PERFORMANCE ANALYSIS OF BENCHMARK PLANT FOR SELECTIVE LITHIUM RECOVERY FROM SEAWATER

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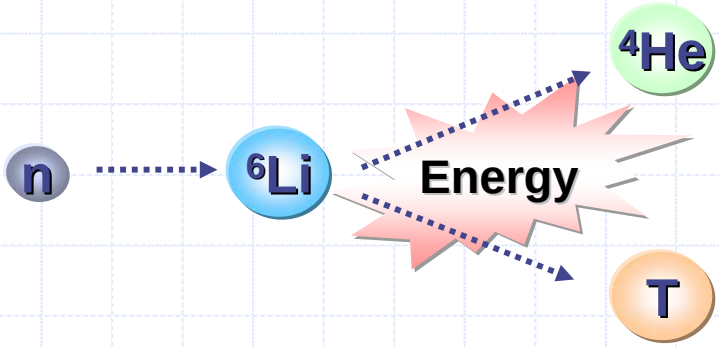
Application Fields of Lithium

Light alloy mixed with Al for aircraft

Electric vehicle without emission

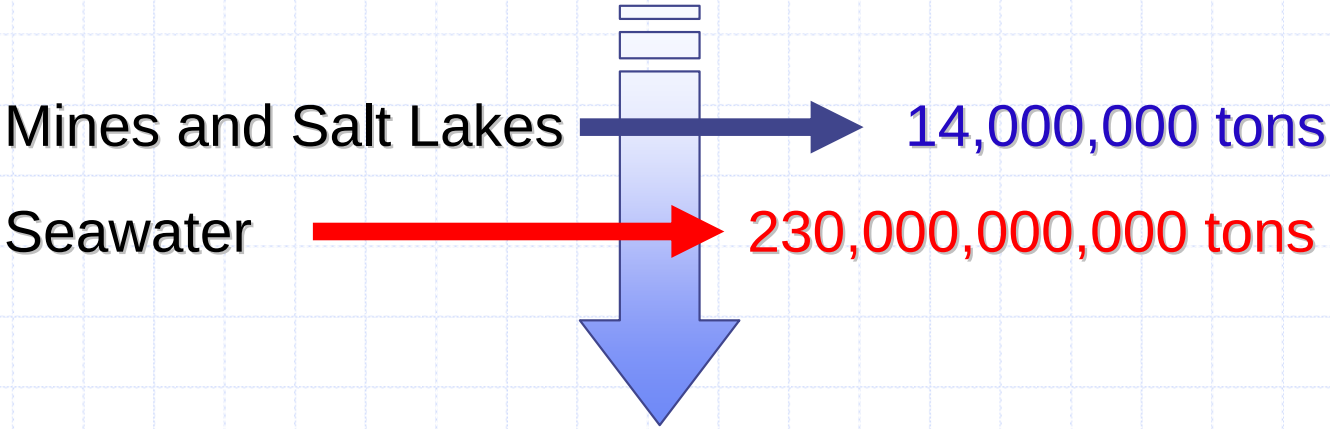


Next energy fuel for nuclear fusion

Rechargeable battery of mobile IT devices

Recovery of Lithium from Seawater

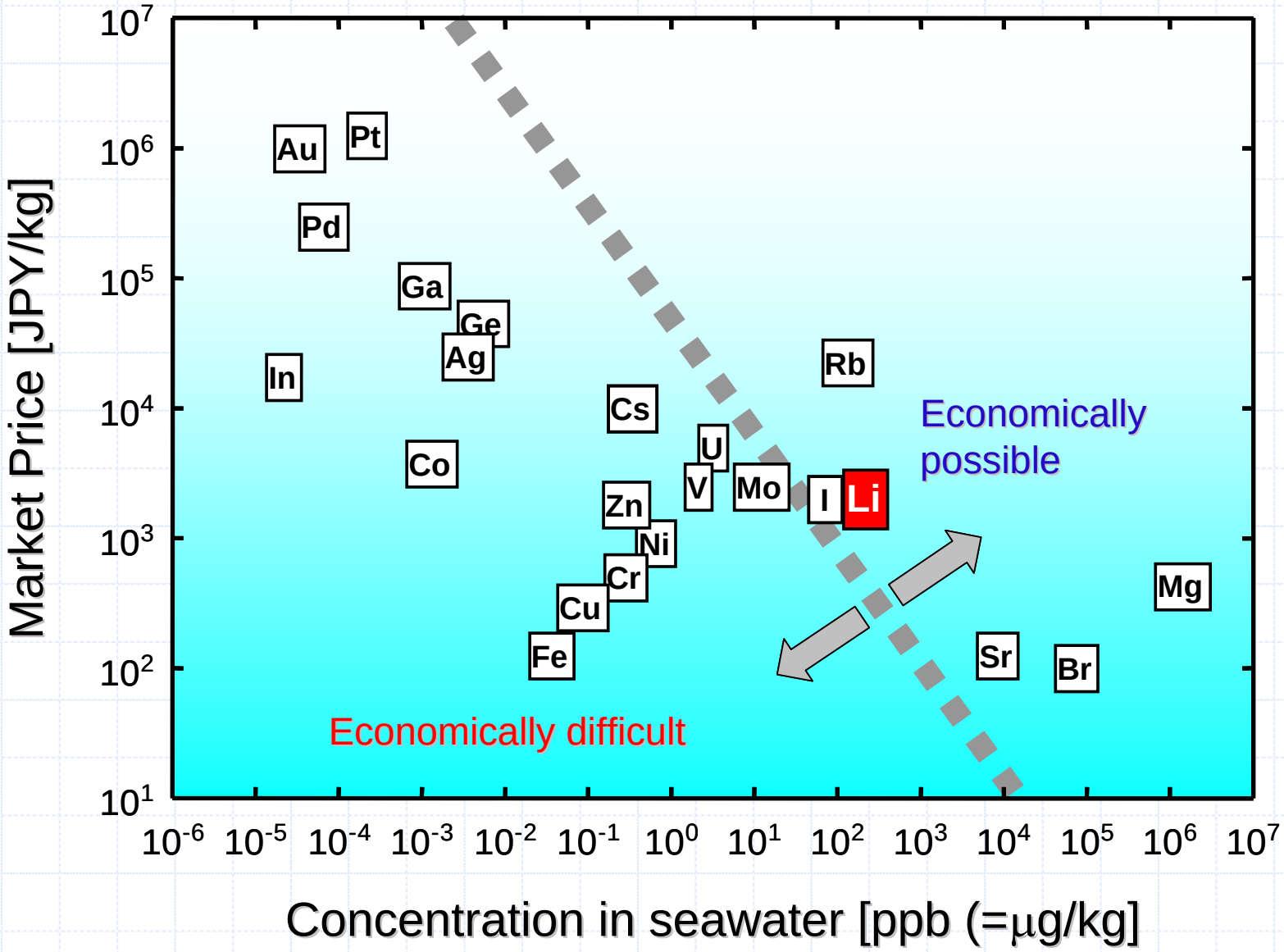
Since the concentration of lithium ion in seawater is quite low (0.1-0.2ppm) as well as that of sodium ion is extremely high (10,800ppm), selective recovery method of lithium ion should be developed.



