

Getting Hydrated Magnesium Chloride from Magnesium Chloride Solutions of Potassium Sulfate Fertilizers Production

Basystiuk Ya I^{1*} and Kostiv IY²

¹Precarpathian National University named after V. Stepanyuk 57, Shevchenko Str, 76025 Ivano-Frankivsk, Ukraine

²State Enterprise Scientific-Research Gallurgi Institute 5a, Fabrichna Str., 76000 Kalush, Ukraine

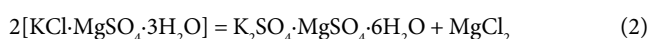
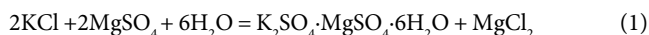
Abstract

This article presents the results of research of the process of cleaning magnesium chloride solution potash production from impurities of potassium chloride and sodium- cooled lighted solution after separation kainite and for the sulfates the evaporation to getting a suspension of finely dispersed sulfate salts (kieserite, langbeinite) in a concentrated solution of magnesium chloride, cooling, which leads to the crystallization of magnesium chloride. At the expense of differences in size, structure and energy of crystals of sulfate minerals and hydrated magnesium chloride different crystalline phases and separated by hydrodynamic method have been formed. The suspension of finely dispersed sulfate minerals with solution have been returned on crystallization kainite and thickened sediment hydrated magnesium chloride has been filtered on a centrifuge to produce a finished product.

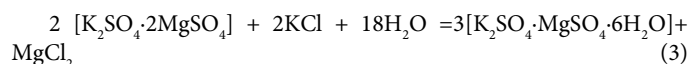
Keywords: Magnesium chloride solution; Evaporation; Crystallization; Kieserite; Kainite; Langbeinite; Potassium chloride; Magnesium chloride; Sodium chloride; Hydraulic separation

Introduction

Production of sulfate potassium-magnesium fertilizer is based on polymineral potassium ores which contain potassium chloride (sylvite KCl) and potassium-magnesium minerals (kainite $\text{KCl}\cdot\text{MgSO}_4\cdot 3\text{H}_2\text{O}$, langbeinite $\text{K}_2\text{SO}_4\cdot 2\text{MgSO}_4$, carnallite $\text{KCl}\cdot\text{MgCl}_2\cdot 6\text{H}_2\text{O}$) is associated with their dissolution in the circulation solutions and crystallization from a saturated solution of schoenite ($\text{K}_2\text{SO}_4\cdot\text{MgSO}_4\cdot 6\text{H}_2\text{O}$). These processes are accompanied by conversion reactions with formation of magnesium chloride and schoenite:



The hydration of hardly soluble langbeinite in the presence of potassium chloride with formation of magnesium chloride occurs by the reaction equation:



As a result of reaction is formed magnesium chloride, which reduces the rate of dissolution and solubility of minerals. That is why part of it in the form of excess schoenite solution separated from the sulfate cycle and thrown into the salt lakes [1], or to reduce loss of valuable components come into contact with a gypsum for binding potassium in synhenit ($\text{K}_2\text{SO}_4\cdot\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$) [2], or sent to evaporation [3] with the return salts which crystallized into the technological process.

In the known technologies on the first stage evaporation of excess schoenite solution to a concentration Mg^{2+} 4.5% in the liquid phase crystallized sodium chloride, in the second stage by evaporation to a concentration Mg^{2+} 6.3- 6.8% i SO_4^{2-} 1.8-3.5- mixture of sodium chloride, potassium chloride, kainite and other sulfate salts, which separated, filtered and called "man-made kainite" returned into the stage in sulfate cycle of dissolution polymineral potassium ore or into crystallization of schoenite. Evaporated solution purified without sulfates by solution of calcium chloride. Herewith gypsum is formed which separated and as waste throw out to the landfill waste. Without sulfates solution continues to evaporate in the third stage with crystallization of mixtures of chloride salts, which called the "artificial"

carnallite. Through its gypsum pollution and excess of calcium chloride in intercrystalline solution, increased gypsum incrustation on hot surfaces and formation of small crystals of salt to use it in the production of potassium sulfate fertilizers is difficult. Therefore, the "artificial" carnallite not find using in the production of potassium fertilizers and it also thrown in the waste. With gypsum and "artificial" carnallite lost 10% potassium and sulfates of their quantity in ore [4].

