

Behavior of Some Trace Elements During the Concentration of Sea Water by Electrodialysis with Ion-Exchange Membranes

K. Hiroi

Central Research Institute
Japan Monopoly Corporation
Yokohama, Japan

ABSTRACT

The method of manufacturing salt in Japan was completely changed from the traditional salt field method to the ion-exchange membrane method by the end of 1971. The manufacture of brine at present is entirely by electrodialysis utilizing ion-exchange membranes.

For the purpose of investigating possible relationships between raw sea water polluted by toxic heavy metal ions and the quality of the salt produced from it, a study was conducted on the extent of permeation of such metal ions from the diluting compartment through the ion-exchange membranes into the concentrating compartment during sea water concentration by electrodialysis.

An attempt was also made to clarify the distribution of these metal ions contained in the brine to such deposits as scale, salt, and bittern during salt crystallization by vacuum evaporation.

INTRODUCTION

The principle of concentration of sea water by electrodialysis with ion-exchange membranes is shown in Figure 1. The apparatus consists of a series of alternate concentrating and diluting compartments divided by alternate cation- and anion-exchange membranes. There are two electrodes at each end of the apparatus.

When sea water is introduced to the diluting compartment and direct current applied between the electrodes, the cations and anions move through the cation- and anion-exchange membranes toward the cathode and anode, respectively. Brine can then be obtained from the concentrating compartments.

Based on this principle, it was possible to switch the manufacture of salt in Japan from the traditional salt field method to the ion-exchange membrane method. All salt manufacturing plants in Japan now produce brine by means of electrodialysis with ion-exchange membranes.

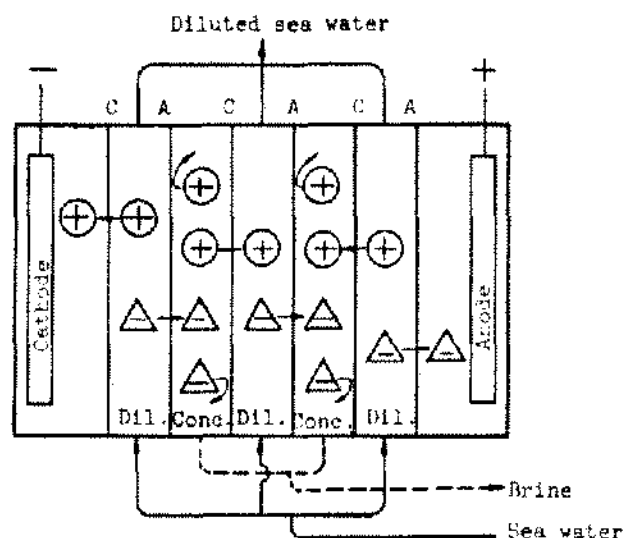


Figure 1. Principle of concentration of sea water by electrodialysis. C = cation exchange membrane, A = Anion exchange membrane.

However, in order to produce solid common salt, concentration of brine by an evaporator is required, as in the salt field method.

As the study of the relationships between polluted raw sea water and the quality of the common salt produced is an important task, the author has carried out investigation of the behavior of concentration of such toxic metals as cadmium, lead, mercury and chromium during concentration of sea water by the ion-exchange membrane method and also the crystallization of salt by the evaporation method.

ANALYSIS OF TRACE HEAVY METAL IONS

As there are only slight traces of heavy metal ions in raw sea water, brine, salt, scale and bittern, they are,

following extraction with an organic solvent or co-precipitation with ferric hydroxide after concentration, analyzed by means of an atomic-absorption spectrophotometer.

Cadmium and lead ions are extracted with dithizone-carbon tetrachloride solution of pH 8 (Hiroi and Tahara, 1970, p. 22). Mercury ions are extracted with dithizone-carbon tetrachloride solution of pH 3. The solvent layer separated from the aqueous layer is then extracted with diluted acid and used for analysis.