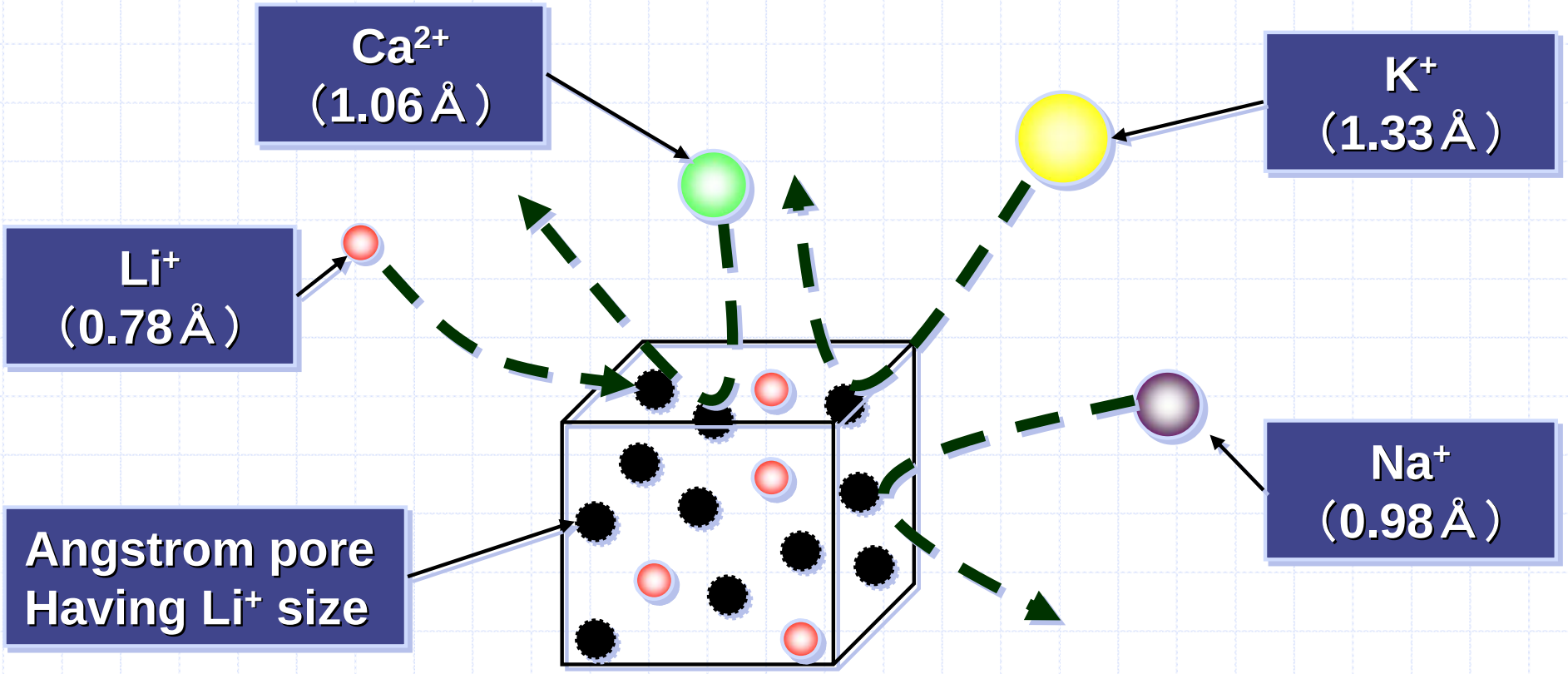
Ion exchange recovery method using MnO_2 type adsorbent having spinel structure (λ-MnO_2)

This adsorbent can be synthesized from lithium manganese oxide ($Li_xMn_yO_4$) using ion exchange of $Li^+$by H^+.

Economical Potential of Lithium Recovery from Seawater



Adsorbent Having High Selectivity for Lithium Ion
Spinel Type $Li_xMn_2O_4$



Ion Size Memorized Adsorbent

Synthesis of $Li_xMn_yO_4$ and λ-MnO_2

Mn_3O_4 + $LiOH \cdot H_2O$

Molar ratio Li : Mn = 1:2 or 1.5:2

Mixing & Grinding (15min)

Pre-sintering 425°C, 5h

Slow-cooling at room temp. for 1.5h

Mixing & Grinding (15min)

Main-sintering 500°C, 5h

Slow-cooling in electric oven for 12h

$Li_xMn_2O_4$

Acid treatment by 1M HCl

To keep the crystal structure, stirring in acid solution of molar ratio $[Li^+] : [H^+] = 1 : 40$ for overnight (Several times repeating)

λ-MnO_2

Ion-recognizable adsorbent of Li^+

pH Dependency of Lithium Adsorption

Batchwise Adsorption Experiment

Metal conc.: Li (5mM) + Na (5mM)

