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# THEORETICAL BASIS AND DEVELOPMENT OF PRODUCTION TECHNOLOGY OF ARTIFICIAL CARNALLITE FROM WASTES BY USING CHEMICAL METHODS

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## ABSTRACT

In the article represented the results of treatment waste products asbestos and -titanium-magnesiums manufacture with receipt artificil karnallite research. We established the conditions of initial products and cristallisations karnallite leaching from solution. This process allows to refuse from import karnallit and to realize the producton in Kazakhstan. Technology was tested in enlarge scale and recommending to implementation.

**Key words**: Magnesium, Potassium chloride, Carnallite, Asbestos waste, Hydrochloric acid, Waste titanium, Leaching, Synthesis.

## INTRODUCTION

There is a lack of carnallite in titanium-magnesium industry of Kazakhstan. It is possible to find native carnallite as the separate lenses at the deposit of Satymola that is not developed and does not have any industrial interest, that's why the only way to procure carnallite in Kazakhstan is its synthesis.

Big quantity of run-off containing chloride appears during the process of procuring the titanium by means of magnesium-thermal technology. This is the spent melting of titanium chlorinators, fume of titanium chlorinator, middling's of carnallite chlorinator, etc. Because of absence of effective technology of recycling, the run-off are kept or after sterilization being dropped into middling's keeper. Approximately, total loss of chlorine run-off is 0.7-0.8 tons per 1 ton of titanium sponge, spent electrolyte 0.4 tons to 1 ton of titanium sponge. Totally, in general, the yields of chloride wastes more than 2 tons per 1 ton of

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titanium sponge. Loss of chlorine and magnesium chloride run-off and the spent electrolyte replenished dehydrated carnallite and chlorine coming from the side[1].

Thus, there is almost everything that is needed at the factory in order to procure the carnallite : chloride run-off, anodic chloride, spent electrolyte. For the replenishment of magnesium, that is being lost during the process of procuring the titanium the run-off asbestos producing can be used. These run-off are hydrous silicates of magnesium, ferrum, calcium and natrium that contain up to 42 % MgO[2].

In this work, there are the results of studying the technology of missed recycling of chloride run-off in titanium-magnesium producing and producing run-off of asbestos with the aim of getting the carnallite. The paper presents the results of studying the technology co-processing of run-off chloride titanium-magnesium production and the production of asbestos run-off to produce carnallite[3]. This task will involve the production of run-off existing facilities to produce import-substituting products, to reduce the environmental load in areas of existing enterprises, ensure the creation of new work places.

## EXPERIMENTAL

### Literature review of the research

In works of Eydenzon[4], the technologies are described that allow engaging in complex processing practically all the run-off production of titanium and magnesium producing in order to form titanium dioxide and carnallite. One of the variants of the regeneration of chloride is the "Magnesium" method, the implementation of which dissolved chlorides of titanium production run-off processed magnesium oxide, and from the purified solution by crystallization-carnallite. The disadvantage of such scheme is the very low velocity of filtration of the pulp during the phase separation due to the formation of hydrogels.

Scheme were offered for recycling the solid waste in carnallite by means of hydrometallurgical method, in which raw materials are the run-off molten titanium and magnesium electrolytic chlorinators of carnallite scheme[5,6]. In our opinion the disadvantage of the method is that during the process of obtaining carnallite from chloride run-off there was added magnesium sulfide, in addition, during the leaching of chloride the hydrogen sulfide is released. It is known that even a small amount of sulfur-containing compounds in the electrolyte adversely negatively affect the performance of the electrolysis process in the electrolytic production of magnesium[7].

In the literature, we studied there is no information about research of carnallite procuring with the usage of asbestos materials that was the main goal of the present research.

The possibility of procuring the magnesium chlorides with the usage of run-off of asbestos producing and chloride-containing run-off of titanium-magnesium production proves by the thermo-dynamic calculations.