Chromic ions are treated with ferric ions and ammonium hydroxide to precipitate as chromic hydroxide absorbed in ferric hydroxide. After chromate ions are reduced by ferrous ions, residual ferrous ions are oxidized to ferric ions and the solution similarly treated with ammonium hydroxide. The precipitant obtained is dissolved with diluted acid and the solution used for analysis (Hiroi, 1972, p. B139). In the atomic-absorption spectrophotometer method, acetylene-air flame is used for cadmium, lead and chromium, while the no-flame method (Koerker, 1970) is used for mercury.

BEHAVIOR OF TRACE HEAVY METAL IONS DURING ELECTRODIALYSIS

Experiment

The two types of experimental apparatus shown in Figure 2 (Type A) and Figure 3 (Type B) were used in the experiment. The Type A apparatus was only used to study the concentration behavior, while Type B was used to study the respective concentration behaviors of anions and cations.

Type A consists of 2 concentrating and 3 diluting compartments and 2 electrode compartments. Membrane spacing is 5 mm in the concentrating compartment and 10 mm in the diluting compartment, while the effective mem-

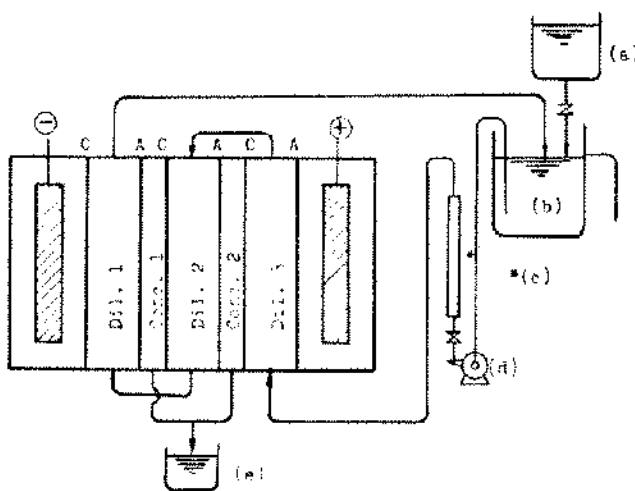


Figure 2. Experimental apparatus for electrodialysis (A). (a) Sea water tank, (b) Reservoir, (c) Flow meter, (d) Circulating pump, (e) Brine tank.

brane area is $3 \times 3 = 9 \text{ cm}^2$. The ion-exchange membranes are inserted between rubber gaskets and kept firmly in place with fastening frames. The anode is made of silver and the cathode of silver-silver chloride. In the Type B apparatus, the diluting compartment Dil. 2, separated from the other diluting compartments, is fed with sea water and Dil. 1 and 3 with 0.5N sodium chloride solution. Therefore, cations in sea water and chloride ions in the sodium chloride solution can permeate to Conc. 1 compartment, and anions in sea water and sodium ions in the sodium chloride solution to Conc. 2 compartment.

The apparatus consists of non-metallic materials; dialyser, flow meter, piping and valve are made of plastics and glass, and a magnet induction pump which has plastic-covered wings is used to circulate the solution.

Ion-exchange membranes used for this study have the characteristic of low permeability concerning bivalent ions.

Cadmium ion

Cadmium content in sea water is about 0.024 to 1.80 $\mu\text{g/l}$. The artificial sea water used for the experiment contains 60 $\mu\text{g/l}$ Cd as chloride. Experiments were carried out under conditions where current density was 1.0, 2.5, 4.0 A/dm^2 , and temperature 25, 35°C, and the value of permselectivity coefficient of cadmium ions, $T_{\text{Na}}^{\text{Cd}}$, were calculated by the following equation:

$$T_{\text{Na}}^{\text{Cd}} = \frac{[\text{Cd}]_{\text{brine}}}{[\text{Na}]_{\text{brine}}} \bigg/ \frac{[\text{Cd}]_{\text{sea water}}}{[\text{Na}]_{\text{sea water}}}$$

The value of $T_{\text{Na}}^{\text{Cd}}$ are shown in Figure 4 (Hiroi and Kaneko, 1971, p. 50).

The result shows that the permeability of cadmium ions is increased with current density and temperature, still is less than that of sodium ions. The permselectivity coefficient of cadmium ions at a salt-making factory is 0.27 and that of magnesium ions 0.28, so the permeability of cadmium ions is similar to that of magnesium ions. The ion-exchange membranes of low permeability to bivalent ions do not pass cadmium ions or magnesium ions, but non-selective membranes permit the permeation of cadmium ions more easily than sodium ions.

