Experimental Studies on Rare Metal Collection from Seawater

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ABSTRACT

The paper presents the results of rare metal collection experiments conducted off the shores of Okinotorishima (Okinotori Islands) and Iriomotejima (Iriomote island), Japan, in 2007 and 2008. The adsorbent materials used in the experiments were developed originally for uranium by the Japan Atomic Energy Agency and for lithium by the National Institute of Advanced Industrial Science and Technology. The purpose of this study is to investigate various factors affecting the adsorption efficiency of rare metals from seawater, e.g., soaking duration, seawater temperature, depth in seawater, and mooring system for adsorbent components. The results presented in the paper focus primarily on the adsorption efficiency involved with uranium and lithium.

KEY WORDS: Seawater; rare metal; uranium; lithium; adsorbent.

INTRODUCTION

About 70% of all elemental ions can be found in seawater, albeit at low concentrations. Although the concentrations are not high, the elemental ions in seawater could become a valuable resource if efficient and economical collection technology can be developed. The concentration of typical rare metals in seawater is shown in Table 1.

The increasing worldwide demand for rare metals is being driven by the economic development of emerging countries as well as by high-tech industrialization, e.g., lithium for high-power/long-lasting batteries, uranium for nuclear electric power generation, vanadium compounds for catalysts, and molybdenum additive for alloy steels.

For the last two decades, the Japan Atomic Energy Agency and the National Institute of Advanced Industrial Science and Technology have been studying adsorbents for the extraction of uranium and lithium, respectively, from seawater. Various adsorbents have been developed, and rare metal extraction efficiencies have improved.

Table 1. Concentration of typical rare metals in seawater.

Resource	Concentration in seawater (mg/ton-seawater)
Cobalt (Co)	0.1
Yttrium (Y)	0.3
Titanium (Ti)	1
Manganese (Mn)	2
Vanadium (V)	2
Uranium (U)	3
Molybdenum (Mo)	10
Lithium (Li)	170
Boron (B)	4,600
Strontium (Sr)	8,000

EXPERIMENT: SETUP AND PROCEDURES

Experiment Location

Since previous studies by the Japan Atomic Energy Agency have shown that higher seawater temperatures result in greater rare metal collection efficiencies, experiments were conducted in May 2007 in Okinotorishima (Okinotori Islands), the southernmost island in Japan (1,740 km south of Tokyo), and from November 2007 to January 2008 in Iriomotejima (Iriomote island), located 2,100 km southwest of Tokyo, as shown in Fig. 1.

Adsorbents

Uranium adsorbent

The uranium-specific adsorbent used in the experiments, an amidoxime adsorbent synthesized by radiation-induced graft polymerization, was developed by the Japan Atomic Energy Agency (Tamada, 2009). A non-woven polyethylene fabric is used as a trunk polymer for grafting. In the grafting process, the polyethylene is irradiated with an electron beam and then put in contact with a reactive monomer. As a result, graft chains are propagated from active sites in the irradiated trunk polymer. In this way, acrylonitrile can be grafted onto the non-woven polyethylene fabric; subsequently, the cyano groups of the grafted polymer chain are then converted into amidoxime groups. This grafting process results in an adsorbent material with sufficient mechanical strength and a high uranium adsorption capacity.

Lithium adsorbent

A granulated manganese oxide developed by the Japan National Institute of Advanced Industrial Science and Technology (Ooi et al., 1986; Chitrakar et al., 2001; Ooi et al., 2002) functions as a lithium-specific adsorbent in the experiments. The ion-sieve-type manganese oxide used has a higher affinity for lithium ions than for other alkali metal ions. This high selectivity arises from the presence of micropores with a size suitable for fixing lithium ions; other alkali metal ions have an ionic radius that is larger than the radius of the micropores and, thus, cannot enter.

Experimental Apparatus

Examples of individual adsorbent components are shown affixed to mooring ropes in Fig. 2. The uranium adsorbent components, in the form of non-woven fabric, are strapped directly to the mooring rope with plastic bands at the upper and lower ends of each individual unit, whereas the granulated lithium adsorbent is put into nylon mesh bags that are strapped individually to the mooring rope.

