Determination of inorganic exchange efficiency of rubidium, cesium, and barium

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ABSTRACT

Reducing environmental pollution needs for modern life. Nowadays, the pollution levels increase with time because there are many causes and sources to affect directly the natural environment. So a necessary improvement of the environment quality would treat and reduce waste. In this paper, the inorganic exchange method was chosen. Two kinds of inorganic salts were used: ammonium phosphomolybdate n-hydrate (AMP), and ammonium phosphotungstate n-hydrate (AWP) for studying on the behavior exchange of Rb(I), Cs(I), and Ba(II). The results showed that the exchange efficiency was high for both rubidium and cesium. The exchange efficiency ratios depended on the kind of inorganic compound and acid concentration.

Keywords: *AMP, AWP, inorganic exchange*

INTRODUCTION

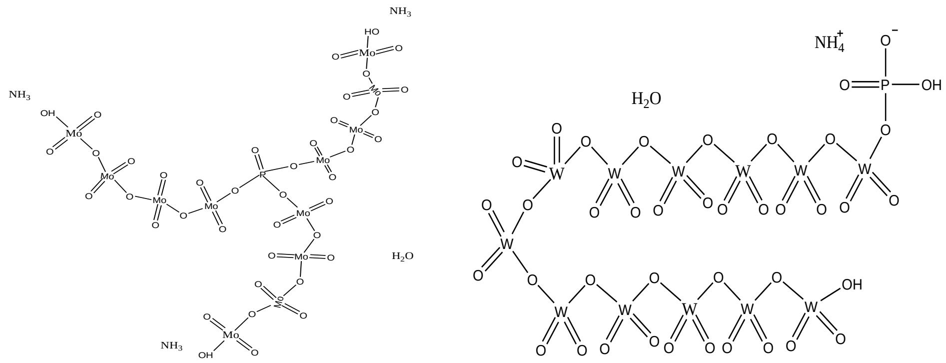
Normally, when a nuclear power plant (NPP) operates, the material playing an important role in the heat transfer is sea water, and it usually comes to the sea again. When the sea water comes out from NPP, it brings itself a lot of metals and their compounds. Most of them are radionuclides having long half-lifes, such as cesium, iodine, cobalt, lithium, rubidium, barium, magnesium, etc. However, NPP systems are often out of their operation due to various system troubles and in the reality the quality of sea water is not enough for requirements to release on ocean. Therefore, the water treatment is necessary to improve life environment.

There are many ways to reduce the radioisotope waste of water containing the radionuclides, such as reused water in NPP, collective ion metals [1, 2], treatment by chemical method [3, 4, 5], etc.

Recently, the adsorption of radionuclides by acidic type resin [4, 5, 6] were used. It has been known that acidic type resin has the high adsorption ability for many kinds of metals. Therefore, the organic compounds created from a chemical reaction were unstable hydrocarbon salts.

The inorganic compounds used in the above-mentioned exchange indicate the behavior of radioactive fall out in soils and NPP [7]. Normally, organics have absorption capacity greater than inorganics, however, the organic structures are affected by radiation interaction. Therefore, inorganics are used to absorb the radioactive isotopes in trace elements in the primary and secondary cycle in NPP.

In this research, inorganics were used as the exchange role to creat the precipitated salts. Ammonium phosphomolybdate *n*-hydrate (AMP), and ammonium phosphotungstate *n*-hydrate (AWP) were used as inorganic exchange parts. The chemical structures of AMP and AWP were shown in the Fig. 1.



