Method of Producing a Naturally Purified Salt Product From Inorganic Salt Mixtures

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Abstract

Sodium chloride of high purity is produced via three major production methods including solution mining, rock mining, and solar salt production. Solar salt production utilizes sources including solution mining solid salt deposits, brine lakes/springs, and sea water. However, in addition to sodium chloride, salt sources often contain a significant proportion of other mineral constituents – including but not limited to magnesium, sulfate, and potassium. Unlike sodium chloride, the other minerals do not precipitate cleanly during solar evaporation and end up as a mixed salt. The utilization of these salts has long been of interest to many producers that manufacture sodium chloride. A brine of these mixed salts can concentrate to form a liquid fraction of predominantly magnesium chloride and a solid fraction of mixed salts. The solid fraction is a potential source of high value "natural" minerals such as magnesium sulfate, magnesium chloride, sodium chloride and to a minor extent, potassium based salts. A number of separation processes have been suggested for the recovery of pure minerals from mixed salts, but these are often too complicated. Recently, Cargill Inc. developed a process to produce naturally purified salts from mixed salts. This process can utilize streams from solar salt production to separate and recover USP Epsom Salt, sodium chloride, and magnesium chloride, while concentrating the potassium component which other processes can refine. The process utilizes the temperature dependence of the solubility of magnesium sulfate in aqueous magnesium chloride brine, the lack of solubility of other compounds in said brine, and the relative size of the solid components. Hot liquid magnesium chloride selectively dissolves magnesium sulfate from the mixed salts; the solution is then cooled resulting in precipitation of pure magnesium sulfate heptahydrate. The liquid magnesium chloride is then re-heated and recycled as the extraction liquor. Solid sodium chloride is recovered by size separation at > 80% purity, which can be recycled back into the solar salt pond system. Through this same step the potassium fraction is concentrated. Finally, this process yields liquid magnesium chloride, which is already a well-known commercial product sold for deicing and road stabilization. This process has the advantages of involving relatively few and simple unit operations (aqueous extraction, precipitation, filtration, and washing) which are routinely performed at many salt production sites, as well as operating at moderate temperatures from ambient to 120°F. It has the further advantage of using components naturally present in solar salt production, requiring no addition of compounds or chemicals.

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Introduction 1.0

Separating solid inorganic salt mixtures can be problematic due to overlying thermodynamic and physical properties. The mixed salts or solids considered contain single and double salts of varying concentrations, agglomerates, insoluble material and sometimes entrained brine. The development of the following method focused on the solubility of natural salts common to solar salt in magnesium chloride solutions in combination with additional common unit operations to separate mixed salt solids. Figure 1.0 is an example of a process flow diagram for this method.