To observe the effect of adsorbent packing density, i.e., concentration in seawater, on lithium adsorption, three different quantities of adsorbent, 10, 40, and 160 mL, were placed into identically sized nylon mesh bags.

The configuration of the experimental apparatus for the Iriomotejima tests is schematically shown in Fig. 3. The test apparatus was installed 150 m offshore: seawater depth of 12 m. The effect of water depth on lithium adsorption was examined by placing the adsorbent components at three distances from the seawater surface: surface zone, 2-4 m in depth; middle zone, 6-8 m; and bottom zone, 9-11 m.

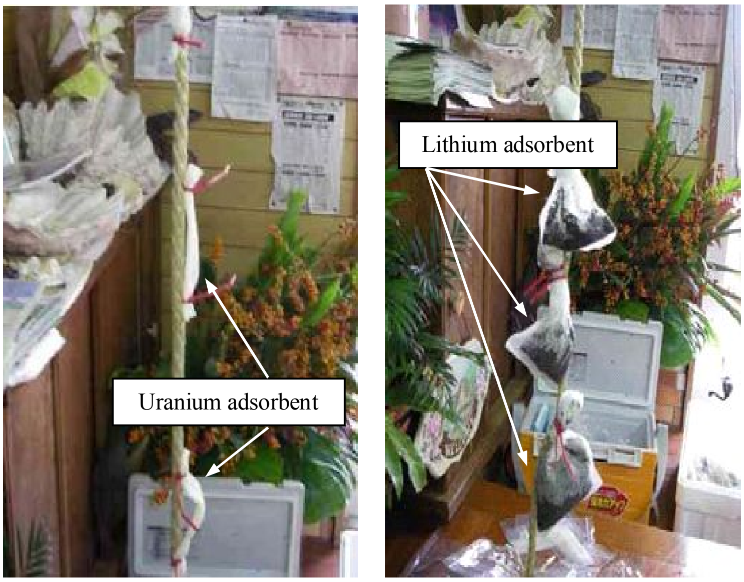


Fig. 2 Uranium (left) and lithium (right) adsorbent components used in Iriomotejima experiments.

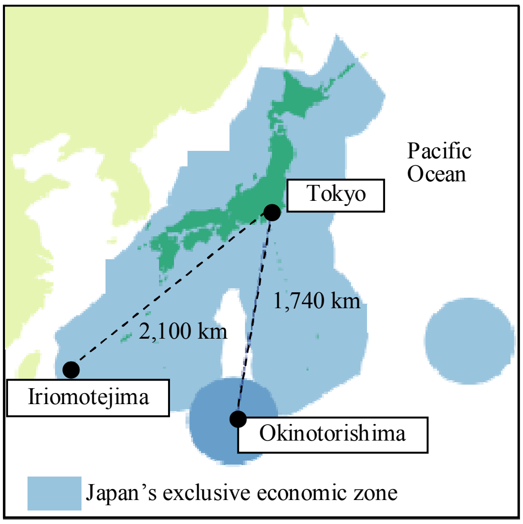


Fig. 1 Experiment locations.

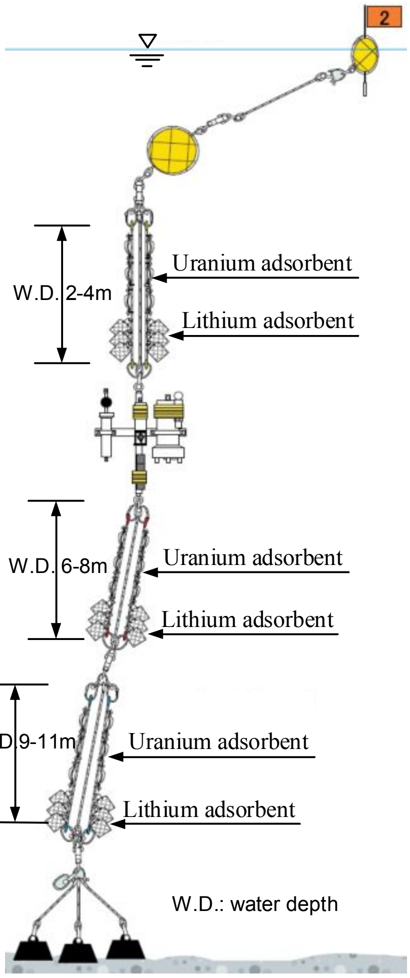


Fig. 3 Test configuration for Iriomotejima experiments.