Adsorbent wt.: 0.02g

Aq. Soln.: 0.1M-NH_4OH-NH_4Cl buffer, 10mL

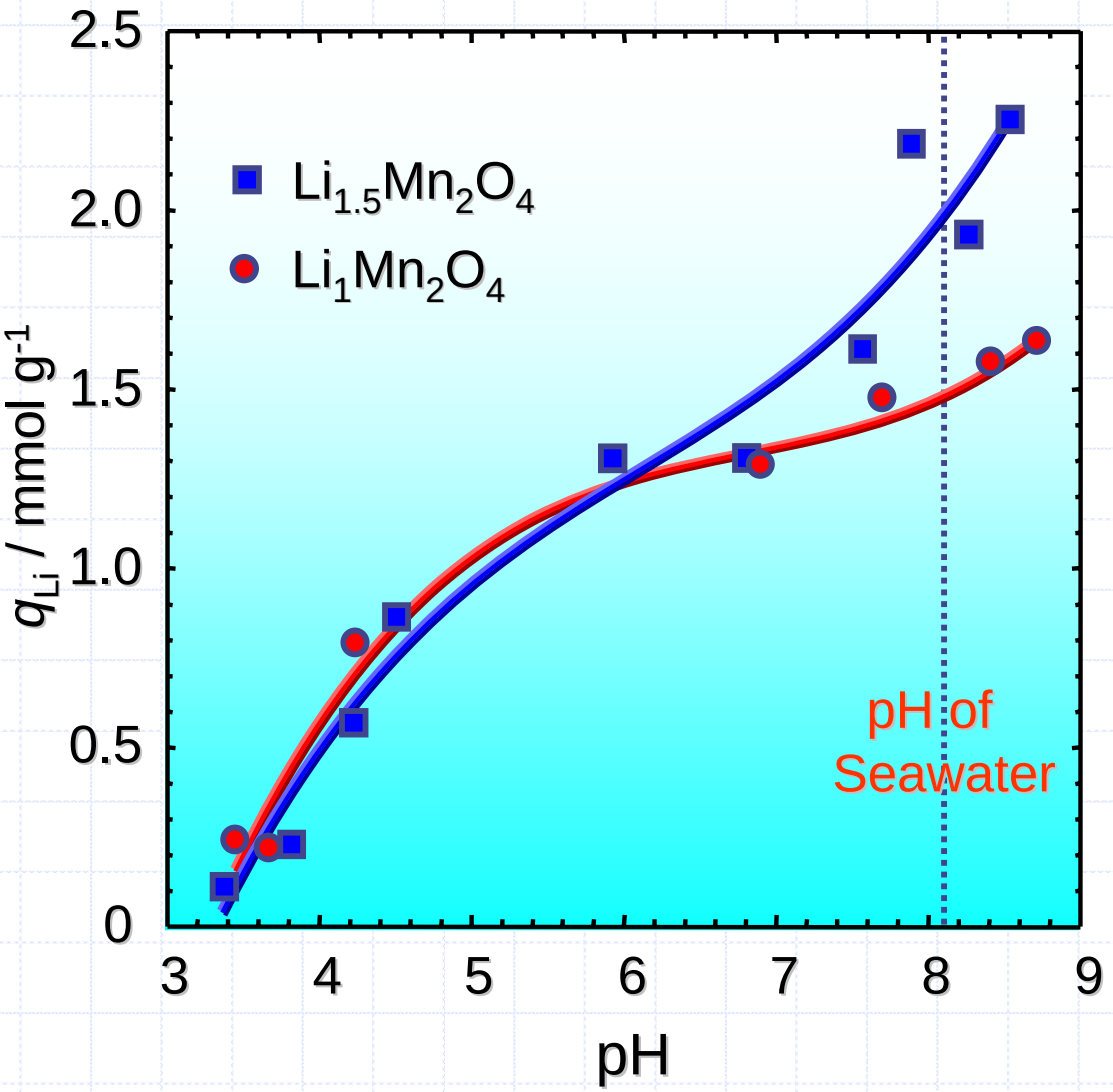
Initial pH: 6.0 - 9.0

Time: 5h

Temp.: 303K

Measurement: AAS

High adsorption ability of Li^+ at pH of seawater



Influence of Metal Ions on Lithium Adsorption

Batchwise Adsorption Experiment

Metal conc.: Li (5mM) + M (5mM~4M)

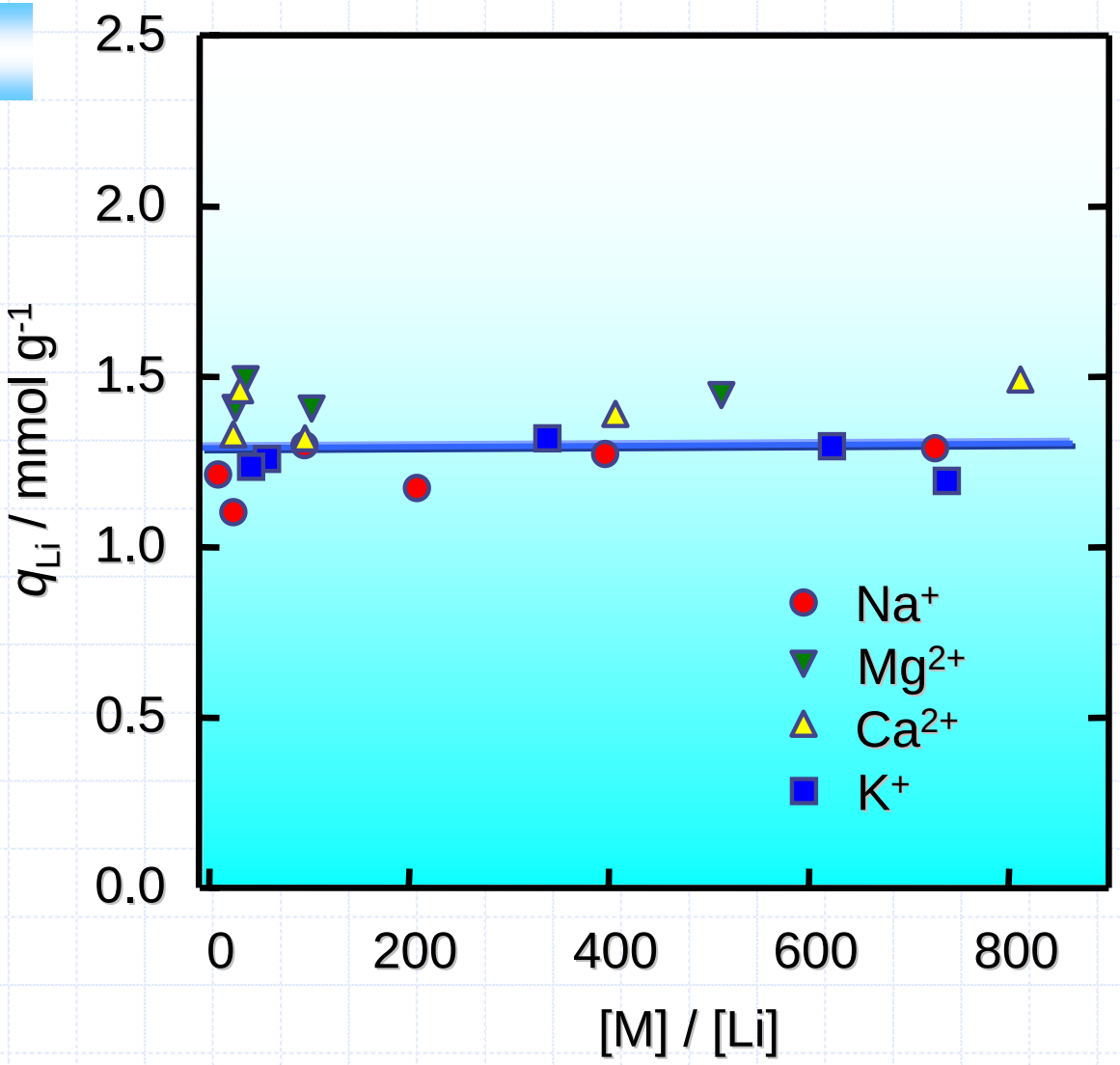
Adsorbent wt.: 0.02g
Aq. soln.: pH 8.1
(0.1M-NH_4OH-NH_4Cl buffer, 10mL)

