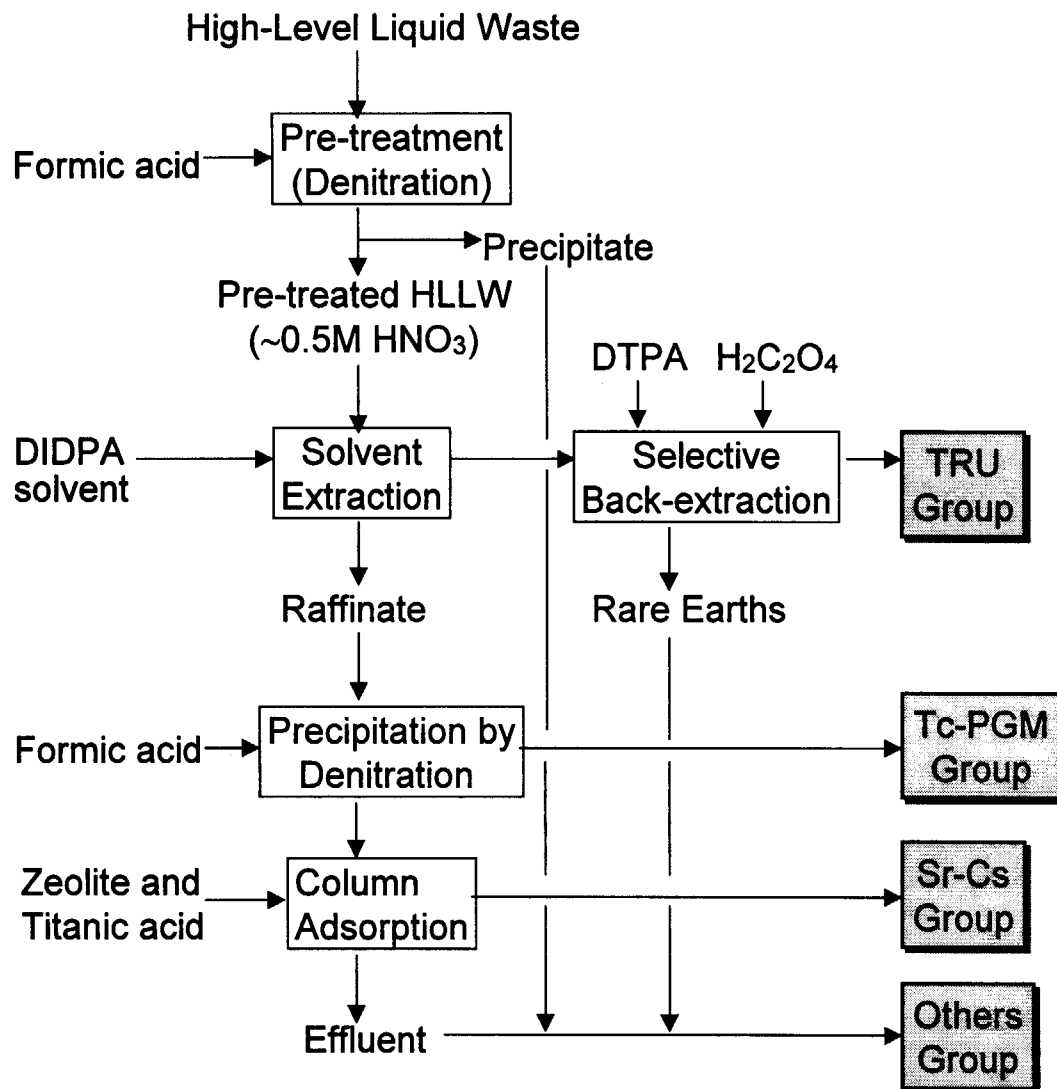


Figure 1.1 4-Group Partitioning Process developed at JAERI

## 2. Cesium Adsorption on Three Mordenite

### 2.1 Introduction

This first experimental period was devoted to compare the adsorption properties of three zeolites toward cesium. One of them, the natural mordenite would be chosen for the treatment of HLLW. The others are two synthetic mordenite type Zeolon 900 Na and H in which the major cation is respectively Na and H. It was well known that they have interesting capacity at low acidity<sup>(13-15)</sup>. But the goal of the work is to demonstrate the recovery of Cs for higher acidity than 0.01 mol/L. The studies present the distribution ratios and the adsorption isotherms at different acidities. The capacity of these zeolites has been determined and compared with other adsorbents in similar conditions.

### 2.2 Experimental

#### 2.2.1 Zeolite Preparation

Natural Mordenite is produced in the suburbs of Sendai, Japan. The two Synthetic Mordenites are produced by Norton company. The chemical composition of a natural mordenite is given in Table 2.1<sup>(15)</sup>. The chemical composition of the natural mordenite used in the present study has not been analyzed, but would be similar to the above.

The zeolites are crushed and sieved to obtain particle size from 20 to 50 mesh. The size lies between 850 and 350  $\mu\text{m}$ . The retained fraction was washed with deionized water until the supernatant becomes clear. The zeolites dried at 45°C for 96 h are stored in a polyethylene bottle at room temperature.

#### 2.2.2 Adsorption Procedure

The solution of cesium was prepared by dissolution of cesium nitrate in nitric acid solution. The initial concentrations of cesium are varied from 0.02 to 5.5 g/L or  $1.5 \times 10^{-4}$  to  $4.10 \times 10^{-2}$  mol/L. 15 ml of aqueous solution containing Cs was shaken with 0.1g of zeolite at  $26 \pm 1$  °C for 24 h. After 3 min centrifugation at 3000 rpm and if necessary dilution, the solution was analyzed by flame emission technique. The initial and final acidities of the solutions were measured by titration with sodium hydroxide solution using titroprocessor.

The adsorption ratio, R, and the distribution coefficient, Kd, are given by the equation :

$$R = \frac{[Cs]_0 - [Cs]_{sol}}{[Cs]_0} * 100, \text{ unit : \%}$$

$$K_d = \frac{[Cs]_0 - [Cs]_{sol}}{[Cs]_{sol}} * \frac{V}{m}, \quad \text{unit: ml/g}$$

where  $[Cs]_0$  = initial concentration of cesium in the solution (mol/L);  $[Cs]_{sol}$  = final concentration of cesium in the solution (mol/L);  $V$  = volume of solution in milliliter, and  $m$  = weight of zeolite in gram.

## 2.3 Results

### 2.3.1 Adsorption Rate

The adsorption rate was studied for a cesium concentration of 0.1 g/L and a concentration of nitric acid in the solution of 0.5 mol/L. Figure 2.1 and Table 2.2 show the increase of the adsorption ratio of cesium with shaking time for three different zeolites.

In the present conditions, it was observed that adsorption equilibrium of cesium was established after 24 hours regardless of zeolites. The behaviors of the two zeolites are different in the first part of the mixing. In the case of the natural mordenite, the cesium was adsorbed faster than with the other zeolites. The difference can be involved on the nature of the cation present in the zeolite. An analysis of the natural mordenite and the two other zeolites would be interesting to have the concentrations of the different present cations.

### 2.3.2 Distribution Coefficient

The first part of the work consisted of a measurement of distribution ratio of Cs at different concentrations in 0.5 mol/L nitric acid solution. The results shown in Figure 2.2 and Table 2.3 revealed that the highest distribution coefficient value was obtained with the synthetic mordenite Zeolon 900H. The fluctuation of the  $K_d$  value may be attributed to a little difference in the initial acidity. Table 2.4 summarizes the values of distribution coefficient.

The influence of acidity of the solution has been examined in the range of the acidity from 0.01 mol/L to about 4 mol/L.

The ion exchange between protons and the cations involved changes the acidity after contact with zeolite. It was observed that for acidity higher 0.1 mol/L there was no variation of the acidity actually after contact with zeolite. At lower acidity than 0.1 mol/L, the acidity of the final aqueous solution is different from the initial and depends on the used zeolite as shown in Figure 2.3 and Table 2.5. In the case of natural mordenite and Zeolon 900Na the final acidity is always lower than the initial. In the case of Zeolon 900H, the final acidity is higher than the initial except for the Cs concentration lower than 0.5 g/L. A similar result was observed for nitric acid concentration at 0.016 mol/L.

The second effect of the proton adsorption is to modify the cesium adsorption, the  $K_d$  values

decreases when the acidity increased as shown in Figure 2.4 and Table 2.6.

### 2.3.3 Adsorption Isotherms

The adsorption isotherms were studied at three different nitric acid concentrations (1, 0.5 and 0.01mol/L). Figure 2.5 and Table 2.3 show the cesium concentration in the zeolite as a function of the cesium concentration in the solution after equilibrium at 0.5mol/L nitric acid. Some similar curves are obtained for the two other acidity and shown in Figures 2.6 and 2.7 and Tables 2.7 and 2.8. Some dispersion appeared specially at high cesium concentrations. In fact this problem is due to a too small difference between the initial and final concentration of Cs.

The ultimate base exchange capacity of a zeolite depends on the chemical composition such as  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio and impurity. The specific exchange capacity varies with a given exchange system. Therefore, the saturation capacity of Cs defined as the maximum Cs concentration in the mordenite were determined at different acid concentrations by using adsorption isotherms and the Langmuir equation<sup>(14)</sup>:

$$[\text{Cs}]_{\text{zeo}} = \frac{K * [\text{Cs}]_{\text{max}} * [\text{Cs}]_{\text{sol}}}{1 + K * [\text{Cs}]_{\text{sol}}} \quad (1)$$

where  $[\text{Cs}]_{\text{sol}}$  (mol/L) and  $[\text{Cs}]_{\text{zeo}}$  (mol/g) are respectively the concentration of Cs in solution and in zeolite ;  $[\text{Cs}]_{\text{max}}$  is the saturation capacity of Cs (mol/g) and K is the Langmuir constant. After rewriting the equation (1), a linear relation can be obtained between the ratio  $[\text{Cs}]_{\text{sol}}/[\text{Cs}]_{\text{zeo}}$  and  $[\text{Cs}]_{\text{sol}}$  :

$$\frac{[\text{Cs}]_{\text{sol}}}{[\text{Cs}]_{\text{zeo}}} = \frac{1}{K * [\text{Cs}]_{\text{max}}} + \frac{1}{[\text{Cs}]_{\text{max}}} * [\text{Cs}]_{\text{sol}} \quad (2)$$

Figures 2.8, 2.9 and 2.10 show the Langmuir plot of Cs for natural mordenite at different acidity. Similar results were obtained with the two other zeolites; the slopes of the different lines are near with each other and therefore the saturation capacity is not very different specially for the high concentration of nitric acid. Table 2.9 summarizes the saturation capacity obtained for each zeolite.

An other method used by Chun-Nun Hsu et al.<sup>(15)</sup> in which the authors explained that the cesium concentration on the zeolite can expressed by :

$$[\text{Cs}]_{\text{zeo}} = [\text{Cs}]_{\text{max}} * (1 - e^{-k * [\text{Cs}]_0 * \frac{V}{n}}) \quad (3)$$

where  $[\text{Cs}]_{\text{zeo}}$  (g/g) and  $[\text{Cs}]_0$  (g/L) are respectively the concentration of Cs in zeolite and in initial solution ;  $[\text{Cs}]_{\text{max}}$  is the saturation capacity (g/g). The use of the relation and the fitting of the equation for the present experiments are given in Figures 2.11, 2.12 and 2.13. The fitting of these curves gives some capacity values

quite similar to those obtained by the Langmuir equation.

Considering the effect of acidity, the obtained saturation capacity for Cs adsorption agree with those obtained by Chun-Nun Hsu et al.<sup>(15)</sup> at lower acidity. Table 2.10 compares the saturation capacity of the three Zeolite and some other adsorbents for cesium<sup>(16)</sup>. The capacity obtained are a little lower than with those obtained with Clinoptilolite.

## 2.4 Conclusion

The kinetics and equilibrium of Cs adsorption on three mordenites have been studied. The obtained results showed that the three mordenite have a similar adsorption behavior. The most important difference was found in kinetics : adsorption rate was faster in the case of the natural mordenite. The saturation capacity of cesium adsorption is found about 0.64mmol/g for natural mordenite at 0.5mol/L nitric acid. Now we have to carry out experiments on the adsorption of other fission and corrosion products and their effects on Cs adsorption, which will be described in the following chapters.

Table 2.1 : Chemical composition of natural mordenite by Chun-Nun Hsu et al.<sup>(15)</sup>

Chemical composition	weight (%)
SiO <sub>2</sub>	72.6
Al <sub>2</sub> O <sub>3</sub>	12.9
Fe <sub>2</sub> O <sub>3</sub>	2.17
CaO	2.58
MgO	0.81
Na <sub>2</sub> O	0.65
K <sub>2</sub> O	1.05
H <sub>2</sub> O	7.26
total	100.02

Table 2.2 : Adsorption rate of cesium as function of shaking time  
at 0.5 mol/L nitric acid  
(volume of solution 15ml, weight of zeolite 0.1g, temperature : 26 ± 1 °C)

time (h)	Natural Mordenite C/C0 (%)	Zeolon 900Na C/C0 (%)	Zeolon 900H C/C0 (%)
0.5	74.8	43.0	56.8
1	80.4	59.5	71.4
2	84.1	70.7	81.2
2	82.6		82.6
4	86.5	79.5	87.9
4	85.0	80.6	85.0
7	86.9	83.1	89.4
7	86.0		89.1
24	89.0	87.5	92.2
24	88.1	87.2	91.7
24	87.6		92.4
48	87.5	87.9	92.4

Table 2.3 : Distribution of cesium at 0.5 mol/L nitric acid  
(volume of solution = 15ml, weight of zeolite = 0.1g, temperature =  $26 \pm 1$  °C)

Natural mordenite		Zeolon 900 Na		Zeolon 900 H	
[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/L	[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/L	[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/L
2.56E-05	2.2E-05	3.05E-05	2.086E-05	1.53E-05	2.312E-05
4.22E-05	4.3E-05	4.83E-05	4.162E-05	3.01E-05	4.434E-05
5.67E-05	6.1E-05	6.35E-05	5.958E-05	4.26E-05	6.270E-05
7.41E-05	8.2E-05	7.98E-05	8.040E-05	5.44E-05	8.436E-05
9.4E-05	1.0E-04			6.6E-05	1.1E-04
9.5E-05	9.9E-05			6.7E-05	1.0E-04
9.4E-05	1.0E-04			6.7E-05	1.1E-04
9.6E-05	1.0E-04			6.7E-05	1.1E-04
9.6E-05	1.0E-04	8.8E-05	1.011E-04	6.0E-05	1.057E-04
2.0E-04	1.95E-04	1.8E-04	1.978E-04	1.4E-04	2.035E-04
1.1E-03	3.11E-04	5.7E-04	3.847E-04	5.5E-04	3.886E-04
1.8E-03	3.88E-04	1.2E-03	4.718E-04	1.4E-03	4.466E-04
2.17E-03	4.498E-04	1.70E-03	5.217E-04	1.84E-03	4.983E-04
4.3E-03	4.88E-04	3.4E-03	6.228E-04	3.9E-03	5.585E-04
6.77E-03	5.767E-04	6.11E-03	6.751E-04	6.18E-03	6.634E-04
1.1E-02	5.72E-04	1.0E-02	6.877E-04	1.1E-02	5.138E-04
1.64E-02	6.056E-04	1.54E-02	7.538E-04	1.60E-02	6.744E-04
2.6E-02	6.15E-04	2.5E-02	7.752E-04	2.7E-02	4.412E-04
3.68E-02	7.310E-04	3.61E-02	8.325E-04	3.72E-02	6.730E-04

Table 2.4 : Distribution coefficient of cesium for different zeolites at 0.5 mol/L nitric acid

Zeolite	Kd (ml/g)
Natural Mordenite	1150
Zeolon 900 Na	1200
Zeolon 900 H	1550

Table 2.5 : Influence of Cs concentration on the acidity of the solution after contact with zeolite ([HNO<sub>3</sub>]<sub>initial</sub> = 0.01mol/L , temperature =  $26 \pm 1$  °C, volume of solution = 15 ml, weight of zeolite = 0.1g )

Cs <sub>init</sub> (g/L)	Natural Mordenite	Zeolon 900Na	Zeolon 900H
0.0682	0.0075	0.0033	0.0096
0.341	0.0085	0.0038	0.0101
0.682	0.0088	0.0049	0.011
1.41	0.0094	0.0067	0.0117
2.728	0.0097	0.0076	0.0123
5.456	0.0098	0.0084	0.0126



Table 2.6 : Influence of nitric acid concentration on the Kd  
 ([Cs]<sub>initial</sub> = 0.1 g/L , temperature = 26 ± 1 °C, volume of solution = 15 ml,  
 weight of zeolite = 0.1g)

Natural mordenite		Zeolon 900Na		Zeolon 900H	
[H] <sub>final</sub> (mol/L)	Kd (ml/g)	[H] <sub>final</sub> (mol/L)	Kd (ml/g)	[H] <sub>final</sub> (mol/L)	Kd (ml/g)
0.0075	7211	0.016	2597	0.023	5280
0.020	4602	0.081	1843	0.097	3196
0.095	2495	0.163	1772	0.171	3053
0.168	2130	0.494	1081	0.494	1691
0.494	1125	0.990	574	0.990	1113
0.990	647	1.950	252	1.950	451
1.950	260	3.800	51	3.800	123
3.800	54				

Table 2.7 : Distribution of cesium at 0.01 mol/L nitric acid  
 (volume of solution = 15ml, weight of zeolite = 0.1g, temperature = 26 ± 1 °C)

Natural mordenite		Zeolon 900 Na		Zeolon 900 H	
[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/g	[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/g	[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/g
1.2E-05	7.5E-05	2.3E-05	7.3E-05	8.8E-06	7.6E-05
8.9E-05	3.7E-04	1.1E-04	3.7E-04	1.1E-04	3.7E-04
7.4E-04	6.6E-04	3.1E-04	7.2E-04	8.1E-04	6.5E-04
4.7E-03	8.3E-04	2.7E-03	1.2E-03	4.9E-03	8.5E-04
1.4E-02	9.9E-04	1.2E-02	1.2E-03	1.5E-02	9.0E-04
3.5E-02	1.1E-03	3.2E-02	1.3E-03	3.6E-02	7.8E-04

Table 2.8 : Distribution of cesium at 1.0 mol/L nitric acid  
 (volume of solution = 15ml, weight of zeolite = 0.1g, temperature = 26 ± 1 °C)

Natural mordenite		Zeolon 900 Na		Zeolon 900 H	
[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/g	[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/g	[Cs] <sub>sol</sub> mol/L	[Cs] <sub>zeo</sub> mol/g
1.0E-04	6.5E-05	1.1E-04	6.4E-05	6.9E-05	7.1E-05
8.3E-04	3.0E-04	7.1E-04	2.9E-04	6.5E-04	3.0E-04
2.7E-03	3.9E-04	2.3E-03	4.6E-04	2.3E-03	4.5E-04
7.3E-03	4.9E-04	6.5E-03	6.2E-04	6.8E-03	5.7E-04
1.7E-02	4.7E-04	1.6E-02	6.4E-04	1.7E-02	5.6E-04
3.8E-02	4.9E-04	3.7E-02	7.2E-04	3.7E-02	6.2E-04

Table 2.9 : The saturation capacity of Cs for each zeolite  
at the different acidity (mmol Cs/g zeolite)

Zeolite	[HNO <sub>3</sub> ] (mol/L)		
	0.01	0.5	1.0
Natural Mordenite	1.11	0.64	0.49
Zeolon 900 Na	1.34	0.80	0.75
Zeolon 900 H	0.78	0.65	0.65

Table 2.10 : Saturation capacities (mmol/g) of different adsorbents for cesium

Sorbent	Ref.	[HNO <sub>3</sub> ] (mol/L)		
		0.5	1.0	3.1
Cd <sub>2</sub> [Fe(CN) <sub>6</sub> ]	(16)	5.4		4.3
Ni <sub>2</sub> [Fe(CN) <sub>6</sub> ]		1.2		1.0
FeMo		2.2		1.3
APM		1.4		0.95
ZrP		0.9		0.9
TiP		0.5		0.3
Clinoptilolite (green)		1.1		0.5
Clinoptilolite (white)	this work	1.0		0.7
Natural Mordenite		0.64	0.49	
Zeolon 900 Na		0.80	0.75	
Zeolon 900 H		0.65	0.65	

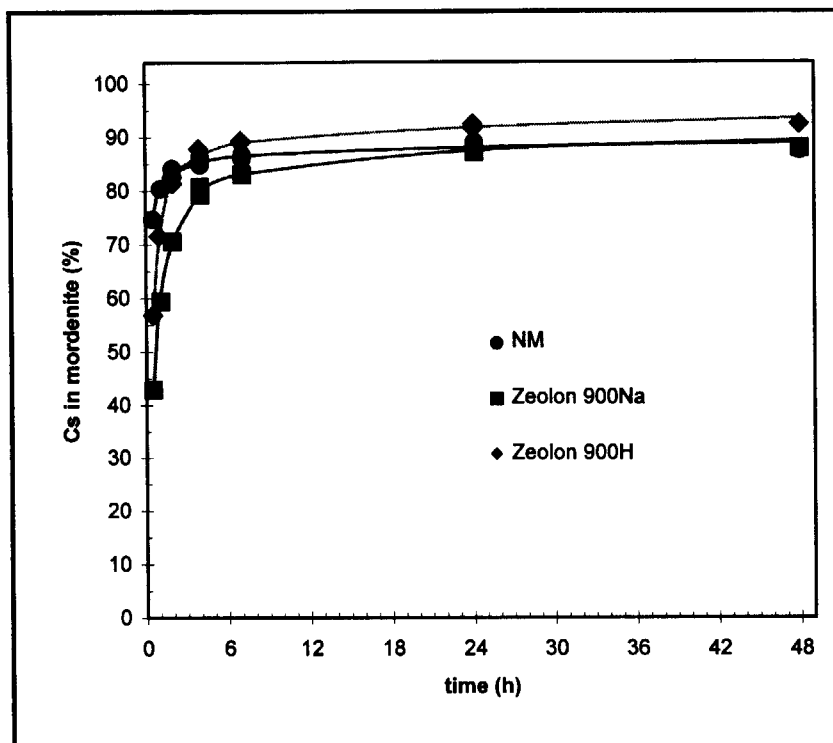


Figure 2.1: Adsorption ratio of cesium as a function of shaking time  
 experimental conditions :  $[\text{HNO}_3] = 0.5\text{mol/L}$ , volume of solution 15ml,  
 weight of zeolite 0.1g, temperature :  $26 \pm 1^\circ\text{C}$ .

