

## Research on the Extraction of Potassium from Seawater by Inorganic Ion Exchange

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### ABSTRACT

This paper studies the adsorbing and exchanging capacity of zeolite and various synthetic molecular sieves — Models 3A°, 4A°, 5A°, 13X and W — with regard to potassium. It is shown that the exchanging capacity of synthetic molecular sieves with regard to potassium in seawater is up to 35.0–41.2 mg/g, while that of zeolite is up to 14.9–18.3 mg/g. In the potassium elution process of the exchangers, the elution effects of eluates such as calcium chloride, magnesium chloride, sodium chloride, sodium carbonate and sodium hydroxide have been examined; sodium chloride is considered to be the most promising eluate. The effects of various conditions such as temperature, concentration and composition on adsorption and elution by using molecular sieve and zeolite as exchangers have been investigated, and the bases for the determination of technological operational conditions have been provided. This method has the potential for industrialization.

### INTRODUCTION

The total amount of potassium salt stored in seawater is about 50 billion t, and is an inexhaustible resource. Since potassium was extracted from seawater using diticrylamine by the Norwegian chemist Kielland (1971), studies have been performed by many scientists. These methods are: (1) chemical precipitation method, which involve the use of phosphoric acid, sodium tetraphenylborate, sodium hypsulphite, perchlorate, gypsum, etc.; (2) organic solvent methods, which involve the extraction of polycyclic ether, and precipitation of polar solvent; (3) membrane separation; (4) organic ion exchange; and (5) inorganic ion exchange. Because inorganic ion exchanger is cheap and has the property of selective exchange for potassium, it is considered to have the most potential for industrialization.

Systematic investigations have been performed by Matsushita and Takagi (1969) and Kobayashi (1976) using inorganic phosphate ion exchangers. These exchangers include zirconium phosphate, polyphosphoric zirconium, molybdic acid, aluminium phosphate, and ferric phosphate; the highest exchanging capacity of potassium in seawater is up to 9.5 mg/g (Matsushita and Takagi, 1969). Thomas (1970) in the USA used aluminosilicate (glaucinite)

as an inorganic ion exchanger, and found its adsorption capacity to be up to 11 mg/g. Knoll (1971) in East Germany used mordenite as an exchanger. Because its eluate concentration is only half that of seawater, it has received no attention. Based on past research, the exchanging capacity of synthetic molecular sieves on potassium in seawater has been studied in this paper and good results have been obtained. Its adsorption capacity is up to 35.2–41.2 mg/g. Zeolite from Zhejiang, China, has been used as exchanger and an adsorption capacity of 14.9–18.3 mg/g has been achieved. Various factors involved in the adsorption and elution process have been investigated, from which it is concluded that the potassium concentration in eluate at special conditions is up to 15–20 g/l, i.e. 50–100 times higher than that of seawater. This provides potential for industrialization.

### EXPERIMENTAL RESULTS

#### Experimental method

Ion exchanger (200 g) was packed into a glass column ( $\varnothing$  1.5 x 1.3 m) with jacket. Firstly, the inorganic ion exchanger was treated with a saturated solution of sodium chloride at 100°C, which transformed it into a sodium ion form. Then seawater was passed through at a flow rate of 50

ml/min. The saturated exchanging capacity was determined. After adsorption saturated, the exchanger was diluted with the eluate at certain concentration, and its elution curve was determined.

### Sources and preparation of the exchangers

#### (a) Commercial molecular sieve

Four kind of molecular sieve such as 3A°, 4A°, 5A°, and 13X of reagent grade, were weighed, treated with sodium chloride solution, and then put into a glass exchanging column for determination.

#### (b) Model W molecular sieve

The structure of phellipsite determines well the selective exchanging ability for potassium, and the Model W molecular sieve belongs to the phellipsite family. Therefore, it is expected that its selective exchanging ability for potassium is fairly good. As there is no Model W molecular sieve on the market, it was prepared by us in the laboratory. This involved seven stages of preparation of the raw material liquor, jelling, aging, crystallizing, filtering and washing, drying and formation. It is proved to be a Model W molecular sieve by chemical composition analysis and X-ray diffraction.

