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TECHNOLOGY OF PRODUCTION OF NaCl AND KCl USING THE METHOD OF CRYSTALLIZATION

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RESUME

Le minerai de sylvinite de la région de Kama est constitué de 26-30 % KCl, 67-70 % NaCl et 3-5 % d'insolubles ; la méthode de recristallisation a servi à produire la potasse. Les produits de queue sont des sous-produits stockés comme déchets. Le chlorure de sodium à 96-97 % NaCl de pureté est obtenu à partir de ces produits de queue, avec des dépenses élevées en chaleur (0,6-0,7 Gcal/t de sel). La consommation de chaleur est abaissée jusqu'à 0,4 Gcal/t de NaCl si KCl et NaCl sont produits en même temps, utilisant la même solution pour les 2 stades de cristallisation. Dans l'intervalle de température 0-100°C, il y a une faible différence de solubilité de NaCl. Ainsi le volume de solution en circulation pour une quantité de sel sera élevé (3 % de NaCl pourront être retirés de la même quantité refroidie). La pureté du NaCl produit ne peut être inférieure à 99,7 % NaCl. L'usine de Solikamsk Gallurgia a utilisé la méthode de traitement complexe de sylvinite pour produire NaCl et KCl dans le même procédé.

L'idée de ce procédé est la suivante : la sylvinite est dissoute dans la solution circulante préchauffée dans l'intervalle de température 95-100°C. La teneur en KCl de la solution se situe entre 45-70 % et tout le NaCl. La solution est refroidie dans un appareil sous vide à plusieurs étages d'abord jusqu'à 45-70°C dans la première partie de la cristallisation sous vide, seul NaCl cristallisant. Le produit en suspension (cristaux de NaCl) est séparé, la solution restante étant encore refroidie dans la deuxième partie de l'appareil de cristallisation sous vide jusqu'à 20-27°C, seul KCl cristallisant. Les cristaux de KCl sont séparés et la solution restante, préchauffée jusqu'à 110-118°C, est renvoyée à la solution de sylvinite. Les produits finaux sont NaCl, avec une teneur d'au moins 98,4 % NaCl et KCl avec une teneur de 95-98 % KCl. Le rendement de production de KCl et NaCl en un cycle dans la méthode de cristallisation dépasse de 2,7-3 fois celui de NaCl dans le cas de la production de NaCl avec la méthode de cristallisation, ce qui entraîne une baisse des prix de revient. La quantité de produits de queue et les pertes d'argile diminuent de 5 %.



Silvinite from the Kama region consists of 28-30% of KCl, 67-70% NaCl and 3-5% of non-soluble components and are separated by crystallization. KCl is dissolved out while the galit ore which does not is put in the underground storage as a waste. Galit consists of 96-97% NaCl.

By using mechanical treatment and eluding the KCl it is possible to get the common salt with 97-98% NaCl content, but that salt will have low organic matter. It is possible to get high quality salt by full crystallization of the galit waste. For the salt crystallization it is necessary to have the evaporation equipment that leads to the large heat consumption (0.6-0.7 Gcal/ton of salt). In common salt production by evaporation of solution during the crystallization of KCl the usage of secondary vapor from the preheating of the solution entering the silvinite solution reduces the heat consumption to 0.4 Gcal/ton of salt.

Both methods of evaporation demand high heat consumption for the evaporation equipment. At present, common salt of high quality is produced in the 4th Kall plant (Berezniki) using the method of crystallization of the rock salt obtained in the mine. The rock salt is dissolved at a temperature of 90°C, that is then cooled in seven vacuum crystallization 7 units. This salt content is not less than 99.7% of NaCl. This method of common salt production could be used for galit wastes during silvinite treatment. But it is necessary to point out that common salt production with this method has one big shortcoming, that is: because of the small difference in solution solubility of NaCl at the temperature of 90-100°C and 20-30°C, eluding the salt from the same cooled quantity is about 3%. So the circulation volume of solution for one unit of salt mass will have to be high. As the circulating solution is preheated every time from 20-30°C up to 110-115°C, the heat consumption will be large too. As a comparison, silvinite treatment by the classical method, the KCl eluded during solution cooling consists 8-9%, and the heat consumption for 1 ton of KCl is 0.45-0.5 Gcal. Then, with the NaCl (3%) and KCl (8-9%) elution combined it is obvious that heat consumption for 1 ton of salt will be 2.7-3 times more than for 1 ton of KCl, that means, 1.2-1.5 Gcal. Similarly, the other production expenditures for 1 ton of salt will be 2.7-3 times more too, in comparison with KCl production, using the silvinite.