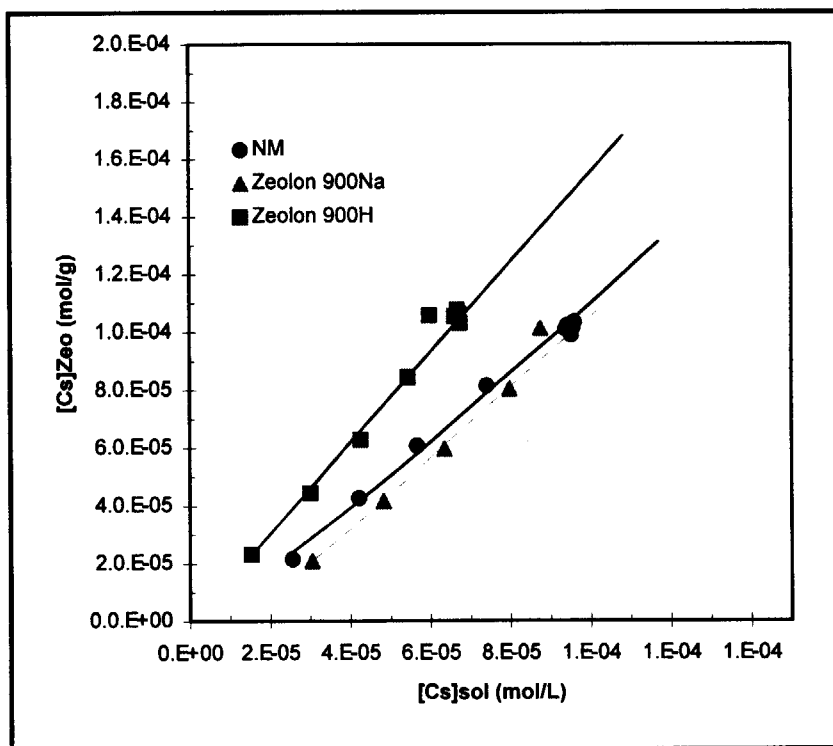


Figure 2.2: Distribution of cesium at 0.5 mol/L nitric acid  
 experimental conditions : volume of solution = 15ml,  
 weight of zeolite = 0.1g, temperature =  $26 \pm 1^\circ\text{C}$ .

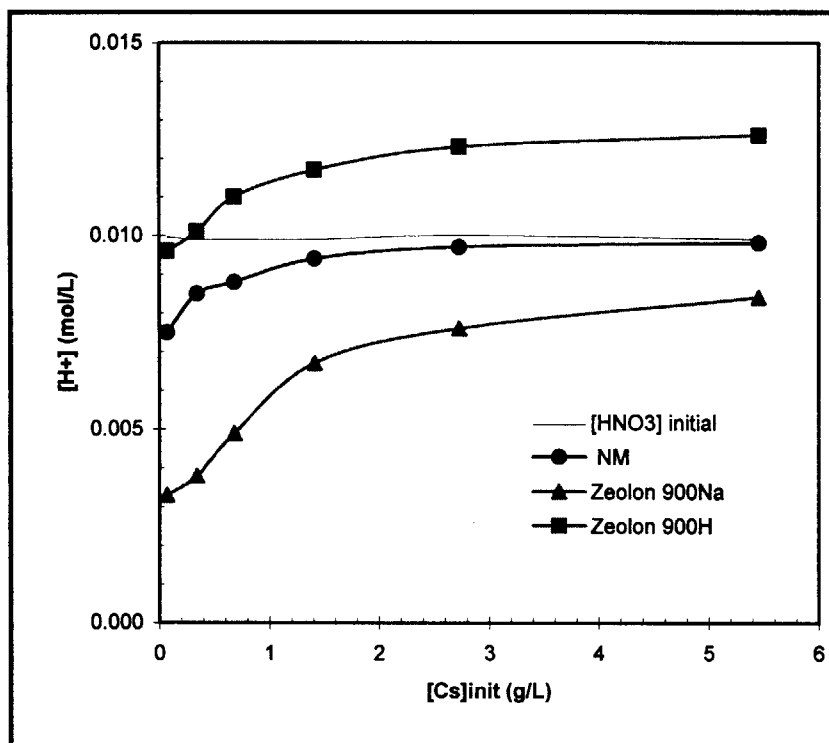


Figure 2.3 : Influence of Cs concentration on the acidity after contact with the zeolite  
 experimental conditions :  $[Cs]_{initial} = 0.1 \text{ g/L}$  ,  $[HNO_3]_{initial} = 0.01 \text{ mol/L}$  ,  
 temperature =  $26 \pm 1 \text{ }^\circ\text{C}$ , volume of solution = 15 ml, weight of zeolite = 0.1g

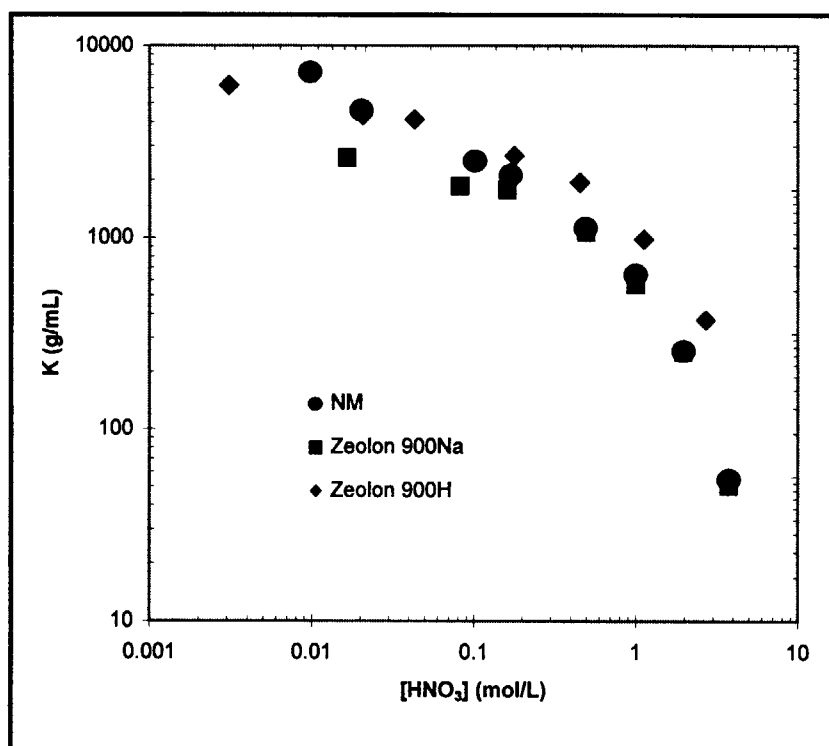


Figure 2.4 : Variation of the distribution coefficient with concentration of nitric acid.  
 experimental conditions :  $[Cs]_{initial} = 0.1 \text{ g/L}$  , temperature =  $26 \pm 1 \text{ }^\circ\text{C}$ ,  
 volume of solution = 15 ml, weight of zeolite = 0.1g

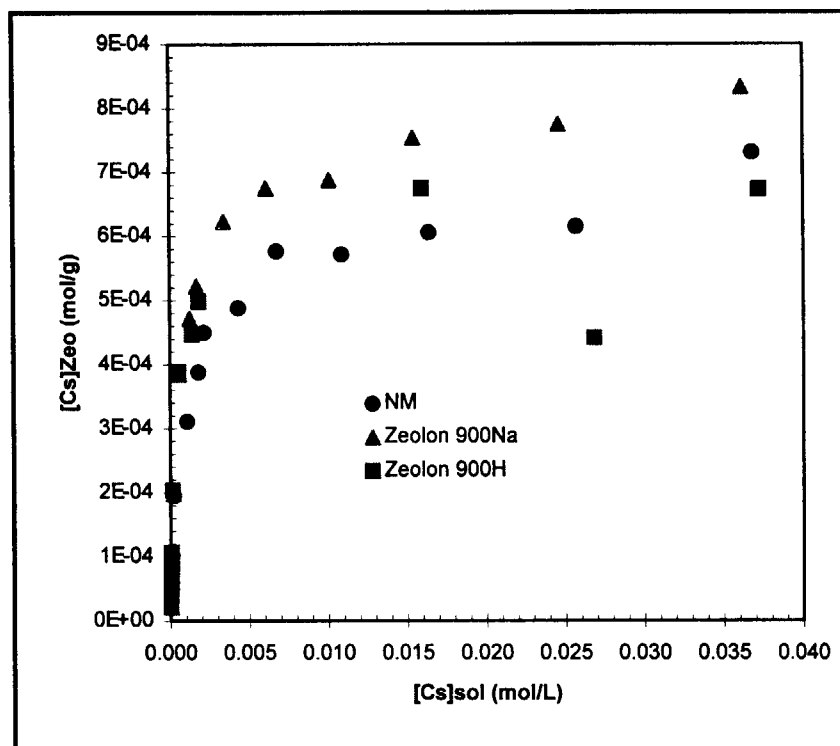


Figure 2.5 : Adsorption isotherms of cesium at 0.5 mol/L nitric acid  
experimental conditions : volume of solution 15ml, weight of zeolite 0.1g,  
temperature :  $26 \pm 1$  °C.

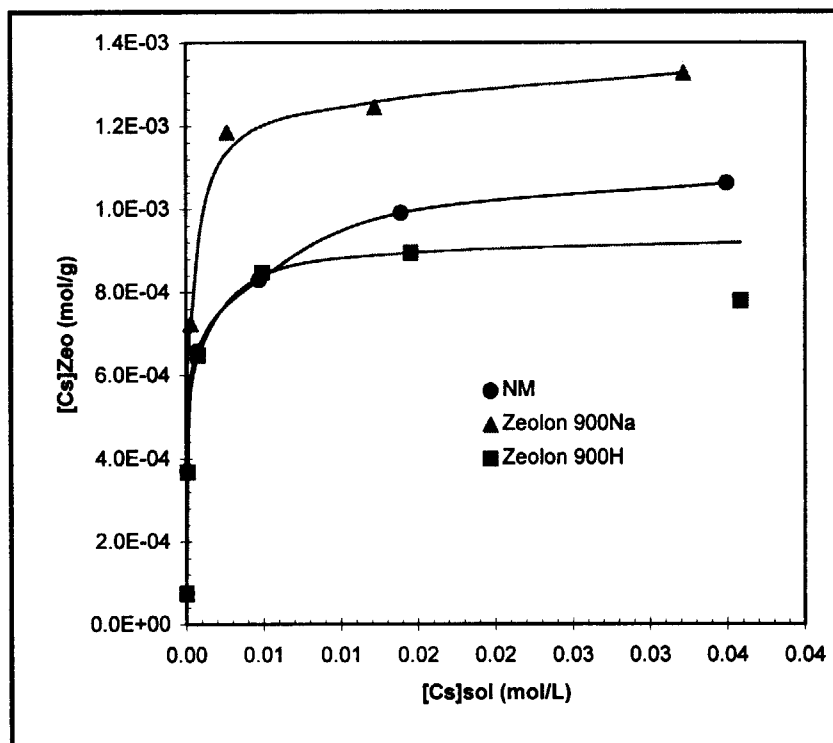


Figure 2.6 : Adsorption isotherms of cesium at 0.01 mol/L nitric acid  
experimental conditions : volume of solution 15ml, weight of zeolite 0.1g,  
temperature :  $26 \pm 1$  °C.

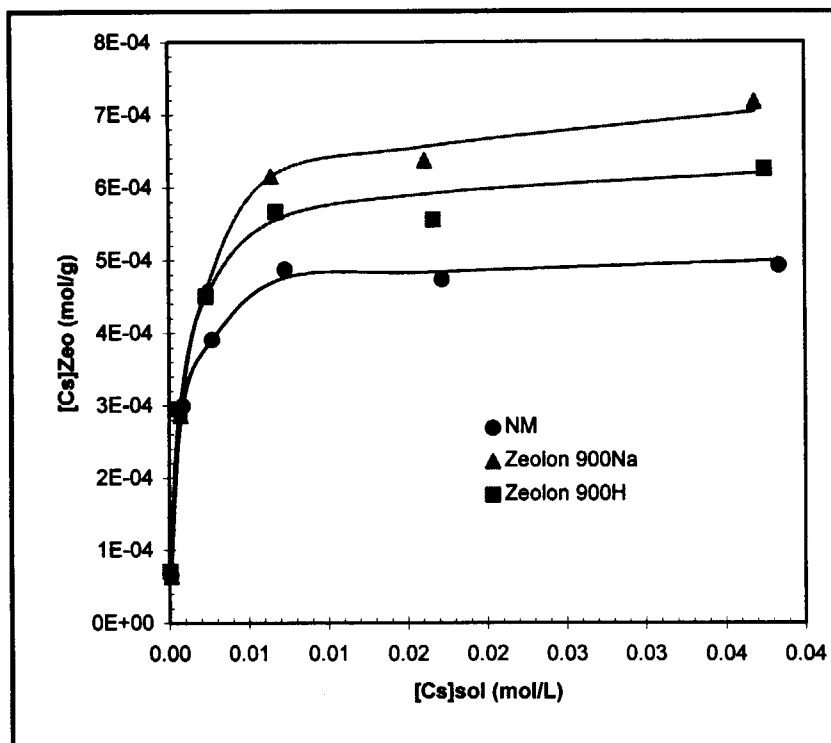


Figure 2.7 : Adsorption isotherms of cesium at 1.0 mol/L nitric acid  
experimental conditions : volume of solution 15ml, weight of zeolite 0.1g,  
temperature :  $26 \pm 1$  °C.

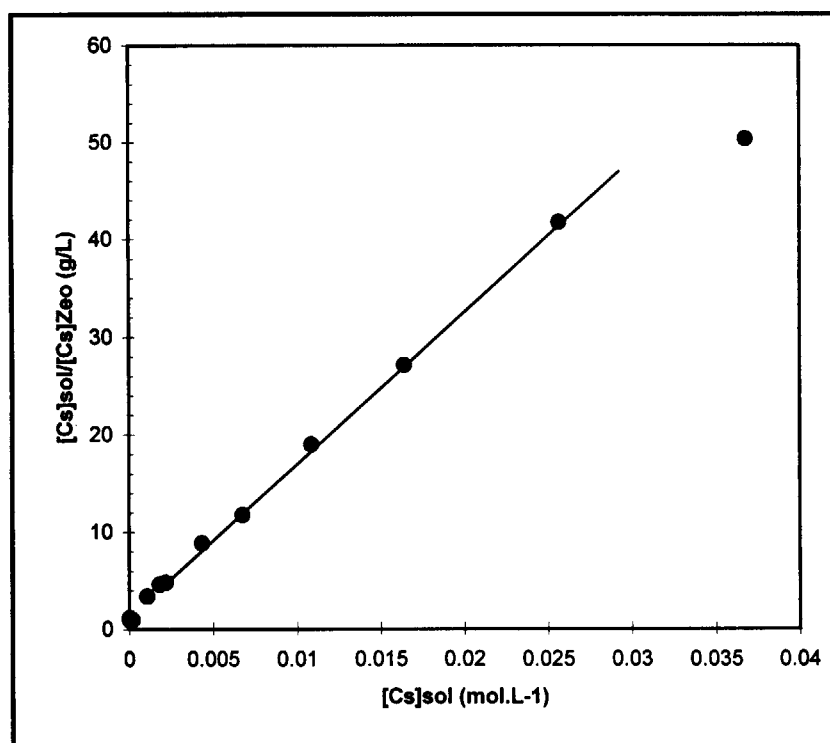


Figure 2.8 :Langmuir plot for Cs adsorption with Natural Mordenite at 0.5 mol/L nitric acid  
experimental conditions : volume of solution 15ml, weight of zeolite 0.1g,  
temperature :  $26 \pm 1$  °C.

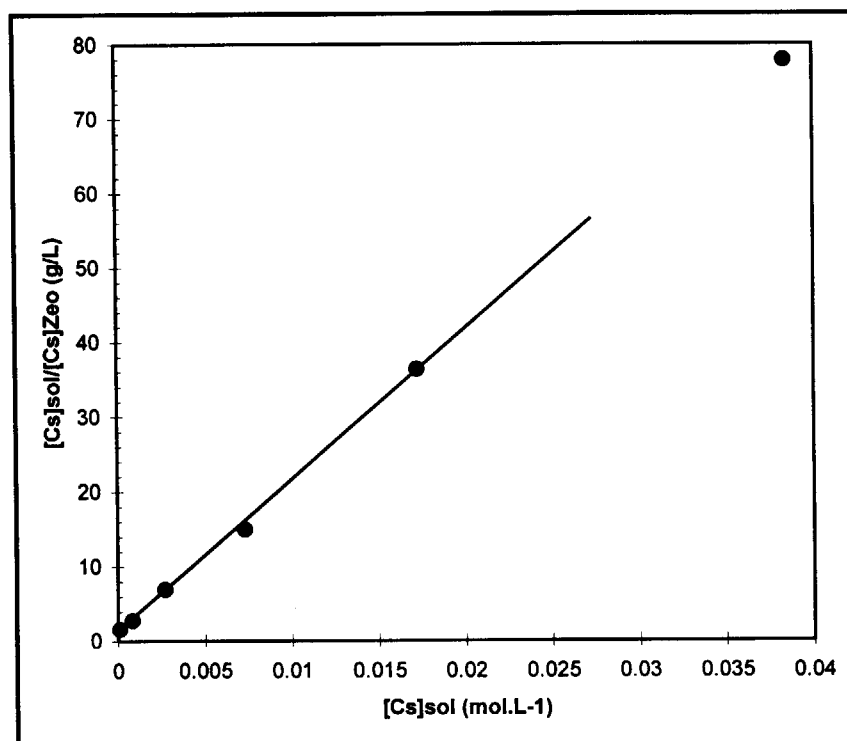


Figure 2.9 :Langmuir plot for Cs adsorption with Natural Mordenite at 1.0 mol/L nitric acid  
experimental conditions : volume of solution 15ml, weight of zeolite 0.1g,  
temperature :  $26 \pm 1$  °C.

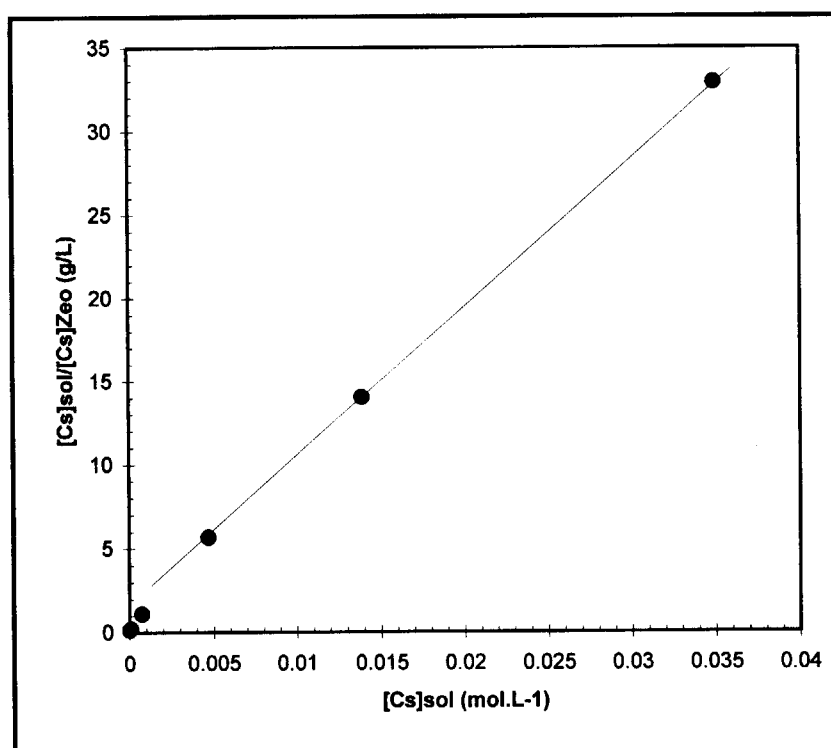


Figure 2.10 :Langmuir plot for Cs adsorption with Natural Mordenite at 0.01 mol/L nitric acid  
experimental conditions : volume of solution 15ml, weight of zeolite 0.1g,  
temperature :  $26 \pm 1$  °C.

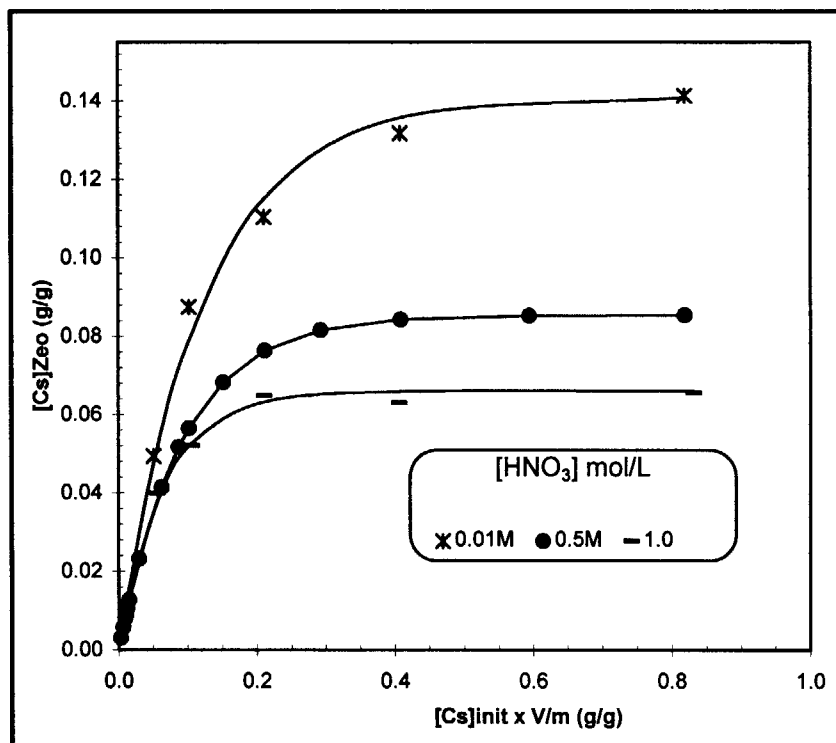


Figure 2.11 : Variation of Cs concentration in Natural Mordenite as a function of the initial concentration.

