

Production of Synthetic Carnallite from The Wastes of Titanium and Magnesium Production with The Extraction of Niobium-Containing Middlings

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Abstract. Analysis of the current state of the titanium and magnesium production in the Republic of Kazakhstan shows the availability of significant amounts of chloride wastes containing valuable components. Magnesium and potassium with an average content of 50-60% potassium chlorides, 25-30% magnesium chlorides are lost among other metals in the wastes of the titanium and magnesium production. Kazakhstan has not mastered the field of magnesium raw materials, so it has to import it in the form of carnallite. Ust-Kamenogorsk Titanium Magnesium Plant JSC (UTMK) currently imports carnallite that is a $KCl \cdot MgCl_2 \cdot 6H_2O$ binary salt at quite high prices. In this regard, the task of extracting these metals from chloride wastes is relevant. Chloride wastes of titanium production, sublimates of dust chambers of a titanium chlorinator, sludge of a carnallite chlorinator has been chosen as the targets of our research. The analysis of niobium distribution within any solid waste of a titanium sludge chlorination process in UTMK JSC showed that the highest content of niobium is in the sublimates of dust chambers of a titanium chlorinator in the ranges from 0.26 to 1.0%. Among the niobium extraction technologies considered, the known method of its extraction from the chloride waste is leaching with weak solutions of mineral acids or bases in order to convert the chloride salts into the solution to be used for synthetic carnallite extraction. Besides niobium, other impurity components are transferred to the cake and shall be separated from the base metals. The effective method for this is the chlorination process enabling niobium transfer into the sublimates in the form of chlorides and thus separating it from the majority of the impurities. The condensed niobium chlorides are hydrolysed transferring it into sediments in the form of oxide. The paper shows the way of the synthetic carnallite production suitable for use in the main flow diagram of titanium and magnesium production with a by-product in the form of middlings enriched with niobium.

1. Introduction

Based on niobium distribution analysis of solid chloride wastes produced in course of titanium slag chlorination process in UTMK JSC the highest niobium content was found in dust chamber (DC)



sublimates of titanium chlorinator. DC sublimates consist of chlorides of alkali and alkaline earth metals [1].

Out of niobium and titanium extraction technological processes studied leaching with weak solutions of mineral acids or alkalis is one of the ways of titanium chloride waste processing in order to convert chloride salts into solution for synthetic carnallite production. Other impurities are also converted into the cake in addition to titanium and niobium and later on they shall be separated from the basic metals [2,3]. Chlorination process is one of the effective methods for doing this, allowing to convert niobium and titanium in sublimates in the form of chlorides, and therefore separate them from the main impurities. Condensed niobium and titanium chlorides are hydrolysed, precipitating them in oxides form [4,5].

Magnesium deposits are not developed in Kazakhstan therefore magnesium raw material is imported from abroad in a form of carnallite. Due to supplies cessation from Russia and China, UTMK JSC has to import carnallite from Israel at the high price. Meanwhile problem of carnallite shortage could have been resolved by titanium-magnesium waste recovery.

Present paper was aimed to investigate secondary cakes chlorination processes produced out of cinders leaching out of titanium chlorinator primary cake DC sublimate roasting and subsequent hydrolytic treatment of chloride hydro sublimates. Solutions of DC leaching sublimates are purified and carnallite is synthesized out of them.

2. Results and Discussions

2.1 Study of synthetic carnallite production out of purified solutions

Titanium chlorinator DC sublimates of the following composition were used in the study, wt.%: 0.7 Nb; 2.8 Ti; 8.2 Fe; 6.3 K; 0.4 Mg; 2.5 Na; 0.27 Cr; 8.4 Al; 0.9 SiO₂; 0.44 Mn. DC sublimates were leached with 5% sulfuric acid solution at 100 °C within 2 hours, at the ratio of S:L=1:10. Obtained slurry was filtered, cakes were dried, then sent to produce middlings, enriched with niobium and titanium. Composition of solution at pH = 0.5 was following, g/dm³: 12.4 Fe; 4.1 Al; 2.5 Mn; 42.0 SO₄²⁻; 7.5 K; <0.1 Mg; 3.2 Na. In order to get synthetic carnallite such solution shall be purified of iron, aluminium, manganese and SO₄²⁻ ion.

Calcium oxide can use to remove SO₄²⁻ ion from the solution obtained in course of DC sublimate leaching that is the most accessible and cheap deposition reagent out of all available. SO₄²⁻ ion content is 42.0 g/dm³ in the solutions of DC sublimates leaching with 5% sulfuric acid solution. It is necessary to add 24 g of CaO per each litre of solution to recover this volume of SO₄²⁻ ion and process in such reaction: CaO+H₂SO₄=CaSO₄+H₂O, but solution after DC sublimates leaching becomes multi-component and calcium oxide also raises the pH level, therefore excess CaO solution was added. To increase CaO activity, it was preliminarily annealed at 950 °C with 1 hour soaking time. 80 g of calcined CaO was added per one litre of heated solution. It was leached during 180 minutes at the temperature of 100 °C and stirring speed of 300 rpm. After that pulp was decanted, clarified solution was drained, precipitated portion was filtered, pH level of filtrate was measured, wet cake was weighed and dried. Solution of following composition was obtained, g/dm³: 1.2 Fe; 1.1 Al; 3.2 Ca; 0.11 SO₄²⁻, pH level of 3.05.