**Table 1: The standard free energy ($\Delta G^0$) leaching processes of magnesium silicates (KDJ)**

| Reaction | Temperature, k | | | |
|---|---|---|---|---|
| | 343 | 353 | 363 | 373 |
| $3MgO·2SiO_2·2H_2O + 6HCl = 3MgCl_2 + 2SiO_2 + 5H_2O$ | 101.3 | 97.7 | 94.3 | 90.9 |
| $3MgO·2SiO_2·2H_2O + 6HCl = 3MgCl_2·H_2O + 2SiO_2 + 2H_2O$ | 15.1 | 12.3 | 9.7 | 7.2 |
| $3MgO·2SiO_2·2H_2O + 6HCl + H_2O = 3MgCl_2·2H_2O + 2SiO_2$ | -38.3 | -40.1 | -41.7 | -43.2 |
| $3MgO·2SiO_2·2H_2O + 6HCl + 7H_2O = 3MgCl_2·4H_2O + 2SiO_2$ | -123.2 | -122.9 | -122.6 | -121.9 |
| $7MgO·8SiO_2·H_2O + 14HCl = 7MgCl_2 + 8SiO_2 + 8H_2O$ | 203.8 | 197.3 | 191.0 | 185.0 |
| $7MgO·8SiO_2·H_2O + 14HCl = 7MgCl_2·H_2O + H_2O + 8SiO_2$ | 2.7 | -2.0 | -6.3 | -10.4 |
| $7MgO·8SiO_2·H_2O + 14HCl + 6H_2O = 7MgCl_2·2H_2O + 8SiO_2$ | -121.9 | -124.3 | -126.3 | -128.0 |
| $7MgO·8SiO_2·H_2O + 14 HCl + 20H_2O = 7MgCl_2·4H_2O + 8SiO_2$ | -319.9 | -317.7 | -314.9 | -311.7 |
| $7MgO·8SiO_2·H_2O + 14HCl + 34H_2O = 7MgCl_2·6H_2O + 8SiO_2$ | -426.0 | -420.25 | -413.9 | -406.9 |

The values of the standard free energy show that the dissolution process is thermodynamically possible in a wide range of temperatures. Magnesium transfers to a solution in form of chloride, by different amounts of hydrated water molecules. The presence of molecules in solution is thermodynamically incredible. As follows from the results of the calculation of thermodynamics dehydration process (Table 2) the complete loss of crystallized water is possible at temperatures above 600 K. Dehydration takes place in steps with increasing temperature according to the scheme.

$$MgCl_2 \cdot 6H_2O \rightarrow MgCl_2 \cdot 4H_2O \rightarrow MgCl_2 \cdot 2H_2O \rightarrow MgCl_2 \cdot H_2O \rightarrow MgCl_2.$$

**Table 2: The standard free energy ($\Delta G^0$) processes of dehydration of magnesium chloride (KDJ)**

| Reaction | Temperature, k | | | | | | |
|---|---|---|---|---|---|---|---|
| | 373 | 423 | 473 | 523 | 573 | 623 | 650 |
| $MgCl_2 \cdot 6H_2O = MgCl_2 \cdot 4H_2O + 2H_2O$ | 13.6 | -0.03 | -13.6 | -27.1 | -40.5 | -53.8 | -60.9 |
| $MgCl_2 \cdot 4H_2O = MgCl_2 \cdot 2H_2O + 2H_2O$ | 26.3 | 11.8 | -2.5 | -16.6 | -30.7 | -44.6 | -52.1 |
| $MgCl_2 \cdot 2H_2O = MgCl_2 \cdot H_2O + H_2O$ | 16.8 | 9.6 | 2.5 | -4.6 | -11.6 | -18.6 | -22.3 |
| $MgCl_2 \cdot H_2O = MgCl_2 + H_2O$ | 27.9 | 21.1 | 14.3 | 7.7 | 1.2 | -5.1 | -8.5 |

To isolate the 6-carnallite and water from unsaturated solutions of magnesium chloride and potassium are two options:

- Evaporation forwarding to the crystallization of carnallite and separating it from the mother solution.
- The evaporation method is accepted for the study in this work.
- The aim of this present work is the research, development and to improve the ecology condition in the regions of the active enterprises.
- The aim of this work is studying, designing and testing the hydrochloride - acid technology carnallite from run-off JSC "Kostanay minerals", and run-off production of titanium dehydration, which will produce import-substituting products, and to improve the ecology condition in the regions of the active enterprises and improve environmental conditions in the areas of active enterprises.

