

A Study on the Collection of Ca^{2+} from Seawater Using A Recycling Oleic Acid System

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An evaluation of the combined process of seawater desalination for drinking water production and solar salt production that uses the effluent from the desalination process is now undertaken by the Taiwan Salt Industrial Corporation (TSIC). It is based on the recently developed technology that can remove more than 75 % of the Ca^{2+} ions from seawater by forming Ca-oleate with oleic acid. As a result, in the following desalination operation, more than 70 % of fresh water can be recovered [1]. The remaining seawater is then transferred to evaporation ponds to produce solar salt. It is estimated that 3/5 pond area and time of evaporation can be saved. Because oleic acid can be recycled and reused in the same process (Figure 1), the cost of Ca-removal is relatively low. This will be beneficial to the solar-salt production and desalination processes in future operation of Taiwan [2,3]. This study presents part of the evaluation work dealing with the technique of removing calcium ions from seawater.

Calcium ion removal from seawater has long been a challenge to the engineer of seawater chemistry, both from the technical and economical considerations. In this study oleic acid is used as a collector to remove Ca^{2+} from seawater by the formation of calcium-oleate, which has an extremely low solubility ($K_{sp} = 4.0 \cdot 10^{-13}$) [4]. Furthermore, the precipitate Ca-oleate itself is a flocculant with a bulk density $< 1.0 \text{ g/cm}^3$, and can float to the top and be readily separated from the seawater. The concentrated calcium oleate flocculates are then decomposed into oleic acid and CaCl_2 by treating with HCl. The recovered oleic acid can be reused to precipitate the calcium ions in the previous de-calcium operation.

Both synthetic and natural seawaters have been tested in this study. The results showed that calcium-oleate precipitates could be easily formed. The removal of Ca-oleate was conducted at pH values

from 8.2 to 9.8 adjusted by NaOH solution. Simple mechanical stirring can bring about the formation of over 90 % of calcium oleate and small amount of Mg-oleate precipitates. The required dosage was 10 ml oleic acid in 1 liter seawater with a stirring rate 1,500 rpm. A well-dispersed or emulsified oleic acid-water system is critical to the formation of the Ca-oleate. It is shown that with the dosage of 5 ml/L of emulsified oleic acid (10 mg/L sodium dodecyl sulfate, SDS, as surfactant), 72 % Ca and 33 % Mg can be removed even the stirring rate is reduced to 300 rpm.

Experimental results also revealed that the amount of Ca-removal was close to the figure of theoretical calculation at the pH around 8.8. The Ca-oleate flocculates can float to the top and be separated from the seawater readily without further treatment. The removal rate was above 96 % for both synthetic and natural seawater. The turbidity of the residual seawaters was 0.5 NTU, which is better than that of city water (1 NTU).

Total organic carbon (TOC) measurements on the floc-removed seawater showed that the TOC value ranged from 60 to 200 ppm. The value increased with the increasing dosage of oleic acid as well as pH values during the Ca-oleate formation operation. The TOC of the seawater can be lowered by filtration through activated carbon. The results showed that the TOC of the treated seawater was reduced to about 30 ppm, which is far below that of the original seawater (41.6 ppm) [5].

The recovered calcium oleate can be decomposed into oleic acid and CaCl_2 by the treatment of hydrochloric acid. The recycled oleic acid is used to precipitate the calcium ions in the previous de-calcium stage. It has been shown that there is no difference in effect between the fresh and the recycled oleic acids.

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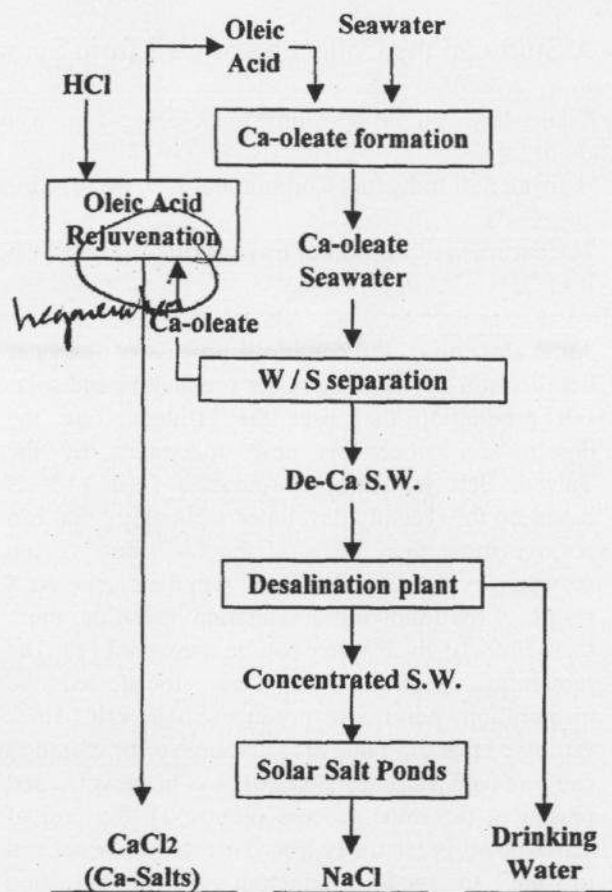


Figure 1. Combination of desalination plant with solar salt production using Ca-removal technology.