Time; 5h

Temp.; 303K

Measurement: AAS

No Influence on lithium adsorption more than [M] / [Li] = 800



Granulation of Adsorbent for Column Packing

LiCl 0.25g + Chitin 0.05g
in N-methyl 2-pyrrolidinone 5ml

↓

+λ-MnO_2 5g under stirring

↓

+ 2-propanol

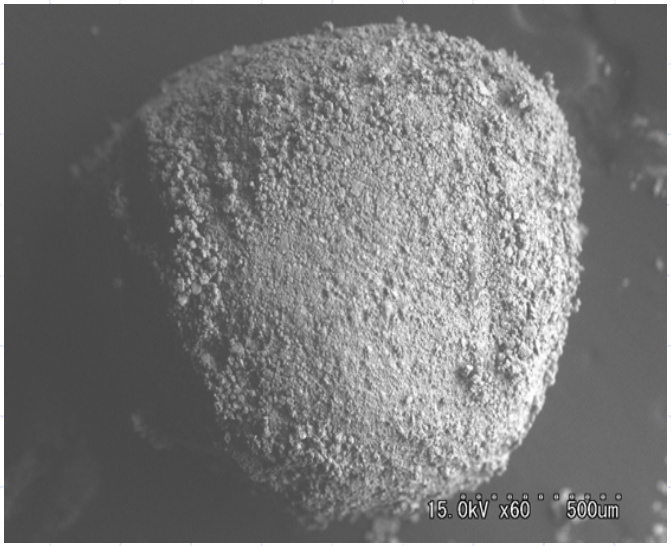