## The raw materials of the research

The selected object of research is asbestos run-off of JSC "Kostanay minerals" – deposits of Zhetikara asbestos tailings plant (JSC) and the spent melt titanium chlorinators JSC "UK TMC" (SMTC) as a source of potassium chloride.

In order to leach AW, there was used the grade chemically pure hydrochloric acid. The run-off SA in chemically combined condition contain a number of elements, including,% MgO - 39.0-42.0; $SiO_2$ - 37.0-41.0, CaO - 1.1-1.6; $Fe_2O_3$ - 1.9-5.4; FeO -1.0-2.7; $Al_2O_3$ - 0.8- 1.4; NiO - 0.1-0.25. In negligible quantities (up 0.32%), there is a presence of cobalt, chromium, manganese, sodium, potassium, titanium and other metals. Mineral foundation of serpentine is $3MgO \cdot 2SiO_2 \cdot 2H_2O$

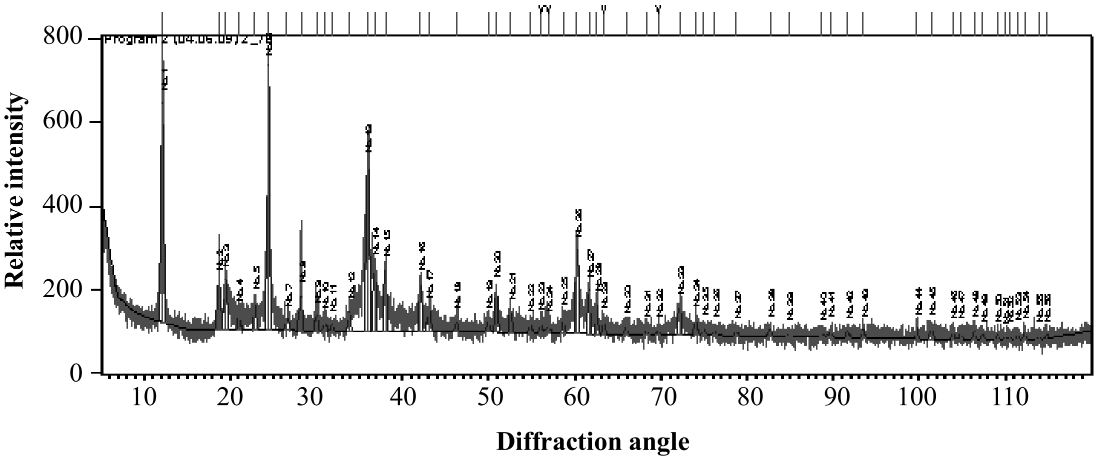

**Fig. 1: X-ray of the initial asbestos products**

**Table 3: The phase of composition of the initial asbestos products**

| Component | Formula | Mass % |
|---|---|---|
| Talc | $Mg_3(Si_2O_5)(OH)_4$ | 27 |
| Brucite | $Mg(OH)_2$ | 6 |
| Magnesium oxide, nickel | $MgNiO_2$ | 2 |
| Antigorite | $Mg\ 39(Si_{28}O_{70}(OH)_{50})$ | 65 |