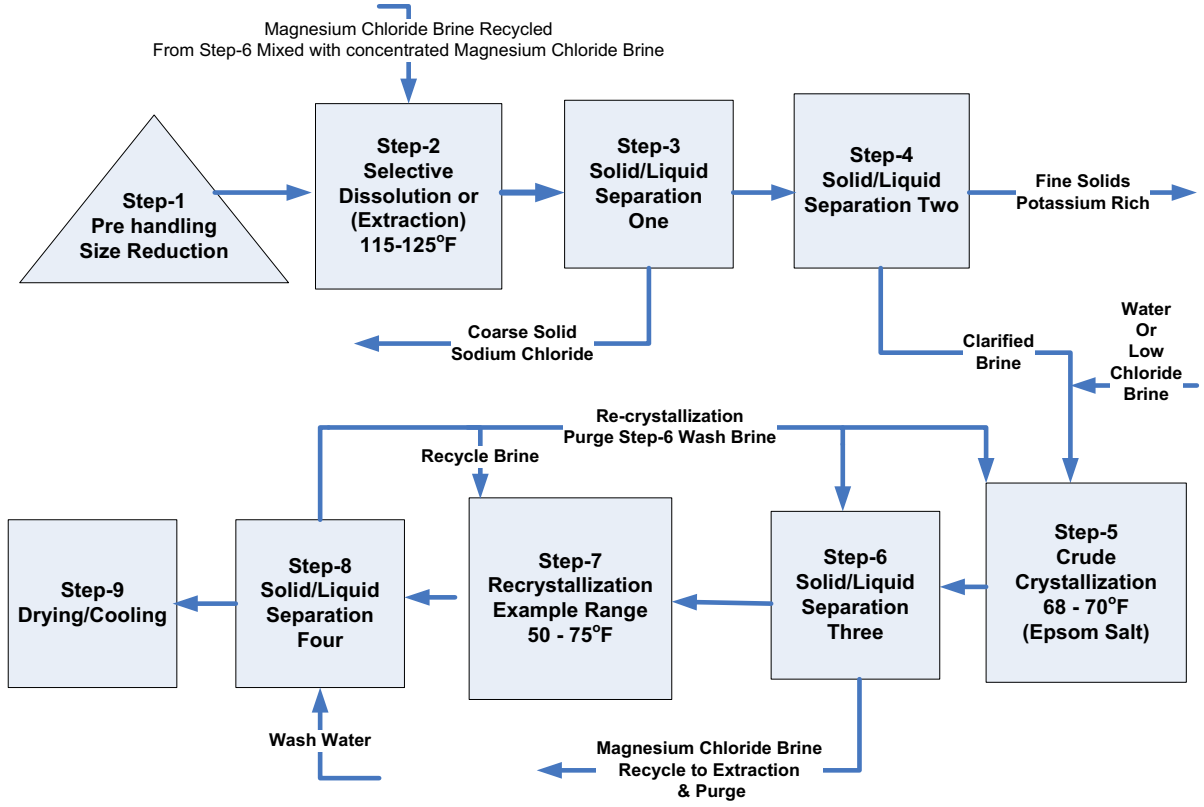

Figure 1.0 – Process flow diagram

Step One Preparation – The solids are collected and separated from entrained non-magnesium chloride brine. Brine containing a significant portion of dissolved solids as magnesium chloride may remain entrained in the solids. The solids are reduced in size to approximately minus one quarter inch to increase surface area and initiate the reduction of existing agglomerates.

Step Two Extraction – In one example, naturally produced 70°F magnesium chloride brine saturated in salts present in the mixed solids referred to in Step One is heated to 120°F. The magnesium chloride concentration ranges from 18 to 25 weight percent. The solids are added to the brine where they are mixed for approximately 10 – 15 minutes. The solids should be fully suspended during the mixing process, wherein magnesium sulfate will be dissolved by the magnesium chloride brine and the agglomerates will continue to decompose. The extraction step may be repeated to improve removal efficiency.

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Step Three Separation One – The coarse solids remaining are separated from the saturated magnesium chloride brine, which remains at or near 120°F. The coarse solids are primarily composed of sodium chloride, which can be re-dissolved and crystallized to produce high purity sodium chloride.

Step Four Separation Two – The fine solids remaining are separated from the saturated magnesium chloride brine, which remains at or near 120°F. The fine solids are primarily composed of a combination of salts including potassium, magnesium, chloride, sulfate, sodium, as single and double salts.

Step Five Crude Crystallization – The clarified magnesium chloride brine is fed to a continuous crystallization stage. The crystallizer is of cooling type, operating in one example between the temperature range of 60 to 75°F. Water removed during crystallization should be added back to the mother liquor to prevent the crystallization of unwanted salts.

Step Six Separation Three – The crude Epsom salt is separated from the mother liquor. Epsom salts or Magnesium sulfate heptahydrate, is formed in the crystallizer ranging between 94 to 97 weight percent as unwashed Epsom salt. The purity can be increased by washing. The separation is typically performed with a pusher type centrifuge. The mother liquor is recycled to the extraction step.

Step 7, 8, 9 Recrystallization – The crude Epsom is dissolved, recrystallized, dewatered and dried to produce a product meeting USP specifications. Key brines concentrated in Epsom salt are used as wash solution and recycled to improve yield.

Experimental 2.0

In order to validate the process described, laboratory bench testing was completed followed by the operation of a pilot plant. As a general indication of scale, the bench testing was carried out at a rate of 10,000 grams of solids fed per extraction batch and 100 to 200 ml/min were fed to the crude continuous crystallization stage. The bench scale testing was necessary to identify the required number of stages in the extraction step, identify the ratio of solids to liquid in extraction step, and size the pilot plant equipment. The bench scale tests were carried out using typical lab equipment with a few exceptions. Grinding (Step One) was performed by hand with a motor & pestle, the extraction (Step Two) was performed in a three gallon 316 stainless steel bucket which was hand mixed to assure good mixing. Separation One (Step Three) the separation of coarse solids was performed by hand with varying sieve sizes to identify the proper mesh for the separation. Separation Two (Step Four) was completed by decanting the saturated magnesium chloride brine from the settled fine material. The clarified brine was then cooled (Step Five) in a stirred four liter glass jar to crystallize the crude Epsom salt.

