

FLUID BED DEHYDRATION OF MAGNESIUM CHLORIDE

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Abstract

Molten salt electrolysis of $MgCl_2$ is commonly used for the production of magnesium metal. However, the electrolysis feed must be completely dry with minimum oxygen content. Therefore, complete dehydration of the $MgCl_2$ brine or the hydrated prill is a required process, which is very challenging because of the ease of thermal degradation due to hydrolysis of magnesium chloride.

Fluidized bed dryers are often used, under hot air and HCl environments. The key features of three different types of fluid bed technologies, which can be applied to $MgCl_2$ dehydration plants, are described in this paper. In addition, a discussion of chemistry, unit operations and advantages associated with each option, is presented.

The background information is provided based on open literature sources, including papers and patents. Most calculations are performed using commercially available metallurgical software, for the thermodynamic calculations and mass/heat balances.

Introduction

For electrolytic production of magnesium, the presence of water and other oxygen compounds in the fused-salt bath has a negative impact on both the product quality and the cell efficiency [1].

Oxygen content of the electrolyte is very detrimental to the operation of the electrolysis cells, through anodic attack and/or insoluble-phase formation. Therefore, not only it is required to effect a complete dehydration of the feed to anhydrous magnesium chloride ($MgCl_2$), but the drying process should also be conducted under such conditions that would minimize the extent of magnesium oxidation.

In practice, the oxide content of the electrolyte, prior to its feeding into the electrolysis cells, is regularly monitored (by sampling) and controlled (in the dryers), in order to avoid upset conditions in the electrolysis cells.

The source of magnesium chloride feed to the electrolysis cells can either be an ore that has been leached with HCl, or the evaporation of salty waters that contain $MgCl_2$. Both routes lead to the production of a typical brine solution with approximately 25-35% $MgCl_2$ by weight [2, 3].

The brine can be further evaporated to produce intermediate magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) prills, before it is sent to a multi-stage fluid bed dryer to produce magnesium chloride dihydrate ($MgCl_2 \cdot 2H_2O$) prills [4]. Alternatively, the 25-35% $MgCl_2$ brine can be fed directly into a fluidized bed spray dryer to produce dihydrate prills [5].

Either way, the dihydrate prills are then dried to anhydrous $MgCl_2$ prills, either using a fluid bed dryer with hot HCl gas, or in a molten-salt electrically-heated chlorinator.

This paper discusses the fluidized beds used for the hexahydrate prills air-drying, brine solution spray drying, and dihydrate prills drying with hot HCl gas. The main challenge is demonstrated as the fact that; removing more and more water from magnesium chloride requires the use of higher and higher temperatures, which in turn can result in the pyro-hydrolysis (breakage under temperature and in presence of water) of the $MgCl_2$ to the unwanted hydroxide or even oxide species.

Figure 1 demonstrates that challenge through a simple thermodynamic calculation using the HSC® software. On the y-axis, 100 moles of hydrated magnesium chloride is heated by hot air, resulting in dehydration as well as hydrolysis at higher temperatures. Consequently, only 10 moles of the initial $MgCl_2$ ends up as a fully dried product, with the rest turning into $Mg(OH)Cl$, at 300°C on the x-axis.

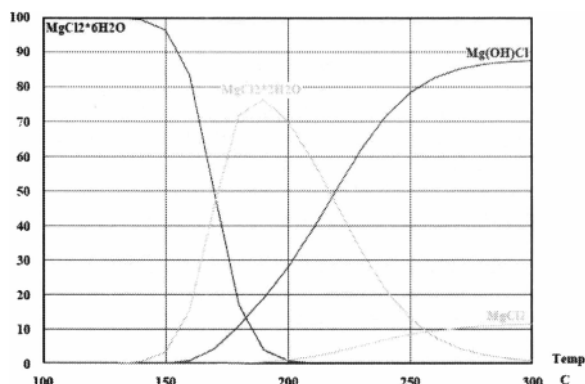


Figure 1. Magnesium chloride hydroxylation, with hot air drying

Fluidized Hot-Gas Dryers

Most fluidized bed dryers operate in the so called 'bubbling regime'. Bubbling fluidization occurs when the hot gas velocity through the bed of solids is more than the minimum to suspend it, with most of the excess gas moving through the suspended solids in bubble-like pockets [6].