Solikamsk Gallurgia factory uses the other method of common salt production, the method of complex silvinite treatment of salt and KCl in the same circuit technological cycle. This method was developed by the Russian Science Research Institute of Gallurgia (author patent N°1837588, 1990, given to Savvatin J.N. and Slobodkinoy G.L.).

The method is as follows: silvinite is dissolved in the preheated recycled solution, producing a solution in the temperature range of 95-100°C and full NaCl content, but with KCl eluding stage at 45-70% (instead of 95 % for KCl production). The solution is cooled in multi-stage vacuum equipment initially at 45-70°C in the first part of vacuum crystallization with the crystallization only of NaCl. From the suspension the hard substance is separated from the crystals of NaCl and the liquid substance. As the solution is near to KCl crystallization point, the cooling is continued in the second part of vacuum crystallization equipment between 20-27°C producing only KCl crystallization.

The KCl crystals are removed from the suspension and the rest of solution after 110-118°C preheating returns to silvinite solution. The extracted NaCl crystals are washed with water on filter, dried and the common salt of the highest quality, having the content not less, then 98.4% of NaCl is ready. The KCl crystals are dried and used as fertilizers and chemicals. Its KCl content is 95-98% of KCl. This method allows the production of varying ratios of common salt and KCl content, by varying the solution content before cooling 45-70% and the first cooling of solution at the limit 40-70°C.

With the saturation stage at 45% and first cooling temperature 40°C, the extraction of NaCl from the solution will be at maximum. The mass quantity of NaCl and KCl will be equal to mass quantity of them in the silvinite ore, that means, galit and sylvinite ores will be totally crystallized in two types of products. While saturation stage of KCl in the solution of 70% and it is first cooling up to 70%, the NaCl and KCl content will be 0.5, that means the common salt eluded will be 33% and KCl 67%.

At Solikamsk Gallurgia factory the saturation stage in KCl is 57% and the first solution cooling in the first part of vacuum crystallization equipment is up to 55°C, with a further solution cooling in the second part up to 20-25°C. With this data, the mass quantity of common salt and KCl is approximately 1:1, that means the equal quantity of product is produced. With different quantities of NaCl and KCl, the total production out of the same mass of cooled solution is equal to the KCl production while silvinite treatment is only for KCl, i.e. 8-9%. This production using rock-salt and galit wastes is 2.7-3 times higher than the common salt production. By using the method of table salt and KCl production from silvinite, the expenditure is lower in comparison with the method of KCl production only.

For example, at a saturation stage of 57% in production of equal product quantity, the ore input in the first case is 2.3 tons for 1 ton of end product. The quantity of NaCl and KCl produced will be equal to the composition in the resource ore, that means the galit and silvinite ores will be totally crystallized into two types of products. With the saturation stage of KCl in the solution of 70% and its first cooling up to 70°C, the NaCl and KCl content will be 0.5, that means the common salt eluded will be 33% and KCl 67%.

Except for that, using the method of common salt and KCl production out of silvinite, the expenditure decreases in comparison with the method for the production of KCl alone. For example, with the saturation stage of 57% in production of equal product quantity, the ore input in the first case is 2,3 tons for 1 ton of end product, but in the second case is 5,1 tons of ore input to 1 ton of KCl.