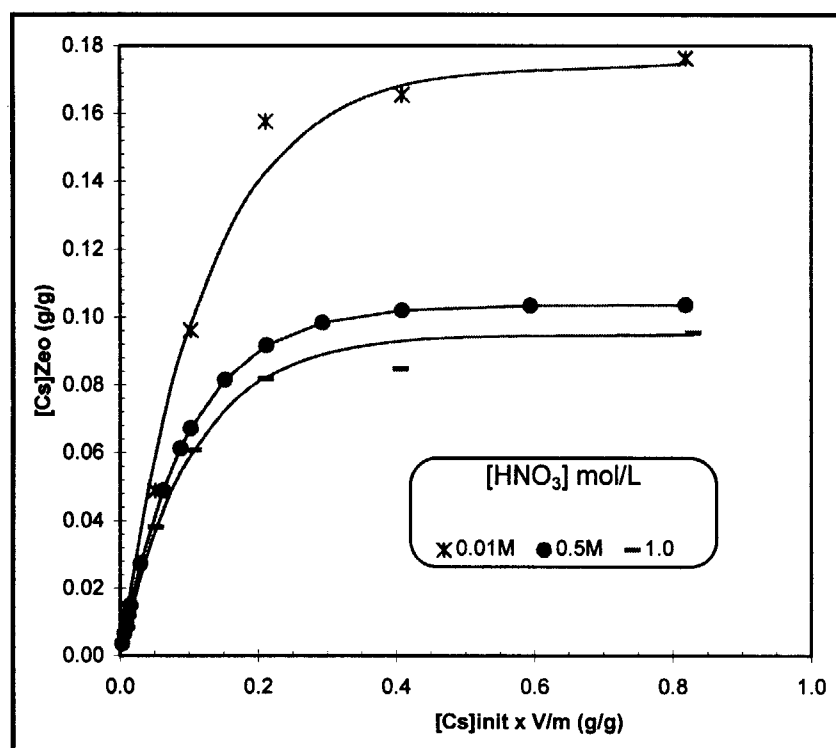


Figure 2.12 : Variation of Cs concentration in Zeolon 900Na as a function of the initial concentration.



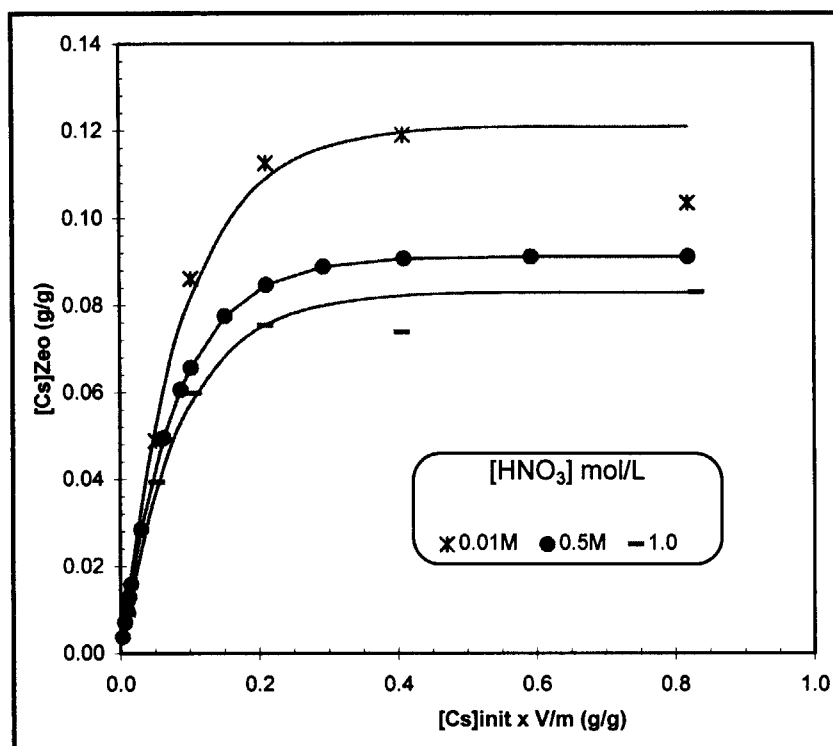


Figure 2.13 : Variation of Cs concentration in Zeolon 900H as a function of the initial concentration.

### 3. Adsorption of other Elements

#### 3.1 Introduction

In Chapter 2, some results have been presented concerning Cs adsorption with three different mordenites. In this chapter, the results concerning adsorption of several fission and corrosion products will be presented. Eight elements have been studied. All are present in the raffinate from DIPDA extraction process. For each element the  $K_d$  values have been determined at several acidities.

#### 3.2 Experimental

The solution of each element was prepared by dissolution of the element in nitrate form in nitric acid 0.5 mol/L. In the case of the platinum group metals (PGM), the elements are already in nitric solution at different concentration ( $[Rh] = 1.0$  wt%,  $[HNO_3] = 3$  mol/L, density = 1.118 ;  $[Pd] = 4.0$  wt%,  $[HNO_3] = 2$  mol/L, density = 1.11,  $[Ru] = 2.5$  wt%,  $[HNO_3] = 0.6$  mol/L). These solutions were purchased from N. E. Chemcat Corp.

The study of acidity influence was performed for an element concentration 0.04 mg/L. For each element seven different acidities have been checked between 0.01 mol/L to 4.0 mol/L of nitric acid. At first, the same procedure described in Chapter 2 has been used for the  $K_d$  determination. Each solution was contacted for 24 hours with 0.1g of zeolite at 26 °C. But for several elements (Sr, Ba, Cr, Ni, and PGM) the adsorption was so weak that one modification has been made to determine the  $K_d$  values for acid concentration higher than 0.1 mol/L. The solutions were contacted with 1g of each zeolite to increase the difference in concentration of each element between the solutions before and after contact with zeolite.

The analyses of sodium and rubidium are performed by flame emission technique with Hewlett Packard machine. For the other elements ICP-AES SPS1200AR from SEIKO is used to perform the simultaneous analyses. All of standards are prepared by dilution of reference solutions at 1000 ppm (1g/L) from each element purchased from Wako Pure Chemical Industries LTD. For the Ru, the standard solution was prepared with the solution used for the adsorption.

#### 3.3 Results

##### 3.3.1 Adsorption of Sodium

The case of sodium is more complicated than the other elements because sodium is present in the zeolite in large amount. First it is important to determine the quantity of sodium in the zeolite. One method

has consisted to contact each zeolite with a nitric solution without sodium. After 24 hours sodium in the solution has been analyzed. The zeolite has been contacted again with a new nitric acid solution. Table 3.1 shows the sodium concentration after each contact. The sodium concentration in mg/g in zeolite are indicated in the third column. The fourth column shows the percentage in weight of sodium in the zeolite. In Chapter 2 the chemical composition for natural mordenite has been given, and Na<sub>2</sub>O represented 0.65% in weight or 0.5% of Na. The two results are close.

An another method was used to determine the quantity of sodium in zeolite with K<sub>d</sub> determination at 0.5 mol/L nitric acid. For the K<sub>d</sub> determination, 5 different solutions with different sodium concentrations have been contacted with the three zeolites. Table 3.2 shows the obtained values of sodium in the aqueous phases before and after contact.

The following relationship (1) expresses the K<sub>d</sub> in the case of sodium present in the initial zeolite :

$$K_d = \frac{[\overline{\text{Na}}]}{[\text{Na}]} \quad (1)$$

where [Na] = sodium concentration in the aqueous phase after contact and  $[\overline{\text{Na}}]$  = sodium concentration in the zeolite after contact.  $[\overline{\text{Na}}]$  can be expressed by relationship (2) :

$$[\overline{\text{Na}}] * \frac{m}{V} = [\text{Na}]_{\text{tot}} - [\text{Na}] = [\text{Na}]_0 + [\overline{\text{Na}}]_0 * \frac{m}{V} - [\text{Na}] \quad (2)$$

where [Na]<sub>0</sub> = initial sodium concentration in the aqueous phase in mg/L,  $[\overline{\text{Na}}]_0$  = initial sodium concentration in the zeolites mg/g, m = mass of zeolite in g and V = the volume of the solution in L.

Using (1) and (2) the relationship (3) can be obtained as following :

$$[\text{Na}] = \frac{1}{1 + \frac{K_d * m}{V}} [\text{Na}]_0 + \frac{[\overline{\text{Na}}]_0}{1 + \frac{K_d * m}{V}} * \frac{m}{V} \quad (3)$$

The use of the relationship (3) permits to calculate the K<sub>d</sub> from the slope of the straight line of sodium concentration after contact as a function of initial sodium concentration as shown in Figure 3.1. The calculated values of K<sub>d</sub> from the slope are given in Table 3.3. In the case of Zeolon 900Na the slope is calculated with the first four points. For the other points the sodium concentrations were at the high limit for the analysis and the calculation gave some negative value for the K<sub>d</sub>.

The values of  $[\overline{\text{Na}}]_0$  can be calculated from the y-intercepts in Figure 3.1 and the K<sub>d</sub> values, and are shown in the second column of Table 3.3.

The two methods have given some similar results for sodium concentration in the three zeolite.

The values of  $[\overline{\text{Na}}]_0$  in Table 3.3 have been used in the study of the influence of the acidity on the K<sub>d</sub>. Table 3.4 gives the different distribution coefficients obtained for each acidity. Figure 3.2 represents K<sub>d</sub> in logarithmic scale as a function of the nitric acid concentration.

### 3.3.2 Adsorption of Rubidium

The adsorption of rubidium has been studied in the range of acidity shown in Table 3.5. Figure 3.3 shows  $K_d$  values for the different acidity of the aqueous solutions. As shown in Figure 3.3 rubidium adsorption is strongly affected by acidity increase as already observed for cesium.

### 3.3.3 Adsorption of Barium and Strontium

A small amount of barium and strontium was found in zeolite, but only in the natural mordenite and in the Zeolon 900Na. The natural mordenite contains about 70  $\mu\text{g/g}$  of Ba and Zeolon 900Na only 5  $\mu\text{g/g}$ . The amount of strontium found is around 30  $\mu\text{g/g}$  in the natural mordenite and 5  $\mu\text{g/g}$  in the Zeolon 900Na.

Table 3.6 shows the values obtained for the  $K_d$  of Ba and Sr. For the Zeolon 900H the  $K_d$  value of Sr is lower than detection limit even at 0.01 mol/L nitric acid.

### 3.3.4 Adsorption of Nickel, Chromium and PGM

Two corrosion products (Ni and Cr) and three PGM (Pd, Rh, and Ru) have been tested for the different acidity. Tables 3.7, 3.8 and 3.9 present respectively the  $K_d$  for natural mordenite, Zeolon 900Na and Zeolon 900H.

### 3.3.5 Comparison with Cs

In this part, the results between Cs adsorption and the other elements will be compared. Tables 3.10, 3.11 and 3.12 show the influence of the acidity on the separation factor for the different zeolites. The separation factor,  $\alpha_{\text{Cs/M}}$ , is the ratio of the  $K_d$  value for Cs to the  $K_d$  for a element M.

Two families can be distinguished. The first group includes elements from the barium to ruthenium. It can be observed in most cases the separation factor is higher than 100. From 0.01 mol/L to 0.2 mol/L of nitric acid, the separation factor increases and decreases later when the nitric acid concentration increases. The second group includes the elements from the same group as Cs. The separation factor are lower than the other group. In the case of rubidium it is lower than 10. For the sodium the separation factor is about 50 for acidity less than 0.5 mol/L. The comparison of the  $K_d$  shows that  $K_{d\text{Cs}} > K_{d\text{Rb}} > K_{d\text{Na}}$ . The result is well known in neutral and alkaline media. The correlation between ionic radius of cation<sup>(17)</sup> and  $K_d$  is observed for different acidity as shown in Table 3.13 and Figure 3.4. The correlation seems to be observed also in the Ba and Sr.

## 3.4 Conclusion

Some data shown in this chapter confirmed that separation of cesium from the solution containing some other elements is possible also in acidic solution. Most cases the separation factor between Cs and

fission products is higher than 1000 (Ba, Sr, Cr, Ni and PGM). It seems that for these elements the separation factor is higher in acidic media than in solution between pH 5 to 8 according to the data by Kanno et al.<sup>(9)</sup>.

For Rb and Na the separation is much lower. Separation factor against cesium was 4.5 for rubidium and 42 for sodium at 0.5 mol/L nitric acid.

Next chapter will describe the adsorption from the solution containing the mixture of cesium and sodium or rubidium. The kinetics of the adsorption from the mixed solution will be also approached.

Table 3.1 : Sodium concentration in zeolites

Zeolite	[Na]		[Na] <sub>0</sub>	
	1 <sup>st</sup> contact mg/L	2 <sup>nd</sup> contact mg/L	mg/g	(weight %)
Natural Mordenite	50	0.5	7.5	0.75
Zeolon 900 Na	215	2	32.5	3.2
Zeolon 900 H	10	nd	1.5	0.015

experimental conditions : [HNO<sub>3</sub>] = 0.5 mol/L ; volume of solution = 15 ml ; weight of zeolite 0.1g ;  
temperature = 26 ± 1°C

Table 3.2 : Sodium concentration in solution before and after contact with zeolites.

[Na] initial in solution		[Na] in solution after contact		
Theo. mg/L	Meas. mg/L	Natural Mordenite mg/L	Zeolon 900 Na mg/L	Zeolon 900H mg/L
0	0	61	201	13
0	0	61	197	12
20	22	77	217	30
40	41.3	91	236	46
80	76.4	127	277	78
100	91.6	142	294	92

experimental conditions : [HNO<sub>3</sub>] = 0.5 mol/L ; volume of solution = 15 ml ; weight of zeolite 0.1g ;  
temperature = 26 ± 1°C

Table 3.3 : K<sub>d</sub> of sodium at 0.5 mol/L nitric acid and initial sodium concentration in zeolites

Zeolite	K <sub>d</sub> ml/g	[Na] <sub>0</sub>	
		mg/g	%weight
Natural Mordenite	20	10	1.0
Zeolon 900 Na	18	33	3.3
Zeolon 900 H	23	2.0	0.020

Table 3.4 : Sodium distribution coefficient as a function of the acidity

[HNO <sub>3</sub> ] mol/L		K <sub>d</sub>		
initial	final	Natural Mordenite ml/g	Zeolon 900 Na ml/g	Zeolon 900 H ml/g
0.01		135 <sup>a</sup>	89 <sup>b</sup>	100 <sup>c</sup>
0.1	0.096	50	37	50
0.19	0.19	42	33	33
0.49	0.48	29	29	40
0.99	0.98	32	27	20
1.97	1.96	26	24	9
3.88	3.85	30	30	12

a : [HNO<sub>3</sub>] = 0.008 mol/L, b : [HNO<sub>3</sub>] = 0.004 mol/L, c : [HNO<sub>3</sub>] = 0.009 mol/L

experimental conditions : Volume of solution = 15 ml ; weight of zeolite 0.1g ; temperature = 26 ± 1°C

Table 3.5 : Rubidium distribution coefficient as a function of the acidity

[HNO <sub>3</sub> ] mol/L		Natural Mordenite ml/g	Kd Rb	
initial	final		Zeolon 900 Na ml/g	Zeolon 900 H ml/g
0.015		2875 <sup>a</sup>	2195 <sup>b</sup>	1959 <sup>c</sup>
0.1	0.1	1015	845	931
0.2	0.2	638	566	648
0.5	0.5	353	309	377
1.0	1.0	155	142	186
2.0	2.0	64	53	87
4.0	4.0	9	4	18

a : [HNO<sub>3</sub>] = 0.013 mol/L, b : [HNO<sub>3</sub>] = 0.007 mol/L, c : [HNO<sub>3</sub>] = 0.014 mol/L  
 experimental conditions : Volume of solution = 15 ml ; weight of zeolite 0.1g ; temperature = 26 ± 1°C

Table 3.6 : Barium and Strontium distribution coefficients as a function of the acidity

	Natural Mordenite			Zeolon 900 Na			Zeolon 900 H		
[HNO <sub>3</sub> ] init	Kd <sub>Ba</sub>	Kd <sub>Sr</sub>	[HNO <sub>3</sub> ] final	Kd <sub>Ba</sub>	Kd <sub>Sr</sub>	[HNO <sub>3</sub> ] final	Kd <sub>Ba</sub>	Kd <sub>Sr</sub>	[HNO <sub>3</sub> ] final
mol/L	ml/g	ml/g	mol/L	ml/g	ml/g	mol/L	ml/g	ml/g	mol/L
0.01	111	28	0.008	156 <sup>b</sup>	32	0.004	< 0.3		0.009
0.1	3.4	< 0.3	0.08	0.3	< 0.3	0.04	< 0.3		0.09
0.2	< 0.3		0.17	< 0.3		0.12	< 0.3		0.19
0.5	< 0.3		0.46	< 0.3		0.41	< 0.3		0.48
1.01	< 0.3		0.96	< 0.3		0.91	< 0.3		0.98
2.08	< 0.3		2.04	< 0.3		1.97	< 0.3		2.03
3.58	< 0.3		3.50	< 0.3		3.42	< 0.3		3.53

experimental conditions : Volume of solution = 15 ml ; weight of zeolite 0.1g ; temperature = 26 ± 1°C

Table 3.7 : Distribution coefficient of several metals as a function of the acidity with Natural Mordenite

[HNO <sub>3</sub> ] mol/L		Kd (ml/g)				
initial	final	Cr	Ni	Pd	Rh	Ru
0.01 <sup>a</sup>	0.008	28	11	7	38	61
0.1	0.08	2.9	1.4	1.3	1.2	4.3
0.2	0.17		< 0.3			2.0
0.5	0.46		< 0.3			1.2
1.01	0.96		< 0.3			0.5
2.08	2.04		< 0.3			0.5
3.58	3.50		< 0.3			0.5

experimental conditions : [M]<sub>initial</sub> = 40 mg/L, Volume of solution = 15 ml ; weight of zeolite 1.0g,  
 (a) weight of zeolite 0.1g; temperature = 26 ± 1°C

Table 3.8 : Distribution coefficient of several metals as a function of the acidity with Zeolon 900Na

[HNO <sub>3</sub> ] mol/L		Kd (ml/g)				
initial	final	Cr	Ni	Pd	Rh	Ru
0.01	0.004	8	6	11.0	16	24
0.1	0.04	< 0.3		16.0	0.5	1.9
0.2	0.12	< 0.3		0.8	< 0.3	0.4
0.5	0.41	< 0.3		1.3	0.5	0.6
1.01	0.91	< 0.3		0.9	< 0.3	0.6
2.08	1.97	< 0.3		1.3	0.6	0.8
3.58	3.42	< 0.3		1.4	0.6	0.9

experimental conditions : [M]<sub>initial</sub> = 40 mg/L, Volume of solution = 15 ml ; weight of zeolite 1.0g,  
(a) weight of zeolite 0.1g; temperature = 26 ± 1°C

Table 3.9: Distribution coefficient of several metals as a function of the acidity with Zeolon 900H

[HNO <sub>3</sub> ] mol/L		Kd (ml/g)				
initial	final	Cr	Ni	Pd	Rh	Ru
0.01	0.008	< 0.3		0.8	< 0.3	
0.1	0.09			< 0.3		
0.2	0.19			< 0.3		
0.5	0.48			< 0.3		
1.01	0.98			< 0.3		
2.08	2.03			< 0.3		
3.58	3.53			< 0.3		

experimental conditions : [M]<sub>initial</sub> = 40 mg/L, Volume of solution = 15 ml ; weight of zeolite 1.0g,  
(a) weight of zeolite 0.1g; temperature = 26 ± 1°C

Table 3.10 : Separation factor between Cesium and different several elements with Natural Mordenite at different nitric acid concentration

[HNO <sub>3</sub> ] <sub>init</sub> mol/L	separation factor $\alpha_{Cs/M}$								
	Rb	Na	Ba	Sr	Cr	Ni	Pd	Rh	Ru
0.01	2.5	53	65	250	261	684	980	190	120
0.1	2.5	50	734	>8320	860	1782	1920	2080	580
0.2	3.3	50			>7100				1060
0.5	3.2	39			>3750				940
1.01	4.2	20			>2160				1300
2.08	4.1	10			>860				520
3.58	6.1	1.8			>180				110



Table 3.11 : Separation factor between Cesium and different several elements with Zeolon 900Na at different nitric acid concentration

[HNO <sub>3</sub> ] <sub>init</sub> mol/L	separation factor $\alpha_{Cs/M}$								
	Rb	Na	Ba	Sr	Cr	Ni	Pd	Rh	Ru
0.01	1.2	29	17	81	330	420	240	160	109
0.1	2.2	50		>6145			115	>6150	970
0.2	3.1	54		>5910			2220	>5910	4430
0.5	3.5	37		>3600			830	>3600	1802
1.01	4.0	21		>1920			640	>1920	960
2.08	4.8	11		>840			190	>840	320
3.58	>13.3	2		>170			40	>170	60

Table 3.12 : Separation factor between Cesium and different several elements with Zeolon 900H at different nitric acid concentration

[HNO <sub>3</sub> ] <sub>init</sub> mol/L	separation factor $\alpha_{Cs/M}$								
	Rb	Na	Ba	Sr	Cr	Ni	Pd	Rh	Ru
0.01	2.7	53		>17600			6600	>17600	
0.1	3.4	64				>10650			
0.2	4.7	93				>10200			
0.5	4.5	42				>5640			
1.01	6.0	56				>3710			
2.08	5.2	50				>1500			
3.58	7.0	10				>410			

Table 3.13 : Comparison of Ionic radii of different elements with K<sub>d</sub> value at different acidities

[HNO <sub>3</sub> ] (mol/L)	Cs	Rb	Na	Ba	Sr
0.01	7211	2875	135	111	28
0.1	2495	1015	50	3.4	0.3
0.5	1125	353	29		
Ionic radius <sup>(17)</sup> (Å)	1.69	1.49	1.33	1.35	1.13