Table 2. Summary of the test conditions in Iriomotejima (2007-2008) and Okinotorishima (2007) experiments.

Test site	Submersion duration/dates	Test water depth	Seawater temperature	Seawater velocity
Iriomotejima	Max. 58 days Nov. 21, 2007, to Jan. 18, 2008	Surface zone: 2 - 4 m Middle zone: 6 - 8 m Bottom zone: 9 - 11 m	22 - 26 °C	At 5 m water depth: Average 2.5 cm/sec Max. 31.6 cm/sec
Okinotorishima	Max. 4 days May 26 to 30, 2007	1 - 2m	27 – 29 °C	At 1 m water depth: Average 9.7cm/sec Max. 39.1 cm/sec
Adsorbents	Uranium adsorbent: amidoxime adsorbent synthesized by radiation-induced graft polymerization (developed by the Japan Atomic Energy Agency). The uranium adsorbent components are shown in Fig. 4 after submersion. Lithium adsorbent: granulated manganese-oxide developed by the National Institute of Advanced Industrial Science and Technology.			
Parameters Measured	Seawater temperature, velocity, salinity, chlorophyll, turbidity, current direction			

Environmental and Test Conditions

Iriomotejima tests

The adsorbent components were submersed in seawater for durations of 4, 8, 14, 28, and a maximum 58 days in the period from November 21, 2007, to January 18, 2008, to observe the effect of immersion time on adsorption. The seawater temperature at depths between 1.5 and 6.5 m ranged from 22 to 26 °C. The average and maximum seawater velocities, 2.5 and 31.6 cm/sec, respectively, were measured at a depth of 5 m. The test conditions in the Iriomotejima (2007-2008) and Okinotorishima (2007) experiments are summarized in Table 2.

Okinotorishima tests

Because of the limited time available at this location, May 26 to 30, 2008, the test duration was limited to four days. The adsorbent components were placed at a depth of 1-2 m since the maximum water depth was only 3 m. At a depth of 1 m, the average and maximum seawater velocities were measured at 9.7 and 39.1 cm/sec, respectively, and the seawater temperature was between 27 and 29 °C.

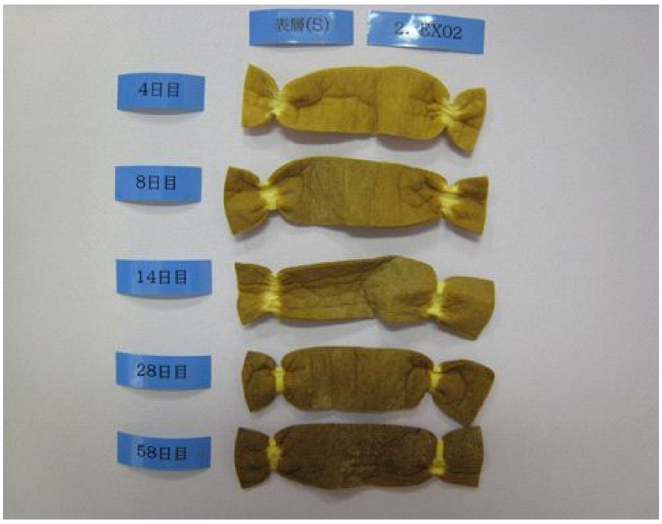


Fig. 4 Uranium adsorbent components after submersion in seawater: the original white color turned brown by adsorption of elemental ions dissolved in seawater.

