

MAGNESIUM CHLORIDE PRODUCTION METHODS

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Annotation

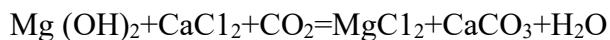
The development of a technology for the production of magnesium chloride using halite waste separated from dolomite ores and magnesium sulfate with constant water hardness and the calculation of a 2-stage evaporator have been improved in the magnesium chloride evaporation department.

Keywords

"Kaiser Refractories", "magnetic" fire magnesite with large periclase grains, filter fluid, seawater and brines, hydrochloric acid, magnesite, dolomite, magnesium chloride, hydroxide and oxide, sodium sulfate and sodium chloride.

Magnesium chloride is obtained from seawater without preconcentrating it and without precipitating NaCl, directly by precipitating magnesium hydroxide with lime water and dissolving it in HCl acid. The 25% Mg (OH)₂ precipitate is mixed with a dilute MgCl₂ solution and neutralized with HCl. The solution containing 15% MgCl₂ is evaporated. This method allows obtaining Mg (OH)₂, which is then used to obtain magnesium chloride free of boron compounds. The boron content in magnesium chloride, which is converted into magnesium metal, should not exceed 0.001%.

A solution of CaCl₂ can serve as a chlorine source for converting a suspension of Mg (OH)₂ into CaCl₂. CaCl₂ is a cheap waste product generated in soda production. Mg (OH)₂ suspension in CaCl₂ solution undergoes 76 carbonation:

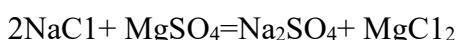


After the precipitate is separated, a solution containing 10% $MgCl_2$ and a small amount of $NaCl$ is obtained.

As a result of evaporation of the solution, up to 35% $MgCl_2$ is separated, and the main part is in a crystalline state.

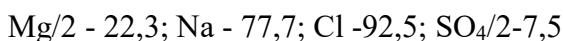
Magnesium chloride ($MgCl_2 \cdot 6H_2O$) is produced from seawater, lake sediments and estuaries by precipitation of salts and subsequent separation of bromine [1,2].

The evaporation process of seawater and brines of marine-type salt lakes can be observed in the isotherms of aqueous systems at 25 °C in the diagram [3].



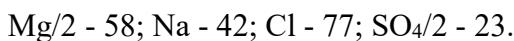
This system is very complex, and is prone to solidification, even in the presence of large amounts of phase, in a metastable state.

The metastable parts of mirabilite, thenardite, halite, and epsomite tend to adhere to the inner surface of astrakhanite (delimited by dotted lines). The salt mass composition of the resulting seawater and saline solutions can be expressed in terms of ion-equivalents at 1 point in %:



In the isothermal evaporation of this solution, the solid phase table salt is separated first.

During the crystallization of sodium chloride, the composition of the solution changes in 1-2 crystallizations according to the light, the composition of the solution at 2 points:



The amount of water evaporated during the stages of the crystallization process can be determined from the water diagram.

If only stable phases crystallize, then during the re-evaporation of water, the composition of the solution changes at 2-3 points on the curve, where halite and astrakhanite dissolve, forming $NaCl$ and $MgSO_4 \cdot 7H_2O$ a mixed precipitate.

This also leads to the formation of an important equilibrium that lasts a long time and is stable under natural conditions.

In many lakes, as a result of the evaporation of seawater, astrakhanite does not precipitate, but instead $NaCl$ and $MgSO_4 \cdot 7H_2O$ begin to crystallize.

The composition of this mixture changes depending on the increase in the concentration of magnesium chloride.

When the triple point $MgSO_4 \cdot 7H_2O$ is combined, magnesium chloride loses 1 molecule of water and turns into $MgSO_4 \cdot 6 H_2O$.