Lead ions

The lead content in sea water ranges over 1.0 to 11.0 $\mu\text{g/l}$. The experiment on lead ions with the Type A apparatus is carried out in the same way as that for cadmium ions, using the artificial sea water containing 120 μg of lead per liter. The permselectivity coefficient of lead ions calculated from these results is shown in Figure 5.

The permeability of lead ions is larger than that of sodium ions, as shown in Figure 5, even when membranes with low permeability to bivalent ions were used. The value of permselectivity of magnesium ions concerning

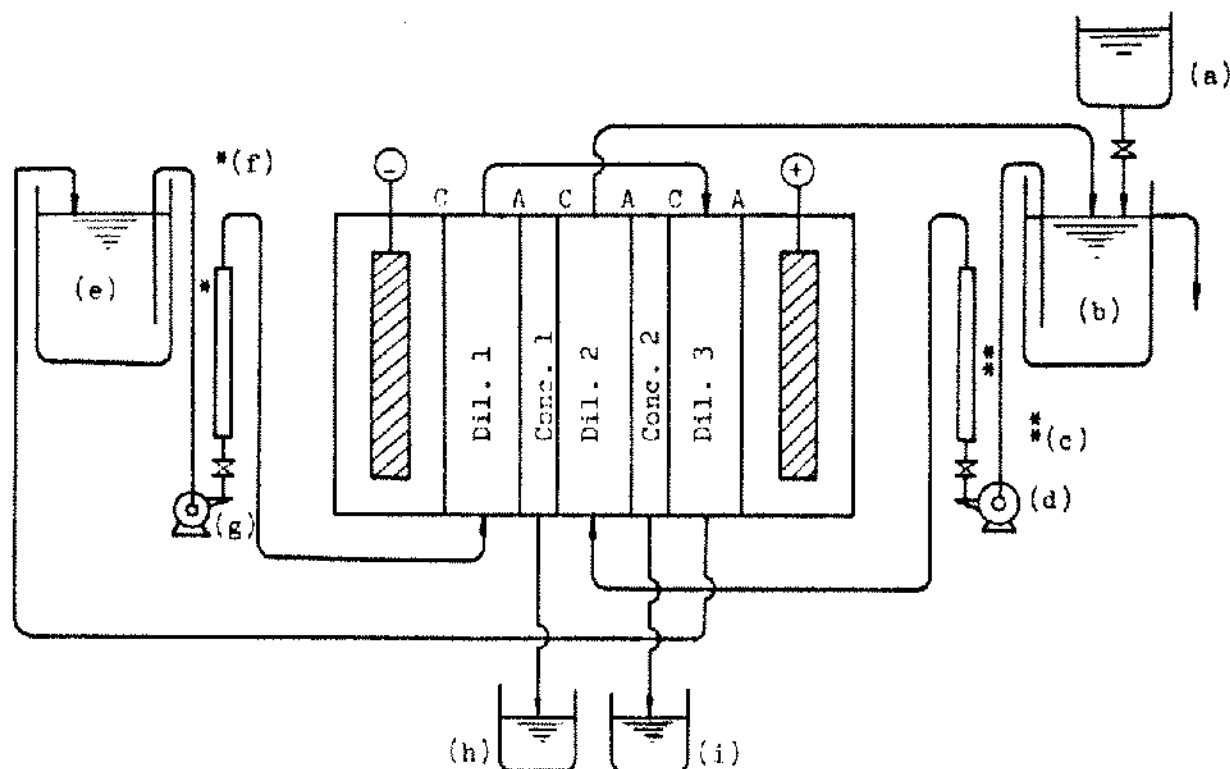


Figure 3. Experimental apparatus for electrodesialysis (B). (a) Sea water tank (b) Reservoir for sea water (c) Flow meter (d) Circulating pump (e) Reservoir for 0.5N-NaCl solution (f) Flow meter (g) Circulating pump (h) Brine (for cation) (i) Brine (for anion).