Figure 2 shows a bubbling fluid bed dryer, where solids are agitated and fully contacted with the hot fluidizing gas. Under bubbling conditions, most of the solids remain in a dense and distinct 'bed' phase, with only a fraction of the fines reporting to the off-gas discharge.

As a solid phase reactor, a simple circular bubbling bed is similar to a well mixed single stage unit where, depending on the bed inventory, an average residence time from several minutes up to many hours can be achieved.

However, a rectangular dryer can operate under a plug-flow regime, with wet feed entering at one end and product withdrawn from the other side of the unit.

Alternatively, a similar plug-flow arrangement can be obtained within a circular cross-section unit, through the use of baffles (separating walls) which can direct the solid feed through a labyrinth, from inlet towards the outlet.

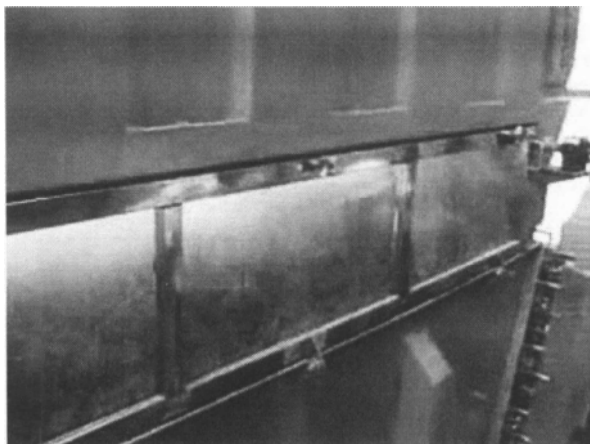


Figure 2. Bubbling fluidized bed dryer

Choice of Fluidization Velocity

In the design of fluid beds, the minimum fluidizing velocity of the particulate solids must be carefully considered. The minimum fluidization velocity is best measured by simple tests. However, it can be approximated by empirical correlations as well [6].

Bubbling fluidized beds normally operate at 3 to 30 times the minimum fluidization velocity, which increases with the particle size and decreases with temperature.

The fluidizing behavior of particles in hot air versus particles in hot HCl gas is somewhat different. Figure 7 depicts the calculated minimum fluidization velocity curves for hydrated $MgCl_2$ (with 2 and 4 molecules of water) at 120°C and 180°C respectively, and the minimum fluidizing velocity for anhydrous $MgCl_2$ at 180°C and 330°C, for a range of spherical particle diameters expected in the fluid bed dryers.

It is advantageous to run the unit at the highest gas velocity possible, in order to achieve the drying duty within the smallest equipment diameter. However, higher velocities result in more elutriation and dust losses to the off-gas.

Fluidized dryers can operate at high velocities to reduce equipment size. However, as the velocity increases, the fluid bed behavior moves from the bubbling regime into the slugging regime, then the turbulent mode, and eventually the entrainment condition. As the fluid bed behavior approaches the entrainment condition, dust losses to the off-gas increase, and solids residence time in the bed decreases.

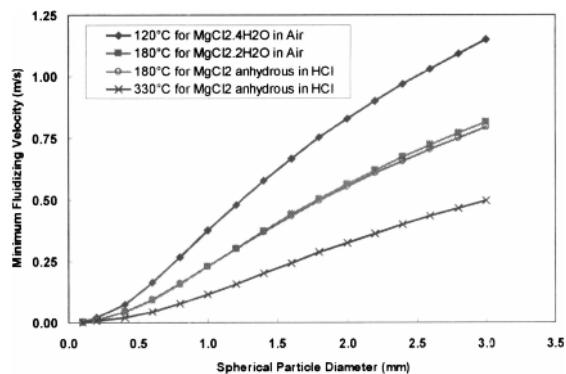


Figure 3. Fluidization velocity and the particulate bed behavior

Dust losses from a fluidized bed are typically related to the terminal velocity of the bed material. At the terminal velocity, a bed particle can be theoretically carried by the exiting hot gas. It is more difficult to measure the actual terminal velocity of specific particles, but given the key physical characteristics, it can be approximated using empirical formulas [6].

