Integrated System for Complete Usage of Components in Sea Water

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Very severe troubles of scale formation might be expected when the recovery of water from sea water increases. The main constituents of the scale are $CaCO_3$, $Mg(OH)_2$ and $CaSO_4$, all of which are salts of alkaline earth metals. Therefore, if a key technology will be developed by which the main constituents of the scale, all alkaline earth metal can be removed and/or separated from sea water, the recovery of desalted water from raw sea water by high pressure reverse osmosis (HPRO) can be increased up to 75-80%, the solubility limit of the remaining scale components. Then, it will be possible to make use of all valuable materials existing in sea water, by an integral system which combines conventional recovery technologies with a set of the proposed technologies such as HPRO, alkaline earth metal ions removal process, inorganic ion-exchangers for recovery of trace elements and so on.

1. Introduction

Sea water contains almost all elements from hydrogen far down to uranium and is composed of 96.7% water and 3.3% dissolved salts. Seven elements (Na, Mg, Ca, K, Cl, S, and Br), account for 93.5% of the dissolved salts.(1) Sea water desalination for the recovery of water, its major constituent, is widely practiced particularly in the Middle East. During desalination, the concentration of the dissolved salts increases resulting into the deposition of scale (e.g. calcium sulfate).(5) Therefore, water recovery is restricted so 35-40% of the solubility limit of the scale components.(8-10) On the other hand, among the many dissolved salts, only the following 4 components are extracted for commercial use: table salt, and its by-products KCl, magnesium and bromide salts. Extraction of U, as fuel for fission reactors and deuterium for fusion reactors, was tried up to a semi-commercial scale, but failed from the economical point of view.(6) The only main reason why other components cannot be used is due to their very low concentration and huge amount of seawater to be handled.

In order to exploit economically the unused components contained in sea water, we should develop new technologies which can be applied to sea water and/or to effluent streams from operating sea water desalination plants. In 1995, we proposed the preliminary concept of the Integrated System for the Complete Usage of Components in Sea Water (ISCUCSW)(7), high pressure reverse osmosis which is one of the proposed new technologies, is now under development aiming as 60% recovery of desalted water from seawater.

This paper presents a scheme for the development of new technologies in order to make complete use of the components in seawater.

2 Concept of the Integrated System for the Complete Usage of Components in Sea Water(ISCUCSW)

In order to maximally exploit the components in the taken in with the raw sea water as much as possible, scale components such as $CaCO_3$, $CaSO_4$, $MgSO_4$, $Mg(OH)_2$, etc. should be removed up stream of the system. If some amount of the scale components could be removed, the recovery ratio of desalted water could be increased up to possibly 75-80%, which is twice the present ratio of 35-40%, because the solubility limit where the components start to deposit increases. To make this feasibility, high pressure reverse osmosis(HPRO) should be developed, accompanied by the development of RO membranes which can withstand high pressures preferably up to 20Mpa.

The concentration of the dissolved salts in the concentrated brine to increases 4-5 times. This means that the concentration of NaCl in the brine is almost now the same as in the electrodialysed brine, 20%.(11) Furthermore, it will be economically feasible to obtain the mono-valence ions such as Na, K, Li with only one additional of the already concentrated RO brine by applying electrodialysis using a mono-valence ion permselective membrane. The concentration of multi-valence ions in the retentate of the electrodialyzer will be increased to 4-5 times of that in the sea water. If the concentrated multi-valence ions could be recovered from this stream, we could make complete use of all the components present in sea water.