TEST RESULTS AND OBSERVATIONS

Effect of Submersion Duration

Lithium

The relationship between the quantity of lithium adsorbed and the duration of submersion in the surface, middle, and bottom zones is shown in Figs. 5(a,b,c), respectively. The figures show adsorbed lithium increasing with submersion duration over the test periods of 4 to 58 days.

Figures 5(a,b,c) also show that the lithium adsorption efficiency increases as the adsorbent concentration in seawater is decreased; decreasing the amount of adsorbent material (160, 40, and 10 ml) placed into identically sized mesh bags, i.e., decreasing the concentration of adsorbent in seawater, increases the interaction between adsorbent and seawater, as illustrated in Figs. 6(a,b,c).

The maximum amount of adsorbed lithium extracted in these tests ranged from about 14 to 15 mg per 1 g-adsorbent (14,000 to 15,000 mg/kg-Ads), regardless of the water depth.

Uranium

The relationship between adsorbed uranium and submersion duration in each depth zone is shown in Fig. 7. Although the amount of adsorbed uranium continues to increase throughout the entire submersion period, maximum of 58 days, the adsorption rate is higher in the first 28 days. The quantity and rate of adsorption appear to be relatively independent of water depth. The maximum quantity of adsorbed uranium in these tests was around 1,000 mg/kg-Ads after 58 days of submersion. The results of previous tests conducted by the Japan Atomic Energy Agency (2001) for uranium and vanadium are shown in Fig. 8: seawater temperature between 16 and 22 °C. The increase in adsorbed quantity of both elements with submersion duration is similar to that shown in Fig. 7. The maximum level of uranium adsorption, 1,900 mg/kg-Ads, attained in the 2001 test is higher than that found in the present test, 1,000 mg/kg-Ads.

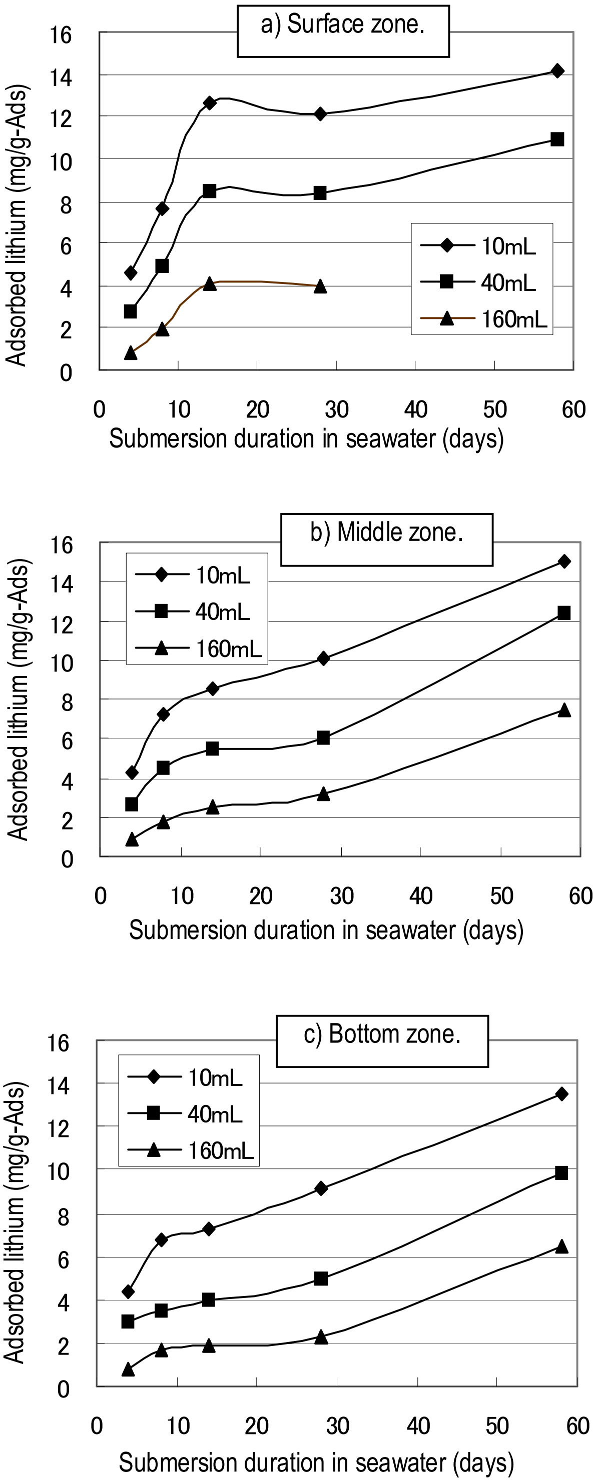
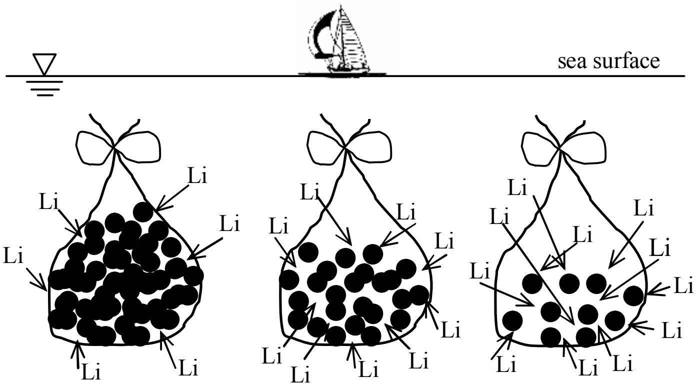


