

Improved Treatment of Waste Brines*

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A technology permitting practically complete utilization of the main components (Na^+ , Mg^{2+} , K^+ , Cl^- and SO_4^{2-}) in the waste brines after obtaining salt from sea water has been developed. This method comprises 4 stages: (i) elimination of SO_4^{2-} ions; (ii) precipitation of $\text{Mg}(\text{OH})_2$ and formation of MgO ; (iii) preparation of KCl , NaCl and $\text{CaCl}_2 \cdot \text{aq}$; (iv) conversion of gypsum into CaCO_3 .

1. INTRODUCTION

The sea-salt production is based on sea-water evaporation, which results in concentration of a significant number of components. When the solution density reaches $1.22 - 1.24 \text{ g/cm}^3$, crystallization of pure NaCl occurs. After the removal of NaCl , the highly concentrated waste brines, which can be used as a source for magnesium, sodium and potassium salts production, are deposited back into the sea. These processes cause an osmotic shock of the living organisms (ecosystems) in the sea.

Various methods are applied worldwide to the partial utilization of waste brines and production of inorganic salts such as KCl and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (Germany), $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and MgO (France)

$\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ and $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ (Bulgaria). The problems associated with the preparation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and $\text{Mg}(\text{OH})_2$ from waste brines in sea salt production as well as the conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to CaCO_3 have been considered in some previous works of ours [1,2].

The technology developed for improved treatment of waste brines from the Sea-Salt Plant "Tchernomorski solnitsi", Burgas, Bulgaria, has 2 aspects: i) a method allowing practically complete utilization of the major components (Na^+ , Mg^{2+} , K^+ , Cl^- and SO_4^{2-}) present in the waste brine after sea-salt production and isolation of some inorganic salts; and ii) a way of protecting the living organisms from the harmful effect of the deposited waste brines.

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2. TECHNOLOGY PROCESS STAGES

The technology comprises 4 stages: (i) elimination of SO_4^{2-} ions; (ii) precipitation of $\text{Mg}(\text{OH})_2$ and formation of MgO ; (iii) preparation of KCl , NaCl and CaCl_2aq ; (iv) conversion of gypsum into CaCO_3 and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. The block - scheme of the processes is shown on Fig. 1.

The main advantage of this technology is that part of the solution obtained after the precipitation of $\text{Mg}(\text{OH})_2$ is involved in a cycle. The concentration of Ca^{2+} ions in this solution suffices for the desulphatization of a new portion of the initial waste brine and preparation of gypsum

without addition of a new precipitating reagent.

2.1. Elimination of SO_4^{2-} ions

Complete precipitation of SO_4^{2-} ions as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) from the initial waste brine was achieved using a diluted solution of CaCl_2 . The chemistry and conditions of this process are given in a previous paper [1]. Precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ during the second and each successive cycle in this technology was performed with brines where a sufficient amount Ca^{2+} ions was present after the precipitation of Mg^{2+} ions.

The precipitation process occurred at about 30°C and a $\text{SO}_4^{2-} : \text{Ca}^{2+}$ ratio of 1:1.5. The initial