↓

Precipitation

vacuum filtration, rinse with deionized water, dry at 60°C

↓

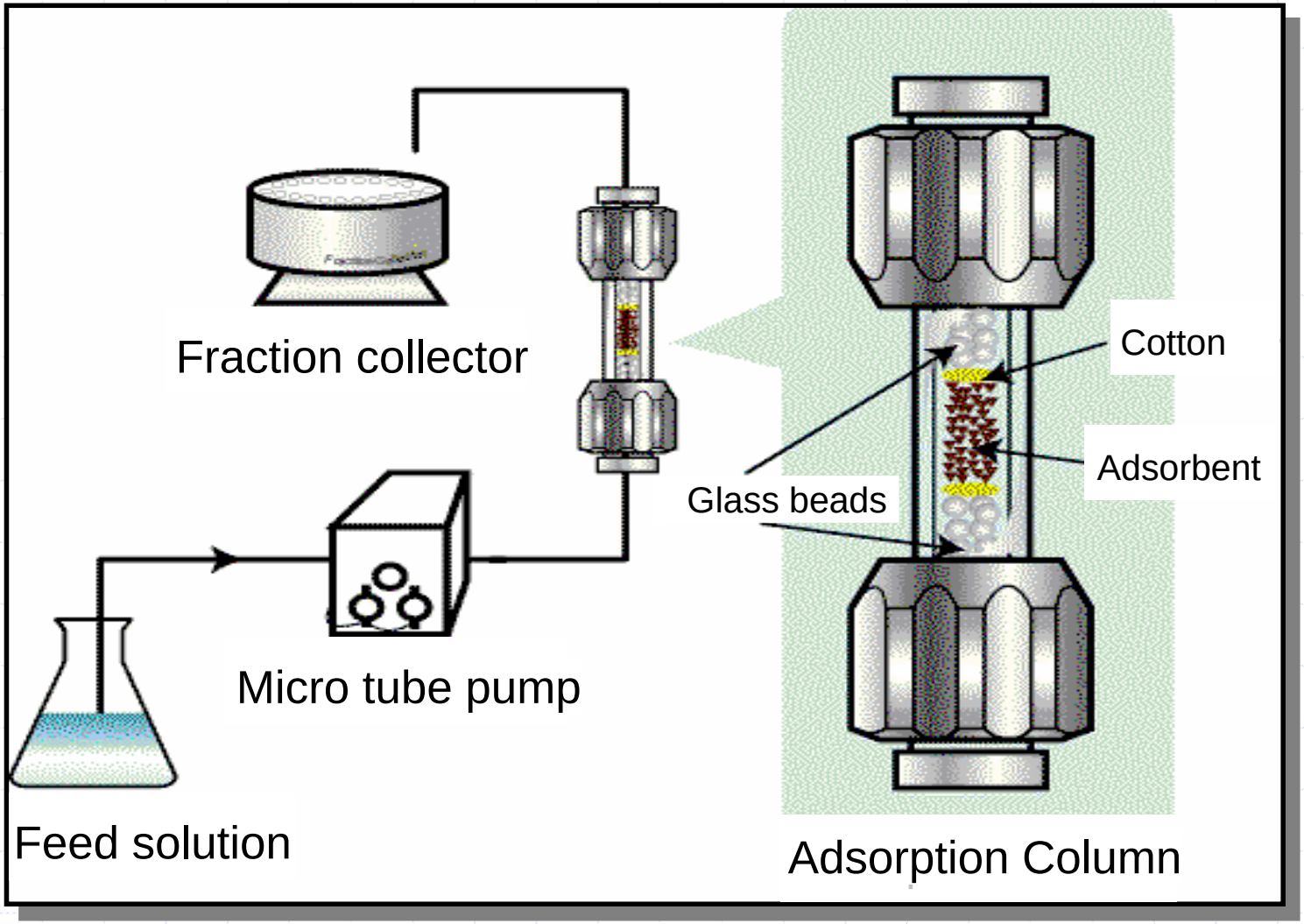
1wt.%Chitin-granulated adsorbent



SEM image of granulated adsorbent (x60)

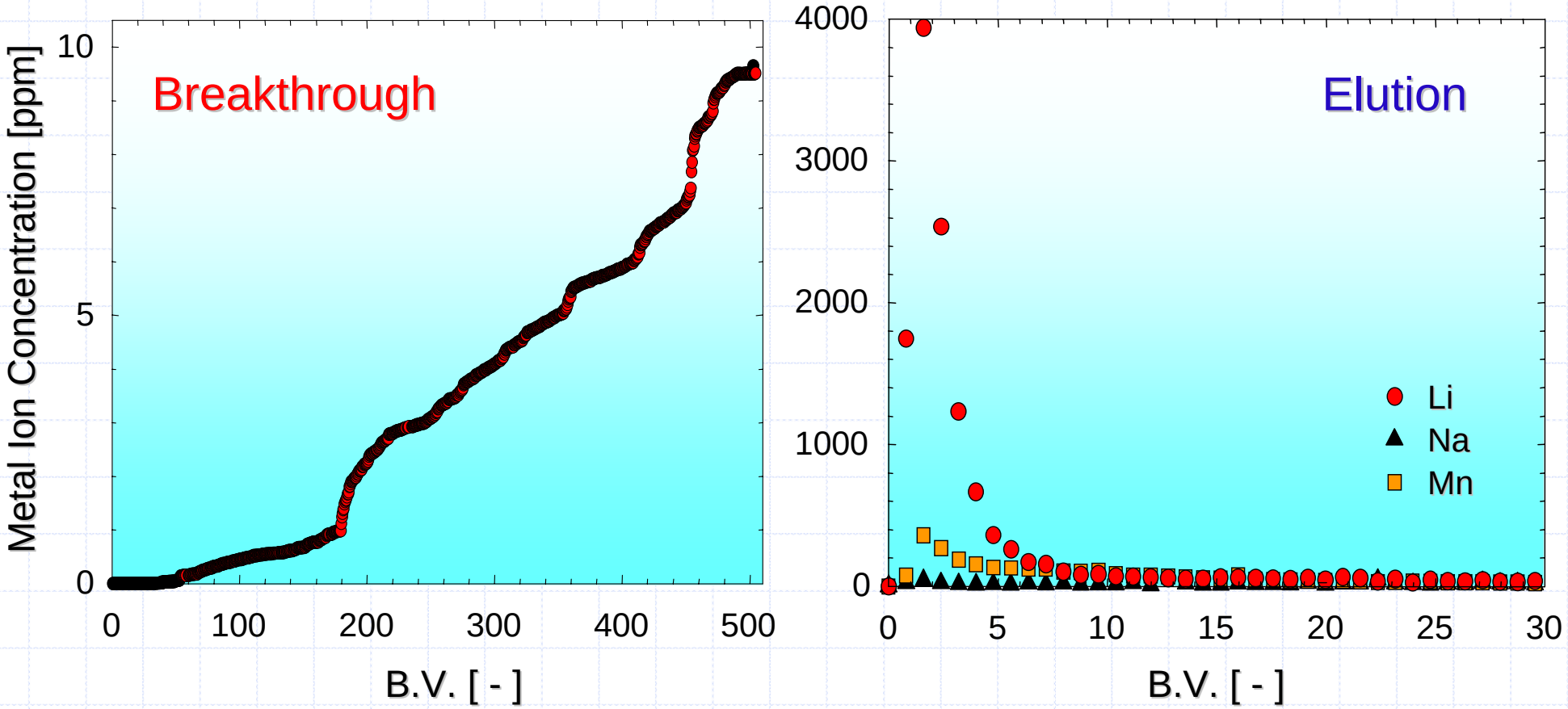
Photograph of granulated and powder adsorbents