Fig. 5 Relationship between adsorbed lithium and submersion duration in Iriomotejima tests: a) surface zone, b) middle zone, and c) bottom zone. To observe the effect of adsorbent packing density, i.e., concentration in seawater, on lithium adsorption, three different quantities of adsorbent (10, 40, and 160 mL) were placed into identically sized nylon mesh bags to represent loose, medium, and dense packing, respectively.



a) adsorbent: 160 ml b) adsorbent: 40 ml c) adsorbent: 10 ml

Fig. 6 Illustrations of three different quantities of adsorbent placed into identically sized nylon mesh bags; black dots represent lithium adsorbent. Decreasing the packing density in bags increases the interaction between adsorbent and seawater, resulting in increased efficiency of lithium adsorption.

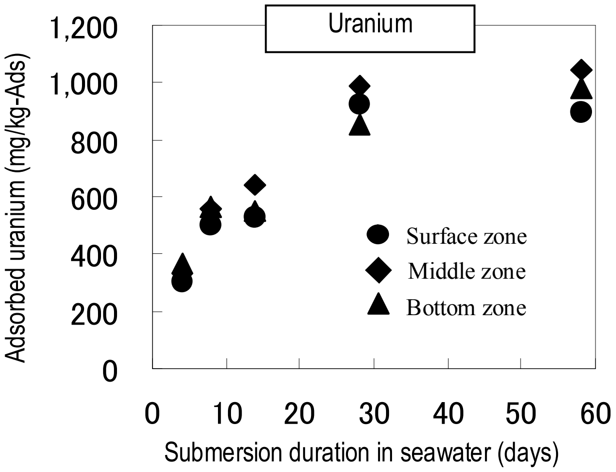


Fig. 7 Relationship between adsorbed uranium and submersion duration in Iriomotejima tests.

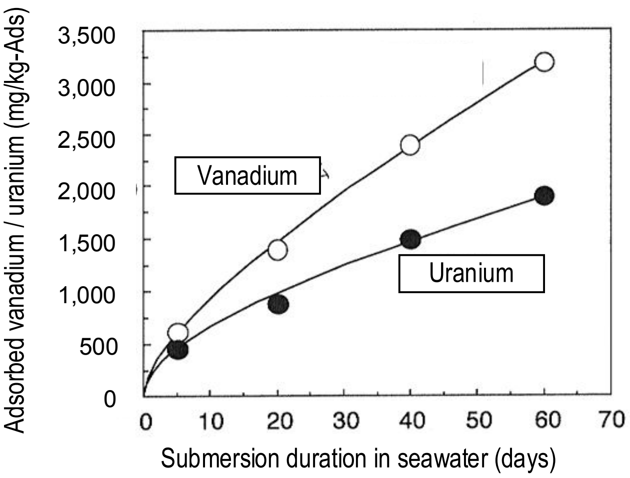


Fig. 8 Relationship between adsorbed uranium and vanadium submersion duration in Japan Atomic Energy Agency tests (2001).