Based on the above approach, we will now propose the Integrated System for the Complete Usage of Components in Sea Water (ISCUCSW) as shown in **Fig. 1**. This system will comprise at least the following 3 sub-systems,

Sub-system 1:Scale components removal process
Sub-system 2:Seawater concentration.desalination process
Sub-system 3:Exploitation process for the recovery of all components

3. Sub-system 1 Scale Components Removal Process

3.1 Suppression of scale deposition

The typical concentrations of Ca and Mg salts in seawater are listed in **Table 1**. With the advancing concentration of the sea water, the concentrations of $CaCO_3$, $CaSO_4$, and $MgSO_4$ etc. will increase and start to precipitate as scale when the concentration crosses the respective solubility curves. The experimental data of the concentration change of salts during the concentration at 40 °C by Ishibashi & Murakami(2) show us that $CaCO_3$ starts to precipitate at 2.2 times concentation,$CaSO_4$ at 5 times and $MgSO_4$ at 6.6 times. Table 1 shows the concentration of the dissolved Ca and Mg salts in the concentrated brines at 4 and 5 times concentration.

If the concentration polarization as the surface of a HPRO membrane is 1.2, the concentration of Mg and Ca increases 6 times at the recovery ratio of desalted water of 5 and scale formation of $CaCO_3$ and Ca SO_4 can be expected. CO_3^- can be removed from the raw seawater by the adjustment of pH. Therefore, the only thing we need to do is to reduce the concentration of $CaSO_4$ in the raw brine to 0.45/6=0.076wt%. This could be achieved by one of the following methods.

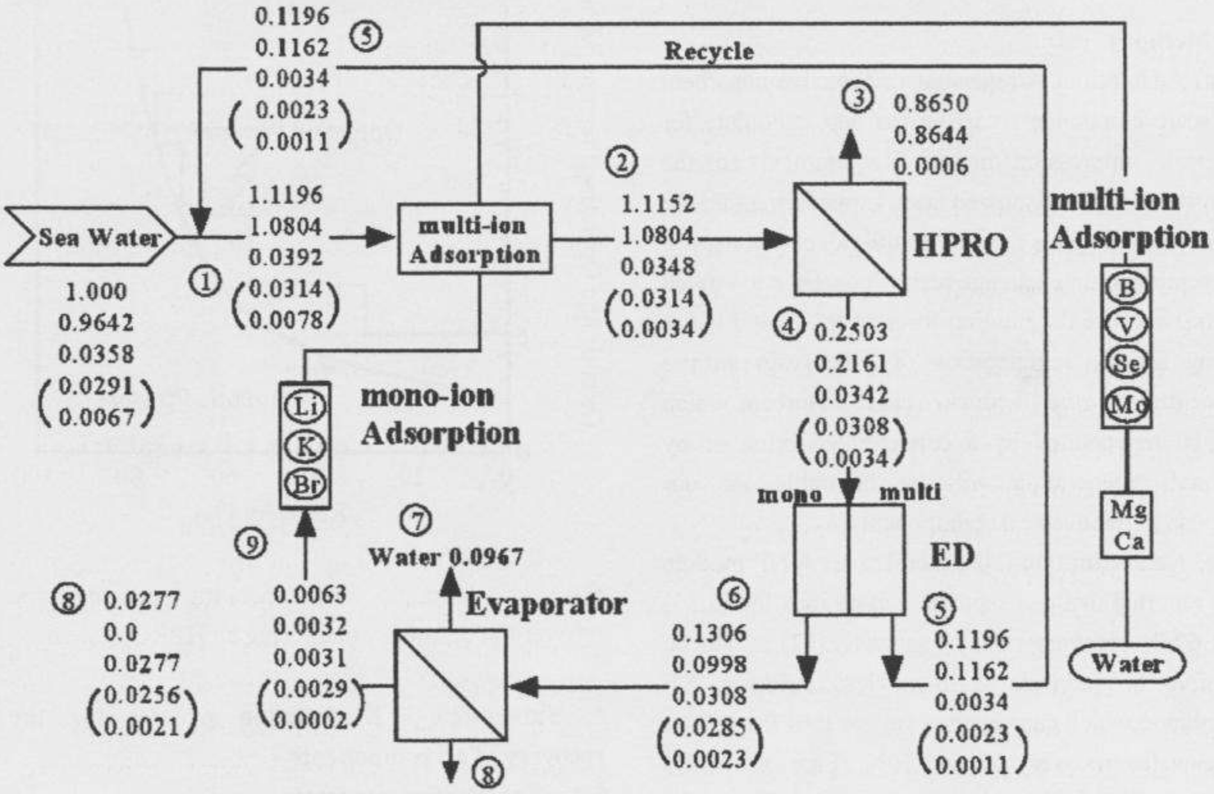

Fig. 1 The weight and composition of each process stream in the case of 80% recovery of desalted water, using an HPRO system (based on 1 kg of raw sea water).