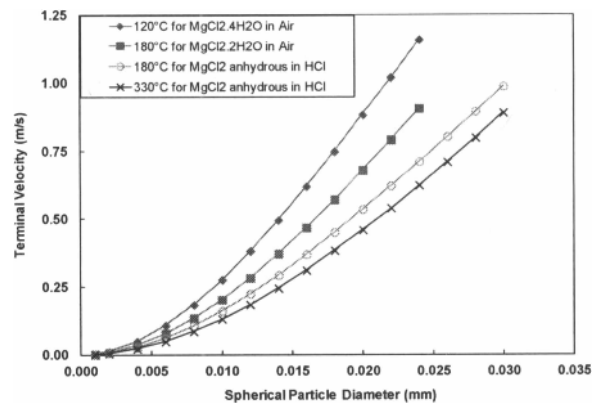


Figure 4. Terminal velocity for single particle carry-over

Knowledge of the minimum fluidizing velocity of prills and terminal velocity for the dust fraction sets the range of velocities at which the fluid bed dryers should be operated.

Prills Hot Air Drying

Heated air drying of the magnesium chloride can start with a solid (prill) feed or a solution (brine). Both processes are typically limited to the production of a dihydrate product ($MgCl_2 \cdot 2H_2O$), as the elevated temperatures required for complete drying can readily form an undesirable oxygenated by-product (Figure 1) [5].

Conventionally, the brine solution is first converted to hexahydrate prills. Prills produced from evaporation and free-fall crystallization of a 30 wt% $MgCl_2$ solution contain a mix of $MgCl_2$ hydrates, but hexahydrate ($MgCl_2 \cdot 6H_2O$) is predominant [4].

Dehydration of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ to the dihydrate ($2\text{H}_2\text{O}$) state can be done using direct contact with hot air or combustion gases, which also serves to fluidize the bed of solids in the dryer [5]. The fluidizing air can be heated through indirect heat transfer or direct flame action.

Direct flame hot gas generation can be achieved in a number of arrangements; however, two commonly utilized systems are the external burner and the in-duct burner. For low and mid-duty applications, the in-duct burners are becoming more popular, due to their simplicity and reasonable cost.

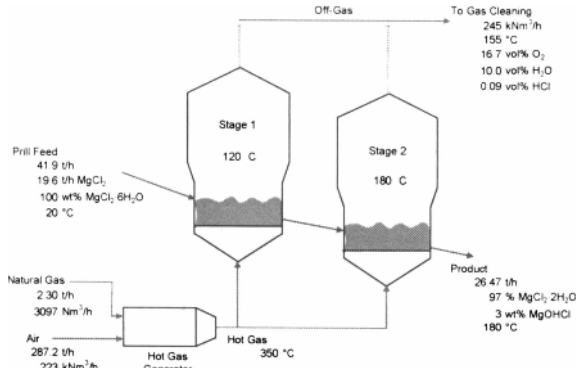
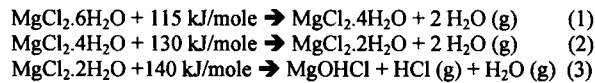


Figure 5. Prill drying for 40,000 t/yr Mg production

The purpose of hot air dryer is to remove moisture from the prills while minimizing oxidation, which produces the undesirable magnesium hydroxychloride. In the presence of water vapor and oxygen, the extent of hydroxychloride production increases rapidly as the moisture content of the prills decreases, likely due to the higher temperatures required to remove the lower hydrates.

The magnesium chloride air-drying is typically carried out in at least two stages, targeting two molecules of hydration-water removal in each stage, so that the drying temperatures can be selected to optimize drying and minimize oxidation. The typical reactions occurring in the dryers are shown below.



A quantitative analysis of the energy input to the fluid bed dryer train is presented, by calculating the mass and energy balance equations, using the METSIM® software platform for a two-stage system. Figure 3 shows the drying of 40 kt/a Mg contained in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ prills. For simplicity, it is assumed that only reaction 1 occurs in the first stage and goes to completion, while reaction 2 only occurs in the second stage and also goes to completion.

In addition, it is assumed that the oxidation reaction 3 only occurs in the second stage and produces 3% MgOHCl by weight. Typically, 2-4% MgOHCl occurs in this stage [7].

