EXTRACTIVE PROCESS FOR PREPARING HIGH PURITY MAGNESIUM CHLORIDE HEXAHYDRATE

This paper reports a method for the preparation of magnesium chloride hexahydrate (bischofite) from Sebkha el Melah of Zarzis Tunisian natural brine. It is a five-stage process based on crystallization by isothermal evaporation and chemical precipitation. The first two steps were dedicated to the crystallization of sodium chloride and potassium-magnesium double salts, respectively. Then, the resulting liquor was desulfated using calcium chloride solution. After that, another isothermal evaporation stage was implemented in order to eliminate potassium ions in the form of carnallite, KCl·MgCl₂·6H₂O. At the end of this step, the recovered solution, primarily composed of magnesium and chloride ions, was treated by dioxan in order to precipitate magnesium chloride as MgCl₂·6H₂O·C₄H₈O₂. This compound dried at constant temperature of 100 ºC gave good quality magnesium chloride hexahydrate. Besides this salt, the various by-products obtained from the different treatment stages are also useful.

Keywords: process; extraction; magnesium chloride; natural brine.

Process description

Choice of the different treatment stages adopted in the conceived process was directed by some previous work [2, 19-22]. The corresponding flowchart is given by Figure 1. It is a five stage process based mainly on isothermal evaporation and salts crystallization as well as chemical precipitation.

The first step consists of evaporating the considered brine at 35 ºC in order to crystallize sodium chloride (halite). During the second treatment, the resulting solution is further concentrated by isothermal evaporation at the same temperature. The precipitated salts are expected to be sodium chloride and substantial amounts of kainite (KCl·MgSO₄·3H₂O). The third step of the process is a chemical precipitation reaction of sulfate ions using calcium chloride solution. After removing calcium sulphate precipitate, the mother liquor is subjected to another 35 ºC isothermal evaporation in order to eliminate partially potassium ions as potassium-magnesium double salt, carnallite (KCl·MgCl₂·6H₂O). The resulting brine, composed essentially of magnesium and chloride ions, is treated by 1,4-dioxan (C₄H₈O₂), which is expected to precipitate the magnesium chloride salt as MgCl₂·6H₂O·C₄H₈O₂ [22-25]. This compound was dried at constant temperature (100 ºC) to eliminate dioxan.
molecules and thus obtain magnesium chloride hexahydrate, MgCl₂·6H₂O.

EXPERIMENTAL

Chemicals

The principal raw material considered in this study is natural brine sampled from Sebkha El Melah of Zarzis. Its chemical composition in major ions is given in Table 1. Besides this highly concentrated aqueous solution, two commercial reagents were also used: calcium chloride dehydrate (99%) and 1,4-dioxan (99%) supplied by Fluka.

Apparatus and analysis methods

All treatments were performed at constant temperature (35 °C) in a thermostatic bath, except the third and fifth ones. These two treatment stages were carried out in a jacketed glass reactor where temperatures (35 and 25 °C, respectively) were controlled by water circulation. In both steps agitation was assured by a mechanic stirrer.

Table 1. Ionic composition of brines (g L⁻¹)

<table>
<thead>
<tr>
<th>Brine</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₀ (initial)</td>
<td>41.32</td>
<td>7.36</td>
<td>53.95</td>
<td>0.40</td>
<td>205.14</td>
<td>30.50</td>
</tr>
<tr>
<td>S₁</td>
<td>21.62</td>
<td>10.95</td>
<td>77.76</td>
<td>0.00</td>
<td>234.57</td>
<td>43.81</td>
</tr>
<tr>
<td>S₂</td>
<td>13.14</td>
<td>12.77</td>
<td>90.52</td>
<td>0.00</td>
<td>265.97</td>
<td>51.89</td>
</tr>
<tr>
<td>S₃</td>
<td>6.64</td>
<td>7.55</td>
<td>70.35</td>
<td>0.00</td>
<td>224.73</td>
<td>6.09</td>
</tr>
<tr>
<td>S₄</td>
<td>4.02</td>
<td>5.88</td>
<td>100.89</td>
<td>0.00</td>
<td>299.35</td>
<td>8.25</td>
</tr>
</tbody>
</table>
Brines and solid phases collected from the different treatment stages of the process were chemically analyzed. The chemical analysis methods applied for sulphate, chloride, magnesium, and alkaline ions were respectively gravimetry, potentiometry (Titrino DMS 716 of mark Ω Metrohm), EDTA complexometry and flame atomic absorption spectroscopy (SAAF).

Furthermore, X-ray diffraction analysis using a Philips instrument (PW 3040 generator, 3050/60 9/2θ) and CoKα radiation (λ = 1.789 Å) were performed.

RESULTS AND DISCUSSION

Ionic composition of the original brine (S₀) and circulating solutions (Sᵢ, i refers to the corresponding treatment) are summarized in Table 1.