Total weight (kg)
water weight (kg)
mono-and multivalent ion (wt%)
(monovalent ion (wt%))
(multivalent ion (wt%))

Table 1 Concentration of Mg and Ca salts in raw (1) and concentrated seawater (wt%)

Components	$MgSO_4$	$MgCl_2$	$MgBr_2$	$CaCO_3$	$CaSO_4$
Raw seawater	.193	.327	.010	.011	.132
4 times concen.	.783	.920	.039	.001	.496
5 times concen.	.960	1.588	.047	.001	.454

Table 2 Total and required energies at each desalted water recovery stage

Water recovery (%)	30	55	70	75	80
Required energy (kWh/m^3)	1.39	1.64	1.88	1.96	2.17
Total energy (kWh/m^3)	1.39	1.73	2.15	2.40	2.68

3.2 Methods

(a) Adsorption: A regenerative selective adsorbent for scale components will be the best candidate for the scale suppression method. Requirements for the adsorbent will be discussed later. Considering that the scale components are multi-valent ions, a conventional ion exchange resin contain a too much ligand, because the binding force of the ligand is too strong for the regeneration of the resin with a concentrated brine. A much weaker adsorbent which can be regenerated by a concentrated brine or by thermal regeneration will be favorable for our purpose to remove scale components.

(b) Nano-filtration (NF) membrane: A NF module was reported that can separate sulfate ions for 93.3% at a 60 % recovery ratio of seawater.(12) It will be possible to fabricate a much less stringent NF membrane which can separate sulfate ions for 80% at a seawater recovery above 70%. First at 73.3% seawater recovery, the concentration of $CaSO_4$ in the rejected stream starts to exceed the solubility limit and scale deposition can occur on the surface of the membrane. Considering that only a 60% recovery ratio of desalted water from seawater is accomplished by HPRO up to now, as far as the salt production concern, NF module does not make.

4. Sub-system-2 Seawater Concentration and/or desalination process

4.1 Minimum work and osmotic pressure

Fig 2 shows the relationship between osmotic pressure and recovery ratio of desalted water from seawater. If the operating pressure increases as shown in Fig.2, the total and required energies at each desalted water recovery stage as calculated are presented in **Table 2**.

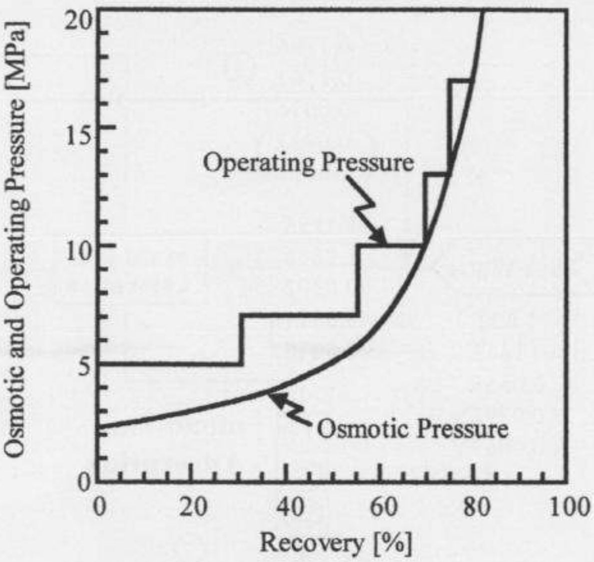

Fig. 2 Osmotic and operating pressure vs. recovery of desalted water, using an HPRO system.