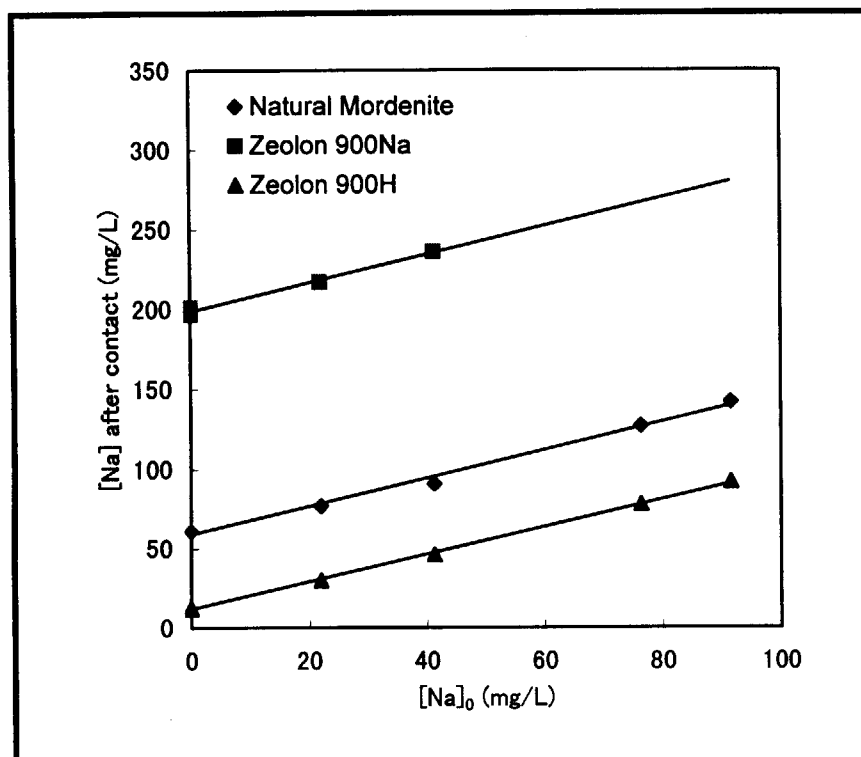


Fig. 3.1 : Sodium concentration after contact with zeolites as a function of the initial concentration  
 experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$  ; Volume of solution = 15 ml ; weight of zeolite 0.1g ;  
 temperature =  $26 \pm 1^\circ\text{C}$

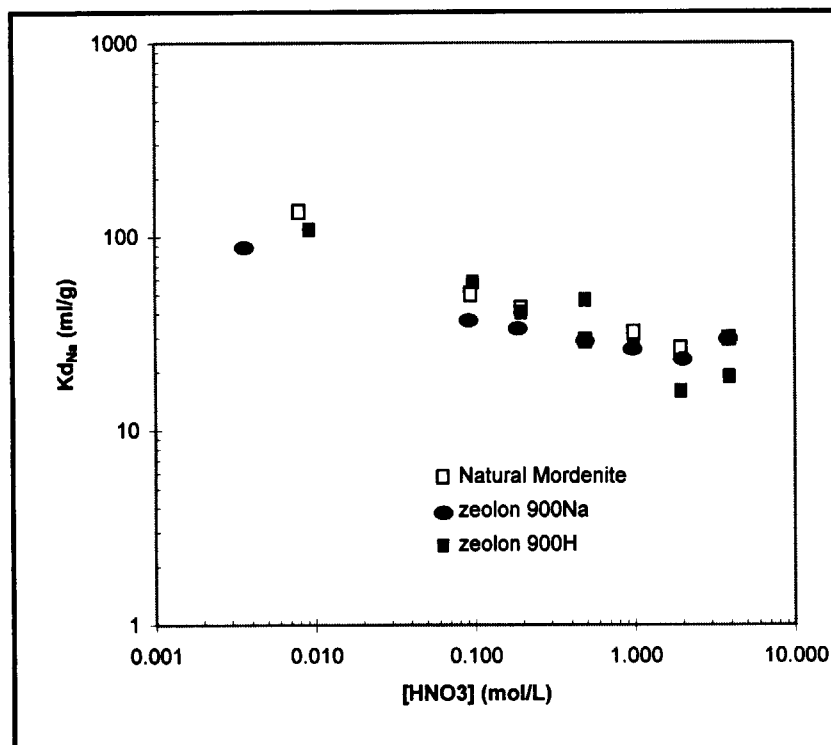


Figure 3.2 : Influence of acidity on the distribution coefficient of sodium in logarithmic scale  
 experimental conditions : Volume of solution = 15 ml ; weight of zeolite 0.1g ; temperature =  $26 \pm 1^\circ\text{C}$

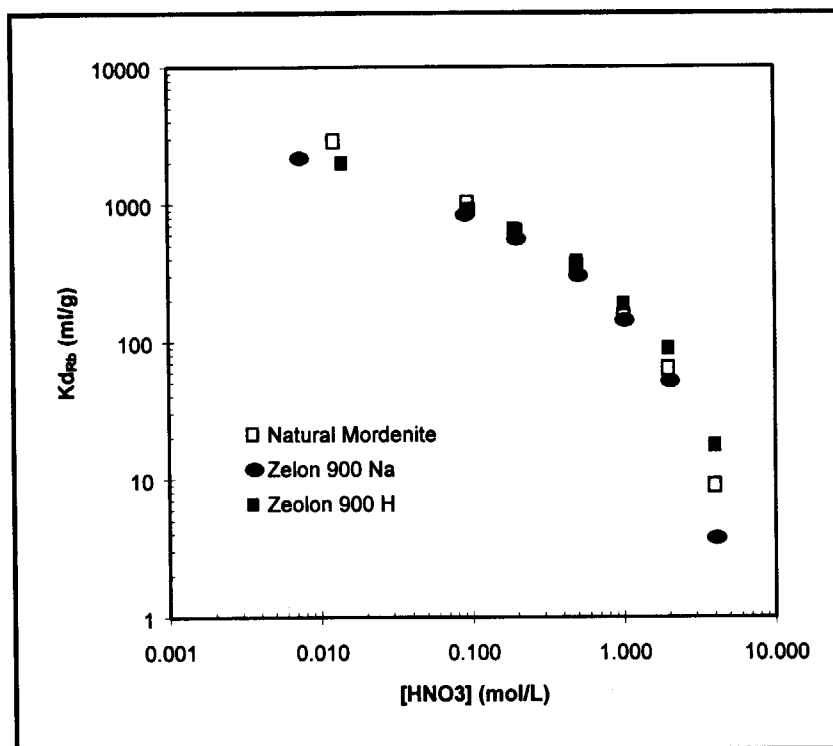


Figure 3.3 : Influence of acidity on the distribution coefficient of rubidium in logarithmic scale  
experimental conditions : Volume of solution = 15 ml ; weight of zeolite 0.1g ; temperature =  $26 \pm 1^\circ\text{C}$

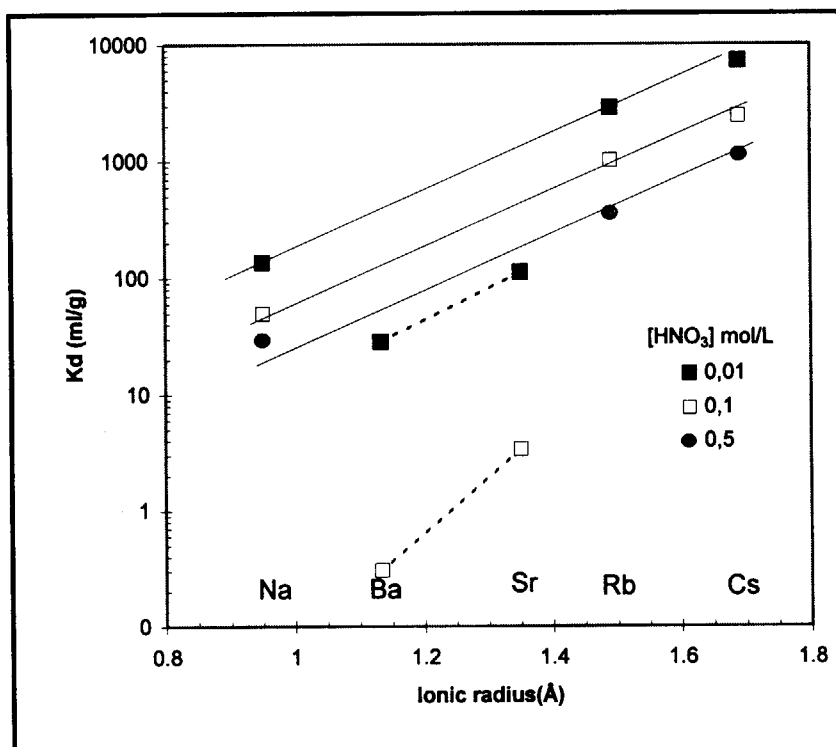


Figure 3.4 : Influence of ionic radius of cation on the distribution coefficient of these cation  
in semi-logarithmic scale

## 4. Influence of the other Alkaline Elements on Cesium Adsorption

### 4.1 Introduction

This chapter completes the results concerning cesium adsorption in batch. After that, the choice of one of the three mordenite will be presented for the cesium adsorption in column. The study in this chapter concerns the cesium adsorption in the presence of other alkaline elements (Na and Rb). The influence on the kinetic of cesium adsorption has been studied for one sodium concentration.

### 4.2 Experimental

The solution of each element (Cs, Na or Rb) was prepared by dissolution of the element in nitrate form in nitric acid 0.5 mol/L. The concentration of the element in stock solution is about 25 g/L. The solutions for experiments were prepared by mixing the different stock solution. Each solution was contacted for 24 hours with 0.1g of zeolite at 26 °C.

The analyses of sodium and rubidium were performed by flame emission technique with Hewlett Packard machine. In this study the problem is to analyze two alkali elements present in the same solution. Sodium or rubidium interfere on cesium analysis and also cesium interfere strongly on rubidium and weakly on sodium. To prevent this problem, two solutions have been used for cesium analysis; one is sodium-cesium standard prepared with sodium for different sodium concentration (0.2 , 2 and 7 g/L), the other is the solution added with potassium in both standard and sample ( $[K] = 10\text{g/L}$ ). The used potassium limits the rubidium effect on the analysis of cesium as shown in Figure 4.1.

In the case of the rubidium analysis it was observed that the cesium interferes with the rubidium signal by increasing the background signal. Figure 4.2 shows the influence of cesium concentration on optical density of rubidium at 780nm. It is possible to analyze rubidium if the solution contained a large amount of cesium. In this case a small variation of cesium concentration of the sample will not affect strongly on the rubidium signal. The analysis are carried out by addition of cesium in the solution to obtain a constant Cs concentration about 10 g/L. By the methods, the errors in the analysis of the mixed solutions were minimized, but were still larger than in the analysis of the solutions containing a single element to be analyzed.

### 4.3 Results

#### 4.3.1 Cesium Adsorption in the Presence of Sodium

In the HLLW which was selected as a starting solution for the study on partitioning process in JAERI, the sodium concentration is 0.076 mol /L ( $\approx 1.8$  g/L)<sup>(18)</sup>. One important parameter to be checked before the start of column adsorption is the influence of sodium concentration on the cesium adsorption. Two different concentrations have been selected, one close to the sodium concentration in the HLLW, and the other one much higher (7 g/L). In the first case, the variation of the cesium Kd has been checked. For the higher sodium concentration only low cesium concentration have been studied. It was observed as shown in Tables 4.1, 4.2 and 4.3 and Figures 4.3, 4.4 and 4.5 that the presence of sodium in the range 0 to 2 g/L did not really modified the cesium adsorption. In the case of higher sodium concentration the Kd of cesium decreases .

Harjula et al.<sup>(19)</sup> have already studied the effect of sodium on the cesium adsorption at pH range 6-9. Cesium adsorption depended with slope -1 for sodium concentration higher than 0.08 mol/L. For lower concentration the effect of sodium decreases.

To check the effect of sodium on the kinetics of cesium adsorption it has been chosen to examine the mordenite contained already some sodium. This mordenite is the synthetic mordenite Zeolon 900Na. For this mordenite it was observed that the kinetics looks a little slower than for the two other mordenites (Figure 2.1). This reduction of the kinetics is perhaps attributed to the sodium including in the mordenite. Since the first result was not enough to concluded on sodium effect, a complementary experiment with sodium included in the initial solution has been carried out. In this case the initial solution contained about 2 g/L of sodium and 100mg/L of cesium. As shown in Figure 4.6 the effect of sodium concentration is not detectable in the adsorption kinetics of cesium. More than 80 % of cesium has been absorbed in the first 4 hours.

#### 4.3.2 Cesium Adsorption in the Presence of Rubidium

In the experiments the rubidium concentration is fixed at  $7.3 \times 10^{-3}$  mol/L. This is the rubidium concentration in the HLLW. It seems that rubidium effect can be neglected for the initial cesium concentration higher than 0.1 g/L as shown in Tables 4.1, 4.2 and 4.3 and Figures 4.7, 4.8 and 4.9. For lower concentration than 0.1 g/L the cesium analysis becomes difficult and it is not possible to conclude on a decrease of the cesium Kd.

#### 4.4 Conclusion

As was shown in this chapter, sodium and rubidium do not modify the behavior of the cesium adsorption.

The results of batch adsorption of cesium with three different mordenites described in three chapters show that the three mordenites have very close behavior with the different parameters studied. The  $K_d$  value with a pure cesium solution is higher than 1000 for each mordenite at 0.5mol/L nitric acid. The kinetics are close with each other but maybe a little slower for Zeolon 900Na. The separation factor is not influenced by nature of the mordenite and in the last experiment it was shown that sodium and rubidium will not interfere on  $K_d$  of cesium. It seems that it is not by these parameters that it is possible to select one of these mordenites; some other aspects have to be used such as chemical behavior in nitric acid or economical aspect. For this aspect the natural mordenite can be selected for its lowest price compared to the synthetic mordenites Zeolon 900Na and 900H.

Table 4.1 : Kd of cesium with natural mordenite for different concentrations of sodium and rubidium

experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$ , volume of solution 15 ml,  
weight of zeolite : 0.1g, temperature :  $26 \pm 1^\circ\text{C}$

$[\text{Na}] = 0 \text{ g/L}$ ,  $[\text{Rb}] = 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	1750
$7.8 \cdot 10^{-4}$	105	1530
$1.7 \cdot 10^{-4}$	23	850
$3.3 \cdot 10^{-4}$	43	1010
$4.6 \cdot 10^{-4}$	61	1070
$6.2 \cdot 10^{-4}$	82	1100
$7.6 \cdot 10^{-4}$	102	1060
$1.5 \cdot 10^{-3}$	199	1000
$3.1 \cdot 10^{-3}$	418	290
$4.4 \cdot 10^{-3}$	584	220
$5.1 \cdot 10^{-3}$	682	210
$7.6 \cdot 10^{-3}$	1010	110
$1.1 \cdot 10^{-2}$	1412	90
$1.5 \cdot 10^{-2}$	1954	50
$2.1 \cdot 10^{-2}$	2728	40
$3.0 \cdot 10^{-2}$	3960	20
$4.1 \cdot 10^{-2}$	5456	20

$[\text{Na}] \approx 2 \text{ g/L}$ ,  $[\text{Rb}] \approx 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	1390
$7.8 \cdot 10^{-4}$	105	940
$3.1 \cdot 10^{-4}$	42	2220
$7.9 \cdot 10^{-4}$	105	800
$3.7 \cdot 10^{-3}$	490	260
$7.3 \cdot 10^{-3}$	969	110
$1.5 \cdot 10^{-2}$	2003	50
$3.7 \cdot 10^{-2}$	4960	20

$[\text{Na}] = 0 \text{ g/L}$ ,  $[\text{Rb}] = 0.62 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$2.9 \cdot 10^{-4}$	39	1140
$6.7 \cdot 10^{-4}$	89	370
$3.6 \cdot 10^{-3}$	479	190
$7.7 \cdot 10^{-3}$	1030	140
$1.5 \cdot 10^{-2}$	1988	50
$3.6 \cdot 10^{-2}$	4748	10

$[\text{Na}] \approx 7 \text{ g/L}$ ,  $[\text{Rb}] \approx 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	520
$7.8 \cdot 10^{-4}$	104	360

Table 4.2 : Kd of cesium with synthetic mordenite Zeolon 900Na for different concentrations of sodium and rubidium

experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$ , volume of solution 15 ml,  
weight of zeolite : 0.1g, temperature :  $26 \pm 1^\circ\text{C}$

$[\text{Na}] = 0 \text{ g/L}$ ,  $[\text{Rb}] = 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	1540
$7.8 \cdot 10^{-4}$	104	1510
$1.7 \cdot 10^{-4}$	23	690
$3.3 \cdot 10^{-4}$	43	860
$4.6 \cdot 10^{-4}$	61	940
$6.2 \cdot 10^{-4}$	82	1010
$7.6 \cdot 10^{-4}$	102	1160
$1.5 \cdot 10^{-3}$	199	1100
$3.1 \cdot 10^{-3}$	418	680
$4.4 \cdot 10^{-3}$	584	380
$5.1 \cdot 10^{-3}$	682	310
$7.6 \cdot 10^{-3}$	1010	180
$1.1 \cdot 10^{-2}$	1412	110
$1.5 \cdot 10^{-2}$	1954	70
$2.1 \cdot 10^{-2}$	2728	50
$3.0 \cdot 10^{-2}$	3960	30
$4.1 \cdot 10^{-2}$	5456	20

$[\text{Na}] \approx 2 \text{ g/L}$ ,  $[\text{Rb}] \approx 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	1590
$7.8 \cdot 10^{-4}$	104	1180
$3.1 \cdot 10^{-4}$	42	2380
$7.9 \cdot 10^{-4}$	105	950
$3.7 \cdot 10^{-3}$	490	370
$7.3 \cdot 10^{-3}$	969	170
$1.5 \cdot 10^{-2}$	2003	80
$3.7 \cdot 10^{-2}$	4960	20

$[\text{Na}] = 0 \text{ g/L}$ ,  $[\text{Rb}] = 0.62 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$2.9 \cdot 10^{-4}$	39	1260
$6.7 \cdot 10^{-4}$	89	390
$3.6 \cdot 10^{-3}$	479	400
$7.7 \cdot 10^{-3}$	1030	180
$1.5 \cdot 10^{-2}$	1988	60
$3.6 \cdot 10^{-2}$	4748	20

$[\text{Na}] \approx 7 \text{ g/L}$ ,  $[\text{Rb}] \approx 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	660
$7.8 \cdot 10^{-4}$	104	490



Table 4.3 : Kd of cesium with synthetic mordenite Zeolon 900H for different concentrations of sodium and rubidium

experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$ , volume of solution 15 ml,  
weight of zeolite : 0.1g, temperature :  $26 \pm 1^\circ\text{C}$

$[\text{Na}] = 0 \text{ g/L}, [\text{Rb}] = 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	2800
$7.8 \cdot 10^{-4}$	104	2430
$1.7 \cdot 10^{-4}$	23	1510
$3.3 \cdot 10^{-4}$	43	1470
$4.6 \cdot 10^{-4}$	61	1470
$6.2 \cdot 10^{-4}$	82	1550
$7.6 \cdot 10^{-4}$	102	1770
$1.5 \cdot 10^{-3}$	199	1450
$3.1 \cdot 10^{-3}$	418	710
$4.4 \cdot 10^{-3}$	584	320
$5.1 \cdot 10^{-3}$	682	270
$7.6 \cdot 10^{-3}$	1010	140
$1.1 \cdot 10^{-2}$	1412	110
$1.5 \cdot 10^{-2}$	1954	50
$2.1 \cdot 10^{-2}$	2728	40
$3.0 \cdot 10^{-2}$	3960	16
$4.1 \cdot 10^{-2}$	5456	18

$[\text{Na}] \approx 2 \text{ g/L}, [\text{Rb}] \approx 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	1290
$7.8 \cdot 10^{-4}$	104	970
$3.1 \cdot 10^{-4}$	42	2010
$7.9 \cdot 10^{-4}$	105	790
$3.7 \cdot 10^{-3}$	490	270
$7.3 \cdot 10^{-3}$	969	120
$1.5 \cdot 10^{-2}$	2003	60
$3.7 \cdot 10^{-2}$	4960	20

$[\text{Na}] = 0 \text{ g/L}, [\text{Rb}] = 0.62 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$2.9 \cdot 10^{-4}$	39	1080
$6.7 \cdot 10^{-4}$	89	310
$3.6 \cdot 10^{-3}$	479	290
$7.7 \cdot 10^{-3}$	1030	150
$1.5 \cdot 10^{-2}$	1988	50
$3.6 \cdot 10^{-2}$	4748	20

$[\text{Na}] \approx 7 \text{ g/L}, [\text{Rb}] \approx 0 \text{ g/L}$

Cs init		Kd g/ml
mol/L	mg/L	
$3.1 \cdot 10^{-4}$	42	560
$7.8 \cdot 10^{-4}$	104	420

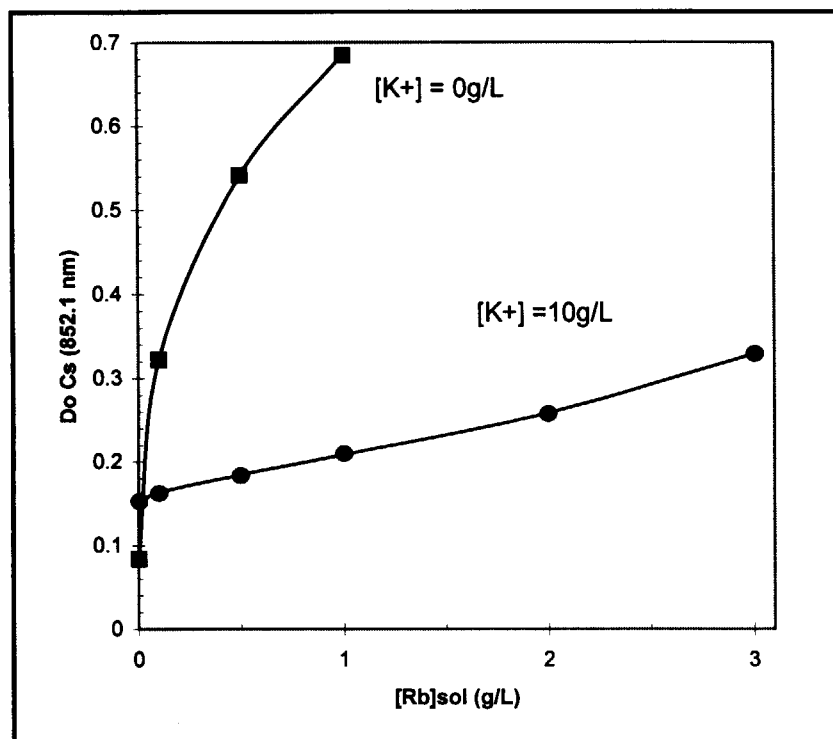


Figure 4.1 : Influence of rubidium concentration on the optical density of the cesium  
Experimental conditions :  $[\text{HNO}_3]$  0.5 mol/L ,  $[\text{Cs}]$  constant, slit width 0.2 nm