A) B)

Fig. 1. Structural formulas of AMP and AWP
A) Ammonium phosphomolybdate *n*-hydrate (AMP); B) Ammonium phosphotungstate *n*-hydrate (AWP)

When AMP or AWP incorporates with RbCl, CsCl, $BaCl_2$ solution, a chemical reaction will happen and create a precipitated salt. The chemical reactions were shown in the following equations:

Case of AMP:

$(NH_4)_3PO_412MoO_3 + 3RbCl \rightarrow Rb_3PO_412MoO_3\downarrow + 3NH_4Cl$ (1)

$(NH_4)_3PO_412MoO_3 + 3CsCl \rightarrow Cs_3(PO_412MoO_3)_2\downarrow + 3NH_4Cl$ (2)

$2(NH_4)_3PO_412MoO_3 + 3BaCl_2 \rightarrow Ba_3(PO_412MoO_3)_2\downarrow + 6NH_4Cl$ (3)

Case of AWP:

$(NH_4)_3PO_424WO_3 + 3RbCl \rightarrow Rb_3PO_424WO_3\downarrow + 3NH_4Cl$ (4)

$(NH_4)_3PO_424WO_3 + 3CsCl \rightarrow Cs_3PO_424WO_3\downarrow + 3NH_4Cl$ (5)

$2(NH_4)_3PO_424WO_3 + 3BaCl_2 \rightarrow Ba_3(PO_424WO_3)_2\downarrow + 6NH_4Cl$ (6)

As HCl solutions having different concentrations, then aforementioned precipitated salts would form ions.

MATERIALS AND ETHOD

Sample preparation

The experiment was set up at the Department of Nuclear system safety Engineering, Nagaoka University of Technology. The experimental technique was mainly based on plasma mass one using the inorganic exchange method in hydrochloric acid solution. The inorganic exchange experiment was carried out with RbCl, CsCl, and $BaCl_2$ species in the 10 mL HCl solutions having different concentrations. Using pure salts: RbCl, CsCl (purity ≥ 99.0 %), called alkaline chloride - ECl, and $BaCl_2$ (purity ≥ 99.0 %), called Alkaline earth chloride - $AECl_2$, which have the concentration of HCl as following:

- 10 mmol/L of RbCl, CsCl in HCl solutions, the concentration of HCl solutions are 0.1, 0.5, 1, 2 and 5 mol/L;
- 10 mmol/L of $BaCl_2$ in HCl solutions, the concentration of HCl solutions are 0.1, 0.5, 1; 2 and 5 mol/L.

Making the samples up was necessary before all exchange experiment tests were performed. Adding ~1 g AMP, and AWP into ACl and $AECl_2$ solutions, called AMP ACl, AMP $AECl_2$, and AWP ACl, AWP $AECl_2$ respectively. All of sample solutions were kept constant at 25 ^{0}C, and shaken in 24 hours by a water shaking machine. After shaking these samples, each extraction (10 mL) of sample solutions was carried out at Minisart® SRP (pore size is 0.45 µm, diameter size is 25 mm) for removal of the insoluble salts in sample solutions. Fig. 2 shows the filter shape, and Fig. 3 shows the shapes of samples.

Fig. 2. The shape of filter

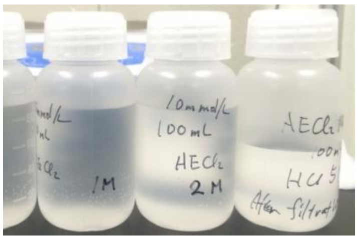


Fig. 3. The ACl and $AECl_2$ solutions with an addition of AMP and AWP

A) B)

Fig. 4. The sample shapes. A) The samples were not filtrated; B) The samples were filtrated

In the next step, adding 1 % HNO_3 concentration solution to AMP ACl, AMP $AECl_2$, AWP ACl, AWP $AECl_2$ solution, which have 50 mL solution included: 49.95 mL 1 % HNO_3 + 0.05 mL each other AMP ACl, AMP $AECl_2$, AWP ACl, AWP $AECl_2$, AWP, AMP. Thus, there were 5 sample solutions of AMP ACL, 5 sample solutions of AMP $AECl_2$, 5 sample solutions of AWP ACL, 5 sample solutions of AWP $AECl_2$, 5 sample solutions of ACL, and 5 sample solutions of $AECl_2$.