As the concentration of the salt solution increases further, it reaches the eutonic point of the liquid phase at point E (molecule 1000 mol of water); $MgCl_2$ - 101.0; $MgSO_4$ - 9.5; $2NaCl$ -

1.1; sodium chloride and $MgSO_4 \cdot 6 H_2O$ begins to separate, and the composition does not change until the salt solution is completely dry. This composition, plus a certain amount of potassium and bromine salts, gives "sunny" magnesium chloride, which is formed as a result of natural evaporation of the precipitate at 25 ° C. At 0 ° C, the amount of $MgSO_4$ in it decreases by about 2.5 times. The isotherm at 0°C [10] (at 65°C and in the following concentration range 7.88-6.79% $MgSO_4$; 7.71-0.9% $MgCl_2$) crystallizes 21.14-21.82% $NaCl$, forming the double sulfate $9Na_2SO_4 \cdot MgSO_4$ [8]. Brine is usually intensively evaporated in the factory, solar heat is used only in the initial process to increase the natural water concentration to 20%.

Regardless of the method of decomposition of magnesium chloride brine carnallite, artificial carnallite after crystallization is evaporated to 6 molecular water magnesium chloride and its dehydration. The content of $MgCl_2$ in such brines is 28-31%. In the work [4], isotherms at 25° C for carnallite systems were studied. The largest surface area of crystallization is occupied by the $NaCl$ and KCl areas. The more soluble carnallite has a larger area, and the bischofite area is very small.

All four areas converge at two double points. At the first point, a saturated solution of carnallite has the following composition (in wt.%): $MgCl_2$ - 25.54 $NaCl$ - 2.36, KCl - 3.2. In the equilibrium state, there are 3 solid phases: $NaCl$, KCl and $KCl \cdot MgCl_2 \cdot 6 H_2O$.

At the double triple point, bischofite has the following composition: $MgCl_2$ - 35.56; $NaCl$ - 0.32 KCl - 0.12. At this point, the saturated solution in equilibrium contains $KCl \cdot MgCl_2 \cdot 6 H_2O$, $MgCl_2 \cdot 6 H_2O$ and KCl .

The line connecting the carnallite and bischofite points corresponds to the final amount of magnesium chloride brine obtained from the processing of carnallite by various methods.

The higher the concentration during the evaporation of magnesium chloride brine, the less they are. Usually, these salts are evaporated until the amount of $MgCl_2$ in the solution is 35%. Then the process is continued to obtain magnesium chloride with 2, 4 and 6 molecules of water.

To purify the magnesium chloride carnallite brine from $NaCl$ KCl , it is treated with gaseous KCl . KCl is easier to process than $NaCl$. Even at low KCl concentrations, carnallite begins to precipitate. At high KCl concentrations (300 g/l), highly pure $MgCl_2 \cdot 6 H_2O$ is obtained. By spraying the solution with air, it is possible to regenerate practically anhydrous KCl [5].

Obtaining pure products by these methods allows for good results in ion exchange processes of KCl .

Regardless of the method by which the brine containing $MgCl_2$ and various impurities is obtained, it is evaporated. The evaporated brine is poured into a container, and after cooling, it crystallizes and turns into a solid, $MgCl_2 \cdot 6 H_2O$ mass. Evaporation to a high concentration is associated with boiling the solution at high temperatures. At atmospheric pressure above 160, $MgCl_2$ practically hydrolyzes and begins to release KCl . Vacuum evaporators are used to evaporate magnesium chloride brines [6].

The apparatus for evaporating before the combustion process is made of cast iron or steel, in which a lined cylinder and a burner are installed.

The temperature of evaporation of water from the solution corresponds to the partial pressure of saturated vapor in the vapor-gas mixture. This is lower than the temperature passing through the entire heated surface. The temperature of the discharged gases can be 1-2 ° C higher than the boiling temperature of the solution. The useful heat coefficient is very high (95%). In the evaporation battery, 3-4 successively added (by liquid) devices with magnesium chloride are evaporated until the concentration of MgCl₂ reaches 34-35%.

To increase the MgCl₂ concentration to 45-57%, after separating the resulting salts (if required) and purifying the solution from calcium (MgSO₄ solution is added to it), it is treated with superheated steam at 25-30 atmospheres.