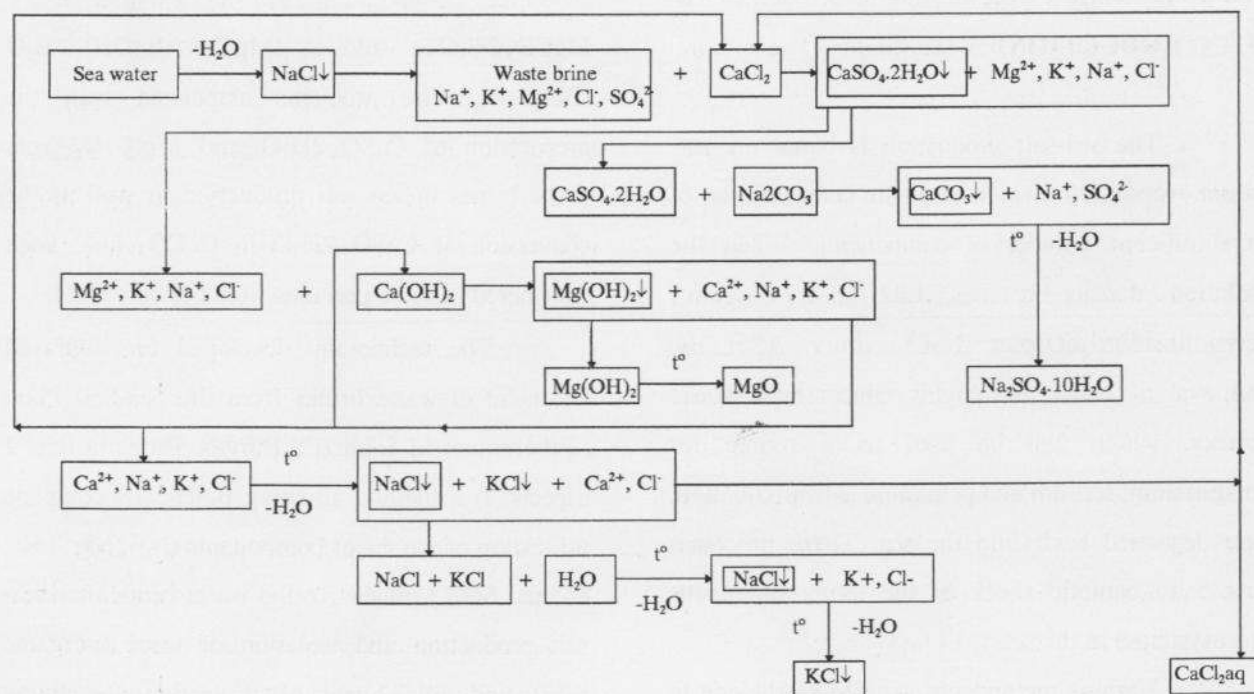


Figure 1. Block scheme of the technological processes

brine was gradually added to the CaCl_2 solution and the mixture was stirred for 1 h. Under these conditions no simultaneous crystallization of $\text{NaSO}_4 \cdot \text{CaSO}_4$, $3\text{NaSO}_4 \cdot 2\text{CaSO}_4$ or $\text{NaSO}_4 \cdot 10\text{H}_2\text{O}$ proceeded.

2.2. Precipitation of $\text{Mg}(\text{OH})_2$ and formation of MgO

The precipitation of Mg^{2+} ions as $\text{Mg}(\text{OH})_2$ was achieved in two steps using $\text{Ca}(\text{OH})_2$. The first step of the precipitation proceeded with an insufficiency of $\text{Ca}(\text{OH})_2$ (90% of the stoichiometric amount) which was suspended in a certain amount of brine where the Mg^{2+} and SO_4^{2-} ions had been eliminated. Only in the beginning of the process H_2O was used for $\text{Ca}(\text{OH})_2$ suspending. The amount of liquid needed for suspending $\text{Ca}(\text{OH})_2$ was determined so as to decrease the MgCl_2 concentration in the brine from about 0.6 - 0.9 mol $\text{MgCl}_2/\text{kg H}_2\text{O}$ to about 0.45 mol $\text{MgCl}_2/\text{kg H}_2\text{O}$ in the final solution. The crystallizing solid phase was a mixture of $\text{Mg}(\text{OH})_2$ and NaCl , no crystallization of double salts being observed. The filtrate containing 1.5 - 2.0 mass % Ca^{2+} ions but no free OH^- ions was suitable for cyclic use and part of it was involved in the desulphatization of new amounts of initial brine. The remaining part of the filtrate was used for crystallization of NaCl и KCl . For that purpose it was additionally treated with $\text{Ca}(\text{OH})_2$ (10 % excess) to achieve complete removal of the Mg^{2+} ions.

Precipitation of $\text{Mg}(\text{OH})_2$ was carried out

with the use of seeds and intense stirring of the suspension resulted in an increase of the particles of the gel-like precipitate.

$\text{Mg}(\text{OH})_2$ is calcined at 920°C to MgO .

2.3. Crystallization of KCl + NaCl

The SO_4^{2-} and Mg^{2+} ion-free solution consisting of the residual waste brines remaining after each cycle is used for obtaining KCl and NaCl . A four-stage process has been proposed:

- (i) *crystallization of pure NaCl* - Evaporation of the solution to a concentration of 15 - 16 mass % CaCl_2 followed by cooling to 0 - 5°C ;
- (ii) *co-crystallization of NaCl and KCl* - Subsequent evaporation of the solution to a concentration of 30-35 mass % CaCl_2 ;
- (iii) *crystallization of $\text{CaCl}_2 \cdot \text{aq}$* - Crystallization of $\text{CaCl}_2 \cdot \text{aq}$ from the residual solution or using of the solution for initial desulphatization of new amounts of waste brine from the sea-salt production;
- (iv) *separation of NaCl and KCl* - Dissolution of the mixture in water and crystallization of NaCl at 110°C .