The solution after evaporation is used for the synthesis of carnallite - raw materials for the production of magnesium metal by electrolysis [5], or continued to evaporate under the influence of open flame in apparatuses "immersed" burning to a concentration of 43-44% MgCl_2 and the resulting melt temperature of 408-411 K cooled in the refrigerator drum to produce scale-like six-hydrated magnesium chloride [6]. In the research and industrial conditions magnesium chloride solution after separation "artificial" carnallite evaporated in the apparatuses "immersed" burning to a concentration 39% of MgCl_2 and temperature of degree of evaporation (α) at different temperatures cooled in the crystallizer to a temperature of 328-333 K. Hydrated magnesium chloride which crystallized is filtered as a finished product containing (wt.%): 43-44 MgCl_2 , 0.3 K^+ + Na^+ , 0.47 Ca^{2+} , 0.09 SO_4^{2-} . The filtrate was returned to evaporation.

By a similar multistage scheme with intermediate separated of chloride and sulfate salts processing solutions of leach kieserite-carnallite ore, chloride-sulfate brines of salt lakes. After saturation of magnesium chloride circulating salts and evaporation with the release of sodium chloride is subjected to cooling to a temperature of 268-278 K with evolution epsomite ($\text{MgSO}_4\cdot 7\text{H}_2\text{O}$), next evaporated and cooled for crystallization carnallite and sodium chloride, which is obtained after filtering magnesium chloride solution with concentration 27.6-

*Corresponding author: Basystiuk Ya I, Precarpathian National University named after V. Stepanyuk 57, Shevchenko Str, 76025 Ivano-Frankivsk, Ukraine, E-mail: yaroslava_artus@ukr.net

Received March 18, 2016; Accepted April 19, 2016; Published April 25, 2016

Citation: Basystiuk YI, Kostiv IY (2016) Getting Hydrated Magnesium Chloride from Magnesium Chloride Solutions of Potassium Sulfate Fertilizers Production. J Chem Eng Process Technol 7: 291. doi:10.4172/2157-7048.1000291

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34.3% $MgCl_2$, 1.4-1.6% SO_4^{2-} , 0.6-2.6% (NaCl+KCl) [7]. Sulfate salts which are crystallized in the form of kieserite [8] or langbeinite [9-11], which are separated after evaporation of the solution at a temperature of 408 K to a concentration of 34% $MgCl_2$. Cleaning the magnesium chloride solution of salts of potassium and sodium is carried out by evaporation, and of sulfates - without sulfates by solution of calcium chloride [12]. But apart to the cost of the reagent during purifying without sulfates happens magnesium chloride solution dilution with water. Binding of sulfate ions in gypsum during purifying without sulfates of solution causes crystallization of free potassium chloride at the stage of crystallization of kainite. Crystals of potassium chloride in size and shape similar to sodium chloride crystals so kainite hard cleaned of impurities sodium chloride, which is why at the stage of crystallization of schoenite occurs additional pollution of sulfate fertilizers by chlorides. The absence of production with utilization of magnesium chloride solution is the main obstacle to the creation of a powerful production without chloride potassium and potassium-magnesium fertilizers based on potassium polymineral raw materials of Carpathians.

Solution of magnesium chloride from enterprises with processing polymineral potassium salts as a commodity product has limited use because of low concentration (27-32%) $MgCl_2$. It is used in the production of magnesium and refractories, magnesium metal and magnesium cement, so separating it in crystalline form presents practical interest because previous without sulfates solution causes costs of calcium chloride and loss of potassium and sulfates. Magnesium chloride as a six water crystalline hydrate exists within temperatures 269.75-389.95 K [13]. There aren't other crystalline forms in this temperature range [14].