Similarly, by using the new method of a solution of 1/3 of galit out of silvinite, and further crystallization of NaCl, the grains of silvinite and galit in the solution process open more, and KCl and galit expenditures are much lower. By lowering the saturation stage (in KCl) of the cooling solution from 95% according the old technology to 57%, the KCl concentration in liquid stage of galit waste and clay slag according to the new technology is lowered from 332 g/1000g H₂O to as low as 200 g/1000g H₂O, thus lower to the availability of KCl in the liquid stage of galit waste and slag at 332:200 or 1,66 times. Further, the losses from lowered galit waste are from 6% or more to 2.6%. By limiting the losses, KCl extraction out of silvinite increases for 5-6%.

The new method, used in Solikamsk Gallurgia factory gives the possibility to increase in 2.7-3 times the extraction of NaCl and KCl out of solution in comparison with a method of only NaCl production, using the galit wastes and rock salt, that leads to lowering of production expenditures (power, heat in 2.7-3 times). So taking into consideration the above fact, the new technology of silvinite treatment leads to lower production costs of NaCl and KCl in comparison to the new technology of NaCl production alone out of galit waste or rock salt production using the crystallization method.

Picture 1 shows the production scheme of NaCl using the new method of multi-stage crystallization.

Picture 2 shows the change of KCl and NaCl concentration with solution temperature. The process shown in the diagram is the salt solution solubility in the system $\text{KCl-NaCl-MgCl}_2\text{-H}_2\text{O}$. In the sylvinite ore, the MgCl_2 content is not high (0.15-0.2%), that is why it is not taken into consideration. The technological processes used are shown in Picture 1, while the details of process are given in Picture 2. From the carriages, the sylvinite passes into solvent (pos. 105-1) which is where the solvent (pos. 105-2) passes to the unsaturated KCl solution. The galit and the rest of sylvinite with fully solubilized KCl passes into the solvent (pos. 105-3) with the help of an elevator. There the cold solution given for galit wastes washes out of tank (pos. 240) and filtering to another tank (pos. 113). Galit wastes with water content of 12-13% are separated from the solvent (pos. 105-3) and passes to the filter (pos. 109-1), where it is further washed with water. The wet galit waste passes to the NaCl production store. The waste is used for filling the empty places of Kali mine.

The process of sylvinite dissolution is shown in Picture 2. The point « d » shows the saturation stage of the solution, at 57% solution cooling, and point « b » is the content of solution when it passes with a sylvinite solution into the solvent (pos. 105-2). In short, the sylvinite solution treatment according the new technology is analogous to the process of dissolution. From the solvent (pos. 105-1), the hot solution with parts of salt and clay slag goes into settlement tanks (pos. 118), where it settles down as salt slag, then further transfer to another settlement tank (pos. 121-1), where the clay slame settles down. The salt slag substance is pumped to the (pos. 105-2) and the clay slame substance is pumped to the waste stock.

The lightened solution with a temperature of 95-100°C from the settlement tank (pos. 121-1) is passed to the tank (pos. 201), then to the 1st vacuum crystallizer (pos. 202) then the solution passes the 2, 3 and 4 vacuum crystallizers. These crystallizers have a total of 9 stages, with the solution (evaporation + vacuum) coolers from 95-100°C up to 60°C crystallizing only NaCl. The process of concentration of KCl and NaCl change while cooling is shown with line « de ». In the point « E », the solution is near the saturation in KCl, but does not reach it. From the stage 9 the developed crystal suspension of NaCl is passed into the tank (pos. 231-A), then is pumped to the settlement tank (pos. 118), then the solution with fine suspended crystals is passed to the tank (pos. 121-2). In this settlement tank the solution is additionally cooled to a temperature of 55°C. In the tanks the crystals of NaCl are settled, the suspension of them (through the tank K-9) passes to the filter (109-2). Filtration, passing the hard stage through the tank pos. 113-a returns to the settlement tank (pos. 121-2), but the wet NaCl is passed from the filter to the drying stage in the apparatus pos. 906. The hot dry product is cooled with air in position 909, then passes to the packing stage as the common salt of the highest quality. The lightened solution with a temperature of 55°C then passes through the tank pos. 240-4, to the tank 201-a, where it is sucked into the 10th vacuum crystallizer (10-stage cooling), then the suspension passes up to 14 stage, cooling from 55°C up to 20-25°C with the KCl crystallization.