Column Apparatus for Lab Scale Experiment



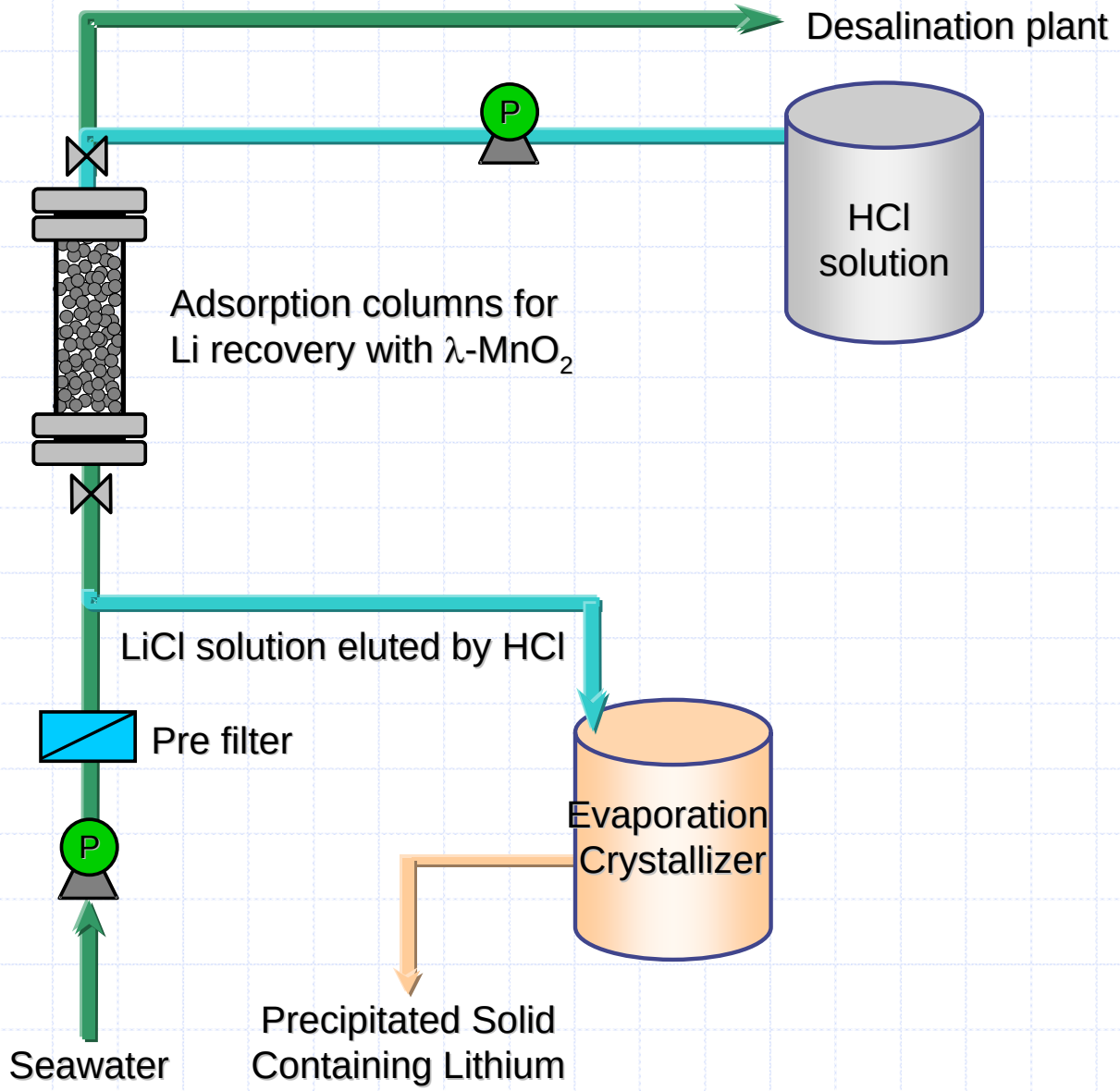
$$\text{Bed volume (B.V.)} = \frac{\text{Flow rate [cm}^3\text{/min]}}{\text{Adsorbent volume [cm}^3\text{]}} \times \text{Supplying time [min]}$$

Column Separation of Lithium from Seawater



Aq. Soln.: Artificial seawater (pH=8.1), Adsorbent wt.: 3.0g,
Flow rate: 0.33cm^3/min, Elutant: 1.0 mol/L HCl