Cleaning the magnesium chloride solution is carried out without reagent by means of their thermal evaporation to a concentration of 38-41% $MgCl_2$ at boiling point with subsequent sedimentation of crystals kieserite $MgSO_4 \cdot H_2O$, halite NaCl, carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$. The liquid phase is cooled to 293-323K with crystallization bishofite [15]. It is known that with increasing temperature chlorides salting sulfates, but with decreasing-sulfates salting chlorides. With approaching the boiling point and with increasing concentrations of chlorides field crystallization of langbeinite increases [16]. Therefore, for the cleaning from sodium chloride and carnallite magnesium chloride solution is evaporated to a concentration which is responsible to the saturation $MgCl_2$ at a temperature of 298-323 K, cooled solution that was evaporated, filtered chloride crystals and repeatedly evaporated filtrate at a temperature of 383-408 K to a concentration of 36-42% $MgCl_2$ separating crystals of sulfates, cool purified solution is filtered and washed sediment bishofite with content 45.2-45.4% $MgCl_2$; 0.4-0.5% KCl + NaCl; less 0.005% $MgSO_4$ [17]. Method is difficult in hardware design, energy-intensive, needs two stages of evaporation, cooling and filtration. Separation of fine sediment kieserite from hot and viscous solution is a very slow process.

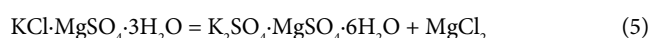
Purifying from chlorides is carried out by dissolving $MgCl_2$ with the intermediate precipitate the liquid phase is evaporated under vacuum at a temperature of 353 K for separation sediment carnallite and sodium chloride, which is returned to the process, and then a temperature of 393 K - for crystallization kieserite. Finely dispersed suspension processing by solution of polyelectrolyte for sedimentation finely dispersed kieserite phase, the precipitate is filtered and cooled liquid phase, separating a mixture of carnallite and sodium chloride, which is returned to the process, get the magnesium chloride solution with a concentration 36.6% $MgCl_2$, 0.58% (NaCl +KCl), 1.66% $MgSO_4$ [18]. The resulting solution of magnesium chloride evaporated under vacuum, cooled and filtered. Obtained crystals of bischofite

composition by weight.%. 46.2 $MgCl_2$, 0.69% (NaCl +KCl), 0.01 SO_4^{2-} and filtrate of the composition, by weight.%. 33.83% $MgCl_2$, 0.52% (NaCl +KCl), 1.35% $MgSO_4$, which is returned to the process. Consequently crystallization of hydrated magnesium chloride in known methods is carried from lighted magnesium chloride solution after separation from him coarse grained chloride salts of sodium and potassium and also finely dispersed - kieserite or langbeinite.

Return sulfate salts in the crystallization process of artificial kainite leads to the binding of potassium chloride in kainite by the reaction:



Kainite as finely dispersed solid phase is easily separated from sodium chloride by hydraulic separation. At the stage of conversion schoenite is crystallized without impurities chlorides by the reaction:



Experimental Section

Evaporation magnesium chloride solution at the stage of crystallization kainite accompanied by an increase in the concentration of $MgCl_2$ liquid phase to 25-27% and decrease of sulfate ions to 1.8-3.5%. The concentration of SO_4^{2-} ions in solution evaporated decreases with increasing temperature evaporation within 323-383 K [19]. After reaching in the liquid phase at 30% concentration of $MgCl_2$ concentration of sulfate ions begins to slowly grow [20].

Therefore evaporation of solutions at the stage of crystallization kainite advisable to carry out with return of concentrated solutions for maintaining in evaporators concentration of solid phase in suspension at a concentration of 30-35% to 1.8% SO_4^{2-} , separating with hot suspension sediment of artificial kainite which returned to the process producing of potassium sulfate or potassium-magnesium, and lighted solution to cool for crystallization of potassium chloride, sodium chloride and carnallite, separate them and return to the stage of evaporation and crystallization artificial kainite. The cooled magnesium chloride solution with a concentration of $MgCl_2$ to 32% is used for obtaining of crystalline bischofite. For this it is evaporated to a concentration 38-39% of $MgCl_2$ to give a finely dispersed suspension sulfate salts (kieserite, langbeinite) in a concentrated solution of magnesium chloride. Her cooling results in crystallization of crystalline magnesium chloride. At the expense of differences in size, structure and energy of crystals of sulfate minerals and hydrated magnesium chloride different crystalline phases and separated by hydrodynamic method have been formed. The suspension of finely dispersed sulfate minerals in a concentrated solution of magnesium chloride have been returned on crystallization kainite and thickened sediment hydrated magnesium chloride has been filtered on a centrifuge to produce a finished product, which meets the requirements the state standard.