Finally, 8 standard samples were made of 11 metals (1000 ppm standard concentration: Cs, Ba, K, Ca, Na, Rb, Li, Sr, Mg, Mo, W). Therefore the content of metals per content of samples were 1 ppb, 50 bbp, 100 bbp, 200 bbp, 300 bbp, 400 bbp, 500 bbp, and 600 bbp. The standard samples were used for calibrating the efficiency of a spectrum machine depending on the contents and kinds of metals. The calibration of the exchanged efficiency of spectrum machine is necessary for calculating the contents of metals in the samples.

All of the sample solutions were measured by using the inductively coupled plasma mass spectrometer Agilent 7700 Series ICP-MS, which is a flexible facility with high performance and high reliable analysis of complex samples in a very short time, or confidently detecting ultra trace metals in high purity. Fig. 5 shows the structure of Agilent 7700 Series ICP-MS.

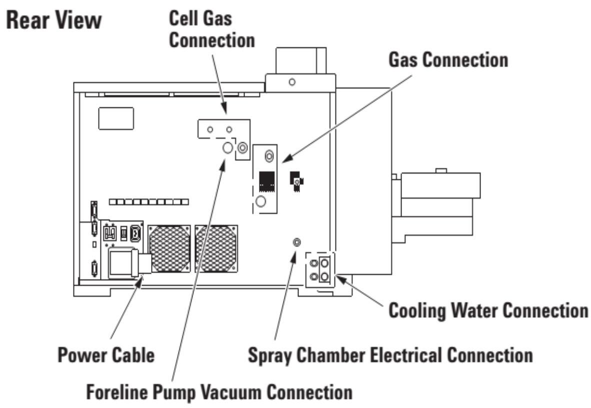


Fig.5. The structure of Agilent 7700 Series ICP-MS plasma mass spectrometer

RESULTS AND DISCUSSION

Firstly, the efficiency of Agilent 7700 Series ICP-MS plasma mass spectrometer must be calibrated with considerated atoms (Rd-85, Cs-133, and Ba-137). Table 1 and Fig. 6 show the experimental data, curve diagrams and fitting functions.

Table 1. The count rate (counts per second) of Rb-85, Cs-133, Ba-137 depended on the content of metal in the sample

Concentration of standard samples (ppb)	Count per second (Rb-85)	Count per second (Cs-133)	Count per second (Ba-137)
1	590315	801518	120346
50	28516218	38613228	5562541
100	57011009	77195577	11114774
200	114012326	154359788	22230974
300	170990199	231524998	33335952
400	227980294	308690209	44428708
500	284970389	385855420	55533686
600	341960484	463020630	66638664