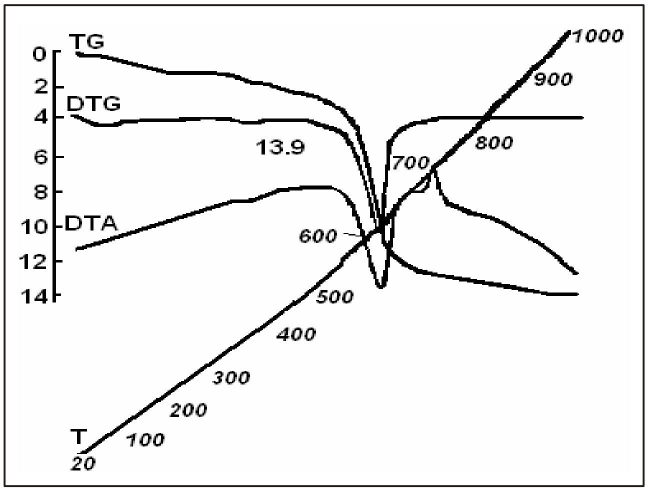

**Fig. 2: DTA, TG and DTG analysis of the asbestos wastes**

According to the results of X-ray diffraction and differential thermal analysis of the sample source of asbestos run-off is identified as a well crystallized mineral of the kaolinite group-serpentine. Thermo analytical and thermo gravimetric parameters allow taking it to a variety of chrysotile asbestos. About the development of the crystalline structure of this formation indicates the presence in the DTA curve (Fig. 2) at 873 K deep endothermic peak, the rolling of 993 K in another exothermic peak direction. Weight reduction, accompanied by endothermic effects due to dehydration and weight loss due to dehydration of serpentine ($\Delta$m 440-700 ºC = 10,2%)[8].

Chemical compound SMTC,mass %*:* $MgCl_2$ – 20.4; KCl -26.0; NaCl -15.0; $CaCl_2$-2.4; $FeCl_2$ - 22.5; $FeCl_3$ – 5.2; $SiO_2$ – 0.08; Cr – 0.17; Mn -0.33; $TiO_2$ - 1.1; C – 7.9; Al – 0.26.

## Methods of research

Leaching of asbestos run-off was carried out at room temperature and at a temperature of 358-363 K. HCl content ranged from 7 to 20%, the ratio of L : S = 2 : 1 and 3 : 1, duration- 2, 4 and 6 pm The solution to the vacuum filter sludge separated from amorphous silica, oxidized ferrous iron with calcium hypochlorite followed neutralizing solution and separating the precipitate. Cleaning solution from the extraction of nickel carried him out of the filtrate with 10% solution of Di-(2-ethylhexyl) phosphoric acid in kerosene. Solution after separation of the organic phase solution was neutralized to pH 7-8 to precipitate impurities -iron and aluminum. Keck was separated by vacuum filtration and sent to the dump, and the filtrate-peeled clear solution of magnesium chloride- for redistribution produce carnallite.

Run-off melts titanium chlorinators dissected by leaching with water at a ratio of L : S = 1.5 : 1 and stirring until the pulp density is 1.3-1.31 g/cm$^3$. During the process of leaching the slurry temperature was raised to 313-323 K (exothermic). Pulp at pH 1.3 was kept, the solution was separated from the sediment. The high degree of purification from impurities such as iron, chromium and aluminum was achieved by neutralization up to pH 7.5-8.0 and then fluff pulp with the addition of 0.1% aqueous solution of polyacrylamide. The precipitate was separated, pressed and went to dump. Purified target solution of magnesium chloride and potassium were used to produce artificial carnallite.

## Getting and dehydration of carnallite

The purified solutions of magnesium chloride and potassium chloride were combined, evaporated, followed by cooling, separation of crystalline carnallite and its dehydration.

Adjustment of the chemical compound of carnallite was performed by mixing the solutions with different volume ratio of AW : SMTC = 1 : 1, 1.6 : 1.2, 1.3 : 1. The results of the experiments are shown in Table 4. As a result, a white crystalline substance, which is identified as a double salt $MgCl_2·KCl·6H_2O$ or synthetic carnallite was received. The ratio of KCl : $MgCl_2$ in carnallite should be ~ 0.8, this combination meets the carnallite obtained from a mixture of solutions with respect to AW : SMTC = 1.65 : 1.

Dehydration of received salt was carried out in an oven at 373 K in a muffle furnace at 673 K.

Raw materials, intermediate products of processing and the resulting compounds were affected by chemical, X-ray diffraction, X-ray and thermal analysis. Thermal analysis was performed with the help of the system derivatograph "Paulik-Paulik-Erdey". Analysis conditions: temperature range is 293-1273 K, dynamic heating mode is 10 degrees/min, atmosphere; reference substance – $Al_2O_3$ : alundum crucibles, weighed sample - 500 mg. Identification of mineral powder samples was carried out on the morphology of the thermal curves using coupled with thermo gravimetric testimony TG lines. Results of the analysis were compared with the data given in the atlas of thermal curves of minerals and rocks[8].