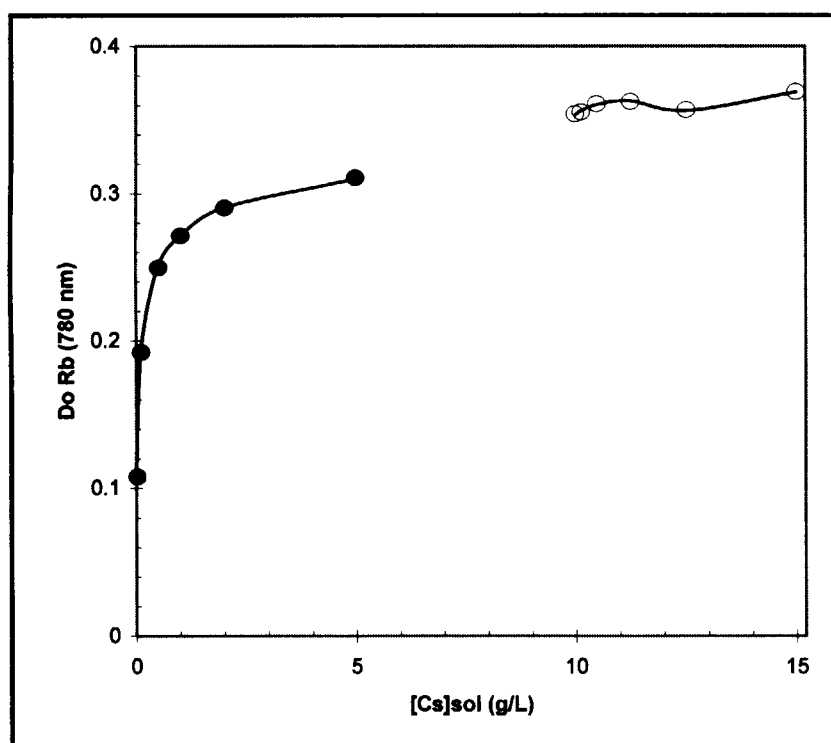


Figure 4.2 : Influence of cesium concentration on the optical density of the rubidium  
Experimental conditions :  $[\text{HNO}_3]$  0.5 mol/L ,  $[\text{Rb}]$  constant, slit width 0.2 nm  
● solutions of cesium and rubidium mixture,  
○ rubidium analyses of solutions after contact with zeolites and the addition on cesium

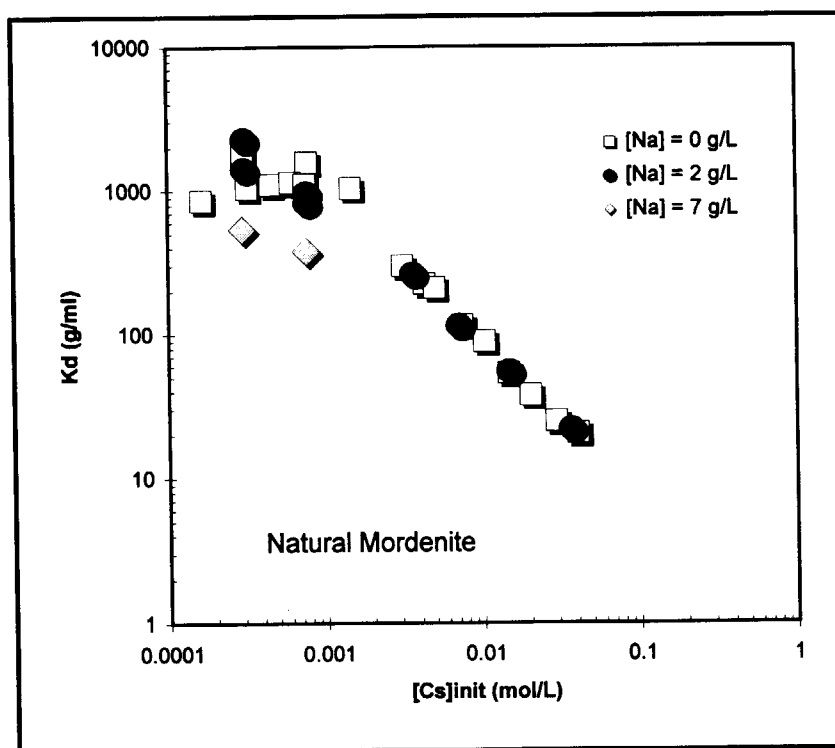


Figure 4.3 : Influence of sodium concentration on cesium  $K_d$  at different Cs concentration with natural mordenite  
 experimental conditions :  $[\text{HNO}_3]=0.5 \text{ mol/L}$ , volume of solution 15 ml, weight of zeolite 0.1g, temperature :  $26\pm 1^\circ\text{C}$

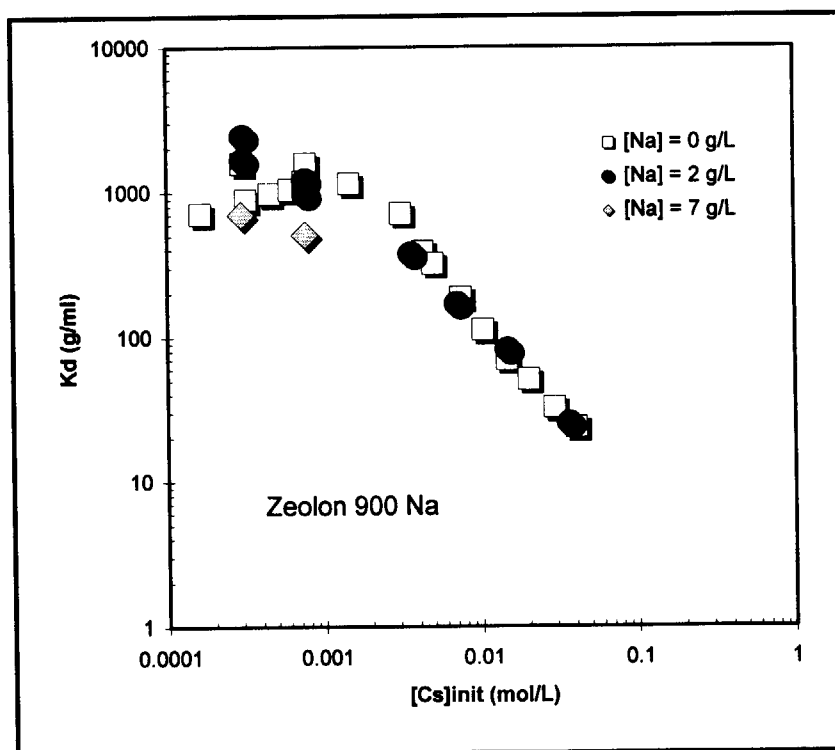


Figure 4.4 : Influence of sodium concentration on cesium  $K_d$  at different Cs concentration with Zeolon 900Na  
 Experimental conditions :  $[\text{HNO}_3]=0.5 \text{ mol/L}$ , volume of solution 15 ml, weight of zeolite 0.1g, temperature :  $26\pm 1^\circ\text{C}$

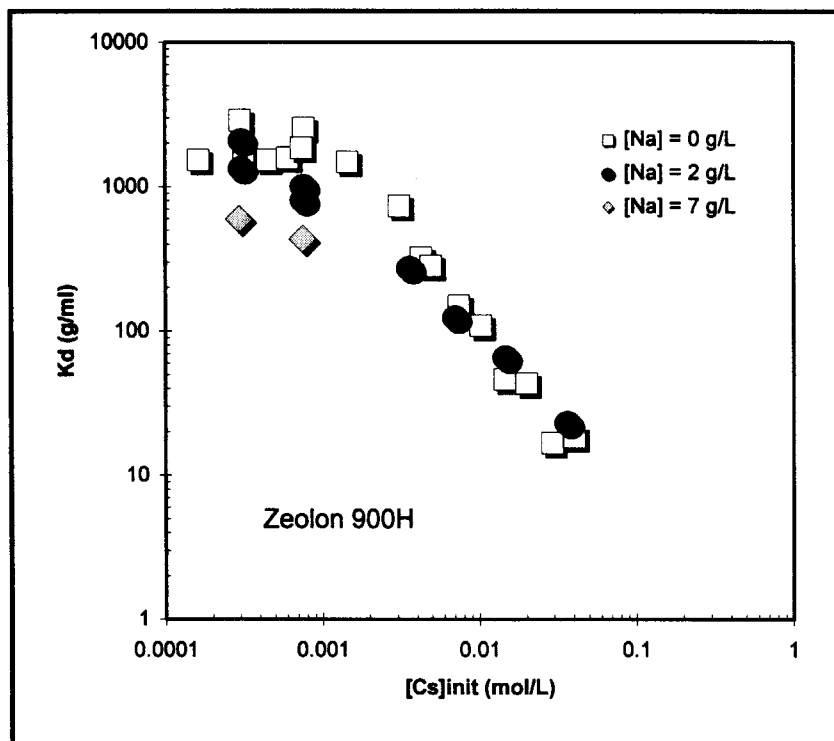


Figure 4.5 : Influence of sodium concentration on cesium  $K_d$  at different Cs concentration with Zeolon 900H  
 Experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$ , volume of solution 15 ml, weight of zeolite 0.1g, temperature :  $26 \pm 1^\circ\text{C}$

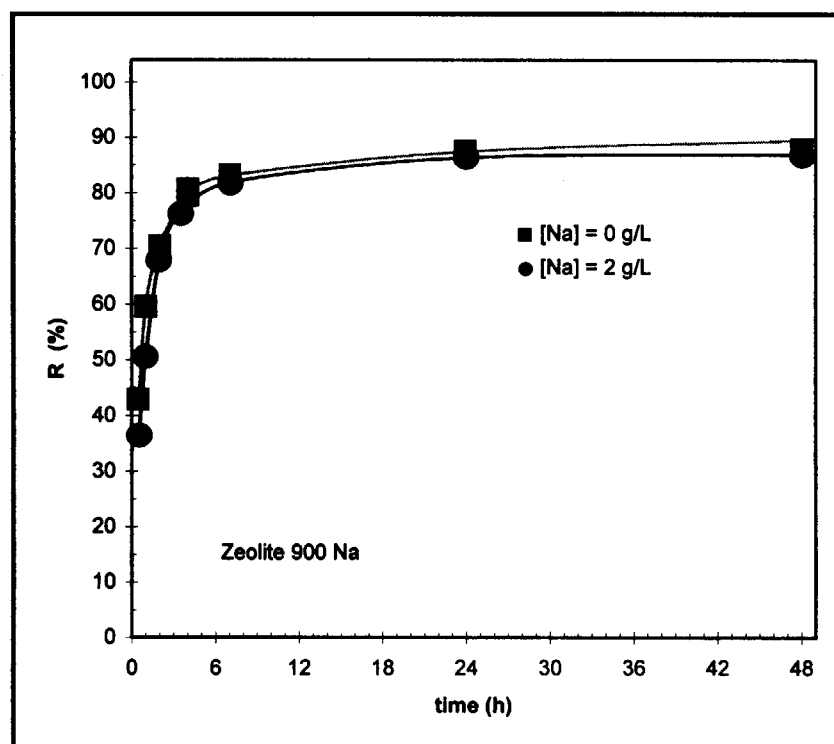


Figure 4.6 : Adsorption kinetics of cesium with synthetic Zeolon 900Na at two concentrations of sodium  
 Experimental conditions :  $[\text{Cs}] = 0.1 \text{ g/L}$ ,  $[\text{HNO}_3] = 0.5 \text{ mol/L}$ , volume of solution 15 ml, weight of zeolite : 0.1g, temperature :  $26 \pm 1^\circ\text{C}$

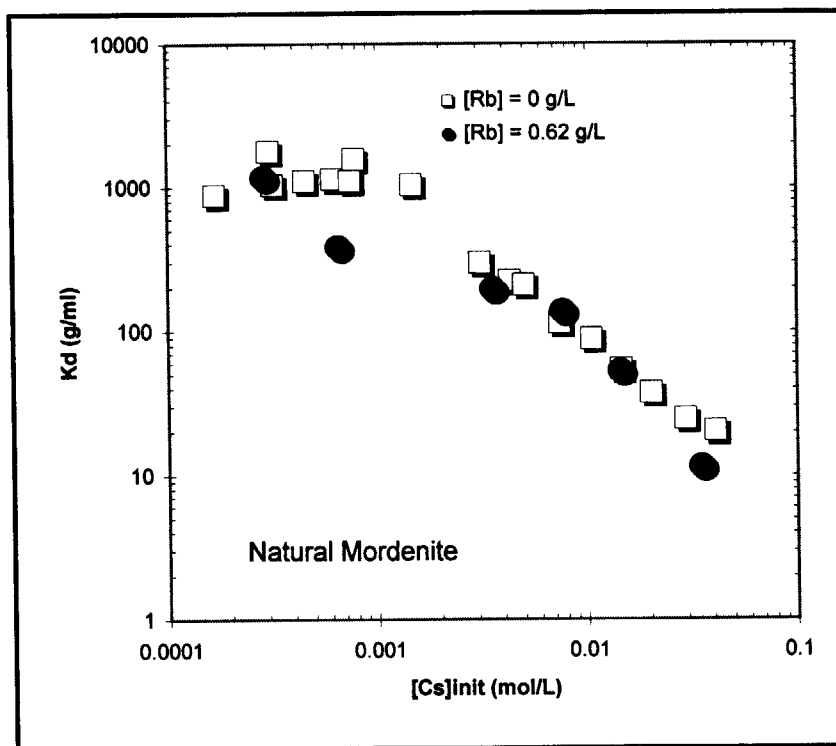


Figure 4.7 : Influence of rubidium concentration at different initial concentration of cesium on Kd of cesium with natural mordenite  
 Experimental conditions :  $[\text{HNO}_3]=0.5$  mol/L, volume of solution 15 ml, weight of zeolite 0.1g, temperature :  $26\pm 1^\circ\text{C}$

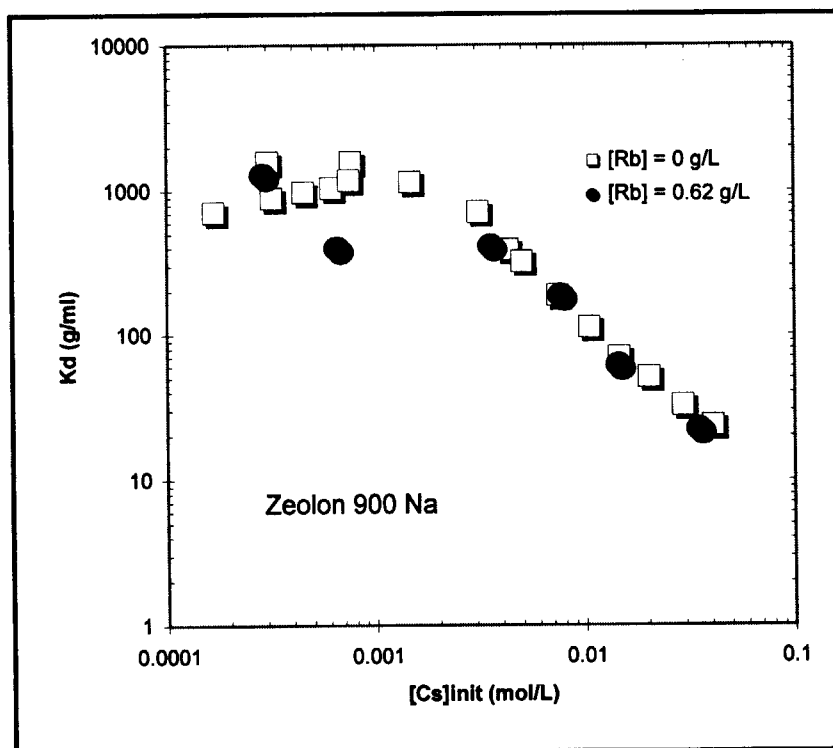


Figure 4.8 : Influence of rubidium concentration at different initial concentration of cesium on Kd of cesium with synthetic Zeolon 900Na  
 Experimental conditions :  $[\text{HNO}_3]=0.5$  mol/L, volume of solution 15 ml, weight of zeolite 0.1g, temperature :  $26\pm 1^\circ\text{C}$

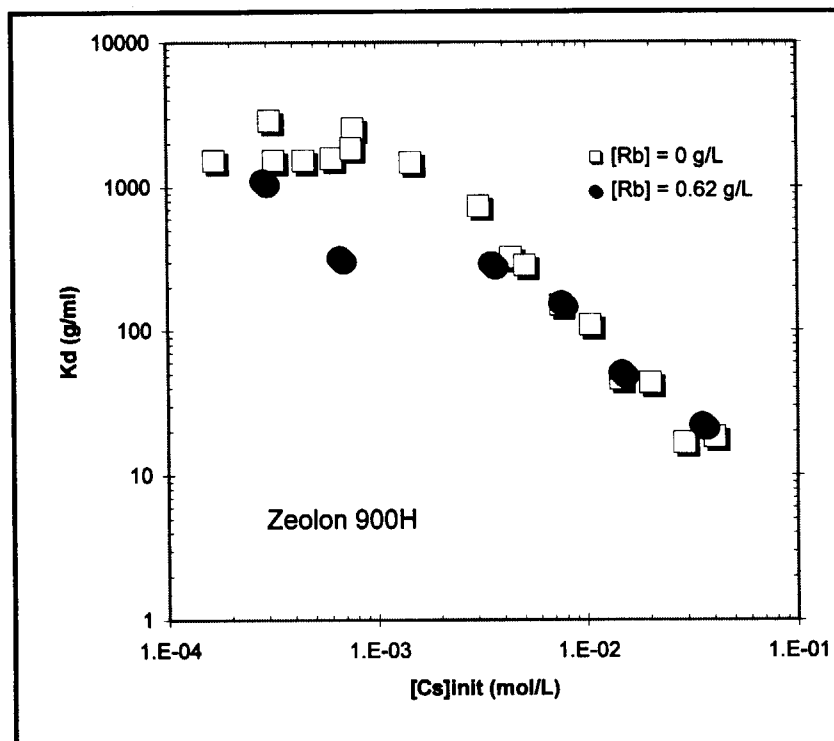


Figure 4.9 : Influence of rubidium concentration at different initial concentration of cesium on Kd of cesium with synthetic Zeolon 900H  
 Experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$ , volume of solution 15 ml, weight of zeolite 0.1g, temperature :  $26 \pm 1^\circ\text{C}$

## 5. Column Adsorption

### 5.1 Introduction

The purpose of this chapter is to confirm the results obtained during the batch experiment in the adsorption of cesium with zeolite by column experiments. The selected zeolite is the natural mordenite. The flow rate of feed solution has been checked. It will be verified that the effect of column temperature on the cesium absorption is negligible in the range 20 to 40°C. The influence of other elements contained in the HLLW on the cesium adsorption was also evaluated by using simulated HLLW at different acidities.

### 5.2 Experimental

The Cs concentration of the feed solution in case of the experiments on the influence of flow rate on the adsorption of cesium on the column was about 2.5 g/L. In case of the feed solution containing mixed elements the concentration of each element is given by the concentration value of the element in the raffinate after the DIDPA extraction step, which is shown in Table 5.1. The feed solutions containing cesium alone were prepared by dissolving cesium nitrate in 100 ml of nitric acid of 0.5 mol/L. For the solutions containing several elements, the volume was 250 ml.

The adsorption of the elements was carried out on a column containing 2g of natural mordenite. Figures 5.1 and 5.2 show the experimental device containing a peristaltic pump, one column and one fraction collector.

The internal diameter of the column is 6mm with maximum height 14 cm. The flow rate was changed in the range of 7 to 57 ml/h using a peristaltic pump. The temperature during the adsorption was kept in the range 21 to 26°C. In case of higher temperature studies, the column, the pump and the feed solution were placed in an air bath thermostatted at 40°C.

The analyses of sodium, rubidium and cesium are performed by flame emission technique with Hewlett Packard machine. As presented in the previous chapter, the analysis of an alkaline element in a solution containing other alkaline elements needs preconditioning prior to the analysis. The concentration of sodium and rubidium in a sample solution were determined after adding 4 g/L of cesium nitrate. The analysis of Cs was carried out in the solution containing 4g/L of sodium to suppress interference of sodium and rubidium. The other components were analyzed by ICP after dilution.

During the experiments several parameters have been used;

Flow rate : ml/h

Volume of feed solution : ml

Volume of column, where the quantity of Natural Mordenite is fixed to 2g : 3.5 cm<sup>3</sup>

Section of column :  $0.28 \text{ cm}^2$

Space velocity : Flow rate/Column volume :  $\text{h}^{-1}$

Linear velocity (L.V.) : Flow rate/Section of column :  $\text{cm/h}$

Bed volume ratio : Effluent volume/Column volume

Breakthrough capacity of cesium at the point of  $C/C_0=0.05$  (B.T.5%) :  $\text{mmol Cs/g NM}$

Total quantity of the interest cation adsorbed ( $Q(M)$ )

= (Adsorbed quantity up to  $C/C_0=1.0$ ) – (Eluted quantity during  $C/C_0>1.0$ )

= Retained quantity after adsorption :  $\text{mmol M/g NM}$

The adsorbed and eluted quantities can be obtained by the determination of the surface area surrounded by axis, ordinate and breakthrough curve.

The  $Q(M)$  value is equal to the total capacity when the  $C/C_0$  does not exceed 1.0, which is the case only for cesium.

Total capacity of Cs adsorbed ( $Q(\text{Cs})$ ) = Adsorbed quantity up to  $C/C_0=1.0$  :  $\text{mmol Cs/g NM}$

### 5.3 Results

#### 5.3.1 Influence of Flow Rate on the Breakthrough Curve of Cesium

The experiments were carried out for the acidity of 0.5 mol/L nitric acid. The concentration of cesium in feed solution was 2.5 g/L (19 mmol/L). This Cs concentration is twice as high as that in the DIPDA raffinate because the flow was too slow to obtain complete breakthrough curve. As expected by the theory the total capacity was not modified by the flow rate in the studied range. Figure 5.3 and Table 5.2 present the breakthrough curves for the three different flow rates. The total capacity was about 0.52 mmol Cs/g NM. The value is about 80% of the saturation capacity obtained from Langmuir equation by batch experiments (Table 2.9).

On the other hand, the breakthrough capacity decreased from 0.45 to 0.39 mmol/g when the flow rate increased from 15 to 43.2 ml/h. Table 5.3 shows the obtained value for each curve. The influence of flow rate on the breakthrough capacity is shown in Figure 5.4. The values are reported in bed volume ratio as a function of the linear velocity. As comparison, the value given by Mimura et al.<sup>(10)</sup> at pH 4 is also plotted.

One experiment carried out at 40° C did not give different result from those obtained at room temperature. This result confirms those obtained by Mimura et al.<sup>(10)</sup>; they said that the adsorption of cesium is not influenced by the temperature in the range 20°C to 50°C.

The obtained total capacity at 0.5 mol/L nitric acid is about 2.5 times less than those obtained by Mimura et al.<sup>(10)</sup> at pH 4. The Cs adsorption is considered to be suppressed by  $\text{H}^+$  co-adsorption.