For research prepared magnesium chloride solution composition (wt.%): K^+ 0.72; Mg^{2+} 7.07; Na^+ 0.64; Cl⁻ 21.42; SO_4^{2-} 1.54; H_2O 68.61, which was diluted with water to prevent crystallization of salts. We took 2 dm³ of diluted solution in isothermal conditions in three of the throat round bottom flask under constant mixing of paddle mixer under vacuum for constant mixing and a temperature of 353 ± 273.65 K evaporated predetermined amount of water that were collected in the receiver graded condensate. Attitude the mass of condensate including water on dilution to the mass of the initial concentrated solution marked as the degree of evaporation. After reaching a given degree evaporation was stopped, the vacuum is turned off, the sample were taken for filtering suspension using Buchner funnel fixed on Bunsen flask under vacuum. The solid phase was filtered an additional from

solution between crystal by 5 min on a laboratory centrifuge by rotor speed of 5000 rev / min. Necessity of additional excretion of liquid phase from the sediment explained by the fact that the solid phase contains theoretically 11.96% Mg^{2+} , and in the liquid phase during evaporation Mg^{2+} concentration reaches 10.00%. The suspension in the flask by constant mixing cooled to a predetermined temperature and under isothermal conditions mixed for 30 minutes. Sampling suspension for filtering and continue cooling suspension to a temperature of 293 K with an intermediate sampling by every 283 K samples suspension for analysis. The obtained liquid and solid phases were analyzed using tetraphenylborate weight method (for K^+ ions), complexometric method (for Mg^{2+} and Ca^{2+} ions), mercurimetry (for Cl^- ions), weight method (for SO_4^{2-} ions), as difference between the sum of equivalents of anions and cations (for Na^+ ions), H_2O - by difference. A result of analysis in a special program material balances were calculated and determined the degree of excretion of components in the solid phase.

Results and Discussion

As can be seen from the data (Figure 1) in the liquid phase during the entire period evaporation and cooling the concentration of ions SO_4^{2-} increases. Concentration of K^+ in the evaporation and cooling gradually decreases and as shown in Figure 2, at a temperature of 353 K allocated in solid phase of K^+ 57%, and at a temperature of 473 K and the degree of evaporation 24%-92%. Thus, evaporation of magnesium chloride solution to the degree of evaporation to 24%, which corresponds to the concentration of Mg^{2+} in terms of $MgCl_2$ 36.08%, and cooled to 293-303 K in solid phase crystallizes over 90% impurities of potassium salt.

The resulting suspension was cooled to a temperature of 293 K for crystallization chloride salts, which separated from the liquid phase and filtered. Lighted solution continued to evaporate at a temperature of 383 K for crystallization of finely dispersed kieserite and langbeinite. Finely dispersed suspension was cooled to a temperature of 293 K by constant mixing. Herewith hydrated magnesium chloride is crystallized. After cooling, the suspension separated, visually observed the formation of two layers of sediment: top- finely dispersed sulfate salts and bottom - with larger size crystals - hydrated magnesium chloride. The upper part of the suspension of finely dispersed crystals was decanted and filtered, and the bottom layer of sediment was also filtered under vacuum. The solid phase additionally filtered for 5 minutes on a laboratory centrifuge for rotor speed of 5000 rev/min. The obtained results are shown in Table 1 and Figure 3.

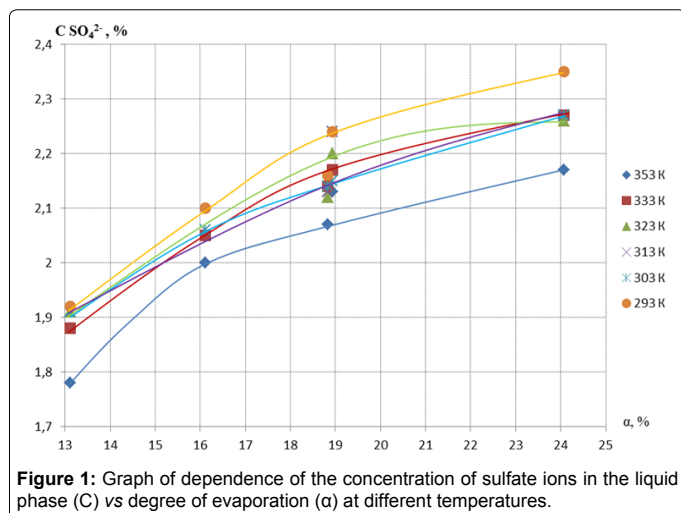


Figure 1: Graph of dependence of the concentration of sulfate ions in the liquid phase (C) vs degree of evaporation (α) at different temperatures.