The primary goals for the pilot plant were to provide final process validation and necessary information to design a production facility. With that in mind, the pilot plant operation was designed with common pieces of process equipment. As a general indication of scale, the pilot plant extraction step was fed 600 to 900 Lbs per batch while the crystallizer was fed at a continuous rate of 0.5 to 1.0 gpm. The following is a detailed description of the pilot operation.

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Step One – Mixed salts sourced from numerous locations from a solar salt facility were the main feed to the pilot operation. These solids were pretreated in different manners such as by gravity draining, washing with water, as well as being collected from multiple locations; this variation tested the robustness of the process. The material was sized with a lump breaker, producing a product of approximately minus one quarter inch in size. Alternative technologies were also trialed for size reduction and found to be satisfactory, a single tiered roller mill with a corrugated roll and a horizontal shaft secondary impact crusher.

Figure 2.0 – Feed mixed

Step Two – The pilot extraction system consisted of two 300 gallon jacketed tanks with top mounted axial flow mixers. The jacketed tanks were heated and temperature controlled via low pressure steam. The solids were gravity fed into the first batch tank which contained magnesium chloride brine produced by the second stage extraction. Following the initial batch, a pusher centrifuge separated the magnesium chloride brine and the remaining coarse solids. The centrifuge contained a screen of in the 300 microns. Following the second stage, the coarse solids were collected and the magnesium chloride brine was transferred to the next extraction stage.

Figure 2.1 – Extraction Tank

Step Three – Following the second stage or final extraction the same pusher type centrifuge as above separated the coarse solids from the magnesium chloride brine.

Step Four –The saturated magnesium chloride brine would then pass through a solid bowl decanter centrifuge separating the fine solids.

Figure 2.2 Pilot plant pusher centrifuge loaded with a cake from extraction

Step Five – The clarified magnesium chloride brine was pumped into a draft tube vacuum cooled crystallizer with a liquid cooled condenser. All condensed liquid was recycled back into the crystallizer to prevent unwanted solids from forming. The crystallizer operated between 60 and 75°F. The continuous discharge was pumped into a holding tank where the slurry was maintained in suspension with an axial flow impeller.

Step Seven – Once the crude Epsom holding tank was full, a pusher type centrifuge with a screen in the range of 200 microns separated the crude Epsom salts from the mother liquor. The mother liquor was recycled back to the extraction stage.

Figure 2.3 Pilot plant pusher centrifuge loaded with crude Epsom salt from crystallizer

Steps Eight & Nine – The crude Epsom solids were recrystallized in the laboratory via a 4 liter jar crystallizer which was vacuum cooled.

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Results 3.0

The pilot plant described in the previous section was operated for five day campaigns to insure the process reached steady state operating conditions. During that period, four different feed solids were tested and key results obtained. Some of these results are presented in the following section.

Step One – A lump breaker was used to reduce the feed solids to the size ranges listed below in Tables 3.0.

Table 3.0 Example Average screen analyses for pilot plant solids feed after size reduction with Lump Breaker

4 mesh	8 mesh	12 mesh	20 mesh	30 mesh	50 mesh	PAN
9%	24%	32%	13%	9%	10%	5%

Step Two – The extraction step produces two solid streams and one liquid. The magnesium chloride brine utilized was naturally produced at a solar salt facility, via solar evaporation. The brine was concentrated and saturated in all components, when heated the brine selectively dissolved magnesium sulfate. A range of the magnesium chloride concentrations tested are displayed in Figure 3.0.