The process of solution cooling and KCl crystallization is shown with a line « a » (Picture 2), the line « e » shows the small solute solution with water before 10th stage. The point « a », it is a solute content in KCl suspension with cooling temperature of 25°C.

From stage 14 the KCl suspension is passed through the hydrotank into the settlement pos. 233, the solution from that settlement with suspended disperse crystals passes into the settlement tank, pos. 236. The solution with fine and large KCl crystals is passed from the settlement tank to mixing system pos. 234, and then to the filter pos. 239. As the filtrate is passed through the receiver pos. 13 and tank 242 back into the settlement pos. 236 for the settlement of fine substances, it passes through a filter, but the wet KCl goes to drying into the apparatus of « boiling delay » position 307. The dry product goes to the stock.

The lightened solution, having a temperature of 20-25°C is passed from the settlement tank pos. 236 to the tanks pos. 240, and then is pumped to the tube condensator pos. 210-218, where it is preheated up to the temperature of 60-70°C with the help of condensation of solution vapour from the vacuum crystallizers. Then the solution is passed through the tank pos. 250 to the last preheating up to 110-118°C to the tube vapour preheaters pos. 136. From the vapour preheaters the hot solution passes into the solvent pos. 105-2 for sylvinite solution. The alkaline solution with salt content in the point « b » is the mixture of solution (point « a ») developed during the process of crystallization of KCl. The crystallizer extrudes the solution with washing water received during crystallizer and equipment washing, etc.

Table 1 shows the total water salt balance of that process with total working schedule at the factory of 170 t/hour is given. From the 170t/hour it will produce 40.81 t/hour of 98% KCl and 39.01 t/hour of common salt of the highest quality. The part of galit ore converted into table salt is :

$$\frac{38.80}{120.58} = 32.18\%$$

TABLE 1:

The total material balance of process the common salt production and KCl for working schedule of 170 t/hour.

Process stage and materials denomination:

Components content in 1 hour process t/hour.

Input:

1. Silvinite
2. Water for washing:
 - a. Galit
 - b. KCl
 - c. NaCl
 - d. Elevator, centrifuge nets, filters, vapour and air tubs and so on
3. Water for addition into alkaline solution before 10 stage of VCS

Output:

1. KCl (98%)
2. Common salt of the highest quality
3. Clay waste:
 - hard stage
 - liquid stage
4. Galit wastes:
 - hard stage
 - liquid stage
5. Evaporated at VCS water
6. Evaporated water:
 - KCl drying
 - NaCl drying

The decrease of KCl galit rests with the clay slag technological extraction of KCl passes:

$$\frac{40.60}{43.18} \times 100 = 94,0\%$$

While mechanical and other losses account for 5%, the final extraction is 89,0%. From the scheme in Picture 1, the suspension of NaCl goes through the 9 stage vacuum crystallizer. If the suspension does not pass through the next 10-14 stages then the suspension will have a mixture of NaCl and KCl at the 14 stage exit. After the extraction of hard substance from suspension the mixed salt of NaCl and KCl will be approximately 1:1. As was previously pointed out, the change of saturation stage in KCl solution during silvinite dissolution will give different ratios of common salt and KCl. The mixed salt can be used for medical common salts.

CONCLUSIONS

The technology for the complex treatment of silvinite with the production of common salt in one cycle and KCl by crystallization of salts has been developed in the Gallurgia factory. The nett production of NaCl and KCl exceeds 2.7-3 times the common salt production using the method of crystallization, and this decreases the production expenditures. The quantity of galit waste and clay losses are less than 5%.