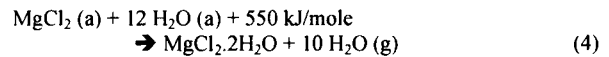
The bed temperature of stage 1 is 120°C, which is within the range of temperatures recommended to produce tetrahydrate

($4\text{H}_2\text{O}$), while the bed temperature for stage 2 is 180°C, which is within the range recommended to produce dihydrate ($2\text{H}_2\text{O}$) [7].

Brine Hot Air Drying

More recently, there has been an attempt for the magnesium chloride brine to be fed directly to a fluid bed (spray) dryer [2]. In this case, the air drying action is imparted on the thin liquid layers that are created on the seed solids (fluidized in the bed), rather than across the whole cross section of every particle.

The drying reaction (for approximately 30 wt% brine) can be approximated as follows:



Just as in the prills dryer, the hydrolysis reaction 3 can also occur in the spray dryer, producing from 1-5% MgOHCl [10].

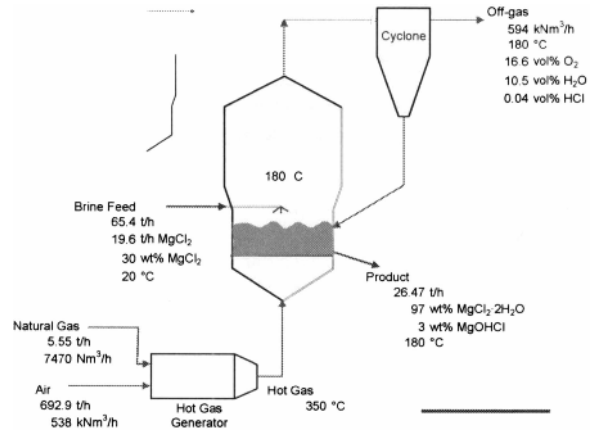


Figure 6. Brine drying for 40,000 t/yr Mg production

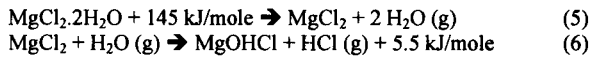
The feed brines should be limited to about 30% MgCl_2 by weight to avoid crystallization in the spray system. Using a similar mass and energy balance basis as the prills dryer, such a brine containing 40 kt/a Mg is modeled to dry in a spray fluid bed dryer at 180°C, for the production of the dihydrate. The calculated results are presented in Figure 4.

As expected, the natural gas usage increases almost proportionally to the water evaporation rate.

Prills Hot HCl Drying

Anhydrous magnesium chloride is normally required for the fused-salt electrolysis cells. As discussed above, drying in a hot air environment at a high temperature can partially oxidize the magnesium into an undesirable byproduct (hydroxychloride).

The key reactions are as follows. Compared to the dehydration reactions, the pyrohydrolysis reaction is slightly exothermic, but normally does not have a significant impact on the overall energy balance.



The production of hydroxychloride is influenced by the temperature and the gaseous environment.

Figure 1 (calculated using the HSC® software) shows how at the 200-300°C range where the dehydration occurs, the equilibrium state of the MgCl₂-H₂O-HCl system favors the formation of hydroxychloride, if the solid phase is simply heated in an inert environment, without any extra gaseous HCl addition.

The hydroxychloride formation can be prevented or reversed if excess HCl gas is provided to the dryer as the heating medium.

Figure 5 (also calculated using the HSC® software) shows how at the same 200-300°C range the equilibrium state is shifted towards the formation of anhydrous MgCl₂ if a high ratio of HCl to H₂O (in this example 10:1) is maintained in the gaseous phase.

As illustrated in Figure 1 and Figure 5, as the ratio of HCl to H₂O concentration decreases, the amount of hydroxychloride increases.

The thermodynamic example of Figure 5 is conducted at the constant temperature of 300°C, which corresponds to the end point temperature of the Figure 1, where only 10% of magnesium chloride survived pyro-hydrolysis, without the addition of gaseous HCl to the environment.

In case of Figure 5, the starting point is 100 moles of the pyro-hydrolysis product (MgOHCl), which is contacted with an increasing amount of gaseous HCl (up to 300 moles on the x-axis). The result is a chemical shift from the undesirable hydroxychloride to the desired anhydrous MgCl₂. Of course at the end of this example case, only 225 moles of HCl gas survive (on the y-axis) as the balance (75 moles) is consumed by MgCl₂ generation.