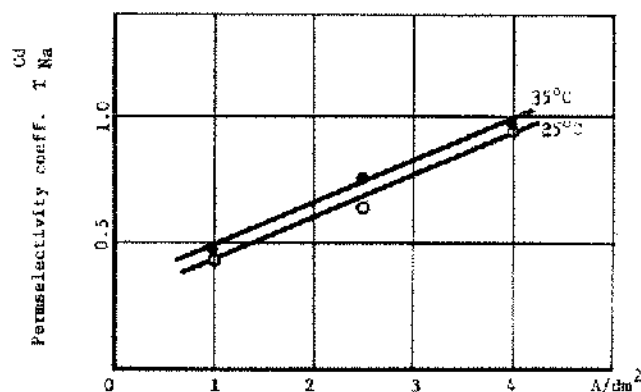


Figure 4. Permselectivity of Cd.

$$T_{Na} = \frac{[Cd]_{brine} / [Cd]_{sea\ water}}{[Na]_{brine} / [Na]_{sea\ water}}$$

these membranes is 0.2 to 0.4. The permeability of lead decreases with increase in current density.

When electrodesialysis was carried out with the Type B apparatus supplied with the same feed solution, a considerable amount of lead permeated the anion exchange membranes. It therefore is assumed that the lead dissolved in the sea water included not only Pb^{2+} but also complex ions. For instance, the lead ion permselectivity coefficient

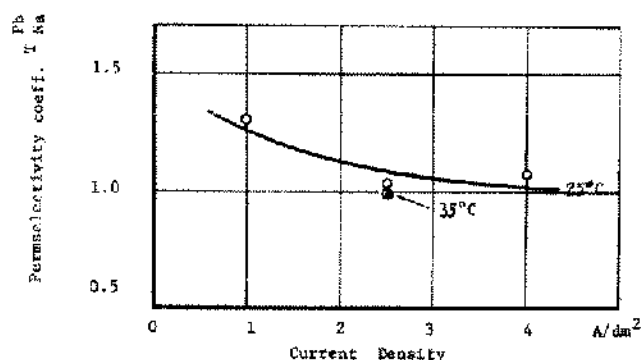


Figure 5. Permselectivity of Pb.

at a salt-making factory was a very large 4.8. This indicates possible contamination emanating from the apparatus used during electrodesialysis.

Mercury ions

As mercury dissolved in sea water forms a complex compound with chloride ions, dissociation is difficult. Results of electrodesialysis of artificial sea water using the Type B apparatus are shown in Figure 6. Mercury hardly permeates either cation- or anion-exchange membranes.

The permselectivity coefficient value of mercury ions

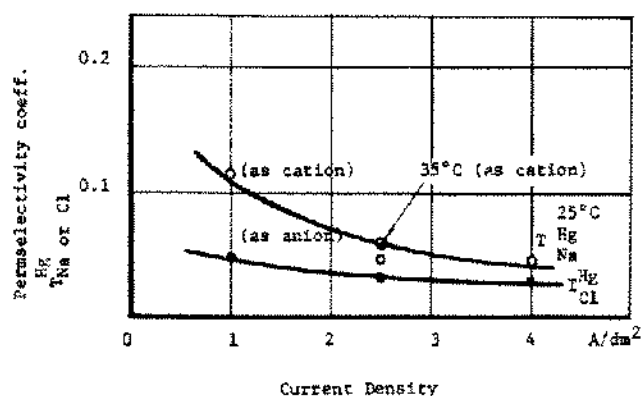


Figure 6. Permeability of Hg.

obtained at a salt-making factory was 0.33, showing little permeation by mercury ions of ion-exchange membranes.