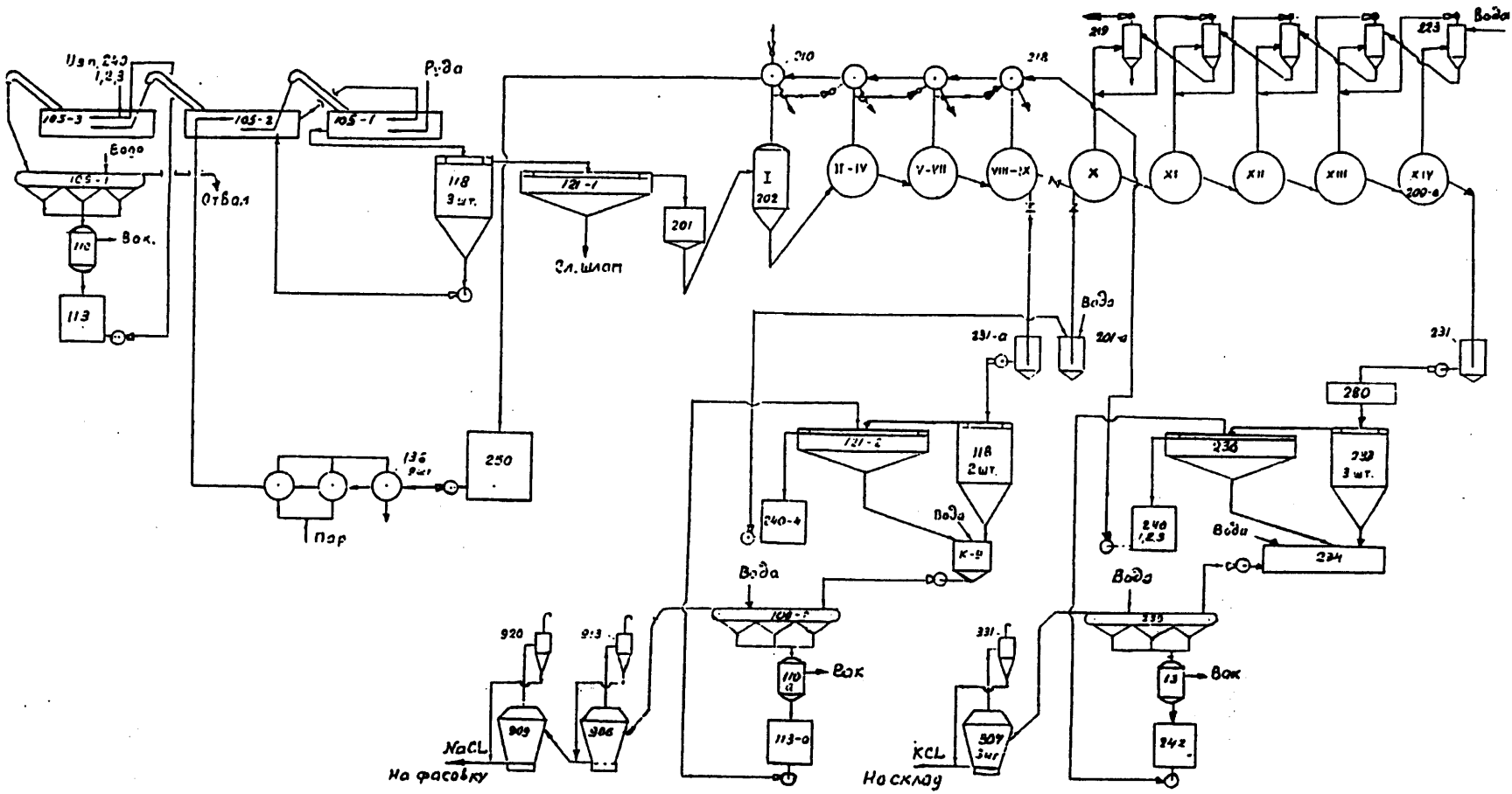


Рис.1 Аппаратурно-технологическая схема получения NaCl и KCl методом последовательной вакуум-кристаллизации

Figure 1

Диаграмма растворимостей NaCl и KCl
 в системе $\text{KCl} - \text{NaCl} - \text{MgCl}_2 - \text{H}_2\text{O}$