Vanadium and Molybdenum

Although the uranium adsorbent used in the present test series has low affinity for alkaline metals such as sodium and potassium ions, transition metal ions, e.g., manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), vanadium (V), yttrium (Y), and molybdenum (Mo) ions, are selectively adsorbed from seawater (Tamada, 2009).

The adsorption results for vanadium and molybdenum are shown in Figs. 9 and 10, respectively; the adsorbed quantity of both elements increased with submersion duration. The total adsorbed vanadium and molybdenum after submersion for 58 days are 1,600 and 23 mg/kg-Ads (bottom zone), respectively.

Effects of Seawater Temperature

Many researchers (Tamada, 2009; Miyai et al., 1996) have reported that warmer seawater enhances chemical adsorption. The average seawater temperature around Okinotorishima was about 4 °C higher than Iriomotejima.

The adsorption results for lithium, uranium and vanadium from both islands are compared in Fig. 11. Since the submersion duration at Okinotorishima was limited to four days, the test results for Iriomotejima in this figure only use the four day results. The 4 °C higher seawater temperature in the Okinotorishima tests markedly enhanced rare metal adsorption, especially that of lithium and vanadium.

SUMMARY AND CONCLUSIONS

Rare metal extraction tests using uranium- and lithium-specific adsorbents were conducted in the southern islands of Japan in 2007-2008. The following is a summary of the experimental findings.

i) Adsorbent materials tested

The uranium adsorbent, an amidoxime adsorbent synthesized by radiation-induced graft polymerization, was developed by the Japan Atomic Energy Agency; the lithium adsorbent, a granulated ion-sieve-type manganese oxide, was developed by the Japan National Institute of Advanced Industrial Science and Technology.

ii) Adsorption as a function of submersion duration

The adsorbed uranium and lithium increased with the submersion duration: test periods of 4 to 58 days. Similar behavior could also be seen with vanadium and molybdenum.

iii) Seawater interaction with adsorbent

The rate that lithium is adsorbed, i.e., its efficiency, increased as the concentration of adsorbent in seawater was decreased; an increase in the interaction between adsorbent and seawater enhances the chemical adsorption.

iv) Adsorption as a function of seawater temperature

Higher seawater temperatures markedly enhanced the chemical adsorption of lithium and vanadium in this study.

DISCUSSION

Although an enormous amount of rare metal and rare earth ions is dissolved in seawater, the concentrations are very low, e.g., 0.0033 g of uranium and 0.17 g of lithium in 1 ton of seawater. To make extraction practical, adsorbent materials with high adsorption efficiency have to be developed. Another promising approach is the use of concentrated seawater that is discharged at elevated temperatures from seawater desalination and electric power plants; the discharge from a desalination plant is typically 1.5-2.0 times more concentrated than the original seawater. Higher adsorption efficiencies can be expected if this discharge can be used for rare metal adsorption, as illustrated in Fig. 12.

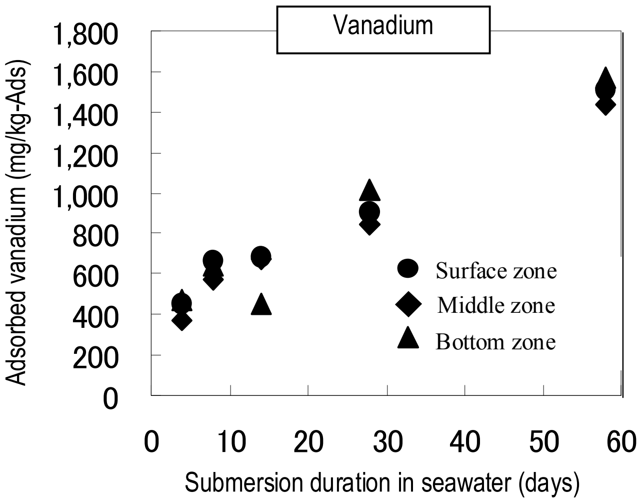


Fig. 9 Relationship between adsorbed vanadium and submersion duration in Iriomotejima tests.