2.4. Conversion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ into CaCO_3

The $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ obtained after desulphatization of the brine is converted to CaCO_3 by means of solid Na_2CO_3 . A maximum conversion degree (98%) without simultaneous crystallization of various double salts is attained when portions of solid Na_2CO_3 are added to a

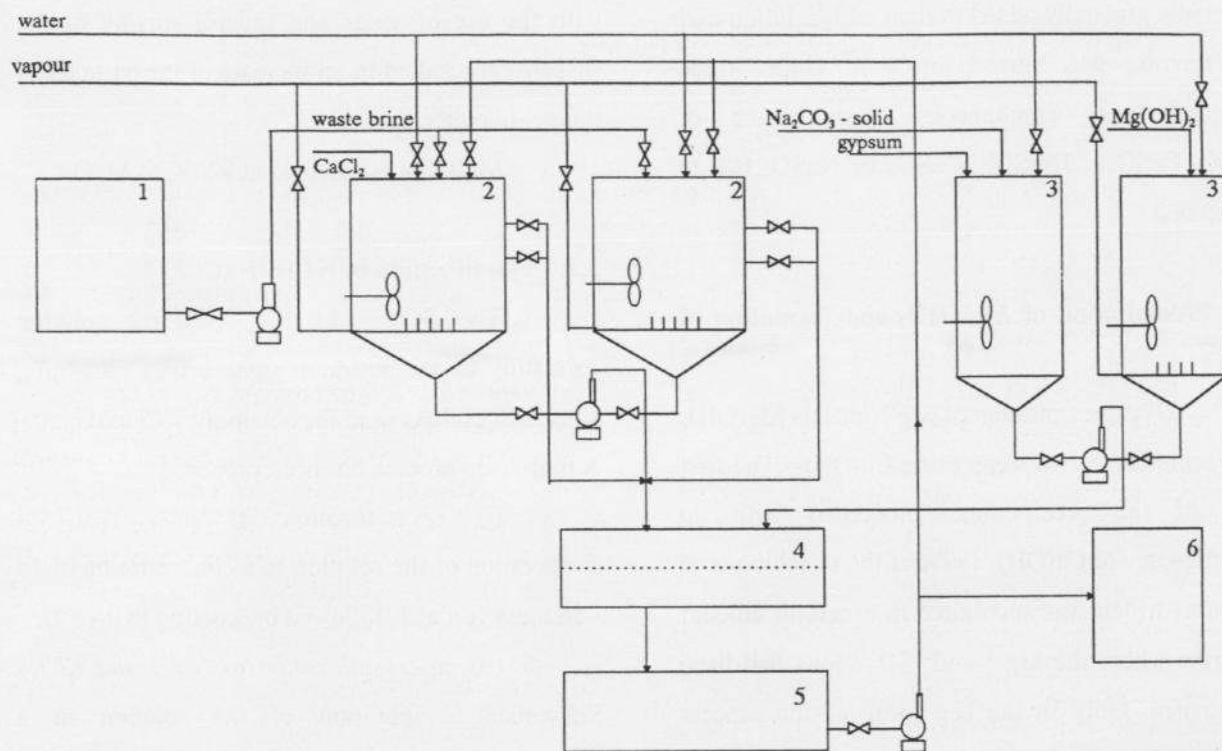


Figure 2 Pilot plant installation for utilization of waste brines: 1 - reservoir for the initial brine; 2 - reactor with stirrer; 3 - collector equipped with stirrer; 4 - vacuum filter (centrifuge); 5 - receiver of the filtrate; 6 - crystallization bed.

suspension of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and H_2O (1:10) for 4-5 h. The molar ratio $\text{Na}_2\text{CO}_3 : \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is 1.1 : 1 (basic medium pH ≈ 11).

The filtrate is evaporated and $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ crystallizes.

3. TECHNOLOGICAL SCHEME

Fig. 2 presents the scheme of a pilot plant installation for application of the method developed for improved treatment and complete utilization of waste brines from sea salt production.

The installation consists of: (1) reservoir for the initial brine; (2) two reactors with stirrers; (3) two collectors equipped with stirrers; (4) vacuum filter (centrifuge); (5) receiver of the filtrate; (6) crystallization bed.

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