When solution after DC sublimates leaching is purified with calcined calcium oxide the pH level of solution raises up to the values of 1.2 and 3.0, while impurities of iron, manganese and aluminium remain in solution. To obtain complete sedimentation it is necessary to increase the pH level to 7.5 - 8.0. Calcined magnesium oxide produced in course of sludge of magnesium production was added in solution purified from SO₄²⁻. Carnallite chlorinator sludge (CCS) was selected. Chemical composition of magnesium production sludge wt.%: 2.02 KCl; 1.2 MgCl₂; 94.0 MgO; 1.6 NaCl; 0.05 TiO₂; 0.1 Fe₂O₃; 0.38 Al₂O₃; 0.006 MnO; 0.3 CaO; 0.3 SiO₂. Magnesium production sludge was pre-leached with water, filtered and dried. Then obtained cake was subjected of roasting at the temperature of 950°C and one hour soaking time.

The following purification method was used: 200 g of calcined MgO obtained from the CCS magnesium sludge was added per one litre of solution, heated to 100 °C, leaching time was 120

minutes. Slurry was filtered, pH value of the filtrate was measured. Composition of solution obtained was following, g/dm³: 14.3 KCl; 1.2 MgCl₂; 8.1 NaCl; 0.01 Fe; 0.03 Al; 0.04 Mn; 0.5 Ca; 0.01 SO₄²⁻, pH value of 7.5. At pH values up to 7.5, impurities content in the purified solution corresponds to the maximum acceptable rated value of solutions coming to carnallite synthesis.

Thus, calcium oxide and CCS magnesium production sludge were selected for purification of solutions obtained in course of DC sublimates leaching with sulfuric acid, as reactants for the impurity sedimentation. First, solution was treated with calcined lime under optimum conditions: S:L=1:12,5; leaching time 180 min; temperature 100 °C; pH level of solution is 2.5-3. Then sludge was filtered, cake was separated, and further filtrate was treated with roasted cake of magnesium sludge under optimum conditions: S:L=1:5; leaching time 120 min; temperature 100°C; pH of 6.5-7.5.

Trial was performed with two solutions, the first solution was out of leaching of CCS magnesium sludge with 5% hydrochloric acid solution of following composition, g/dm³: 24.4 KCl; 156.0 MgCl₂; 4.33 NaCl. carnallite value of 0.16. The second solution was purified solution out of DC sublimates leaching with sulfuric acid of above composition. Solutions were combined in 0.5 litre, heated to 90°C, excess sodium chloride was sedimented and removed by filtration. 46 g of KCl was added to obtain carnallite value and carnallite was crystallized. Salt mass was 0.18 kg and its composition was following, wt. %: 28.1 KCl; 31.2 MgCl₂; 4.2 NaCl. carnallite value was 0.9. The phase analysis consisted of sixaqua carnallite KMgCl₃6H₂O 36.0%. twoaqua carnallite KMgCl₃•2H₂O 38.4%. sylvite KCl 21.6%. halite NaCl 4.0%. Final sample of synthetic carnallite corresponded to GOST 16109-70 in appearance of crystalline white salt.

Thus, synthetic carnallite was produced out of purified solutions produced in course of DC sublimates leaching and magnesium sludge leaching.

2.2 Study on production of middlings enriched with niobium

Primary cake obtained out of DC sublimates leaching with 5% sulfuric acid solution. was mixed with soda Na₂CO₃ at the ratio of 1:1.5 out of stoichiometrically required. and carbonaceous reducing agent. Composition of the cake was following mass. %.: 3.73 Nb; 23.8 Ti; 2.23 Fe; 1.7 Al; 8.7 SiO₂; 0.47 Mn.

The charge consisted of 84% of primary cake. 13% of soda. 3% of reducing agent. Sintering process was performed in graphite crucible at the temperature of 900°C. soaking time was 1 hour. Cinder output was 67-70%. Later on cinder was milled and leached with 1% NaOH during one hour at the ratio of S:L=1:8. after that it was filtered and washed with hot water in the filter at S:L=1:4. Secondary cake produced out of leaching with sodium hydroxide solution was dried and prepared for chlorination. Charge mix consisting of 88% of secondary cake. 11% of reducing agent and 1% molasses was pelletized. Pellets were cylindrical in shape of 3-4 mm size.