#### (c) Zeolite

Because zeolite is very cheap and has certain selective exchanging capacity for potassium, it has its own advantages as an exchanger. In cooperation with the Geology Institute of Academia Sinica, zeolite from Zhejiang was chosen as the exchanger. The crude ore of zeolite obtained from Zhejiang is breccia dike and is fused by volcano glass. Its chemical composition (wt. %) is: SiO<sub>2</sub>, 70.45%; Al<sub>2</sub>O<sub>3</sub>, 12.35%; Fe<sub>2</sub>O<sub>3</sub>, 0.95%; K<sub>2</sub>O, 1.14%; Na<sub>2</sub>O, 1.09%; CaO, 1.66%; MgO, 1.68%; MnO, 1.68%; TiO, 0.19%; sintering loss, 10.60%. It is ground to powder and sieved; 0.246–0.350 mm of the powder was taken as a sample and examined. In addition, natural ores such as glauconite, vermiculite, and smectite have been examined. They are not discussed here in detail because their exchanging capacities are very low.

### Preparation of adsorbate and eluate

#### (a) Preparation of adsorbate

The adsorbate at definite concentration, temperature and flow rate pass through the exchanger, and the adsorption capacity can be determined by measuring the amount of adsorbate in the adsorbent after adsorption. The adsorbates are seawater and its solutions with various components. Seawater was taken from the shore of Tanggu Sea, Tianjin, and the

Bohai Gulf. The other solutions were prepared with chemically pure reagent in certain proportions.

#### (b) Preparation of eluent

After passing through adsorbate, the exchangers carry potassium ion. Potassium ion was exchanged into eluate after passing through eluate at certain concentrations through exchangers carried with potassium. The elution ratio and potassium content in eluate were calculated by measuring the potassium concentration in the eluate.

### Determination of adsorption curve and saturated adsorption capacity

The process of contacting adsorbate with sodium ion exchanger is called adsorption. The reverse process is called elution. In the adsorption process, the potassium concentration in the adsorbate after adsorption varies with the volume of out-flowing fluid. This process can be divided into three stages. The first is the adsorption stage in which the potassium concentration is nearly zero after adsorption. The second is the penetration stage, where potassium concentration gradually increases. In the third stage, adsorption is almost saturated. Potassium content in the eluate is almost equal to that in adsorbate. Potassium ion concentration is saturated and there is no potassium exchange. The seawater potassium exchanging capacities of various exchangers at room temperature are shown in Table 1.

### Effects of various cations in seawater on the potassium adsorption exchanging capacity

The effects of various cations in seawater on the potassium adsorption exchanging capacity have been determined by using zeolite-2 as exchangers. The results are shown in Table 2.

It can be seen from Table 2 that all the magnesium, calcium, and sodium ions in seawater decrease the exchanging capacity of potassium. The exchanging capacity of pure potassium solution whose potassium concentration is equivalent to that of seawater is up to 58.8 mg/g. The existence of magnesium decreases its exchanging capacity to 51.5 mg/g, and calcium decreases it to 43 mg/g, while the existence of sodium ion decreases its capacity to 16.32 mg/g. Therefore, the key factor affecting the exchanging capacity of potassium is sodium, the second is calcium, and the third is magnesium.

The results in Table 2 prove that the ratio of sodium to potassium concentration plays a dominant role in the exchanging process of zeolite.

TABLE 1

Seawater potassium saturated adsorption capacity of various exchangers

		Adsorption exchanging capacity (mg/g)
Molecular sieve model	3A°	16.3
	4A°	13.0
	5A°	7.3
	13X	14.0
	Average	12.7
Model W number	W-9	35.0
	W-10	40.8
	W-11	39.6
	W-12	41.2
	Average	39.2
Zeolite number	Zeolite-1	18.3
	Zeolite-2	14.9
	Zeolite-3	17.4
	Zeolite-4	17.1
	Average	16.9

### The relationship between temperature and adsorption exchanging capacity

By varying the circulating water temperature in the thermostatic jacket of the glass exchanging column, it can be seen that the lower the temperature, the higher the adsorption exchanging capacity. The detailed measuring results are as follows:

Temperature: 12°C; exchanging capacity: 20.01 mg/g.

Temperature: 19.4°C; exchanging capacity: 18.08 mg/g.

Temperature: 27.5°C; exchanging capacity: 17.33 mg/g.

Temperature: 40°C; exchanging capacity: 16.08 mg/g.