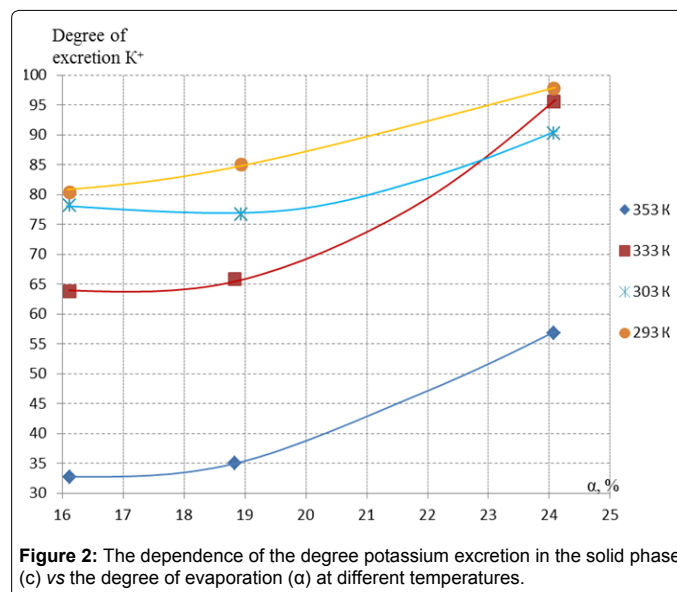


Figure 2: The dependence of the degree potassium excretion in the solid phase (c) vs the degree of evaporation (α) at different temperatures.

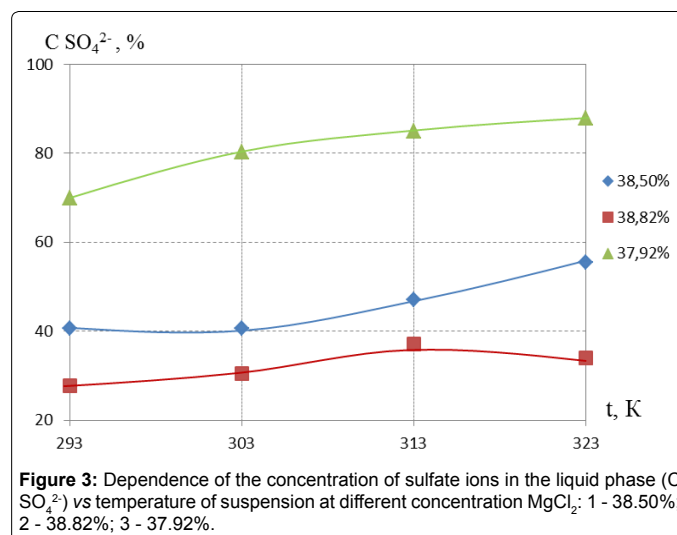


Figure 3: Dependence of the concentration of sulfate ions in the liquid phase ($C SO_4^{2-}$, %) vs temperature of suspension at different concentration $MgCl_2$: 1 - 38.50%; 2 - 38.82%; 3 - 37.92%.

As seen from the data obtained on Figure 3, the solution evaporated to the degree of evaporation of 8.6%, corresponding to 9.68% Mg^{2+} or calculated on $MgCl_2$ 37.92%, containing 3.57% SO_4^{2-} and during the cooling to a temperature of 313 K crystallized small amount of salt. At 293 K concentration of Mg^{2+} decreases to only 9.54% or 37.37% $MgCl_2$, and SO_4^{2-} to 3.47%. In the liquid phase is in this case 69.9% SO_4^{2-} . In the top phase of suspension is 27.3% SO_4^{2-} . In the bottom phase is 14.5% Mg^{2+} and 2.8% SO_4^{2-} . Don't wash solid phase containing 0.78-0.82% SO_4^{2-} . Consequently the degree of evaporation of a solution of 8.6% is not enough for a singly separate of sulfate salts and bischofite.