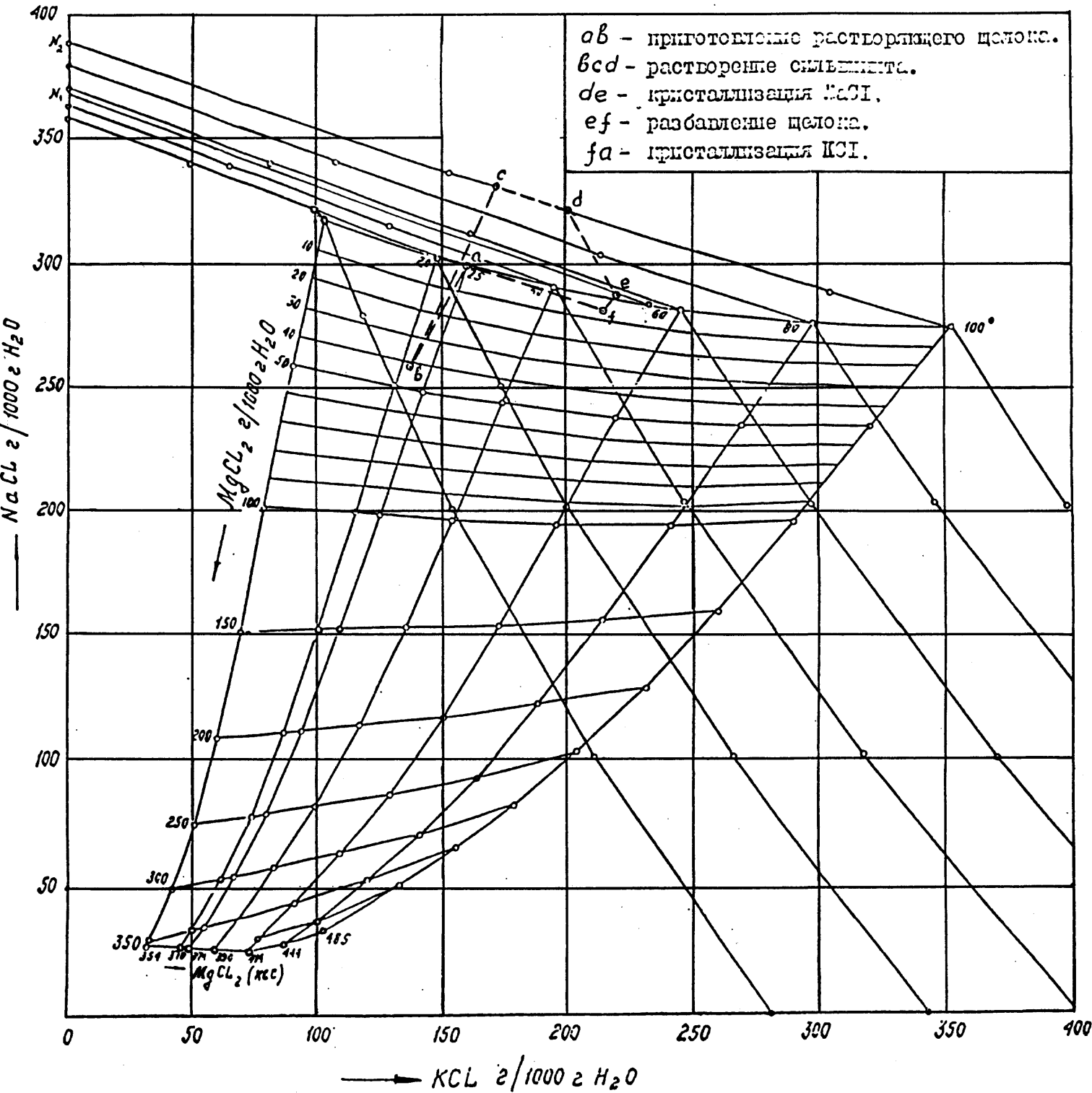


Рис. 2 Изображение хода процесса.

Figure 2