5. Sub-system-3 Exploitation process for the recovery of all components

5.1 Exploitation processes

Electrodialysis may work to separate and further concentrate mono-valent ions. Crystallization process may work to remove water and precipitate NaCl and residual multi-valent ions as crystals. Inorganic adsorbents having a very special affinity for a specific ion can work to separate it from concentrated aqueous solution of mixture of mono- and multi-valent ions.

5.2 Material balance

Material balance was calculated for 1 kg of raw seawater at 80% recovery of desalted water, with the following 3 assumptions;

1. As a basis for the calculation, concentrations of each mono-valence ion are assumed as given in **Table 3.**

2. Main constituents of multi-valence ions are separated by a multi-valence ion adsorption column and their concentrations are reduced to 0.18%

Table 3 Monovalent ions in the raw seawater(wt%)

Components	Concentration
Li	$1.66x10^{-5}$
Na	1.02
K	.0371
Cl	1.85
Br	$6.34x10^{-3}$
Total	2.91

3. Electrodialysis is applied
   1. to separate multi-valence ions into the diluted stream 5 in Fig. 1,
   2. to reduce the concentration of NaCl in the diluted stream 5 to a value below in raw sea water,
   3. to concentrate NaCl in the concentration stream up to 20%.

For the electrodialyzer **Table 4** shows the concentration of mono-valent and multi-valent ions in the feed and in the two streams of either the concentrated of mono-valent ions or concentrated multi-valent ions. The concentrations of NaCl and KCl in the mono-valence ions concentrated stream are 20.0 wt% and 0.524 wt%, respectively. The mono-valent ions concentrated brine is sent to the evaporation process and concentrated until the concentration of KCl reaches 11.5 wt%; its solubility limit.(6) The compositions of the effluent from the crystallizer are shown in **Table 5.**

Table 4 Concentration of mono- and multi-valent ions at electrodialyzer (wt%)

	Mono-Valent ion	Multi-Valent ion
(in)	12.30	1.35
(out) Concentrated side of Monovalent ion	21.82	1.76
Multivalent ion	1.92	0.91

Table 5 Composition of the effluent stream from evaporator

Components	Concentration (wt%)
Water	52.1
NaCl	8.5
KCl	11.5
Others	27.9

5.3 Concentrations

This system makes very high recovery of desalted water possible with HPRO and a crystallization process as shown in Fig.1. Therefore, at the entrance of the mono-valent and multi-valent ion adsorption columns, the concentrations in the adsorption columns are high, and also recovery or exploitation of each ion can be carried out. The total amount of components entering the columns are calculated as 6.6 g /1 kg of raw seawater taken in. Hence, each ion is concentrated by 1000/6.6 times, and its concentration is shown in **Table 6**, together with its concentration in seawater.

Table 6 Composition of mono- and multivalent ions in the solutions before entering into the two down adsorption columns (wt%)(1)

Components	Raw seawater	Concentrated Seawater
(Monovalent)		
Li	$1.75x10^{-5}$	.027
K	.037	6.1
Br	$6.3x10^{-3}$	1.0
(Multivalent)		
B	$4.5x10^{-3}$	0.74
V	$2.0x10^{-6}$	$3.2x10^{-4}$
Se	$3.9x10^{-7}$	$6.4x10^{-5}$
Mo	$9.8x10^{-6}$	$1.5x10^{-3}$

6. Approach

To order to make the proposed ISCUCSW system feasible, research and/or development on the following themes should be conducted;

1. Development of an adsorbent for scale forming ions that can be regenerated by concentrated brine or thermal treatment.

2. Development of a reverse osmosis membrane which works at a very high pressure of 20Mpa.
3. Development of highly selective adsorbents for both mono-or multi-valent ions present in a NaCl saturated brine, and a methods for their regeneration.

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