In the evaporated solution to the degree of evaporation 11.3%, which corresponds to 38.50% $MgCl_2$, concentration of SO_4^{2-} decreased to 3.32% and during the cooling to 293 K decreases only to 2.46%. Concentration of Mg^{2+} decreases only to 9.56%, which corresponds to 37.45% $MgCl_2$. Contents in the top phase at temperature 293 K is: Mg^{2+} - 20.1%, and SO_4^{2-} - 48.7%, and in the bottom phase- respectively 24.7 and 10.1%. In the filtrate is 55.2% Mg^{2+} and 40.6% SO_4^{2-} . Don't wash solid phase containing 0.78-1.80% SO_4^{2-} .

In the evaporated solution to the degree of evaporation 12.8%, which corresponds to 38.82% $MgCl_2$, concentration of SO_4^{2-} decreased

C %	t, K	Contents of components in layers of suspension, %					
		Lower layer		Top layer		Filtrate	
		Mg ²⁺	SO ₄ ²⁻	Mg ²⁺	SO ₄ ²⁻	Mg ²⁺	SO ₄ ²⁻
37.9	303	14.5	2.6	10.7	17.1	74.8	80.3
	293	14.5	2.8	17.8	27.3	67.7	69.9
38.5	323	19.8	3.7	17.5	40.8	62.7	55.5
	313	23.1	9.1	16.4	43.8	60.5	47.1
	303	26.1	9.7	20.7	50.6	53.2	40.7
	293	24.7	10.7	20.1	48.7	55.2	40.6
38.8	323	5.7	1.9	13.3	64.1	75.0	34.0
	313	6.3	1.8	17.7	60.9	75.9	37.2
	303	20.4	7.5	19.1	62.0	60.5	30.5
	293	27.0	13.4	18.3	57.9	53.7	27.7

Table 1: Dependence of contents components in the top and lower layers of thickened suspension from concentration (C) MgCl₂ in evaporated solution and temperature (t°C).

to 1.92% and during the cooling to 293 K decreases only to 1.80%. Concentration of Mg²⁺ decreases only to 9.55%, which corresponds to 37.41% MgCl₂. Contents in the top phase at temperature 293 K is: Mg²⁺ - 18.3% and SO₄²⁻ - 49.8%, and in the bottom phase- respectively 28.0 and 13.4%. In the filtrate is 53.7% Mg²⁺ and 28.7% SO₄²⁻. The higher degree of evaporation achieved fails because suspension is thickened. Consequently it is expedient evaporated to a concentration of not more than 38.8% MgCl₂. In the case of thickening suspension it can be diluted by solution after filtering of bischofite. Don't wash solid phase containing 1.22-1.95% SO₄²⁻. From don't wash solid phase prepared saturated aqueous solution, which was washed sediment on the filter and additionally filtered in a centrifuge. As a result obtained sediment containing 11.62% Mg²⁺ i 0.52% SO₄²⁻.

Consequently as a result of the research for the first time presents the possibility of separation from magnesium chloride solution by processing of polymineral potassium ores in solid phase coarse grained potassium and sodium chloride also carnallite and finely dispersed phases of sulfate salts. Coarse grained phase of chloride salt can be easily separated by precipitating and decanting. Finely dispersed phase of sulfate salt during cooling is not the center of crystallization hydrated magnesium chloride due to different energy of crystal and their structure. Therefore, after cooling and crystallisation hydrated magnesium chloride, decanting the suspension and filtration its, finely dispersed sulfate phase is separated along with concentrated magnesium chloride solution, and after additional washing precipitate by lighted solution of magnesium chloride and filtration contains about 0.5% SO₄²⁻ and as a technical bischofite can be used in the industry. Also sulfates can be completely return them to the production of potassium sulfate and potassium-magnesium and provide a comprehensive processing of polymineral potassium ores production in the absence of utilization of magnesium chloride wastes.

Return sulfates on stage of crystallization kainite results to the binding of potassium chloride in finely dispersed kainite, which is easily separated from the potassium and sodium chloride by hydroseseparation, resulting in sulfate fertilizer are less polluted by impurities chlorides.

We have developed the method which can be used during the processing of polluted by sulfate salts solutions of natural bischofite, polymineral Carpathian potassium ores and wastes processing of langbeinite ores of USA and kieserite ores of Germany.

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