To perform the study special facility was assembled for chlorination of primary cake produced after DC sublimates leaching. Chlorine has produced upon known method of potassium permanganate and concentrated hydrochloric acid reaction: $2\text{KMnO}_4 + 8\text{HCl} = 2\text{MnO}_2 + 3\text{Cl}_2 + 2\text{KCl} + 4\text{H}_2\text{O}$. This facility consisted of tubular furnace with quartz tube. cooler. trap system. Chlorine was formed in the three-neck flask by concentrated hydrochloric acid interaction to potassium permanganate. Under argon pressure chlorine was delivered from cylinder to the quartz tube of tubular furnace. where a tray with pellets was located. then passed through the cooler and the trap system consisting of two flasks with 1% hydrochloric acid solution and following two flasks with alkaline solution of NaOH to neutralize excess chlorine gas. Air supply was regulated by the reducer and measured with a rheometer at the rate up to 4 dm³/min. The pressure in the system was controlled by the U-shaped manometer. Chlorine and argon mixture before coming to the quartz tube passed through the dryer with sulfuric acid to absorb the residual water vapour generated in the three-neck flask upon potassium permanganate and concentrated hydrochloric acid interaction. Sublimate was recovered in the condenser cooler.

Pellets prepared were chlorinated according to the established parameters: chlorine flow rate of 0.2 dm³/min. temperature 750 °C. time of 120 minutes. Figure 1 shows that at chlorine consumption of 0.2 dm³/min. the temperature increases the niobium extraction, slightly varying from 91.4 to 95.6%.

The optimum temperature was 750 °C. when the niobium extraction in sublimates was up of 95.2%. Overall pellets chlorination degree at chlorine flow rate of 0.2 dm³/min ranged from 79.3 to 89.5%.

Sublimates obtained in course of secondary sludge chlorination were hydrolytically processed as follows. Chloride sublimates collected in the condenser cooler, were washed with 1% HCl solution. This solution was diluted with water. then boiled at 100 °C during 120 minutes. After cooling. solution was adjusted with ammonia water to pH=10. filtered and the sediment was dried. Niobium extraction in residue was 92%. Sediment content obtained in course of sublimates hydrolysis during chlorination. wt. %: 20.2 Nb; 25.8 Ti; 0.7 Fe; 0.86 Al; 0.4 Si; 0.05 Mn.

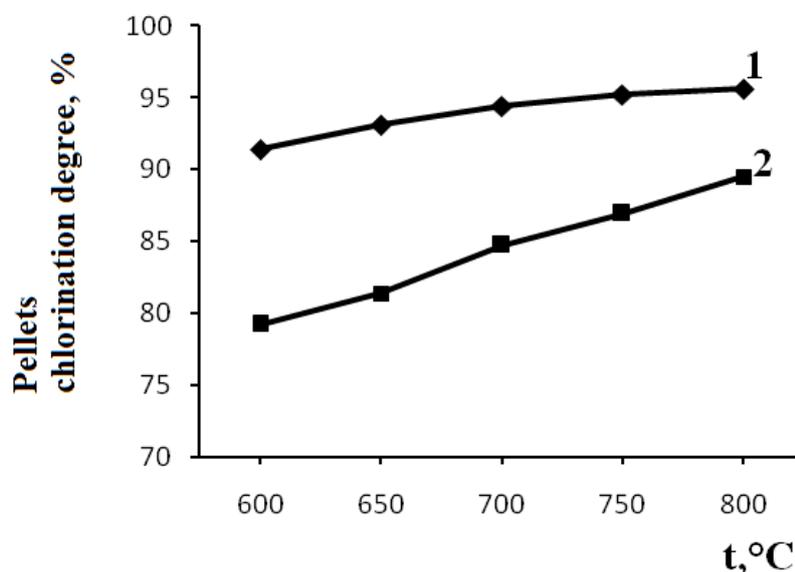


Figure 1. Dependence of pellets chlorination degree and temperature at chlorine flow rate of 0.2 dm³/min; 1 – niobium chlorination degree; 2 – total degree of pellets chlorination

Thus. by means of sintering process cake obtained after DC sublimates leaching is mixed with soda at the ratio of 1:1.5 upon stoichiometrically required. and carbonaceous reducing agent. The optimum temperature for the sintering is 900 °C. holding time is 1 hour. Cinder is leached after calcination with 1% NaOH solution. by washing with hot water in the filter. and secondary cake is produced. Pellets are made out of secondary cake. carbon reducing agent and binder. Pellets are chlorinated at the temperature of 750 °C. during two hours. chlorine consumption is 0.2 dm³/min. Chloride sublimates are washed from the condenser cooler with 1% HCl solution. diluted with water and boiled at 100 °C for 120 min. After cooling. solution is adjusted with ammonia water to pH=10. Solution is filtered residue, dried and middlings produced are than enriched with niobium.

3. Conclusions

Calcium oxide and CCS magnesium sludge were selected as reactants for the impurity component sedimentation to purify solutions obtained after DC sublimates leaching with sulfuric acid solution.

Synthetic carnallite of following composition was produced. wt. %: KCl 28.1; MgCl₂ 31.2; NaCl 4.2; Fe 0.001; SO₄²⁻ 0.01. H₂O 4.95. Final sample of synthetic carnallite met requirements of GOST 16109-70 and was suitable for electrolytic magnesium production.

Middlings enriched with niobium and titanium of following composition was produced. wt. %: 20.2 Nb; 25.8 Ti; 0.7 Fe; 0.86 Al; 0.4 Si; 0.05 Mn.

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