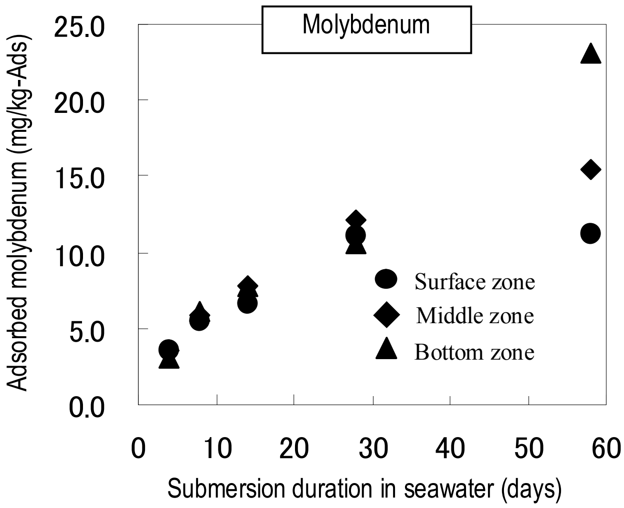


Fig. 10 Relationship between adsorbed molybdenum and submersion duration in Iriomotejima tests.

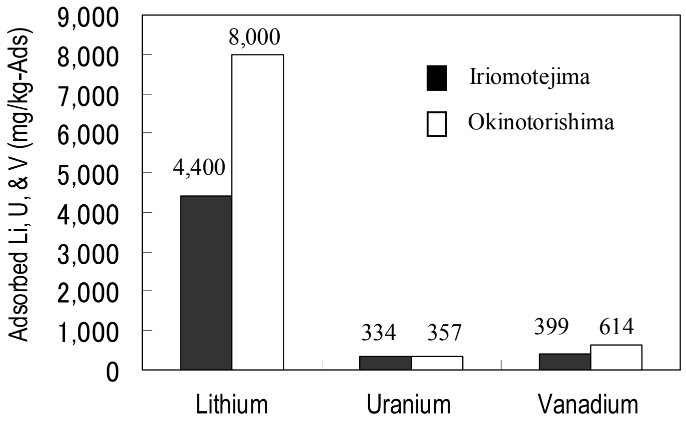


Fig. 11 Comparison of adsorbed lithium, uranium, and vanadium between Iriomotejima tests (seawater temp. of 22 - 26 °C) and Okinotorishima tests (seawater temp. of 27 – 29 °C).

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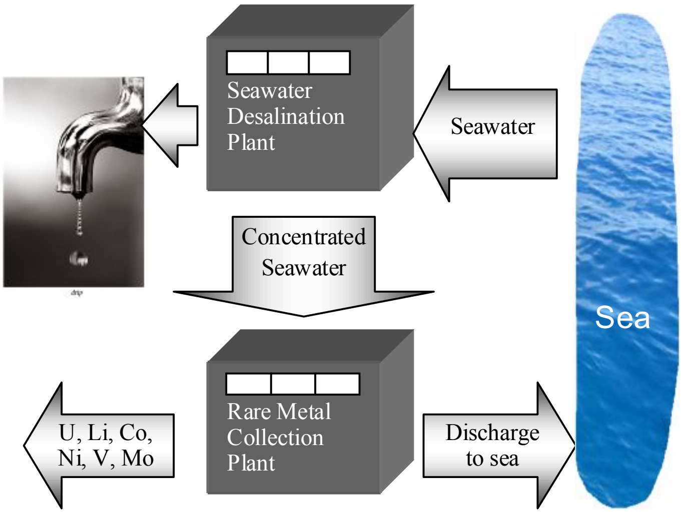

Fig. 12 Schematic drawing showing a rare metal adsorption plant using the highly concentrated seawater discharged from a desalination plant.