As expected, the first four treatment stages gave a magnesium chloride solution (S₄) containing smaller amounts of sodium chloride, potassium chloride and magnesium sulphate. Thus, such solution may be suitable for magnesium chloride salt precipitation by di-oxan as MgCl₂·6H₂O·C₄H₈O₂.

Chemical composition evolution of the treated brine is well seen in Figure 2. It represents a section of the 35 °C isotherm of the quinary system Na⁺, K⁺, Mg²⁺/Cl⁻, SO₄²⁻//H₂O usually used to describe brines equilibrium states. In this diagram, the coordinates of a considered solution are expressed as follows:

\[ \%K_2 = \frac{100n_{K_2}}{D}, \]
\[ \%Mg = \frac{100n_{Mg}}{D}, \]
\[ \%SO_4 = \frac{100n_{SO_4}}{D}, \]
\[ D = n_{K_2} + n_{Mg} + n_{SO_4}. \]

where \( n_i \) is the mole number of the \( i \) entity.

Geometrical positions of the original brine (S₀) and the mother liquors resulting from the four considered treatment stages (S₁, S₂, S₃ and S₄) in the equilibrium diagram show the brine’s evolution towards the crystallization field of magnesium chloride hexahydrate (MgCl₂·6H₂O).

Regarding the recovered solid phases (Sₜ), their ionic compositions are given in Table 2. Besides chemical analysis, they were also characterized by X-ray diffraction. Results of this characterization are represented by Figures 3 and 4.

Table 2. Ionic compositions of solid phases (mass%)

<table>
<thead>
<tr>
<th>Brine</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sₜ₁</td>
<td>35.90</td>
<td>0.26</td>
<td>1.02</td>
<td>0.00</td>
<td>56.25</td>
<td>2.55</td>
</tr>
<tr>
<td>Sₜ₂</td>
<td>35.10</td>
<td>0.37</td>
<td>1.27</td>
<td>0.00</td>
<td>55.29</td>
<td>2.42</td>
</tr>
<tr>
<td>Sₜ₃</td>
<td>1.92</td>
<td>2.32</td>
<td>1.53</td>
<td>21.06</td>
<td>2.15</td>
<td>50.46</td>
</tr>
<tr>
<td>Sₜ₄</td>
<td>0.62</td>
<td>14.02</td>
<td>8.13</td>
<td>0.00</td>
<td>38.32</td>
<td>0.89</td>
</tr>
<tr>
<td>Sₜ₅</td>
<td>0.06</td>
<td>0.05</td>
<td>7.94</td>
<td>0.00</td>
<td>23.10</td>
<td>0.00</td>
</tr>
<tr>
<td>Sₜ₆</td>
<td>0.11</td>
<td>0.09</td>
<td>11.61</td>
<td>0.00</td>
<td>34.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>
Figure 3. Diffractograms of the solid phases $S_{d1}$ (a), $S_{d2}$ (b), $S_{d3}$ (c) and $S_{d4}$ (d).
Solids resulting from the first two treatment stages (Sd1, Sd2) are sodium chloride salts containing less than 5% impurities (mainly ions from coating solution). The chemically precipitated compound, Sd3, is almost pure gypsum. Salt Sd4 is basically carnallite (KCl·MgCl2·6H2O) containing little quantities of halite (NaCl). Solid Sd5 precipitated by dioxane corresponds to the compound MgCl2·6H2O·C4H8O2 including substantial amounts of sodium, potassium and sulphate ions. Finally, the end-product obtained by drying Sd5 solid phase is an extremely pure magnesium chloride hexahydrate salt. Its purity is more than 99.5%. When treating one liter of brine, 155 grams of this salt were recovered, i.e., an overall process yield of 40%.

Considering the information provided by the experimental results regarding the solid phases recovered, only one difference was noted in comparison with our predictions. It is the absence of double salt KCl·MgSO4·3H2O (Kaïnite) in Sd2 solid phase. Lack of this salt could be explained by its low crystallization rate. In fact, magnesium ions exist in aqueous solutions predominantly as [Mg(H2O)6]2+ which promote the formation of salts having six water molecules in their structures.

To show the importance of prepared salt, we studied its industrial application in Sorel cement manufacture. The compressive strength and setting time of the obtained cement paste were determined and were 86 MPa and 62 min, respectively. These values are comparable to those found when using commercial magnesium chloride hexahydrate.
CONCLUSIONS

This work is a contribution to the vaporization studies of Tunisian natural resources dealing with the extraction of magnesium chloride hexahydrate salt from Sebkha el melah natural brine. To perform this task, a five stage process based on isothermal evaporation and chemical precipitation was performed. The conceived process gave good quality magnesium chloride hexahydrate (purity higher than 99.5%) which was successfully checked in Sorel cement manufacture. Besides this chloride, all the collected by products are also useful.

REFERENCES

[3] A. Chaabouni, Extraction of KCl from Chott el Jerid, DEA, Faculty of Sciences of Tunis, Tunisia, 1980