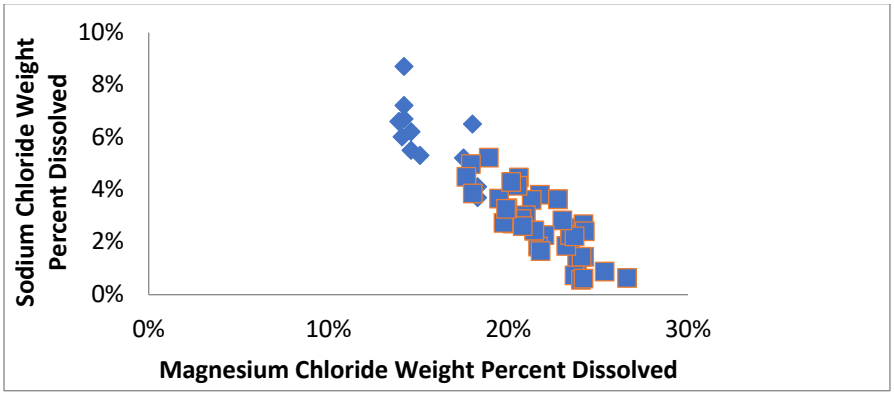

Figure 3.0 – Extraction brine post extraction. Sodium chloride saturation weight percent vs. weight percent of magnesium chloride anhydrous, at temperatures ranging from 115°F to 145°F.

Step 3 – Over seven trials, the coarse solids recovered following the extraction were found to be primarily composed of sodium chloride with a purity of 87 weight percent as anhydrous sodium and potassium chloride on average. The average composition of the solids are presented in Table 3.2.

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Table 3.2 – Average weekly pilot operation data.

Operation Example	Feed Solids Source	Percent of Feed solids Retained as Coarse Solids (NaCl Solids)	Purity of Recovered Coarse Solids (NaCl) Anhydrous	Weight Percent Feed Solids Discharged as (Fine Solids)
Example 1	Solid 1	39%	91%	21%
Example 2	Solid 2	44%	86%	31%
Example 3	Solid 3	37%	81%	14%
Example 4	Solid 3	34%	82%	14%
Example 5	Solid 4	33%	95%	21%

Step 4 – The fine solids recovered following the extraction step with the decanter centrifuge were composed of multiple compounds. The fine solids typically contain 15 weight percent entrained brine. Table 3.3 lists the purity of the solids minus the entrained brine.

Step 5 – The crude crystallization is fed the clarified brine from Step Four and cools the brine by use of vacuum evaporation. Water or dilute chloride brine composed primarily of magnesium sulfate is added for two reasons: replace all the water evaporated and prevent the sodium chloride from crystallizing. By adding the water or dilute chloride brine, the chlorides in the brine will remain under saturated preventing crystallization. The operating temperature of the crystallizer is set based on phase chemistry and is limited by the cooling technique and the boiling point rise of the magnesium chloride brine; the target operational temperature was 68°F. The magnesium chloride brine concentration produced from the extraction was approximately in the range of 18 to 19 weight percent magnesium chloride after the addition of the diluent. Higher concentrations would cause increased boiling point elevation and reduced yield, as well as possible formation of magnesium sulfate hexahydrate which is not desired due to processing complications with washing and breakage. Lower concentrations will approach phase chemistry regions where the formation of double salts are possible. Table 3.3 lists the purity of crude solids produced by the pilot plant operation. The dominant crystal size produced by the crude crystallizer was 200 to 350 micron

Table 3.3 – Four unwashed and washed example purities produce by pilot plant operation.

Example	Washed / Unwashed	MgSO4	MgCl2	KCl	NaCl	Water
Example 1 – A	Unwashed	49%	0.3%	0.0%	2.9%	48%
Example 1 – B	Washed	48%	0.0%	0.0%	3.4%	48%
Example 2 – A	Unwashed	45%	1.9%	0.0%	0.3%	52%
Example 2 – B	Washed	47%	0.7%	0.0%	0.6%	51%
Example 3 – A	Unwashed	46%	1.5%	0.0%	0.0%	52%
Example 3 – B	Washed	45%	1.9%	0.0%	0.0%	54%
Example 4 – A	Unwashed	44%	2.7%	0.0%	0.0%	55%
Example 4 – B	Washed	46%	1.1%	0.0%	0.0%	53%

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Step 6 – Separation of the crude magnesium sulfate from the mother liquor is necessary to eliminate impurities and increase the yield in the second crystallization. Lower impurities transferred into the second crystallization reduces the amount of mother liquor purged, increasing yield. The crude magnesium sulfate would be washed with brine purged from the second crystallization.