## RESULTS AND DISCUSSION

Leaching results AW and SMTC are presented in Tables 4-6 and in Fig. 3.

**Table 4: Extraction of magnesium from AW in solution (α, %) and magnesium content in the solution (β, g/L) depending on process conditions**

| Concentration HCl (%) | 2 hours | | 4 hours | | 6 hours | |
|---|---|---|---|---|---|---|
| | β | α | β | α | β | α |
| L : S = 3 : 1 | | | | | | |
| **7** | 38 | 48 | 40 | 50 | 43 | 53 |
| **10** | 41 | 51 | 60 | 75 | 60 | 75 |
| **15** | 50 | 63 | 65 | 81 | 68 | 85 |
| **18** | 55 | 69 | 70 | 88 | 75 | 94 |
| **25** | 60 | 75 | 72 | 90 | 77 | 96 |

Cont…

| **Concentration HCl, %** | **2 hours** | | **4 hours** | | **6 hours** | |
|---|---|---|---|---|---|---|
| | **β** | **α** | **β** | **α** | **β** | **α** |
| | | | **L : S = 2 : 1** | | | |
| **7** | 39 | 32 | 40 | 33 | 41 | 34 |
| **10** | 41 | 34 | 55 | 46 | 58 | 48 |
| **15** | 47 | 33 | 60 | 50 | 63 | 53 |
| **20** | 55 | 46 | 65 | 54 | 71 | 59 |
| **25** | 60 | 50 | 70 | 58 | 80 | 66 |

The results received (Table 4, Fig. 3) shows that as the concentration of HCl extraction of magnesium from the AW and magnesium content in the solution increases. However, when the concentration of hydrochloric acid > 20% significantly reduced the rate of filtration of the pulp due to the formation of hydrogels. This is due to the formation of hydrated 6-magnesium chloride with water molecules, which causes a deficiency of the solvent (water) in the system. The best results on the filtration rate obtained with the acid concentration of 18%. Thus the high degree of extraction of magnesium- 95%.

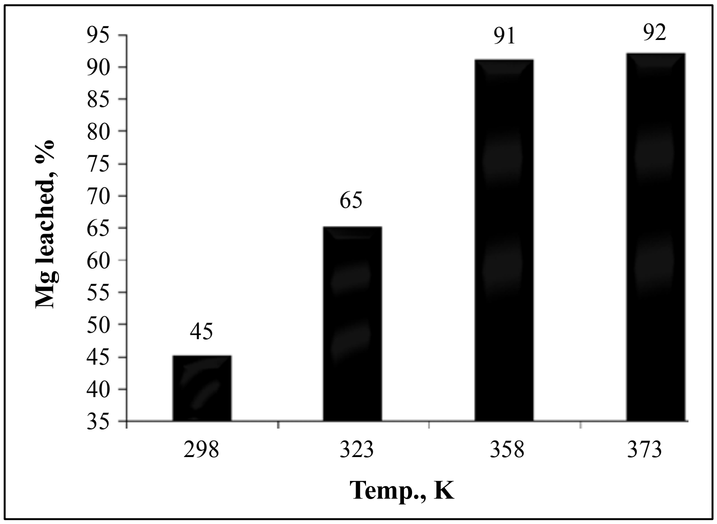

**Fig. 3: The dependence of the extraction of magnesium from the AW to the solution from the leach temperature (The concentration of acid - 18%, duration - 6 hrs, L: S = 3 : 1)**

The extraction of magnesium in solution of AW has the influence on attitudes L : S, (Table 5), the optimal ratio of L : S = 3 : 1. A further increase of the proportion of the liquid phase is not desirable, because it greatly increases the material flows.

Increase of temperature (Fig. 1) is beneficial to the extraction of magnesium. At 358 to the extraction of magnesium is 95%.

Radiographs initial AW and leach residue confirm complete leaching of magnesium. If the original AW contain magnesium-containing compound, in the leaching residue magnesium containing compounds not detected (Table 3, 5, Fig. 1, 4).