### Comparison of elution results among different eluates

Experiments have been performed by selecting various eluates one after another. The results show that the elution effect of calcium chloride or magnesium chloride solution is very poor. The highest potassium concentration in the eluate is only 3 g/l, even when eluted with high concentrated solution at 100°C, and the re-adsorption capacity decreased after the exchanger was eluted. The highest potassium concentration of sodium sulfate eluent is 3.9 g/l. When sodium hydroxide and carbonate are chosen as eluates, even though the potassium concentration is fairly high (the highest value is 15 g/l),

TABLE 2

The effects of various cations in seawater

Solution	Ion concentration (g/l)				Saturated exchanging capacity (mg/g)
	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	
Pure potassium solution	0.37	0	0	0	55.8
Solution containing magnesium	0.38	1.25	0	0	51.8
Solution containing calcium	0.40	0	0.36	0	43
Solution containing sodium	0.38	0	0	9.3	16.3
Seawater	0.40	1.4	0.36	9.5	14.9

the exchanger tends to be effloresced and its life is diminished. Therefore their prospects for industrialization are also very poor. The elution effect of sodium chloride saturated solution at 100°C is fairly good, and there is a marked potassium concentration difference between the eluate and the adsorbate. The highest potassium concentration is up to 8–10 g/l and is 20–30 times thicker than seawater.

### The effects of elution temperature and adsorption capacity of exchanger on the potassium concentration of eluate

The elution temperature has a direct effect on the elution results when saturated sodium chloride solution was chosen as eluent. The higher the temperature, the higher the potassium concentration in eluate and the higher the elution ratio.

At the same elution conditions, i.e. with sodium chloride saturated solution at 100°C as eluent, the higher the adsorption capacity of the exchangers, the higher the potassium concentration in the eluate (see Table 3).

## DISCUSSION

It can be seen from the above experimental results that the seawater potassium selective exchanging capacity of the Model W molecular sieve is fairly high. Its exchanging capacity is up to 35–40 mg/g, which is far superior to that of various inorganic ion exchangers reported previously. The seawater potassium exchanging adsorption capacity of zeolite without chemical processing and treatment is up to 14.9–18.3 mg/g, which is also superior to the capacities of various synthetic inorganic ion exchangers

TABLE 3

The relationship between elution temperature and high concentration eluate

Feed		Eluate volume (ml)	K <sup>+</sup> concentration in high concentration eluate (g/l)				
K <sup>+</sup> concentration (g/l)	NaCl/KCl		100°C	90°C	75°C	50°C	Room temp. (26–31°C)
0.37	37	500	7.87	7.83	7.71	6.28	5.10
7.92	20.24	350	12.24	12.04	11.32	9.57	7.93
12.19	12.49	300	19.08	18.79	16.77	13.90	11.48
19.25	7.62	300	24.16	22.65	21.43	18.72	15.87

previously reported in the literature. Therefore, molecular sieve zeolites can be considered to be inorganic ion exchangers whose seawater potassium exchanging capacity is very excellent.

The reason that molecular sieve zeolite has such properties is dependent on its structure. Not only can the cations of molecular sieve zeolite be displaced by one another at certain conditions, but they also form various circles and body cavities with definite diameters because of the different structures of silicon (aluminium) oxygen frame. The radii of various cations in aqueous solutions are different and so different selective exchanging capacities are shown by some molecular sieve zeolites for definite cations.

Sodium chloride saturated solution has been chosen as the eluate throughout the experiments, its characteristic being that both elution and regeneration are in the same process. Although the high concentration zone of the eluted solution is not so centralized in the elution curve distribution, the effects of potassium enrichment can be realized. Because sodium chloride solution is cheap and easy to obtain, there exists the possibility of industrialization.

The adsorption exchanging capacity of the exchanger depends on the ratio of NaCl to KCl in the feed stream. For high NaCl content solutions such as seawater, the NaCl/KCl ratio of eluate varies after adsorption and elution operation, so there is the possibility of re-enrichment of potassium. Eluate which is 50–100 times thicker than seawater is expected to be obtained if the methods of cool adsorption and hot elution, partial elution and second enrichment were adopted in determining the technological process. Potassium chloride preparation is then technologically feasible after evaporation and separation. This provides the potential for industrialization of the technology of potassium separation from seawater.

## CONCLUSIONS

This paper describes the method of potassium extraction from seawater by using a Model W

molecular sieve and zeolite as exchangers.

The seawater potassium exchanging capacity of Model W molecular sieve is up to 35–40 mg/g, and that of zeolite is up to 14.9–18 mg/g.

The eluate of hot sodium chloride saturated solution makes the material cheap and easy to obtain, both elution and regeneration belong in the same process. The eluted exchanger can go in for the next adsorption.

The effects of adsorbate composition, adsorption temperature and elution temperature on the exchanging process has been reported in this paper, which establishes a foundation for the technological determination of seawater potassium extraction.

The suggestion of technological processing of seawater potassium extraction has been proposed, whose characteristics are cool adsorption and hot elution, partial elution and re-enrichment. With such a process, the potassium concentration in the eluate would be 50–100 times richer than that in seawater, and potassium chloride could be prepared after evaporation and separation.

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