Benchmark Plant of Lithium Recovery from Seawater in IOES



Performance of Equipment

Adsorbent weight: 60 kg

Adsorbent volume: 0.6 m^3

Eluting aq. soln.: 0.8 M HCl

Flow rate of seawater supply: 200 L/h

Benchmark Plant of Lithium Recovery from Seawater in IOES

Performance of Equipment

Adsorbent weight: 60kg x 2 columns

Adsorbent volume: 0.6m^3 x 2 columns

Eluting aq. soln.: 1-0.2M HCl

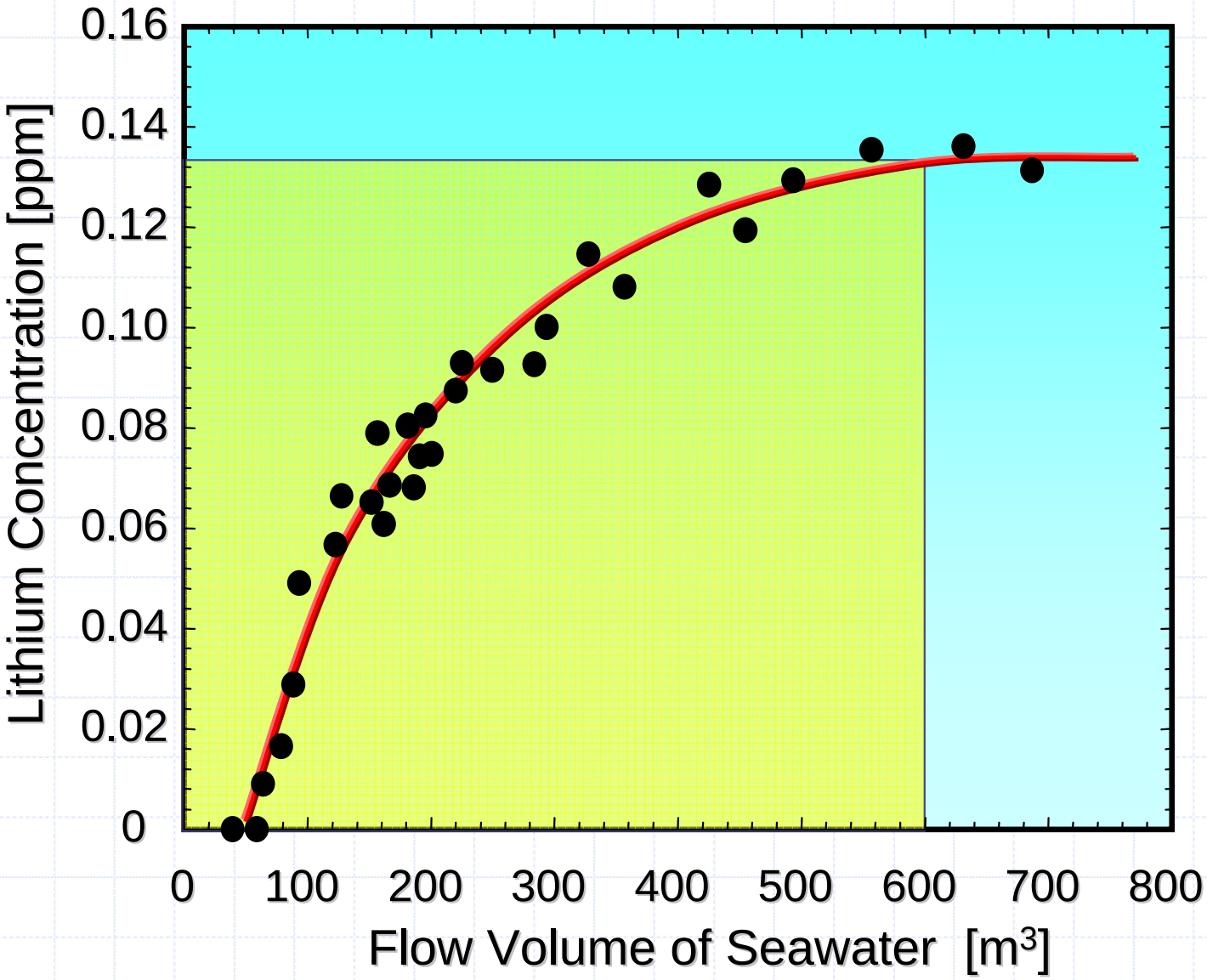
Flow rate of seawater supply: 200L/h

Benchmark Plant of Lithium Recovery from Seawater in IOES

Adsorption Column

Evaporation Crystallizer

Breakthrough Curve of Lithium Using Benchmark Plant for 150 Days Operation (2004/12/21～2005/7/13)



Evaporated Salt Obtained from 150 Days Operation

Dried precipitate 791g

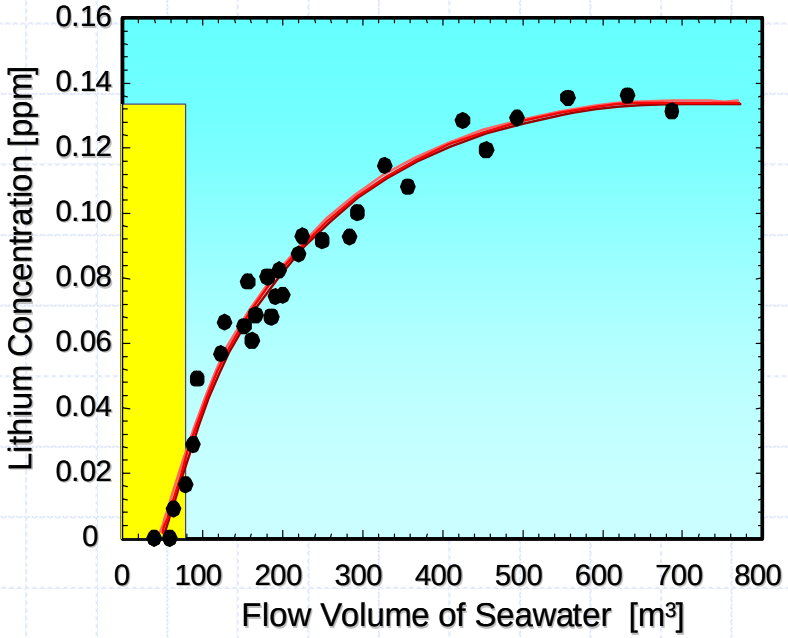
The Components of the Precipitate Salt Obtained from 150 Days Operation

Element	Content [wt%]	Concentration ratio [%]	Content in seawater [wt%]
LiCl	33.3	11,000	0.003
NaCl	20.4	0.26	78.1
KCl	3.3	0.94	3.5
$MgCl_2$	8.2	0.57	14.3
$CaCl_2$	13.4	4.11	3.26
$MnCl_2$	19.4	–	n.q.
$SrCl_2$	2.0	50.0	0.04

Performance of Lithium Recovery from Seawater

1 cycle of adsorption stage would be required to 10 % of breakthrough of Li^+ concentration:

Li^+ Adsorption stage : 80 m^3 (400 h)
washing stage : 1 m^3 (5 h)
Elution stage : 0.6 m^3 (3 h)
Adsorbent washing stage : 1 m^3 (5 h)



1 cycle of full operation = 413 h
(18 days)
20 cycles of full operation / year
5 kg of LiCl