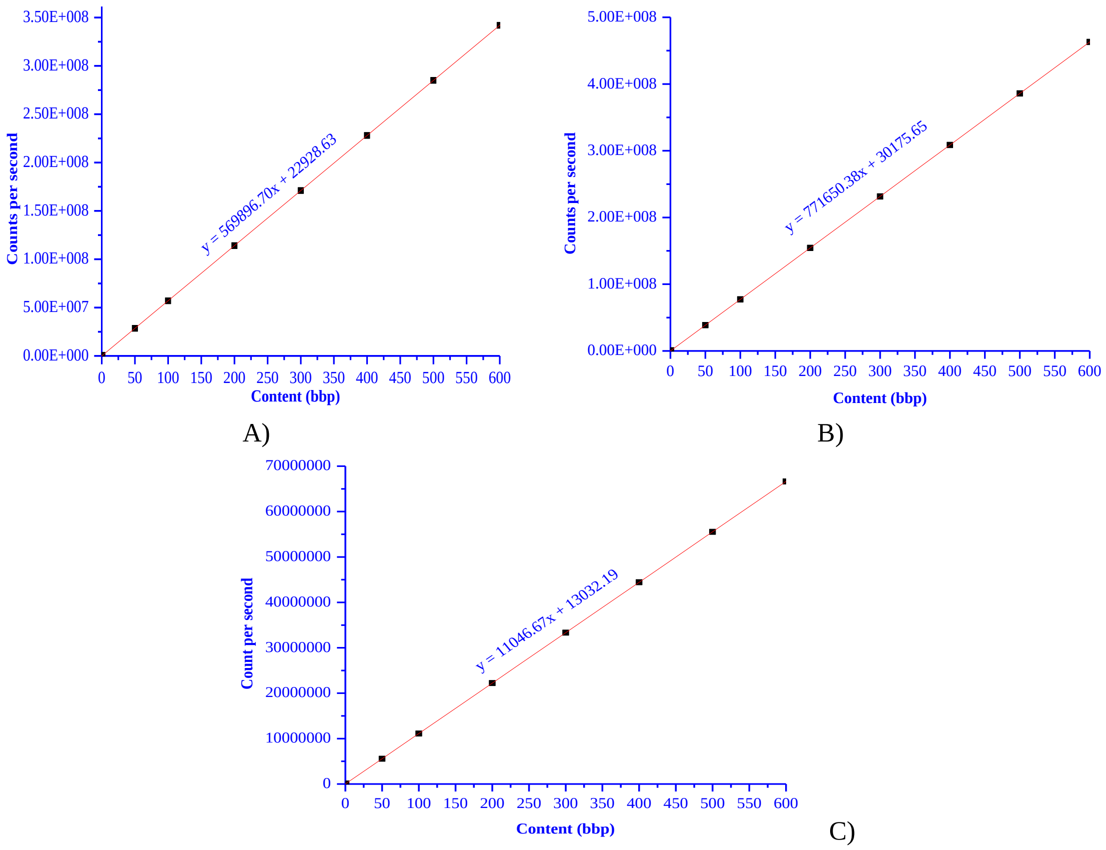


Fig. 6. The experimental efficiency curves and fitting functions
A) Case Rb-85; B) Case Cs-133; C) Case Ba-137

As a result, the fitting functions for three metals in the standard samples are the following ones:

Case Rb-85:

$$y = 569896.70x + 22928.63 \quad (7)$$

Case Cs-133:

$$y = 771650.38x + 30175.65 \quad (8)$$

and case Ba-137:

$$y = 111046.67x + 13032.19 \quad (9)$$

where y is counts per second, and x is the content of metal per the content of sample (ppb).

Before the metals in the samples were exchanged by AMP and AWP, the initial contents of Rb-85, Cs-133, Ba-137 in these samples were shown in Table 2.

Table 2. The content of metals in the initial samples

	The concentration of HCl solution (M)				
	0.1	0.5	1	2	5
Rb-85 (cps)	101171634	99077280	93224397	100673003	106095850
Content (ppb)	177.49	173.85	163.58	176.65	185.99
Cs-133 (cps)	177301005	181112966	161906545	176166676	182108397
Content (ppb)	229.73	234.67	209.78	228.26	235.96
Ba-138 (cps)	25775677	25017207	25257074	25505826	25272621
Content (ppb)	232.03	225.20	227.36	229.60	225.41

After the metals in the samples exchanged cation (or anion) and were insoluble by AMP and AWP, the final contents of Rb-85, Cs-133, Ba-137 in the samples were shown in Table 3, and Fig. 7. The metals exchange and insoluble ability depends on organics (AMP and AWP) and acid concentration in the samples were expressed by the exchanged efficiency (%).

Table 3. The content and exchanged efficiency of metals in samples after exchanging

Case of Rb-85

	The concentration of HCl solution (M)				
	0.1	0.5	1	2	5
Rb-85 (cps) exchanged by AMP	31535437	38992623	36872591	51604531	106095850
Content (ppb)	55.30	68.42	64.70	90.55	96.18
Exchanged efficiency (%)	68.85	60.65	60.45	48.74	48.29
Rb-85 (cps) exchanged by AWP	5582147	33795126	36923882	40143823	106095850
Content (ppb)	9.76	59.30	64.79	70.44	81.13
Exchanged efficiency (%)	94.50	65.89	60.39	60.12	56.38