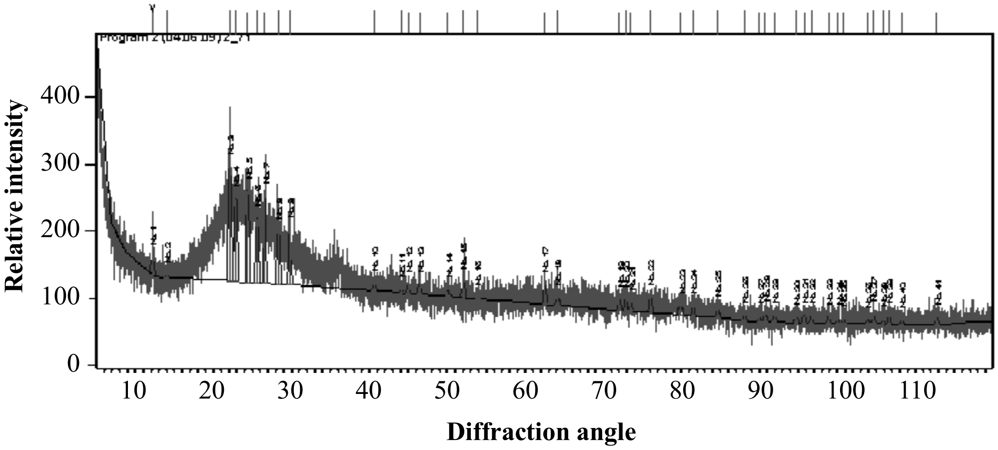

**Fig. 4: X-ray diffraction spectra of post-reaction samples**

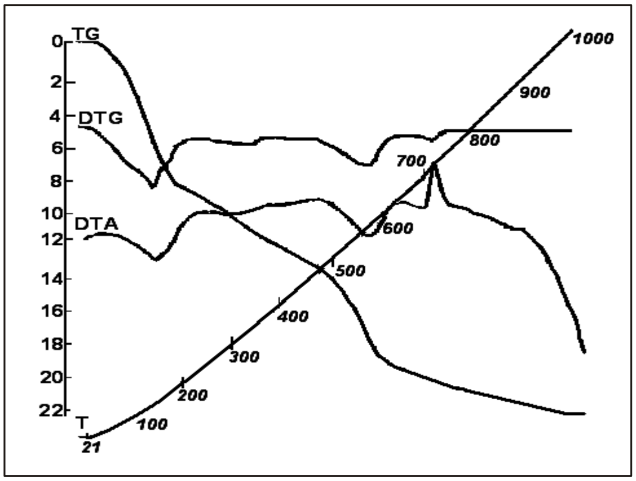

**Fig. 5: DTA, TG and DTG analysis of the residue leaching**

Thermo gravimetric analysis of the residue after leaching (Fig. 5) showed that treatment with hydrochloric acid, a natural compound of this leads to a change in the thermal behavior of the sample, especially in the low end of the range. Leached chrysotile asbestos revealed the presence in its structure (in addition to the constitutional water) three more groups of water. In dehydration samples they leave on the differential thermo gravimetric curve of three inscribed one another peak at 383, 413 and 443 K, indicating that the three stages of removing molecules $H_2O$. The total number of lost hydrates in the range 413-483 K for these stages of dehydration is 8.45% of the sample mass.

Along with the stepped character of the dehydration test, thermogravimetry is over the temperature records continuous mass loss of the sample. Apparently, the leaching of asbestos leads to the disordering structure, which provides the appearance of the mineral lattice in a wide range of electrical idle capacities to different energy levels on retention in the molecules of $H_2O$ and OH groups.

**Table 5: The phase composition of the leach residue of asbestos products**

| Component | Formula | Weight content (%) |
|---|---|---|
| Silica | $SiO_2$ | 97 |
| Magnesia | MgO | 3 |

On the basis of the researches the recommended mode to leaching of asbestos run-off is treatment of crushed asbestos run-off after fractionation (fraction 1 mm 100%) hydrochloric acid solution containing 18-20% HCl with constant stirring for 6 hours at a temperature 358-343 K. Branch, this solution on the vacuum filter of amorphous precipitate silica, washing the precipitate with water.