### 5.3.2 Influence of other Elements on the Cesium Adsorption on Column

It has been shown in batch experiments that the cesium has high separation factor versus the other elements even with the alkaline elements. This behavior should be confirmed also with column experiments. In this experiment the various elements presented in Table 5.1 were added to the feed solution. The volume of the feed solution is about 250 ml. The flow rate selected is 15 ml/h (linear velocity : 53 cm/h). As comparison a linear velocity is 74 cm/h (the flow rate is 400 ml/h and the square section of column is 5.38 cm<sup>2</sup>) at an experimental equipment in NUCEF<sup>(8)</sup>, which was prepared for the demonstration test of the 4-Group Partitioning Process with real HLLW.

The acidity of the feed solution is 0.5 mol/L. In this experiment the determination of the dead volume is given by the volume obtained for 50% concentration of the element that is not adsorbed on the column. All PGM, Ni, Cr, Sr and Ba were not adsorbed on the column as shown in Figure 5.5 and Table 5.4. The volume at 50% concentration is 9ml. From this value, it is possible to determine the quantity of each alkaline element which is adsorbed and eluted from the column. Figures 5.6 and 5.7 show breakthrough curves of alkaline metals and Sr expressed in the molar concentration and its ratio to the initial concentration ( $C/C_0$ ). A small amount of Na is adsorbed at the beginning and is completely replaced by rubidium and cesium later. The same behavior was observed for rubidium but its elution is started after 20% breakthrough of cesium. This behavior can be explained by the higher  $K_d$  value of Rb compared to Na.

The results for  $Q(M)$  are given in Table 5.5. The amount of Na found in the effluent is more than that fed to column. It can be explained by the elution of the sodium present in the mordenite before experiment but the quantity of Na adsorbed or eluted are very small and the analysis are carried out in the region close to the detection limit.

The total quantity of Cs and Rb adsorbed in the mordenite (0.51 mmol/g) is almost the same as those obtained in the experiment with Cs alone (0.52mmol/g), but the total capacity of cesium is lower (0.49 mmol/L) because a small amount of rubidium is loaded on the column. The quantity of Rb which was retained on the column is 0.02 mmol/g. The molar percentage of Cs and Rb retained in the zeolite were 96 and 4%, respectively.

### 5.3.3 Influence of Nitric Acid Concentration on the Column Adsorption of Cesium and Alkaline Metals and Comparison of the Capacity Obtained from the Batch Adsorption

During batch experiment it was shown that the separation factor between cesium and rubidium increased with acidity, when it is higher than 0.5 mol/L of nitric acid. In the following paragraphs present two experiments to check the influence of acidity on the column adsorption and a validity of the result obtained at 0.5 mol/L. For each experiment cesium and rubidium loaded on the column were eluted. The purpose of the elution is to check the results obtained from breakthrough curves and the quantity of cesium and rubidium removal from the column.

The elements present in each experiment are Na, Rb, Cs and Sr except for the second (at 0.01 mol/L nitric acid) where Ni was added in the feed solution to check the behavior of Sr at low acidity.

In the first part, the presented results concern the adsorption step and a comparison with the results of the batch experiments at 0.5 mol/L nitric acid. The second part presents the results concerning the elution step by 4 mol/L nitric acid, which was carried out in both experiments at 2 mol/L and 0.01 mol/L nitric acid in the feed solution.

#### (1) Adsorption step

Figures 5.8 and 5.9 present the breakthrough curves obtained with the feed solution of 2 mol/L nitric acid. (Data was listed in the upper part of Table 5.6.) Since strontium is not adsorbed on the column at 2 mol/L nitric acid, the area calculation of surface gives the quantities of cesium, sodium and rubidium absorbed, which are reported in Table 5.7. The total quantity of cesium and rubidium adsorbed decreased to 0.37 mmol/g, but the ratio of rubidium was 5%, which is almost the same as that at the acidity of 0.5 mol/L. The result did not agree with the expected one. Since the separation factor was higher at 2.0 mol/L than 0.5 mol/L, rubidium retained should be less. Perhaps the separation factor obtained in batch experiment is not exact due to the difficulty to determine the concentration of those elements after adsorption at high acidity. The adsorption is low but some dilution is needed to decrease acidity for the analysis. The behavior of cesium and rubidium presented in Table 3.10 showing a higher separation factor for the acidity higher than 1 mol/L should be corrected and the separation factor between cesium and rubidium should be probably decreased as the separation factor between cesium and sodium, or might be constant.

Concerning the adsorption carried out at the acidity of 0.01 mol/L, the adsorption was interrupted before the complete saturation of the column with cesium as shown in Figures 5.10 and 5.11. (Data was listed in the upper part of Table 5.8.) That means that the total capacity can be obtained only by extrapolation. Table 5.9 gives the quantity of cesium and rubidium adsorbed up to 200 ml of effluent and also those calculated by extrapolation of breakthrough curves to 260 ml of effluent. It can be concluded that the total quantity of cesium and rubidium adsorbed is enhanced by factor 1.7 at the low acidity but the quantity of rubidium increased more comparing to the cesium and the separation factor decreases. In Figure 5.12 the results concerning the total adsorbed quantity ( $Q(\text{Cs}+\text{Rb})$ ) are shown as a function of the acidity. As comparison the saturation capacities,  $Q(\text{Cs})_{\text{sat}}$ , obtained from Langmuir equation are plotted.

The two curves are almost parallel, it is possible to obtain a relationship between the two capacities.

$$\log(Q(\text{Cs})_{\text{sat}}) = -0.17 \log[\text{H}^+] - 0.279$$

$$\log(Q(\text{Cs}+\text{Rb})_{\text{column}}) = -0.17 \log[\text{H}^+] - 0.366$$

From this relationship the following can be derived :

$$Q(\text{Cs}+\text{Rb})_{\text{column}} = 0.82 Q(\text{Cs})_{\text{sat}}$$

The relationship is useful to estimate the column capacity at different acidity by using the data obtained from one column experiment and several batch ones; but it would be important to confirm the

influence column size or particle size on this relationship.

Another comparison between batch and column can be conducted with the adsorbed quantity at the same cesium concentration. The  $Q(\text{Cs})_{\text{batch}}$  equilibrated with 9.5 mmol/L Cs was obtained by the plots in Figures 2.8, 2.9 and 2.10 and are listed in Table 5.10. The  $Q(\text{Cs})_{\text{column}}$  was about 85% of  $Q(\text{Cs})_{\text{batch}}$ .

## (2) Elution step

Figure 5.13 and 5.14 show the concentration profile of each element during the three steps of adsorption, washing (scrubbing) and elution (stripping) at the acidity of 2.0 mol/L and 0.01 mol/L respectively in the adsorption step. After the adsorption, the column was washed with 30 ml of deionized water. Then rubidium and cesium were eluted with 4.0 mol/L nitric acid.

Table 5.11 shows the quantity of cesium and rubidium adsorbed. There is a good agreement between the results given by breakthrough curves and the quantity of cesium removed from the column. The difference obtained in the second case (0.01 mol/L nitric acid) can be due to the non saturation of the column during the adsorption step and further adsorption of cesium during the washing step.

The results show that all of cesium and rubidium can be removed from the column at high nitric acid concentration, but the zeolite would be damaged by the concentrated nitric acid. It should be interesting to analyze aluminum, which is the main component of zeolite, in the eluate. Mimura et al.<sup>(20)</sup> reported that mordenite has a rather high acid resistance compared with other zeolites. Mordenite can be used in 0.1 mol/L nitric acid solution at least, but the structure of mordenite begins to collapse by the contact with 1 mol/L nitric acid. It is important to examine the acid resistance of mordenite at 0.5 mol/L nitric acid.

## 5.4 Conclusion

The adsorption of cesium obtained with natural mordenite on column are similar to those obtained from the batch experiment. The total quantity of cesium and rubidium adsorbed on the column is about 80% of the saturation capacity obtained by Langmuir plot. The flow rate modified only the 5% breakthrough point. Temperature is not a predominant parameter during the adsorption of cesium. The selectivity towards cesium is high and only a small amount of the rubidium is adsorbed together with cesium, but its proportion is low. The capacity of natural mordenite towards cesium is about 0.5 mmol/g (66 mg/g) at 0.5 mol/L nitric acid contaminated with 4% of rubidium. All of the other elements examined were not detected in the eluate, which confirms that there was no adsorption on the mordenite column.

Table 5.1 : Concentration of fission and corrosion products in the feed solution

element	concentration	
	mmol/L	g/L
Na	19.0	0.437
Rb	1.9	0.162
Cs	9.5	1.263
Sr	4.2	0.368
Ba	5.0	0.687
Cr	2.3	0.120
Ni	1.5	0.088
Ru	9.0	0.910
Rh	2.0	0.206
Pd	4.5	0.479

Table 5.2 : Determination of breakthrough curves of Natural Mordenite with cesium for different flow rate at 0.5 mol/L nitric acid

Flow rate (ml/h)					
15.2		24		42	
Volume ml	[Cs]/[Cs] <sub>init</sub> %	Volume ml	[Cs]/[Cs] <sub>init</sub> %	Volume ml	[Cs]/[Cs] <sub>init</sub> %
0.0	0	0.0	0	0.0	0
42.3	1	36.0	0.1	33.4	0.1
43.3	0	38.4	0.1	34.9	0.4
44.4	1	39.7	0.4	36.3	0.8
45.4	1	40.9	0.4	37.8	1.4
46.4	1	42.1	1.0	39.2	2.7
7.4	2	43.4	2.2	40.6	4.3
48.5	5	44.6	4.6	42.1	6.5
49.5	11	45.8	7.7	43.5	9.1
50.5	20	47.1	11.6	44.9	12.7
50.5	20	48.3	15.8	46.4	16.6
51.6	23	49.5	20.7	47.8	21.4
52.6	35	50.8	27.5	49.3	27.1
54.6	51	52.0	34.0	50.7	32.6
56.7	62	53.2	41.8	52.1	39.9
58.8	73	55.7	55.6	53.6	46.3
60.8	79	58.2	67.6	55.0	50.8
62.9	85	60.6	78.3	57.9	63.6
68.0	93	63.1	82.5	60.8	71.7
73.2	97	65.6	88.1	63.7	79.8
78.3	99	70.5	93.1	66.5	83.4
78.3	101	76.7	95.2	69.4	88.8
83.5	100	82.8	97.5	75.2	94.9
		89.0	100.0	82.4	98.3
				89.6	100.0
				96.7	100.0

Table 5.3 : Influence of flow rate on bed volume ratio and adsorbed quantity of cesium  
at 5% breakthrough point

experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$ ,  $[\text{Cs}]_{\text{init}} 2.5 \text{ g/L}$ ,  
weight of NM : 2.0g, temperature :  $24 \pm 2^\circ\text{C}$

flow rate ml/h	bed volume ratio	adsorbed quantity (mmol/g)
15.0	13.8	0.45
24.6	12.7	0.42
43.2	11.8	0.39

Table 5.4 : Composition of effluent solution of fission and corrosion products after adsorption of Natural Mordenite column at 0.5 mol/L nitric acid

Volume ml	[Cs] mg/L	Volume ml	[Rb] mg/L	Volume ml	[Na] mg/L
0	1225	0	171	0	444
3.0	4.3	3.0	0.4	3.0	64.5
12.0	7.9	6.0	0.5	6.0	56.1
30.1	10.0	9.0	2.2	9.0	43.7
60.2	34.4	12.0	3.5	12.1	38.3
90.3	33.8	30.09	4.6	15.0	44.0
108.3	340.7	60.2	5.3	30.16	474.7
120.4	897.5	66	9.6	60.3	517
135.4	1138	72.2	23.5	90.5	500
150.5	1222	78.2	67.7	118.6	459
165.5	1219	84.3	160.0	150.5	445
180.6	1255	90.3	308.0	180.6	436
210.7	1278	90.3	303.8	210.7	440
237.7	1259	93.3	371.1	237.7	445
		96.3	433.0		
		99.3	451.9		
		102.3	465.1		
		111.3	376.7		
		120.4	272.3		
		120.4	269.3		
		129.4	221.1		
		138.4	201.5		
		150.5	186.4		
		180.6	171.9		
		210.7	168.8		
		237.7	169.6		

volume ml	Sr mg/L	Ba mg/L	Cr mg/L	Ni mg/L	Ru mg/L	Pd mg/L	Rh mg/L
0	359	466	123	80	646	480	195
3.0	0	0	0	0	0	0	0
6.0	10	19	10	2	16	21	6
9.0	178	231	36	34	246	269	89
12.0	300	384	93	67	465	415	163
15.0	336	434	115	76	565	459	181
30.1	342	442	121	78	629	459	184
90.3	352	440	120	77	634	478	192
120.4	346	443	119	77	630	478	196
150.5	345	447	120	78	637	487	191
180.6	343	442	116	76	604	468	194
210.7	346	442	118	76	619	468	195
237.7	351	452	120	78	636	489	196

Table 5.5 : Material balance of alkaline elements during adsorption from 0.5 mol/L nitric acid

	adsorbed	eluted	balance	retained	
	mg	mg	mg	mmol/g	%
Na	4.7	5.3	-0.6		
Rb	11.7	8.4	3.3	0.02	4
Cs	130.7	0	130.7	0.49	96

Table 5.6 : Composition of effluent solution of fission and corrosion products after adsorption (2 mol/L nitric acid), washing (deionized water) and elution (4mol/L nitric acid) steps on Natural Mordenite

	Volume ml	[Cs] mg/L	Volume ml	[Rb] mg/L	Volume ml	[Na] mg/L	Volume ml	[Sr] mg/L
Adsorption	0	1248	0	171.8	0	426.8	0	366
	39	9.5	39.3	3.4	4.0	35.3	4.0	0
	55	4.5	54.6	28.0	8.0	24.3	8.0	0
	62	7.6	62.3	138.0	11.8	15.2	11.8	112
	70	15.4	66.2	223.0	15.7	14.4	15.7	336
	78	125.0	70.0	309.3	19.7	131.0	19.7	358
	86	475.7	74.0	357.5	23.7	336.7	39.3	358
	93	845.4	78	379.8	27.7	451.2	116.8	357
	101	1052	81.7	358.7	31.5	479.6	155.7	365
	117	1174	85.7	320.0	35.3	488.0	242.6	357
	132	1223	89.6	280.1	39.3	469.2		
	156	1243	93.5	244.0	79.2	446.5		
	195	1263	97.2	220.9	116.8	418.2		
	243	1257	101.1	207.6	155.7	417.3		
			116.8	184.9	242.6	419.6		
			132.3	177.2				
			155.7	175.7				
			175.6	177.2				
			195.4	176.1				
			242.6	171.9				

	Volume ml	[Cs] mg/L	[Rb] mg/L	[Sr] mg/L
Washing	259.0	681.4	105.7	233.3
	279.6	7.3	1.1	1.7
	295.1	2.7	0.2	0.2

	Volume ml	[Cs] mg/L	Volume ml	[Rb] mg/L
Elution	346.1	2	346.1	0.0
	354.1	2513	354.1	195.8
	362.1	2109	362.1	37.7
	370.2	1254	378.2	4.7
	378.2	880.1	394.3	2.4
	386.3	674.6	418.5	1.4
	402.4	454.8	498.9	0.6
	418.5	350.5	579.3	0.3
	458.7	202.2		
	498.9	138.3		
	539.1	105.1		
	579.3	79.3		



Table 5.7 : Material balance of alkaline elements during adsorption from 2.0 mol/L nitric acid

	adsorbed	eluted	balance	retained	
	mg	mg	mg	mmol/g	%
Na	3.4	3.4	0		
Rb	7.8	4.6	3.1	0.02	5
Cs	94.3	0	94.3	0.35	95

Table 5.8 : Composition of effluent solution of fission and corrosion products after adsorption (0.01 mol/L nitric acid) washing (deionized water) and elution (4mol/L nitric acid) steps on Natural Mordenite

	Volume ml	[Cs] mg/L	Volume ml	[Rb] mg/L	Volume ml	[Na] mg/L	Volume ml	[Sr] mg/L	[Ni] mg/L
Adsorption	0	1252.7	0	159.9	0	419.6	0	367	87
	36.9	18.2	73.9	1.0	3.7	88.3	3.7	0	0
	51.7	9.8	147.8	38.1	7.4	93.6	11.1	1	1
	59.1	15.1	158.9	217.0	11.1	137.5	14.8	66	45
	66.5	18.3	166.3	392.9	14.8	286.2	18.5	193	70
	73.9	19.6	173.65	531.6	18.47	304.3	22.17	257	75
	81.3	20.1	184.7	571.6	22.2	296.4	29.56	311	82
	88.7	39.6	192	462.0	25.9	363.8	36.9	335	85
	96.1	37.0	199.5	348.7	29.6	449.6	110.8	371	88
	110.8	40.6	206.9	267.4	33.3	488.6	206.9	366	89
	125.6	56.7			36.9	503.0			
	147.8	208.5			44.3	527.4			
	206.9	846.9			51.7	513.2			
					59.1	506.8			
					73.9	506.6			
					110.8	504.8			
					147.8	465.4			
					166.3	410.6			
					184.7	395.3			
					206.9	394.0			

	Volume ml	[Cs] mg/L	[Rb] mg/L	[Sr] mg/L	[Ni] mg/L
Washing	221.4	607	178.1	245.6	61.8
	235.8	14.4	0	0	0
	250.5	0			

	Volume ml	[Cs] mg/L	Volume ml	[Rb] mg/L
Elution	277.6	2	277.6	0
	281.3	2	281.3	0
	285.0	15940	285.0	1409
	288.7	16455	288.7	565
	292.5	5455	292.5	38
	296.2	3437	296.2	14
	303.6	1821	303.6	8
	311.1	1232	333.5	3
	329.7	649	363.3	2
	363.3	347	437.8	0
	400.5	148	497.4	0
	497.4	97		

Table 5.9 : Material balance of alkaline elements during adsorption from 0.01 mol/L nitric acid

	adsorbed mg	eluted mg	Balance Mg	retained		retained *	
				mmol/g	%	mmol/g	%
Na	1.9	13.2	-11.3	0		0	
Rb	35.4	22.2	3.3	0.08	9	0.06	7
Cs	202.3	0	202.3	0.76	91	0.8	93

\* obtained by extrapolation of the breakthrough curve

Table 5.10 : Comparison of adsorbed quantity, Q (mmol/g), in Natural Mordenite at 0.5 mol/L nitric acid

Nitric acid mol/l	Batch		Column	
	Saturation Capacity $Q(Cs)_{sat}$	$Q(Cs)_{batch}$ equilibrated with 9.5mmol/L Cs	$Q(Cs+Rb)_{column}$	$Q(Cs)_{column}$
0.01	1.11	0.94	0.86	0.80
0.5	0.64	0.59	0.51	0.49
1	0.49	0.46	-	-
2	-	-	0.37	0.35

Table 5.11 : Determination of cesium and rubidium adsorbed on column by breakthrough curves and by the analysis of the eluate

nitric acid mol/l	breakthrough curves				eluate			
	Rb		Cs		Rb		Cs	
	mg	mmol/g	mg	mmol/g	mg	mmol/g	mg	mmol/g
2.0	3	0.02	94	0.35	2	0.02	102	0.38
0.01	11*	0.06	212*	0.80	8	0.05	231	0.87

\* obtained by extrapolation of the breakthrough curve

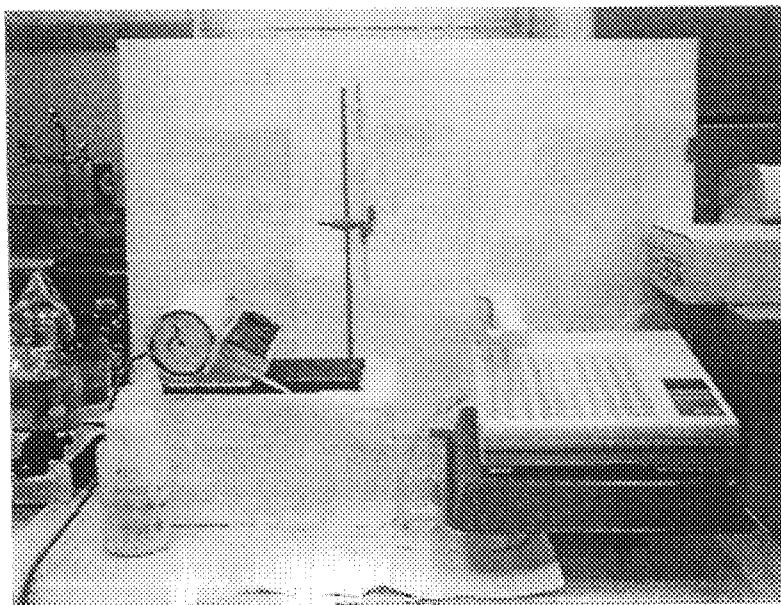


Figure 5.1 : Photo of the experimental device

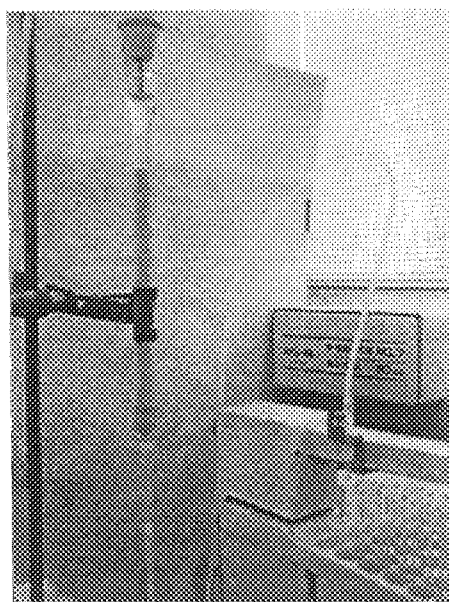


Figure 5.2 : Photo of the column

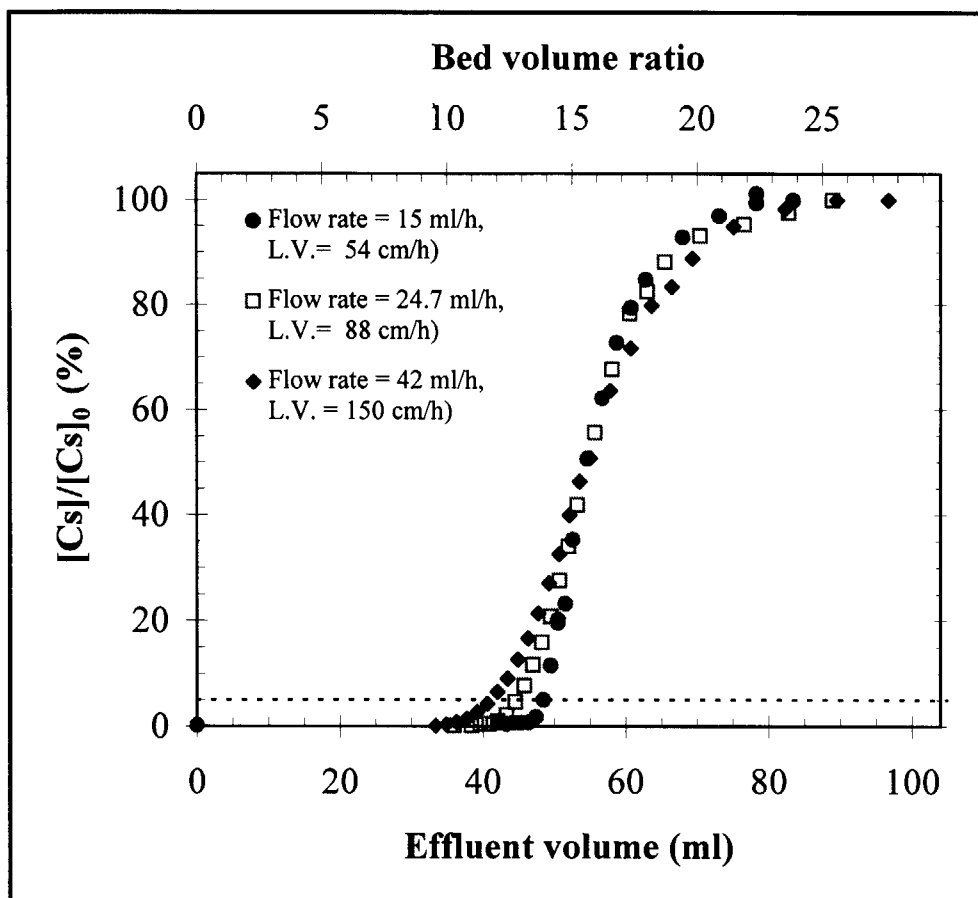


Figure 5.3 : Influence of flow rate on the breakthrough curve  
 Experimental conditions :  $[\text{HNO}_3]$  0.5 mol/L ,  $[\text{Cs}] = 2.5$  g/L, N.M. = 2g  
 Internal diameter of the column : 6mm