Case of Cs-133

	The concentration of HCl solution (M)				
	0.1	0.5	1	2	5
Cs-137 (cps) Exchanged by AMP	18626182	31883165	24429006	36806306	40865196
Content (ppb)	24.10	41.28	31.62	47.66	52.92
Exchanged efficiency (%)	89.51	82.41	84.92	79.12	77.57
Cs-137 (cps) exchanged by AWP	7560691	20802241	32076078	20354683	27739393
Content (ppb)	9.76	26.92	41.53	26.34	35.91
Exchanged efficiency (%)	95.75	88.53	80.20	88.46	84.78

Case of Ba-137

	The concentration of HCl solution (M)				
	0.1	0.5	1	2	5
Ba-137 (cps) exchanged by AMP	21416973	21203757	21696818	24328698	25272621
Content (ppb)	192.78	190.86	195.30	219.00	227.50
Exchanged efficiency (%)	0.90	4.11	5.09	3.19	0.87
Ba-137 (cps) exchanged by AWP	21611310	22113255	22859509	25129367	25272621
Content (ppb)	194.53	199.05	205.77	226.21	229.50
Exchanged efficiency (%)	16.16	11.61	9.50	1.48	0.01

Table 3 and Fig. 7 expressed that in most of cases, the exchange ability depends on acid concentration and kind of organic material. In the case of Rb-85, the exchange efficiency reached up to ~95 % at low acid concentration, and reduced down to half ~50 % at 5 M concentration of HCl solution. Among the two inorganic materials (AMP and AWP), the exchange efficiency of AWP was higher than that of AMP. Of these metals, Cs-133 has the highest exchange efficiency. At the low acid concentration, it reached completely the adsorption (~96 %), the lowest exchange efficiency was more than half of the content of Cs-133 (78 %). Similar to Rb-85, AWP has more higher exchange efficiency than AMP.

In the case of Ba-137, the exchange efficiency has low observation. It was found that the precipitated salt was a little. The result showed that insoluble salt formed with Ba-137 was unclear.

In the HCl solution, the quantity of precipitated salt was reduced because the precipitated salt was splitted negative and positive ions which performed more suspension. This is a cause to reduce the exchange ratio.