SMTC leaching was carried out at room temperature with the sample weight of 200 g As the results (Table 6) extraction of potassium and magnesium in solution increases with M : T. However, the increase in L : S from 1.5 to 3.0 is insignificant effect on the extraction of potassium and magnesium the solution. However, the solutions obtained (pulp density-1.20), and the processing of dilute solutions requires additional expenses for the stage of dehydration. Thus, the optimum leaching conditions SMTC : L : S = 1.5 : 1, duration - 2 hrs. The feed to the leach water does not require heating. Due to exothermic reactions in the leach slurry temperature rises to 413 K.

For cleaning solutions obtained from the impurities of iron, manganese and chromium neutralize the solution to a pH of magnesium oxide = 8. Under these conditions, the above impurities digested and removed. The magnesium content in the purified solution - 30 g/L of potassium - 48 g/L of iron, manganese and chromium less than 0.02 mg/L. Behavior of titanium and other impurity metals are not considered.

**Table 6: Effect of leaching to extract SMTC sylvite and impurities**

| L : S | Density (g/sm$^3$) | | Recovery (%) | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Of pulp | Of filter liquor | $Mg^{2+}$ | $K^+$ | $Na^+$ | $Fe_{total}$ | $Mn^{2+}$ | $Cr^{3+}$ |
| 1.0 : 1.0 | 1.45 | 1.36 | 68.5 | 61.0 | 35.7 | 75.0 | 48.5 | 13.9 |
| 1.5 : 1.0 | 1.31 | 1.30 | 85.3 | 80.0 | 50.3 | 37.8 | 56.1 | 15.0 |
| 2.0 : 1.0 | 1.25 | 1.24 | 87.2 | 83.0 | 55.7 | 90.5 | 60.6 | 19.1 |
| 3.0 : 1.0 | 1.20 | 1.19 | 88.1 | 83.1 | 62.0 | 96.3 | 62.1 | 19.7 |

In carnallite used for electrolysis, the molar ratio of KCl : $MgCl_2$ is 0.8. To obtain the desired compound of carnallite studied the effect on the crystallization ratio of supply solutions from the leaching of the AO and the composition of the resulting SMTC carnallite.

Research results (Table 7) show that the relationship between KCl and $MgCl_2$ is achieved at a ratio of volumes of solutions AG : SMTC equal to 1.65.

**Table 7: Effect of volume ratio of solutions AW and SMTC coming for a carnallite, the ratio of KCl: $MgCl_2$ in the resulting product**

| $MgCl_2$ | MgO | KCl | NaCl | $H_2O$ | $CaCl_2$ | Ti | Fe | Si | KCl /$MgCl_2$ molar |
|---|---|---|---|---|---|---|---|---|---|
| **The ratio of volumes of solutions of AW: EMTC = 1:1** | | | | | | | | | |
| 20.5 | 0.35 | 58.2 | 15.1 | 11.2 | 0.58 | 0.003 | 0.01 | 0.01 | ≈ 2,8 |
| **2:1** | | | | | | | | | |
| 28.8 | 0.58 | 50.5 | 10.7 | 14.2 | 0.56 | 0.0032 | 0.01 | 0.005 | ≈ 1,75 |
| **1.65:1** | | | | | | | | | |
| 48.7 | 0.15 | 38.6 | 3.0 | 22.7 | 0.42 | 0.0023 | 0.01 | 0.01 | ≈ 0,8 |
| **3:1** | | | | | | | | | |
| 28.8 | 0.06 | 39.6 | 11.8 | 23.2 | 0.66 | 0.0029 | 0.01 | 0.009 | ≈1,37 |

## CONCLUSION

Thus, it is shown that by engaging in the processing of only two dump products may receive conditioned synthetic carnallite, which can be used to produce magnesium metal at Ust-Kamenogorsk Titanium-Magnesium Combine (UKTMC). The developed technology will be disposed of dumping products, get quality carnallite, extract valuable components, which are now irretrievably lost, and convert waste into non-toxic mineral formations, from the point of view of ecology is safe and beneficial.

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