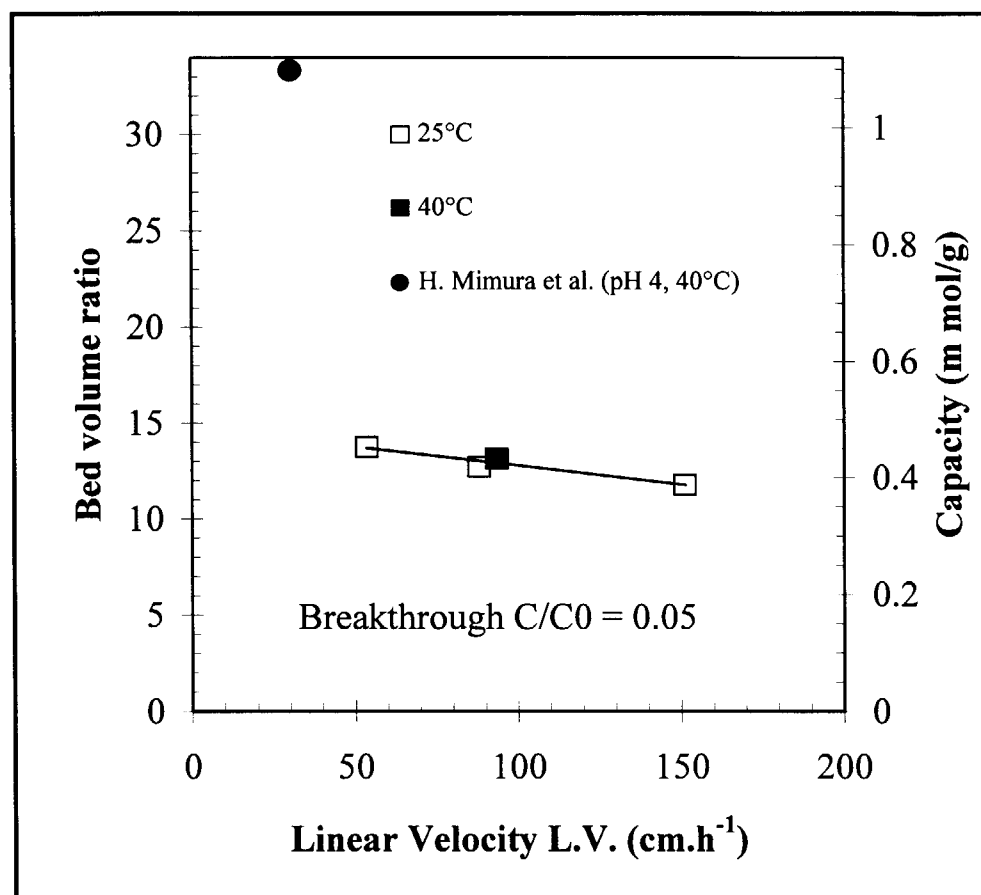


Figure 5.4 : Influence of linear velocity on the bed volume ratio at 5% breakthrough and the breakthrough capacity

Experimental conditions : [HNO<sub>3</sub>] 0.5 mol/L, [Cs] = 2.5 g/L, N.M. = 2g  
Internal diameter of the column : 6mm

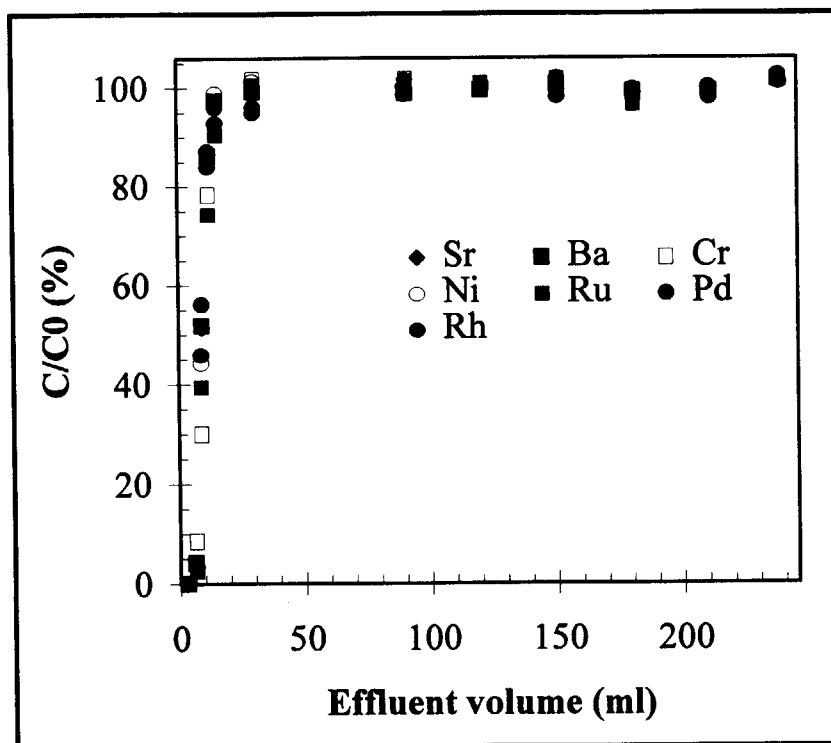


Figure 5.5 : B.T. curves of some elements which are not adsorbed.  
 Experimental conditions :  $[\text{HNO}_3]$  0.5 mol/L,  $[\text{Cs}] = 2.5$  g/L, N.M. = 2g  
 Internal diameter of the column : 6mm

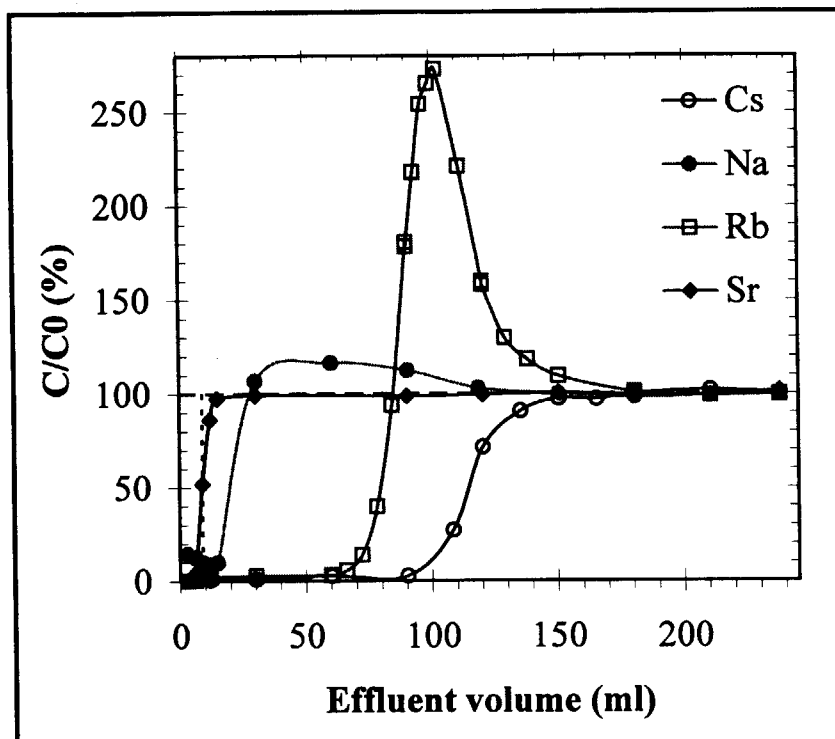


Figure 5.6 : Percentage of elements in solution after adsorption  
 Experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$  ,  $[\text{Cs}] = 2.5 \text{ g/L}$  , N.M. = 2g  
 Internal diameter of the column : 6mm

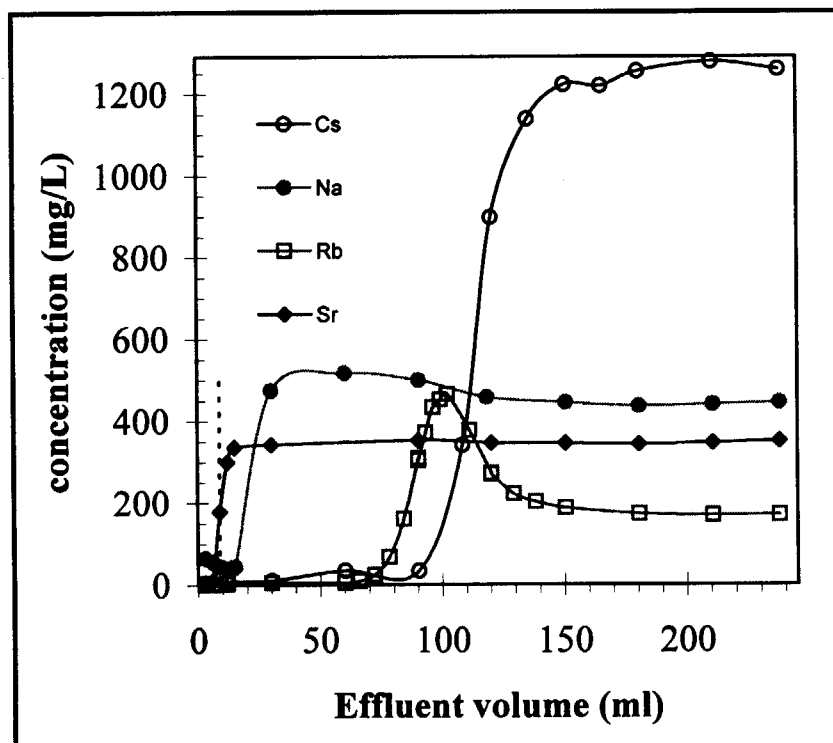


Figure 5.7 : Concentration of elements in solution after adsorption  
 Experimental conditions :  $[\text{HNO}_3] = 0.5 \text{ mol/L}$  ,  $[\text{Cs}] = 2.5 \text{ g/L}$  , N.M. = 2g  
 Internal diameter of the column : 6mm



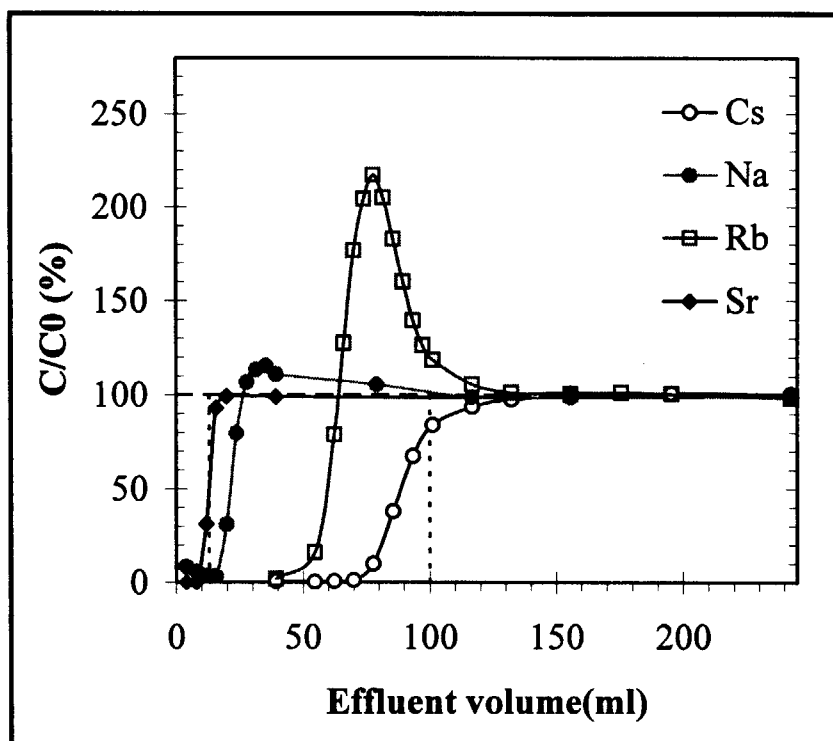


Figure 5.8 : Percentage of elements in solution after adsorption  
 Experimental conditions :  $[\text{HNO}_3] = 2.0 \text{ mol/L}$  ,  $[\text{Cs}] = 2.5 \text{ g/L}$  , N.M. = 2g  
 Internal diameter of the column : 6mm

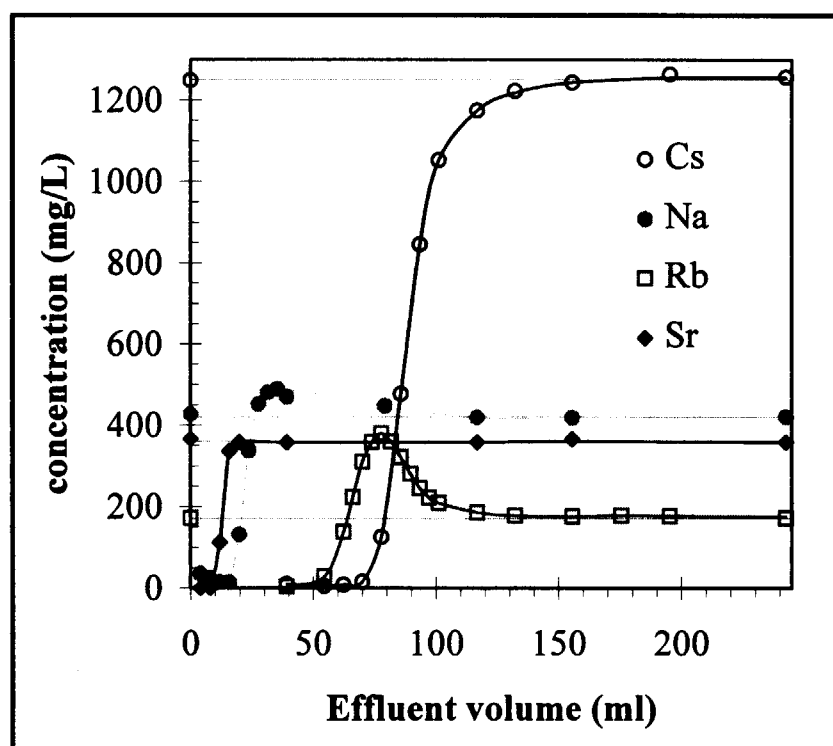


Figure 5.9 : Concentration of elements in solution after adsorption  
 Experimental conditions :  $[\text{HNO}_3] = 2.0 \text{ mol/L}$  ,  $[\text{Cs}] = 2.5 \text{ g/L}$  , N.M. = 2g  
 Internal diameter of the column : 6mm

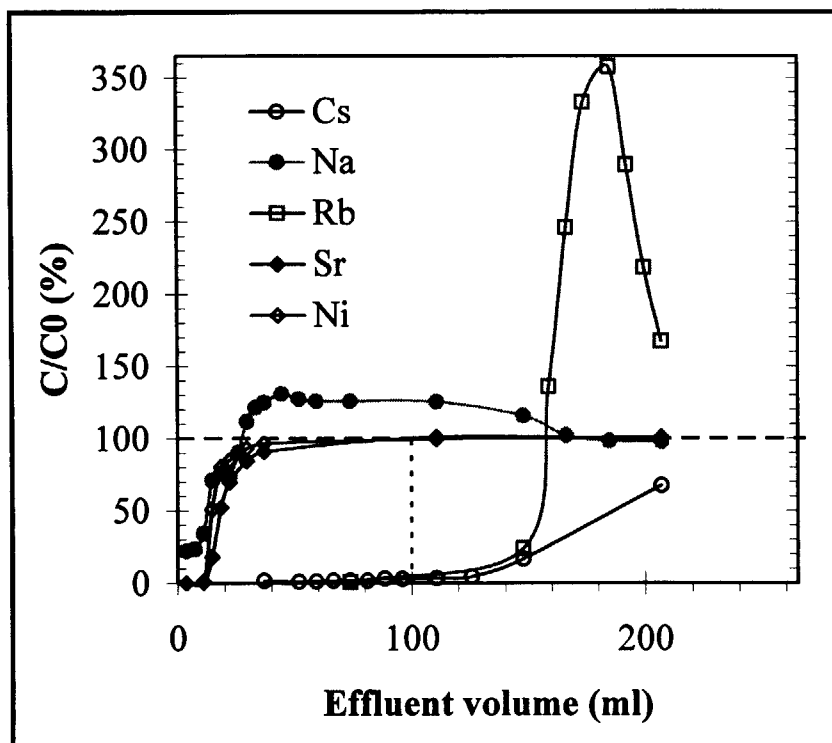


Figure 5.10 : Percentage of elements in solution after adsorption  
 Experimental conditions :  $[\text{HNO}_3] = 0.01 \text{ mol/L}$  ,  $[\text{Cs}] = 2.5 \text{ g/L}$  , N.M. = 2g  
 Internal diameter of the column : 6mm

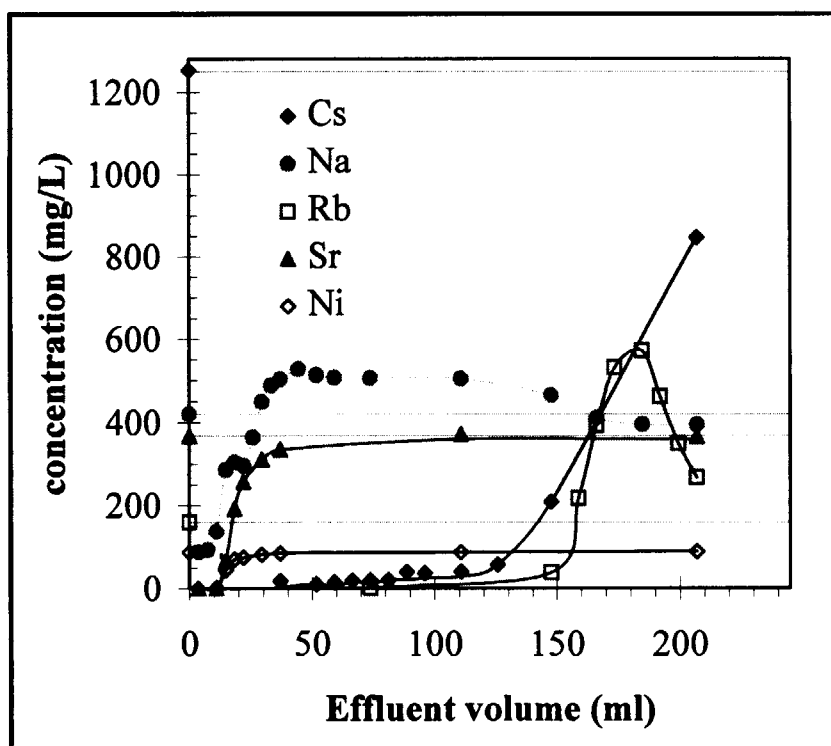


Figure 5.11 : Concentration of elements in solution after adsorption  
 Experimental conditions :  $[\text{HNO}_3] = 0.01 \text{ mol/L}$  ,  $[\text{Cs}] = 2.5 \text{ g/L}$  , N.M. = 2g  
 Internal diameter of the column : 6mm

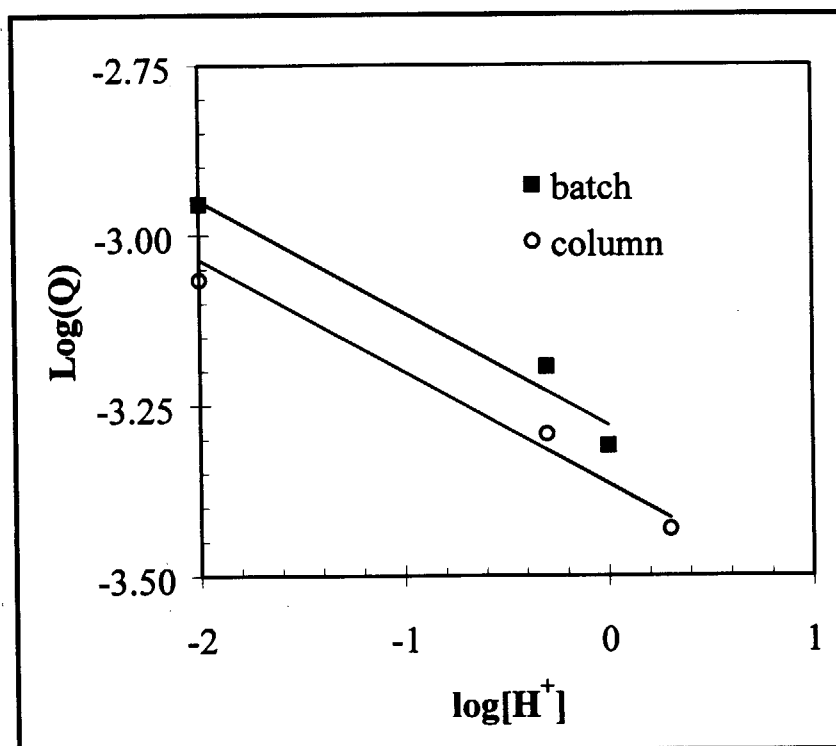


Figure 5.12 : Variation of the total quantity of cesium and rubidium adsorbed on the column and the saturation capacity in batch (mol/g) with the acidity (mol/L)