Therefore, the HCl dryer typically requires a large amount of hot HCl gas recycle, as energy source of drying and to create a large HCl over-pressure for the desired chemical equilibrium. However, only a small portion of the HCl reacts and requires a fresh make-up, if the incoming partially-dried magnesium chloride is only slightly pyro-hydrolyzed.

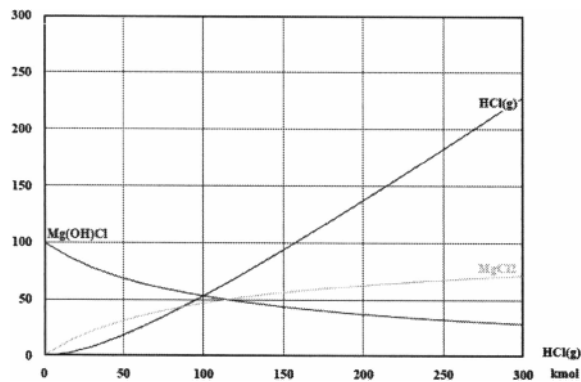


Figure 7. MgOHCl conversion at 300°C with excess HCl

To remedy that problem, the drying of dihydrate to anhydrous can be done inside a dryer fluidized with hot HCl gas. Maintaining a high concentration of HCl and low concentration of moisture drives the pyrohydrolysis reaction in reverse to produce magnesium chloride.

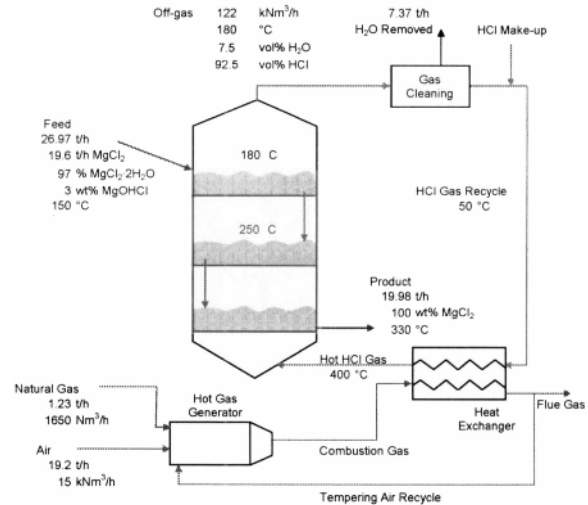
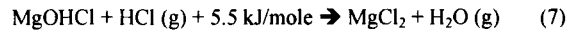


Figure 8. HCl dehydration for 40,000 t/yr Mg production

To maintain the HCl to H₂O ratio throughout the drying process, a multi-stage dryer with dry HCl gas contacting the feed counter-currently can be utilized [4].

A numerical example of the energy input to the HCl fluid bed dryer is provided, for a triple-stage stacked design. Mass and energy calculations results are provided in Figure 6.

Operating History

Based on the published information, at Norsk Hydro facilities in Bécancour, Canada, a MgCl₂ brine was produced from dolomite leaching. At Porsgrunn, Norway, in addition to dolomite leaching, the brine is also obtained through evaporation of MgCl₂ laden seawater [3]. The brines are evaporated and sprayed into a tower to produce a mixture of hexahydrate and tetrahydrate prills, which are then dried in an air fluid bed dryer, followed by an HCl fluid bed dryer to produce anhydrous prills with low MgO content ready for the IG Farben electrolysis cells [4].

Similarly, the State Research and Design Titanium Institute reports that air fluidized bed dryers are used to dehydrate carnallite (KCl.MgCl₂.6H₂O) feedstocks in Russia, Kazakhstan and Ukraine. It also reports use of HCl injection into a second stage of fluid bed drying as an alternative to electric chlorinators [8].

The Magnolia process involved spraying MgCl₂ brine produced by leaching serpentine ore, into a fluidized bed dryer to produce granules of mostly MgCl₂.2H₂O [9]. These granules were then

sent to their “super-chlorinator”, which contacted HCl gas with the granules to reduce MgO content, through melting the granules and removing the remaining moisture. The molten salt was then sent for electrolysis in Alcan-MPC cells [2].

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