Chromium

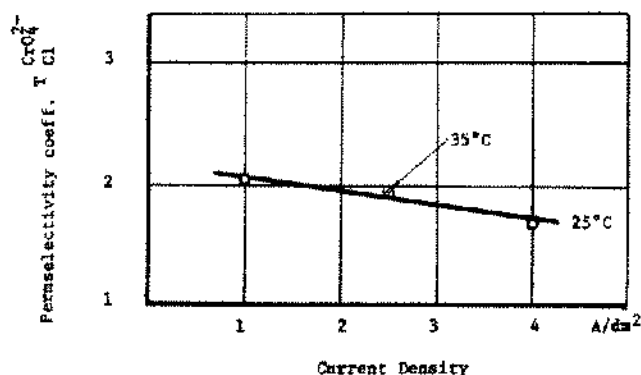
Chromic and chromate ions are present when chromium is dissolved in sea water. Electrodialysis experiments using artificial sea water containing chromic ions or chromate ions were carried out with Type B apparatus. The results are shown in Figure 7.

Chromate ions permeate the anion-exchange membrane and enter the concentration compartment. As seen from Figure 7, the permeability of chromate ions is twice that of chloride ions. Chromic ions were expected to permeate cation-exchange membranes, but were not found in the brine, indicating they cannot permeate cation- or anion-exchange membranes.

BEHAVIOR OF TRACE HEAVY METAL IONS DURING EVAPORATION

Experiment

A rotary vacuum evaporator is used to evaporate sea water, artificial sea water, and brine. A flask containing the solution is dipped in a boiling water bath to create a

Figure 7. Permeability of CrO_4^{2-} .

vacuum until the solution slightly boils. When the degree of concentration becomes one-tenth the starting volume, scale deposited is removed by filtration and the filtrate further evaporated. When deposition of common salt is completed, the volume contained in the flask is one-fortieth the starting volume. The salt is then separated from the mother liquor and bittern is left.

Cadmium

Samples obtained during concentration of artificial sea water and brine were analysed. The results are shown in Table I.

TABLE I
Distribution of Cd among Salt, Scale and Bittern

Sample	Distribution ratio (%)		
	Laboratory		Factory
	Seawater	Brine*	Brine*
Salt	99.4	95.3	80.0
Scale	0.5	2.8	20.0
Bittern	0.1	1.9	0

*Calculated from concentration ratio

Cadmium penetrates salt crystals during concentration. It has been well known that impurities bring about such crystal habit modification. It indicates there is a risk of cadmium contaminating salt. A similar experiment with brine obtained by the saltfield method gave the same results as above. In order to compare this result with the result in a salt-making factory, samples of a factory were analyzed.

Lead

Lead content in nature is higher than cadmium, and this holds true for sea water. Experiments involving evaporation of sea water and analysis of the samples obtained were carried out. The results obtained are shown in Table II.

TABLE II
Distribution of Pb among Salt, Scale and Bittern

Sample	Distribution ratio (%)	
	Laboratory (Seawater)	Factory (Brine)*
Salt	43.7	55.6
Scale	41.4	19.4
Bittern	14.9	25.0

*Calculated from concentration ratio

In this experiment, about 44% of the total lead penetrated the salt and most residual part of it penetrated the scale. It is well known that lead ions also penetrate the salt crystals as the crystal habit modifier. Therefore, if lead

ions are concentrated in the brine, there is a risk of contamination of the salt by the lead. Results of analysis of samples obtained from a salt-making factory show that about half of the lead dissolved in brine penetrates the salt.

Mercury

Evaporation of artificial sea water was carried out, and samples obtained analyzed. The results, outlined in Table III, show that about 28% of the total mercury in sea water penetrates the salt, and about 50% of that the bittern, with the residual penetrating the scale.

TABLE III
Distribution of Hg among Salt, Scale and Bittern

Sample	Distribution ratio (%)	
	Laboratory (Seawater)	Factory (Brine)*
Salt	28.1	28.0
Scale	21.9	32.0
Bittern	50.0	40.0

* Calculated from Mg concentration ratio

Results of analysis of samples in a salt-making factory were similar to those obtained in the laboratory.

Chromium

Experimental evaporation of artificial sea water to which either chromium potassium sulfate or potassium chromate had been added as chromic or chromate ions was carried out.

TABLE IV
Laboratory: (Seawater)

Sample	Distribution ratio (%)	
	Cr (VI)	Cr (III)
Salt	0.7	1.5
Scale	0.6	94.5
Bittern	98.7	4.0

Factory: (total Cr, Brine)*

Salt	24.7
Scale	46.5
Bittern	28.7

* Calculated from Mg concentration ratio. Concentration of total Cr in brine is 0.009 mg/kg brine, and total amount of Cr in samples is 0.010 mg.