Steps 7 through 9 – In order to confirm the final recrystallized Epsom product would meet the required specifications, a study was performed in the laboratory. Crude solids were produced by the same techniques described with sufficient replicates to complete proper confidence analysis with the Student t-Tables. The solids were washed, dissolved and recrystallized but with added impurities in the mother liquor from lab grade chemicals. This was done to confirm the final purity of the Epsom salts operating at steady state conditions, where the mother liquor in the recrystallization stage is recycled and utilized to dissolve the crude solids with a minor purge.

The crude unwashed solids produced from Feed Solids 3 had a purity of 90.2 ± 8.4 weight percent as anhydrous magnesium sulfate with a confidence level of 95 percent. From Feed Solids 4, an average unwashed purity was calculated as 90.2 ± 1.2 weight percent as anhydrous magnesium sulfate with a confidence level of 90 percent. Refer to Table 3.5 for crude solids analyses.

The final Epsom product did meet USP grade specifications. Three recrystallization runs were performed with the purity falling between the required 99.0-100.5 weight percent for USP grade Epsom salt. The chlorides were below the 140-ppm specification, averaging 40 ppm. A 95 percent confidence level was calculated for the chlorides content (40 ± 20 ppm chlorides). Refer to Table 3.4 for the purity analyses of the USP grade Epsom salts produced and Table 3.7 for the particle size distributions.

Table 3.4 – Average of crude unwashed solids analysis for magnesium sulfate originating from Feed Solids 3 and 4 produced during recrystallization testing. Note the significant mass of impurities was in the brine phase as indicated by the weight percent magnesium chloride present.

$MgSO_4$	$MgCl_2$	KCl	NaCl	Water	Chemical Purity $MgSO_4$ Anhydrous
43.0%	3.7%	0.2%	1.0%	52.2%	89.8%

Table 3.5 – Average of recrystallized washed solids analysis for magnesium sulfate. Units are weight percent unless specified otherwise.

$MgSO_4$	$MgCl_2$	KCl	NaCl	Water	PPM Chlorides	Chemical Purity $MgSO_4$ Anhydrous
46.37%	0.00%	0.00%	0.00%	53.63%	40	99.0+

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Table 3.6 – Average screen analyses of recrystallized magnesium sulfate solids percent retained

U.S. Std Sieve	Example 1
12	3.0%
20	65.1%
30	20.9%
40	8.2%
50	2.3%
70	0.5%
Pan	0.03%

Conclusion 4.0

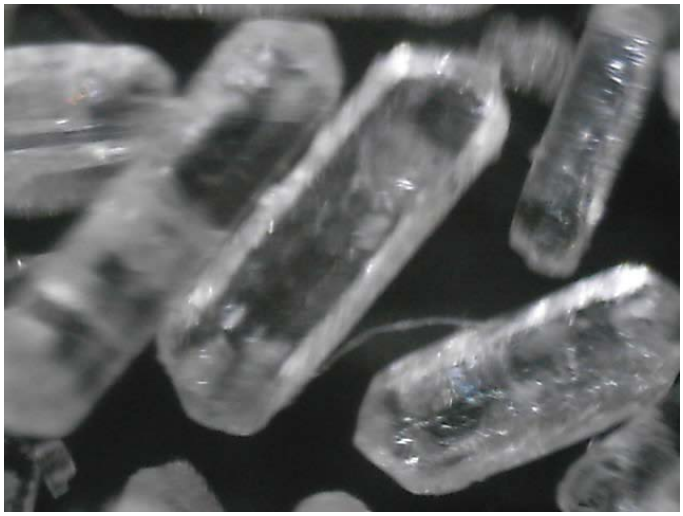

Figure 4.0 – Recrystallized Epsom Salt described in section 3.0

A novel process has been developed for the separation of mixed salts to common salt products. The process can be used to separate common mixed salts formed by solar evaporation into Epsom salt and sodium chloride. A USP grade Epsom salt was produced meeting the defined industry specifications. Also, a high purity sodium chloride solid, averaging 87 weight percent as sodium chloride, was recovered, which could be recombined into the brines of typical solar salt facility production brines. Two additional benefits include the freeing of entrained brine and the pre concentration of a secondary fines solids stream for further refinement. The process utilized the selectivity of natural brines as well as the natural habit of crystal size to separate the compounds. Due to the operational temperature ranges, there are fewer problems with the separation of impurities common to operations at temperatures ranging near 32°F. Also, due the nature of the extraction step very little water is required, which reduces the amount of brine created compared to alternative processes. This process was verified at the bench scale as well as with a pilot plant.

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