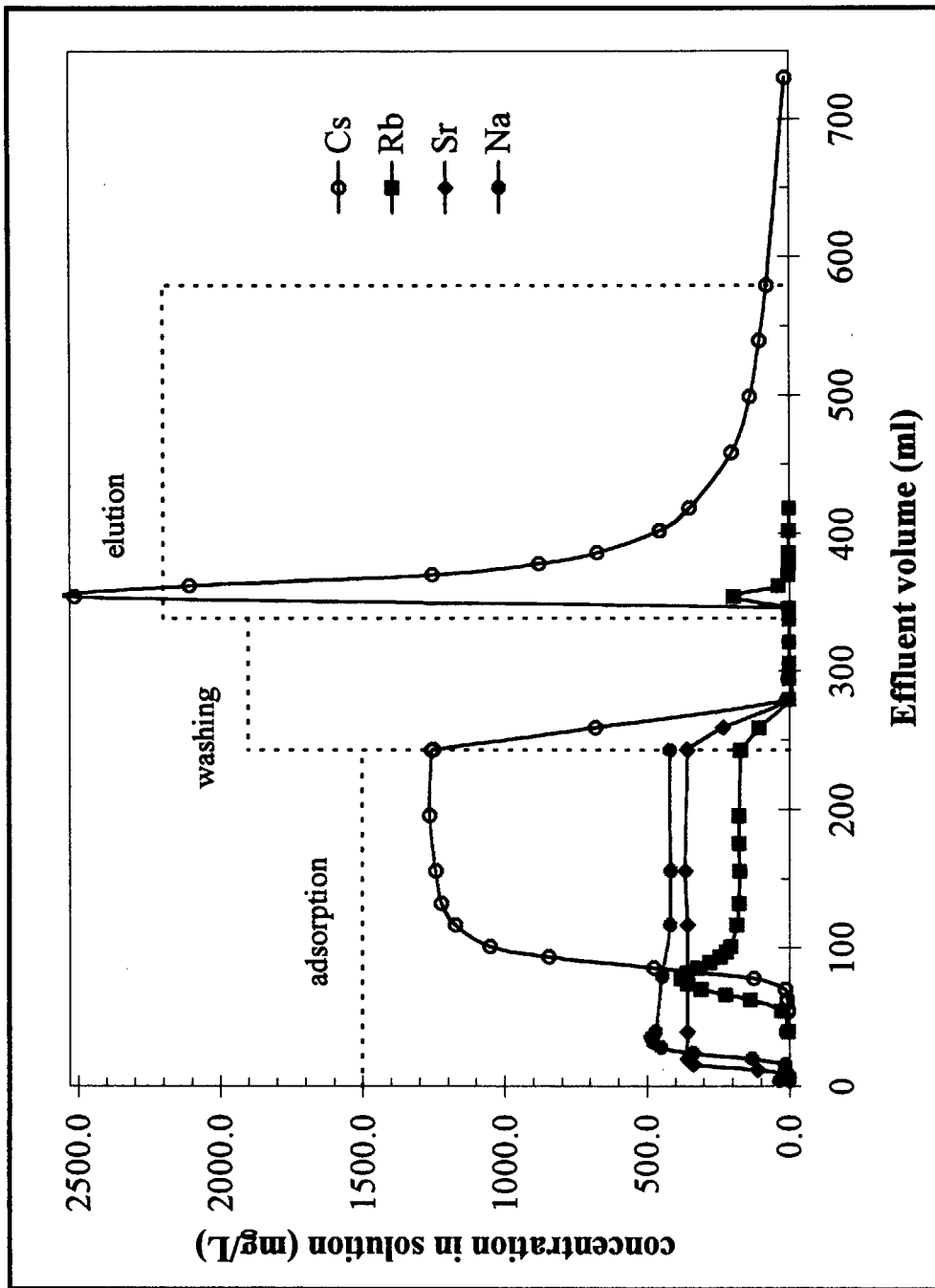


Figure 5.13 : Concentration profile of each element during adsorption, washing and elution steps  
 Experimental conditions : NM : 2g, flow rate : 15.6ml/h, [Cs]<sub>initial</sub> = 1.25 g/L,  
 adsorption : [HNO<sub>3</sub>] = 2.0 mol/L, washing : water, elution : [HNO<sub>3</sub>] = 4.0 mol/L

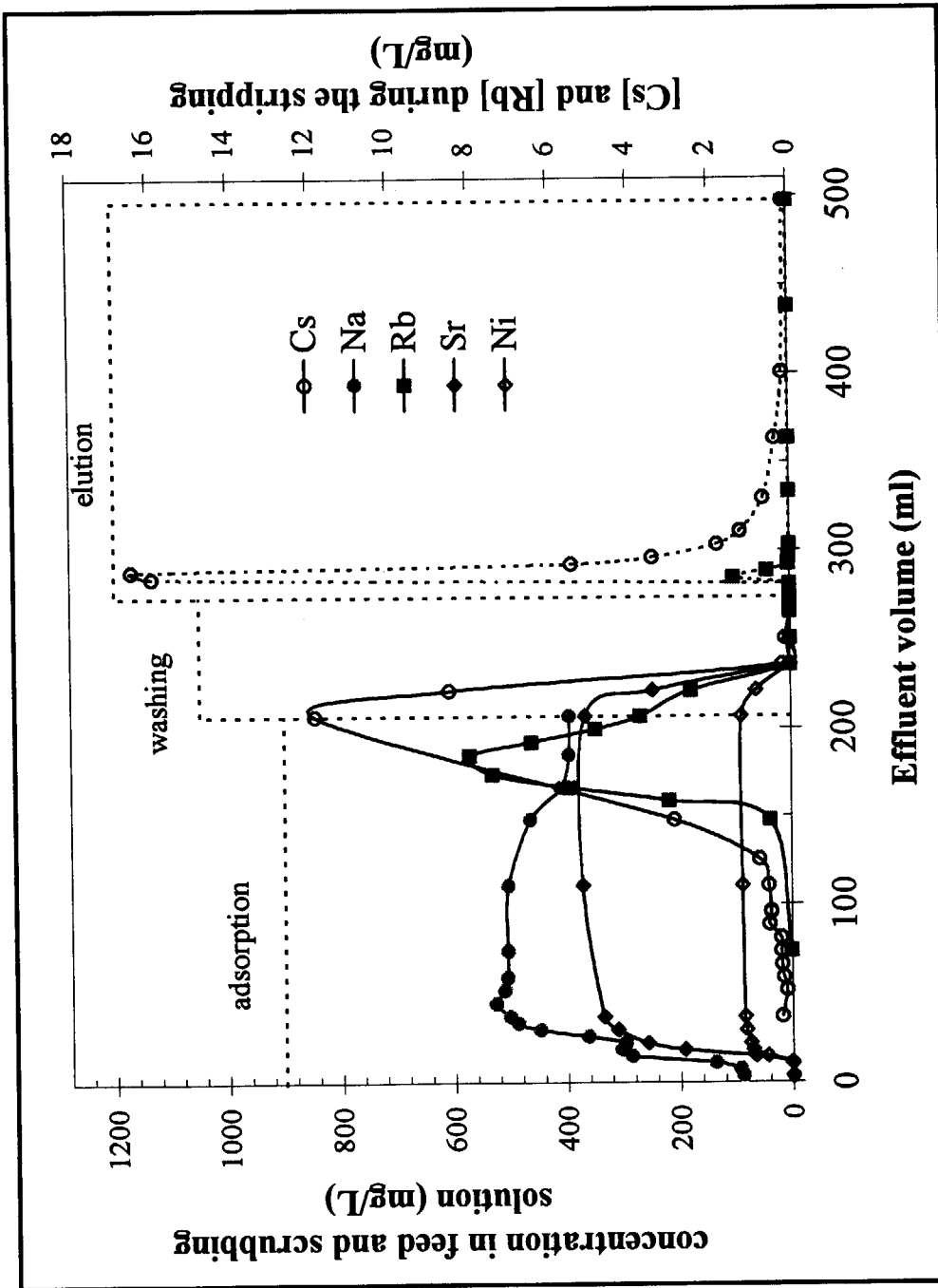


Figure 5.14 : Concentration profile of each element during adsorption, washing and elution steps  
 Experimental conditions : NM : 2g, flow rate : 14.8 ml/h,  $[Cs]_{initial} = 1.25$  g/L,  
 adsorption :  $[HNO_3] = 0.01$  mol/L, washing : water, elution :  $[HNO_3] = 4.0$  mol/L

## 6. Conclusion

The present study revealed that it is possible to separate cesium from an acidic solution such as 0.5 mol/L nitric acid solution by adsorption with mordenite. This shows the possibility to design a new separation scheme for partitioning of HLLW.

The parameters studied in batch experiments were adsorption kinetics, the saturation capacity by Langmuir equation, dependence of distribution coefficient on the Cs concentration and the nitric acid concentration, adsorption of other elements, separation factor toward Cs and the influence of Na and Rb on the Cs adsorption. Three mordenites examined (natural mordenite and two synthetic mordenites Zeolon 900Na and 900H) have very close behavior with these parameters. In the Cs adsorption with the natural mordenite at 0.5 mol/L nitric acid, distribution coefficient was 1150 ml/g and the saturation capacity was 0.64 mmol/g. Even at 1.0 mol/L nitric acid, they were 650 ml/g and 0.49 mmol/g respectively. The separation factors toward Cs were 3.2 for Rb, 39 for Na, 940 for Ru and more than 3750 for Ba, Sr, Cr, Ni, Pd and Rh at 0.5 mol/L nitric acid. Sodium and rubidium have almost no effects on the Cs adsorption when their concentrations lie in the practical region for the HLLW.

After these batch experiments, the adsorption of Cs on column was examined using the natural mordenite, which is considered the best adsorbent among the three because of its lowest price. The flow rate of the Cs solution modified only the 5% breakthrough point and gave no influence on the total capacity of Cs. Temperature was not a predominant parameter. Column experiments with a mixed solution showed that cesium was adsorbed very selectively. Sodium and rubidium were once adsorbed but were eluted as the mordenite became saturated with cesium. Only about 4% of rubidium as a molar ratio to the sum of Cs and Rb were retained in the column. The total quantity of Cs and Rb adsorbed decreased with the increase of nitric acid concentration, and was 0.51 mmol/g at 0.5 mol/L nitric acid, which is about 80% of the saturation capacity by Langmuir equation.

Elution of Cs (and Rb) with 4 mol/L nitric acid was performed against the column used in the adsorption experiments at 2 mol/L and 0.01 mol/L nitric acid. The adsorbed Cs and Rb were well eluted, and a good mass balance was obtained between the adsorbed quantity by breakthrough curves and the quantity found in the eluate. If the column is used repeatedly in a practical process, it is necessary to examine the acid resistance of the mordenite.

## Acknowledgement

The authors wish to thank Dr. Mimura in the Institute for Advanced Materials Processing, the Tohoku University. He kindly gave the authors the synthetic mordenites Zeolon 900Na and 900H and some useful information.

## References

- (1) Kubota, M., Dojiri, S., Yamaguchi, I., Morita, Y., Yamagishi, I., Kobayashi, T. and Tani, S., *"High-Level Radioactive Waste and Spent Fuel Management"*, Slate, S. C., Kohout, R. and Suzuki, A., Eds., The American Society of Mechanical Engineers, p.537 (1989).
- (2) Kubota, M., Yamaguchi, I., Morita, Y., Kondo, Y., Shirahashi, K., Yamagishi, I. and Fujiwara, T., *Proc. of Int. Conf. on Future Nuclear Systems: Emerging Fuel Cycles and Waste Disposal Options (GLOBAL'93)*, p.588 (1993).
- (3) Kubota, M., *Proc. of 4th Int. Conf. on Nuclear Fuel Reprocessing and Waste Management (RECOD'94)*, vol. I (1994).
- (4) Morita, Y., Fujiwara, T., Shirahashi, K., Watanabe, M., Tatsugae, R. and Kubota, M., *Proc. of Int. Conf. on Evaluation of Emerging Nuclear Fuel Systems (GLOBAL'95)*, p.1163 (1995).
- (5) Yamaguchi, I. and Kubota, M., JAERI-M 87-034 (1989) [in Japanese].
- (6) Mizoguchi, K., Yamaguchi, I., Morita, Y., Fujiwara, T. and Kubota, M., JAERI-Research 97-071 (1997) [in Japanese].
- (7) Kubota, M., Okada, K., Yamaguchi, I. and Morita, Y., *Radioactive Waste Manag. Nucl. Fuel Cycle*, **7**, 303 (1986).
- (8) Morita, Y., Yamaguchi, I., Fujiwara, T., Mizoguchi, K. and Kubota, M., *Proc. of 4th Int. Information Exchange Meeting on Actinide and Fission Product Partitioning and Transmutation*, Mito, Japan, 11-13 September 1996, OECD/NEA, p. 375 (1997).
- (9) Kanno, T. and Mimura, H., IAEA-TECDOC-337, p.237 (1985)
- (10) Mimura, H., Kobayashi, T. and Akiba, K., *J. Nucl. Sci. Technol.*, **32**, 60 (1995).
- (11) Mimura, H., Kimura, T. and Kanno, T., *Bull. Res. Inst. Min. Dress. Met.*, **37**, 145 (Report No. 857) (1981) [in Japanese].
- (12) Horioka, M., *J. At. Ener. Soc. Jpn.*, **11**, 406 (1969) [in Japanese].
- (13) Mimura, H. and Kanno, T., *Sci. Rep. Res. Inst. Tohoku Univ. (SCI. REP. RITU)*, **30**, 126 (1981).
- (14) Mimura, H. and Akiba, K., *J. Nucl. Sci. Technol.*, **30**, 436 (1993).
- (15) Chun-Nan Hsu, Dai-Chin Liu and Hwai-Ping Cheng, *J. Radioanal. Nucl. Chem., Articles*, **185**, 319 (1994).
- (16) Süss, M. and Pfrepper, G., *Radiochim. Acta*, **29**, 33 (1981).
- (17) Moeller, T., *"Inorganic Chemistry an Advanced Textbook"* (Modern Asia Edition), John Wiley & sons, Inc., NY (1958).
- (18) Kubota, M., Nakamura, H., Tachimori, S., Abe, T. and Amano, H., *"Management of Alpha-Contaminated Wastes"*, p.551 (IAEA-SM-246/24) (1981).
- (19) Harjula, R. and Lehto, J., *Nucl. Chem. Waste Manag.*, **6**, 133 (1986)
- (20) Mimura, H. and Kanno, T., *J. At. Ener. Soc. Jpn.*, **19**, 170 (1977) [in Japanese].

This is a blank page.



# 国際単位系 (SI) と換算表

表1 SI基本単位および補助単位

量	名称	記号
長さ	メートル	m
質量	キログラム	kg
時間	秒	s
電流	アンペア	A
熱力学温度	ケルビン	K
物質の量	モル	mol
光度	カンデラ	cd
平面角	ラジアン	rad
立体角	ステラジアン	sr

表3 固有の名称をもつSI組立単位

量	名称	記号	他のSI単位による表現
周波数	ヘルツ	Hz	$s^{-1}$
力	ニュートン	N	$m \cdot kg / s^2$
圧力、応力	パスカル	Pa	$N / m^2$
エネルギー、仕事、熱量	ジュール	J	$N \cdot m$
工率、放射束	ワット	W	$J / s$
電気量、電荷	クーロン	C	$A \cdot s$
電位、電圧、起電力	ボルト	V	$W / A$
静電容量	ファラド	F	$C / V$
電気抵抗	オーム	$\Omega$	$V / A$
コンダクタンス	ジーメン	S	$A / V$
磁束	ウェーバ	Wb	$V \cdot s$
磁束密度	テスラ	T	$Wb / m^2$
インダクタンス	ヘンリー	H	$Wb / A$
セルシウス温度	セルシウス度	$^{\circ}C$	
光束度	ルーメン	lm	$cd \cdot sr$
照射度	ルクス	lx	$lm / m^2$
放射能	ベクレル	Bq	$s^{-1}$
吸収線量	グレイ	Gy	$J / kg$
線量等量	シーベルト	Sv	$J / kg$

表2 SIと併用される単位

名称	記号
分、時、日	min, h, d
度、分、秒	$^{\circ}, ', ''$
リットル	l, L
トン	t
電子ボルト	eV
原子質量単位	u

$$1 \text{ eV} = 1.60218 \times 10^{-19} \text{ J}$$

$$1 \text{ u} = 1.66054 \times 10^{-27} \text{ kg}$$

表4 SIと共に暫定的に維持される単位

名称	記号
オングストローム	$\text{\AA}$
バー	b
バル	bar
ガリ	Gal
キュリー	Ci
レントゲン	R
ラド	rad
レム	rem

$$1 \text{ \AA} = 0.1 \text{ nm} = 10^{-10} \text{ m}$$

$$1 \text{ b} = 100 \text{ fm}^2 = 10^{-28} \text{ m}^2$$

$$1 \text{ bar} = 0.1 \text{ MPa} = 10^5 \text{ Pa}$$

$$1 \text{ Gal} = 1 \text{ cm/s}^2 = 10^{-2} \text{ m/s}^2$$

$$1 \text{ Ci} = 3.7 \times 10^{10} \text{ Bq}$$

$$1 \text{ R} = 2.58 \times 10^{-4} \text{ C/kg}$$

$$1 \text{ rad} = 1 \text{ cGy} = 10^{-2} \text{ Gy}$$

$$1 \text{ rem} = 1 \text{ cSv} = 10^{-2} \text{ Sv}$$

表5 SI接頭語

倍数	接頭語	記号
$10^{18}$	エクサ	E
$10^{15}$	ペタ	P
$10^{12}$	テラ	T
$10^9$	ギガ	G
$10^6$	メガ	M
$10^3$	キロ	k
$10^2$	ヘクト	h
$10^1$	デカ	da
$10^{-1}$	デシ	d
$10^{-2}$	センチ	c
$10^{-3}$	ミリ	m
$10^{-6}$	マイクロ	$\mu$
$10^{-9}$	ナノ	n
$10^{-12}$	ピコ	p
$10^{-15}$	フェムト	f
$10^{-18}$	アト	a

(注)

- 表1-5は「国際単位系」第5版、国際度量衡局1985年刊行による。ただし、1 eVおよび1 uの値はCODATAの1986年推奨値によった。
- 表4には海里、ノット、アール、ヘクトールも含まれているが日常の単位なのでここでは省略した。
- barは、JISでは流体の圧力を表する場合に限り表2のカテゴリーに分類されている。
- E C閣僚理事会指令ではbar, barnおよび「血圧の単位」mmHgを表2のカテゴリーに入れている。

換算表

力	N (=10 <sup>5</sup> dyn)	kgf	lbf
	1	0.101972	0.224809
	9.80665	1	2.20462
	4.44822	0.453592	1

粘度  $1 \text{ Pa} \cdot \text{s} (\text{N} \cdot \text{s} / \text{m}^2) = 10 \text{ P (ポアズ)} (\text{g} / (\text{cm} \cdot \text{s}))$

動粘度  $1 \text{ m}^2 / \text{s} = 10^4 \text{ St (ストークス)} (\text{cm}^2 / \text{s})$

圧	MPa (=10 bar)	kgf/cm <sup>2</sup>	atm	mmHg (Torr)	lbf/in <sup>2</sup> (psi)
	1	10.1972	9.86923	$7.50062 \times 10^3$	145.038
力	0.0980665	1	0.967841	735.559	14.2233
	0.101325	1.03323	1	760	14.6959
	$1.33322 \times 10^{-4}$	$1.35951 \times 10^{-3}$	$1.31579 \times 10^{-3}$	1	$1.93368 \times 10^{-2}$
	$6.89476 \times 10^{-3}$	$7.03070 \times 10^{-2}$	$6.80460 \times 10^{-2}$	51.7149	1

エネルギー・仕事・熱量	J (=10 <sup>7</sup> erg)	kgf·m	kW·h	cal (計量法)	Btu	ft·lbf	eV
	1	0.101972	$2.77778 \times 10^{-7}$	0.238889	$9.47813 \times 10^{-4}$	0.737562	$6.24150 \times 10^{18}$
	9.80665	1	$2.72407 \times 10^{-6}$	2.34270	$9.29487 \times 10^{-3}$	7.23301	$6.12082 \times 10^{19}$
	$3.6 \times 10^6$	$3.67098 \times 10^7$	1	$8.59999 \times 10^5$	3412.13	$2.65522 \times 10^6$	$2.24694 \times 10^{25}$
	4.18605	0.426858	$1.16279 \times 10^{-6}$	1	$3.96759 \times 10^{-3}$	3.08747	$2.61272 \times 10^{19}$
	1055.06	107.586	$2.93072 \times 10^{-4}$	252.042	1	778.172	$6.58515 \times 10^{21}$
	1.35582	0.138255	$3.76616 \times 10^{-7}$	0.323890	$1.28506 \times 10^{-3}$	1	$8.46233 \times 10^{18}$
	$1.60218 \times 10^{-19}$	$1.63377 \times 10^{-20}$	$4.45050 \times 10^{-26}$	$3.82743 \times 10^{-20}$	$1.51857 \times 10^{-22}$	$1.18171 \times 10^{-19}$	1

$$1 \text{ cal} = 4.18605 \text{ J (計量法)}$$

$$= 4.184 \text{ J (熱化学)}$$

$$= 4.1855 \text{ J (15}^{\circ}\text{C)}$$

$$= 4.1868 \text{ J (国際蒸気表)}$$

$$\text{仕事率 } 1 \text{ PS (馬力)}$$

$$= 75 \text{ kgf} \cdot \text{m/s}$$

$$= 735.499 \text{ W}$$

放射能	Bq	Ci
	1	$2.70270 \times 10^{11}$
	$3.7 \times 10^{10}$	1

吸収線量	Gy	rad
	1	100
	0.01	1

照射線量	C/kg	R
	1	3876
	$2.58 \times 10^{-4}$	1

線量当量	Sv	rem
	1	100
	0.01	1

(86年12月26日現在)

**DEVELOPMENT OF PARTITIONING METHOD: ADSORPTION OF CESIUM WITH MORDENITE IN ACIDIC MEDIA**