The results are shown in Table IV. Most of the chromic ions penetrated the scale and most of the chromate ions the bittern, so neither ion penetrates the salt. But salt from a salt-making factory contains a fair amount of chromium, and the total amount of chromium in the samples obtained by evaporation was more than in the case of brine. This

fact shows that contamination of chromium by salt-making apparatus had occurred. In this case, it is assumed that chromium dissolved in the brine is in the form of chromic ions because the scale had the highest distribution ratio among the samples.

CONCLUSIONS

In concentration of sea water by the ion-exchange membrane method, cadmium, mercury and chromic ions have a low rate of permeation concerning ion-exchange membranes which feature low permeability of bivalent ions. But the permeability of lead ions is about the same as sodium ions, and chromate ions are more permeable than chloride ions.

On the other hand, in crystallization by evaporation, cadmium and lead ions penetrate the common salt crystals as crystal habit modifiers, whereas mercury, chromic and chromate ions can hardly penetrate the salt.

Behavior of some trace metal ions are summarized in Figure 8.

If heavy metal pollution of sea water should occur, those ions other than lead ions may be removed in the salt-making process, but there is some risk that lead ions

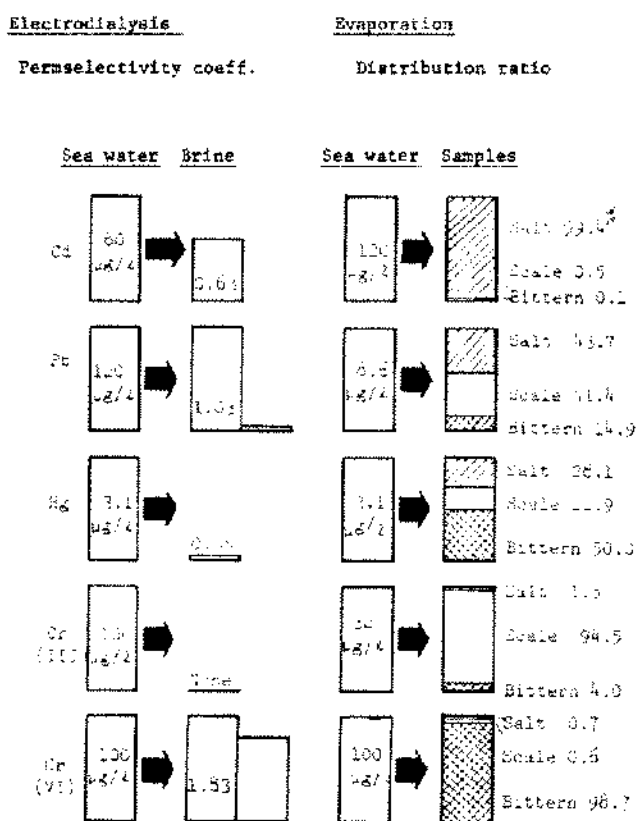


Figure 8. Behavior of trace metal ions.

may penetrate the salt crystals. However, there is nothing to fear at present in regard to contamination of common salt by heavy metals.

REFERENCES

- Hiroi, K., and Tahara, H., 1970. Determination of cadmium in sea water, brine, salt and bittern by atomic absorption spectrophotometric method, *Japan Society of Sea Water Science*, Annual Meeting, Tokyo, 22 pp.
- Hiroi, K., and Kaneko, K., 1971. Behavior of cadmium in the concentration of sea water by ion-exchange membrane method, *Japan Society of Sea Water Science*, Annual Meeting, Osaka, 50 pp.
- Hiroi, K., 1972. Determination of chromium in sea water, brine, salt and bittern by atomic absorption spectrophotometric method, *Japan Society for Analytical Chemistry*, Sendai, Annual Meeting, B. 188 pp.
- Koerker, F. W., 1970. The Dow Chemical Co., Determination of mercury (Atomic absorption spectrophotometric method), CAS-AM-70.13.