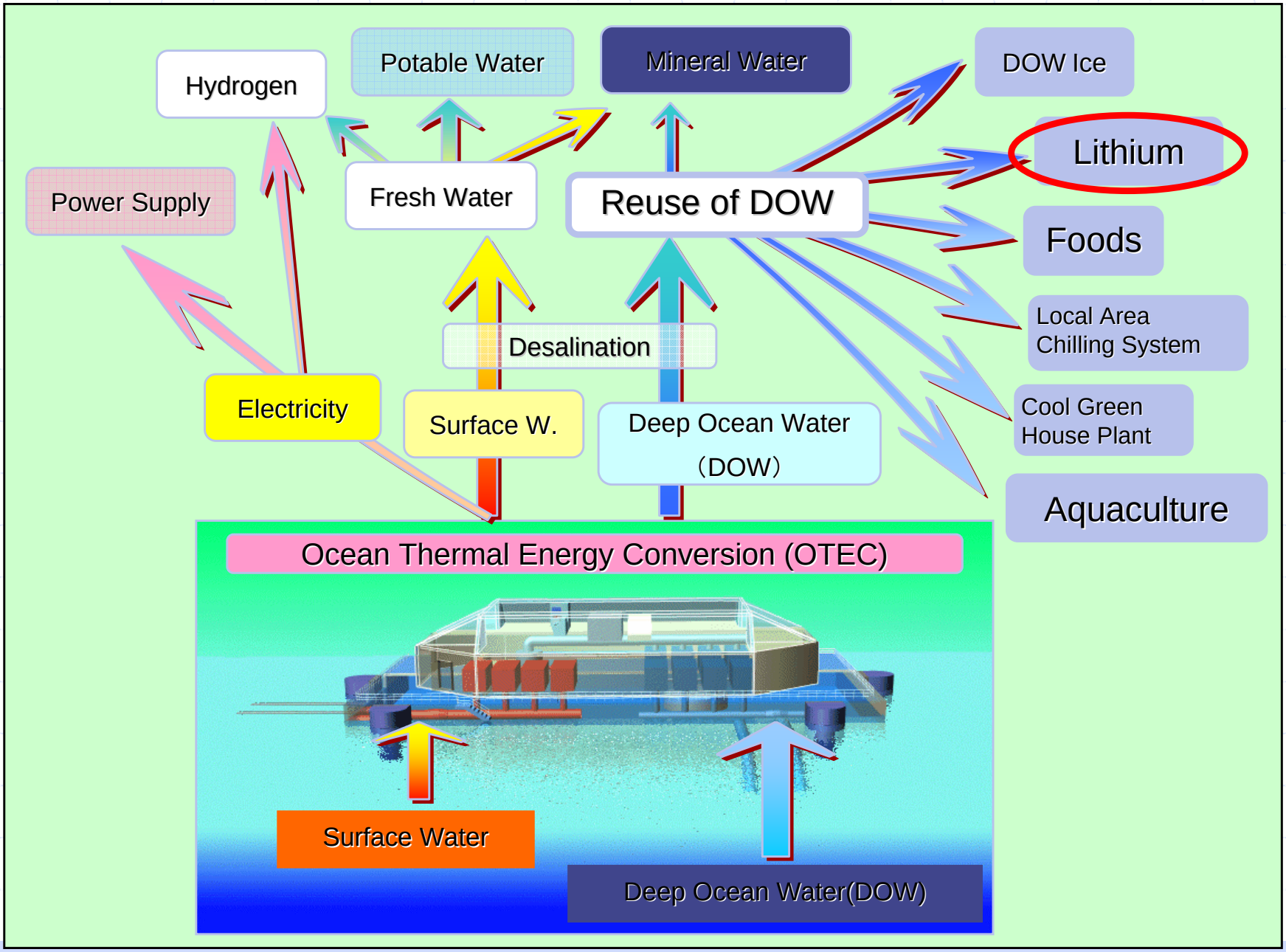
Economical Analysis of Lithium Recovery

Analysis software: Powersim

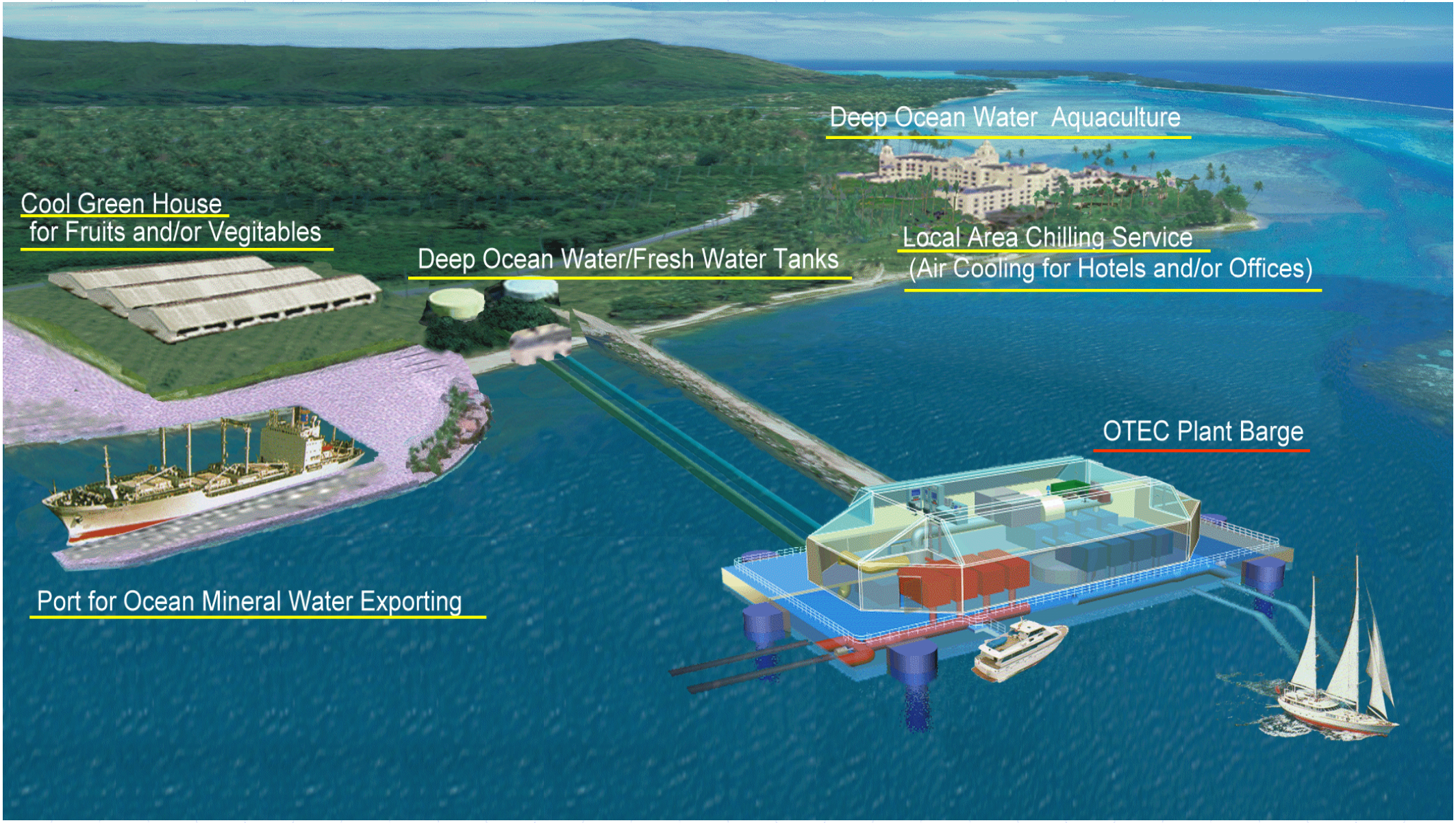
	Unit	Present case	Proposed case
Adsorbed Li	g/year	450	5,300
Energy consumed	kWh	165,400	34,100
Water consumed	m^3	13,300	34,100
Energy requirements	kWh/g-Li	385	80

Energy requirement can be reduced to 1/5.

Multiple Utilization of Ocean Energy and Resources



Multiple Utilization of Ocean Energy and Resources




T−09
T−12