When placing the evaporated broth directly in a container, the area of the iron-lined drum should be large for cooling. In addition, it is difficult to remove the cooled mass from the container, and the container itself is quickly corroded, that is, under the influence of magnesium chloride.

These disadvantages are eliminated by obtaining magnesium chloride in the form of flakes. In this case, plywood boxes and barrels or multilayer kraft cellulose bags can be used as containers. When evaporating the brine to obtain granular magnesium chloride, it crystallizes in a rotating steel drum (density 1.56 g/cm³) and is cooled internally with water.

When producing magnesium chloride from dolomite, fully burned dolomite is quenched with water at 95-100°C. The resulting pulp, which contains 11% solids, is subjected to carbonization at 60-40°C. Only calcium hydroxide, which is converted to calcium hydroxide, is carbonated [7].

Carbonated pulp pH=7-8 If KC1 is added slowly to prevent the dissolution of CaCO₃, the neutralization rate of OH is 16%. Part of this solution is settled and evaporated.

At a temperature below 40°C, a suspension of dolomitic water is recommended to be carbonized with calcium sulfate and alkali metal chloride (MgO: CaSO₄: MgCl₂=1:1:1 molar ratio) [8]. After carbonation of the suspension, it is heated to boiling. The resulting CaCO₃ is separated from the solution. Then the alkali metal sulfate is crystallized from it, and the main solution containing MgCl₂ is evaporated.

To obtain MgCl₂, which does not contain CaCl₂, it is recommended to carbonize dolomitic water obtained by quenching burning dolomite with NH₄Cl solution [16].

During the carbonation process, the double salt CaCO₃ Mg (OH)₂ precipitates, while MgCl₂ remains in solution. The precipitate is treated with NH₄Cl to convert Mg (OH)₂ MgCl₂.

In soda production, dolomite water can be used instead of lime water to regenerate ammonia, which produces MgCl₂. [17]

When treating the distillation heat exchange fluid with dolomite water, NH₄Cl reacts with Ca(OH)₂.

Mg(OH)₂ reacts second, after the ammonia has been released at 95 degrees.

If NH₃ is not removed, the reaction between Mg (OH)₂ and NH₄Cl will only reach 45-50%, and the reaction will proceed very slowly, depending on the activity of magnesium oxide.

The brine discharged from the production of K₂SO₄ contains: 2,9-3.2 % K⁺; 5,5-6,5% Mg⁺; 17-18% Cl⁻; 5-125 SO₄²⁻, and it has been proposed to recycle it by the following methods [9].

Initially, the brine is evaporated and langbeinite crystallizes, releasing up to 80% SO₄²⁻. The remaining SO₄²⁻ is precipitated with calcium chloride. SO₄²⁻ is separated. The solution is evaporated, from which carnallite and halite crystallize. The resulting magnesium chloride solution is sent for evaporation.

In the USA, the method of heating MgO with ammonium chloride is used to obtain anhydrous MgCl₂ for soda production. In several countries, Dow Chemical Co. has patented a method for producing high-quality MgCl₂ continuously (99.5% MgCl₂) by treating an aqueous solution of MgCl₂ with ammonia in the presence of NH₄Cl. The released magnesium chloride hexaammonium is separated and subjected to thermal decomposition by regenerating ammonia. The ammonia concentration in the reaction mixture is maintained at a temperature of -20 °C to +10 °C until it reaches 36-65%. The process is carried out in a two-stage system of continuously operating reactors.

The yield of magnesium chloride hexaammonium chloride is 70%. The washed and filtered precipitate is calcined for 4 hours at 400 °C.

Other known options are, for example, dehydration of MgCl₂ 2 H₂O with gaseous ammonia at 2 atm. pressure and 200 °C in a fluidized bed; the resulting ammonia is decomposed in zone 2 of the apparatus at 1 atm. pressure and 400 °C to convert it into MgCl₂ and NH₃ [10].

Thus, the products of processing natural resources are sea water and brine, carnallite, magnesite, dolomite, serpentinite, magnesium chloride, hydroxide and oxide. In the processing of rapa and brine, sodium sulfate and sodium chloride are additionally obtained.

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