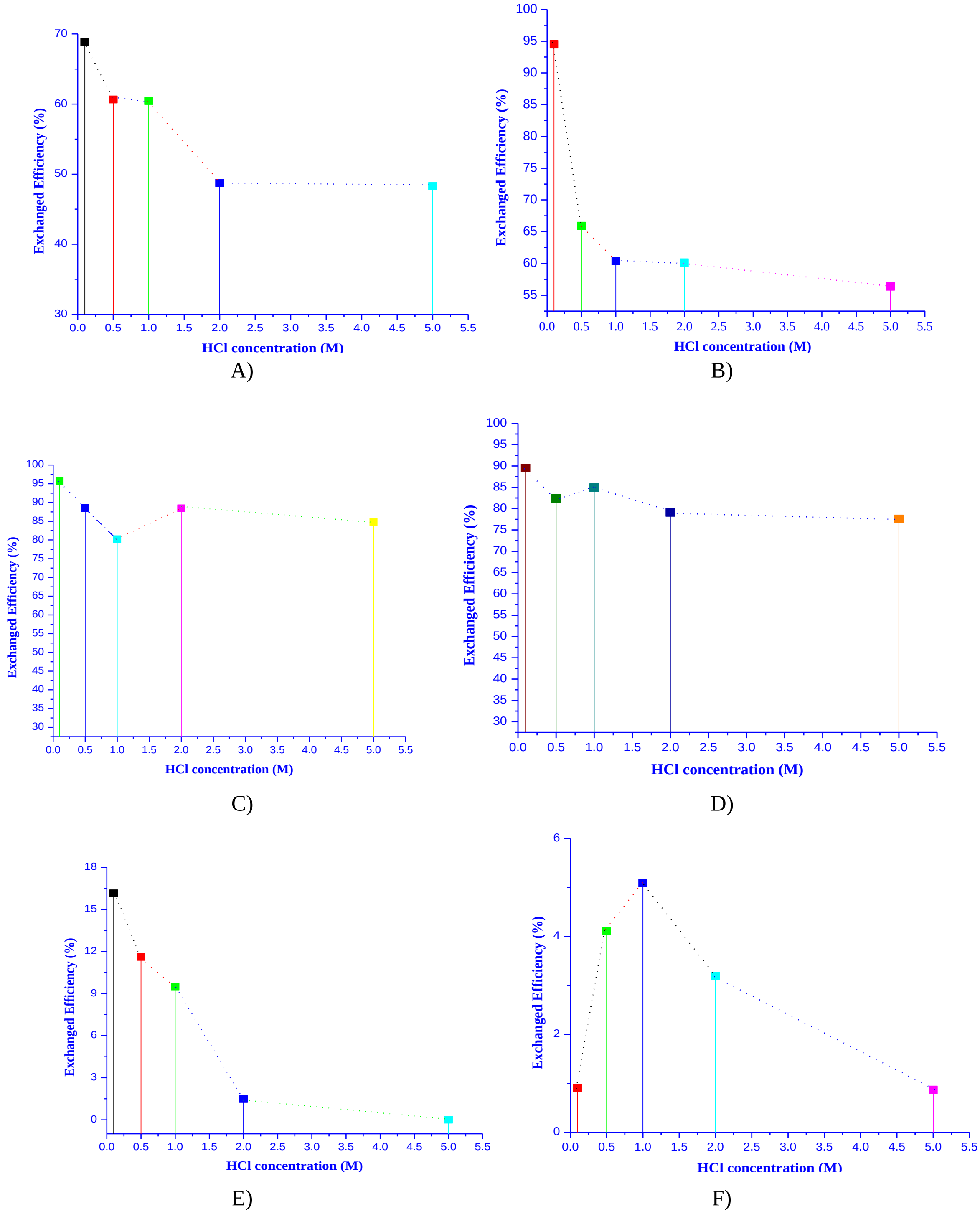


Fig. 7. A) The dependence on Rb-85 exchanged by AMP; B) The dependence on Rb-85 exchanged by AWP; C) The dependent on Cs-133 exchanged by AMP; D) The dependence on Cs-133 exchanged by AWP; E) The dependence on Ba-137 exchanged by AMP; F) The dependence on Ba-137 exchanged by AWP

CONCLUSION

In this research, the exchange efficiencies of rubidium, cesium, and barium on inorganic compounds were obtained. The exchange behaviors of rubidium and cesium were almost similar. According to these results, the exchange abilities of Rb, Cs on AMP and AWP can be controlled by hydrochloric acid. It was also said that the developed AMP and AWP can be insoluble Cs(I), Rb(I) salts in the solution is with different acid concentrations. Besides, the results showed that the exchange abilities consisting of the inorganic compound had high efficiencies of Rb(I), Cs(I), except Ba(II). Therefore, this method can be applyed for the environment treatment.

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Xác định hiệu suất trao đổi vô cơ của rubidium, cesium và barium

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TÓM TẮT

Giảm thiểu ô nhiễm môi trường là cần thiết trong cuộc sống hiện đại. Ngày nay, mức độ ô nhiễm môi trường ngày càng tăng theo thời gian, bởi do quá nhiều nguyên nhân và nguồn ô nhiễm ảnh hưởng trực tiếp đến môi trường. Do vậy, sự cần thiết phải cải thiện chất lượng môi trường bằng các biện pháp giảm thải chất thải và xử lý chúng. Trong bài báo này, bằng phương pháp trao đổi trong hợp chất vô cơ, hai muối vô cơ là ammonium phosphomolybdate n-hydrate (AMP), và ammonium phosphotungstate n-hydrate (AWP) được sử dụng trong nghiên cứu sự trao đổi của các ion Rb(I), Cs(I), và Ba(II). Kết quả cho thấy hiệu suất trao đổi cao ở cả rubidium, cesium; đồng thời cũng chỉ ra sự phụ thuộc của quá trình trao đổi đối với từng hợp chất vô cơ và nồng độ acid trong mẫu chất.

Từ khóa: *AMP, AWP, trao đổi hợp chất vô cơ*

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