

## Subchloride Waste-Free Sublimation of Sillimanite Concentrates

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### Abstract

The possibilities for sublimation of silicon and aluminium – basic components of refractory aluminium silicates – to gas phase have been demonstrated by way of thermodynamic computations and experiments with minerals of sillimanite tribe. The proposed method is founded on alternate action of chlorine on aluminium silicates in the presence of carbon-bearing reductant and aluminium subchloride as a reductant, with the results that low-boiling salts of aluminium and silicon are produced. This method was demonstrated to be economically feasible by direct expenditure of electric energy on the return of aluminium subchloride to the cycle solely in the case of joint production of aluminium and silicon from minerals of sillimanite tribe.

### INTRODUCTION

Essentially all world's primary aluminium is produced from high-quality bauxites of limited reserves by procedures developed back 120 years. At the same time, reserves of non-traditional aluminium ore deposits (low-quality bauxites, porcelain clays, mineral components of coals, minerals of sillimanite tribe, and others) are practically unbounded. The content of aluminium oxides in continental crust comprises ~15 %, but the utilization of these starting materials in aluminium industry is presently impracticable because of lack of technology of their economically profitable processing into  $\text{Al}_2\text{O}_3$  in existing alumina works. What is more, the cost of  $\gamma$ -alumina amounts up to nearly 50 % aluminium cost even with high-quality raw material. In this connection the development of fundamentally new technology oriented primarily to aluminium production from non-traditional resources and excepting the step of alumina production [1] is of currently central importance.

To this know-how can be related electrolysis of aluminium chloride in melt or subchloride method of aluminium extraction from ox-

ide polycomponent ores that is based on the reduction of aluminium chloride up to subchloride in hydrogen plasma with relatively low direct expenditure of electric energy [1, 2]. Aluminium chloride, as such, can be obtained practically from any one of aluminium-containing resources. The peculiarities of chlorination of  $\alpha$ - and  $\beta$ -alumina, gibbsite, boehmite, bauxite, and kaolinite were previously studied [3,4]. The use of these minerals presents no special problems for  $\text{AlCl}_3$  large-capacity production. The minerals of sillimanite tribe (kyanite, andalusite, sillimanite) having the general formula  $\text{Al}_2\text{SiO}_5$  were not yet regarded as resources for aluminium production in traditional or chlorine metallurgy in spite of their purity in respect of impurities, the great explored reserves in Russia [5], and the favourable thermodynamics of chlorination of aluminium component of the mineral [1]. The reason is that aluminium silicates with a great content of aluminium – sillimanites and mullites – are related to inactive low-chlorinated ores [3] and used for the moment in minor quantities only in refractory compositions.

The results of our experiments with kyanite concentrate have shown that the processing

of sillimanite ores (and mullite) can be economically feasible under specific conditions. Aluminium subchlorides, which are reactive toward oxygen, can be used as gaseous reducing agents for oxides of elements that have a more limited affinity for oxygen by comparison with aluminium. The action of aluminium subchloride on kyanite ( $\text{Al}_2\text{SiO}_5$ ) that is a mineral of the tribe of sillimanites, which are presently used only for the preparation of refractory compositions, has been discussed. Our experiments have shown that chlorine has no marked effect on this mineral, even though the reducing agent is present.

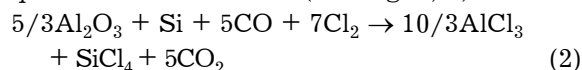
### EXPERIMENTAL

On etching aluminium from macroparticle surface, the residual layer of silicon dioxide prevents ingress of gaseous reagents into the interior of the particle and egress of products ( $\text{AlCl}_3$ ,  $\text{CO}_2$ ) at the surface. To solve this problem, we have advanced that this layer of silicon dioxide, which is inert to chlorine, should be reduced to silicon by gaseous aluminium subchloride ( $\text{AlCl}$ ) in accordance with the reaction  $\text{Al}_2\text{SiO}_5 + 2\text{AlCl} \rightarrow \text{Si} + 2/3\text{AlCl}_3 + 5/3\text{Al}_2\text{O}_3$  (1). Experiments on subchloride sublimation were in progress in tube furnace at 1000–1200 °C with the use of powdered kyanite concentrate, grains of 0.074 mm in size, of the following composition (mass %):  $\text{SiO}_2$  38.79,  $\text{TiO}_2$  0.69,  $\text{Al}_2\text{O}_3$  59.64,  $\text{FeO}$  0.44,  $\text{MnO}$  0.10,  $\text{CaO}$  0.02,  $\text{K}_2\text{O}$  0.05,  $\text{P}_2\text{O}_5$  0.01; loss of ignition – 0.25. If only  $\text{CCl}_4$  is used as chlorinating agent, a decrease in specimen mass is minor (%): 2.7 per 30 min, 3.5 per 60 min, 4.2 per 90 min. For the purpose of etching the arisen passivating layer of  $\text{SiO}_2$  at the surface of kyanite macroparticles the mixture of helium and aluminium subchloride ( $\text{AlCl}_x$ , where  $x < 3$ ) was passed over the prechlorinated specimen. The duration of specimen stay in aluminium subchloride vapour comprised 90 min. Kyanite particles turned black during the course of the process. The availability of silicon at the surface is confirmed by the results of X-ray analysis. Thereupon specimen was rechlorinated by  $\text{CCl}_4$  during 1 h. A decrease in mass comprised 30 %. An additional 30 % can be distilled off on second standing

of concentrate in aluminium monochloride vapour. It takes at least eight reduction-oxidation cycles under this productivity, which is comparable by overall time with the time of kaolinite chlorination [3]. Upon separating the bound water and collapsing the crystal lattice on igniting at temperatures in excess of 900 °C, kaolinite breaks down into silicon dioxide and  $\gamma\text{-Al}_2\text{O}_3$ , which is able to be chlorinated [4]. The number of cycles and their duration can be reduced by rise in content of  $\text{AlCl}$  in  $\text{AlCl}_x$ .

### RESULTS AND DISCUSSION

The results of thermodynamic calculation of equilibrium composition of products of the reaction (1) are presented in Fig. 1, a. It is evident that this reaction can be performed over a wide range of temperatures. Solid products of the reaction (1), which remain at the macroparticle surface, are exposed in the following half-cycle to chlorine action in the presence of CO and pass into a gas phase in consequence of the reaction (see Fig. 1, b) :



The reductant cycle is closed by the reaction  $2/3\text{AlCl}_3 + 4/3\text{Al} \rightarrow 2\text{AlCl}$  (3)

By this means the efficient superficial etching of kyanite takes place during the cycle reduction-oxidation process at 1000–1200 °C. In the absence of CO, only silicon selectively transfers to the gas phase. The chlorine and aluminium subchloride cycle is closed by the following reduction of aluminium and silicon chlorides. In addition to CO, which can be prepared by the gasification of organic fuel, an electric energy is necessary that aluminium chloride should be restored to the cycle of the process described above. The quantity of this energy is of fundamental importance for commercial realization of the advanced method of kyanite processing. The material balance on desired products, from Eqns. (1) and (2), shows that 4 mol of  $\text{AlCl}_3$  and 1 mol of  $\text{SiCl}_4$  are contained in the products of complete sublimation of 1 mol of kyanite. Half this aluminium chloride ( $2\text{AlCl}_3$ ) is recycled to the process, among them  $4/3\text{AlCl}_3$  are reduced to metal and used in reaction (3). The reduction of this amount of alu-

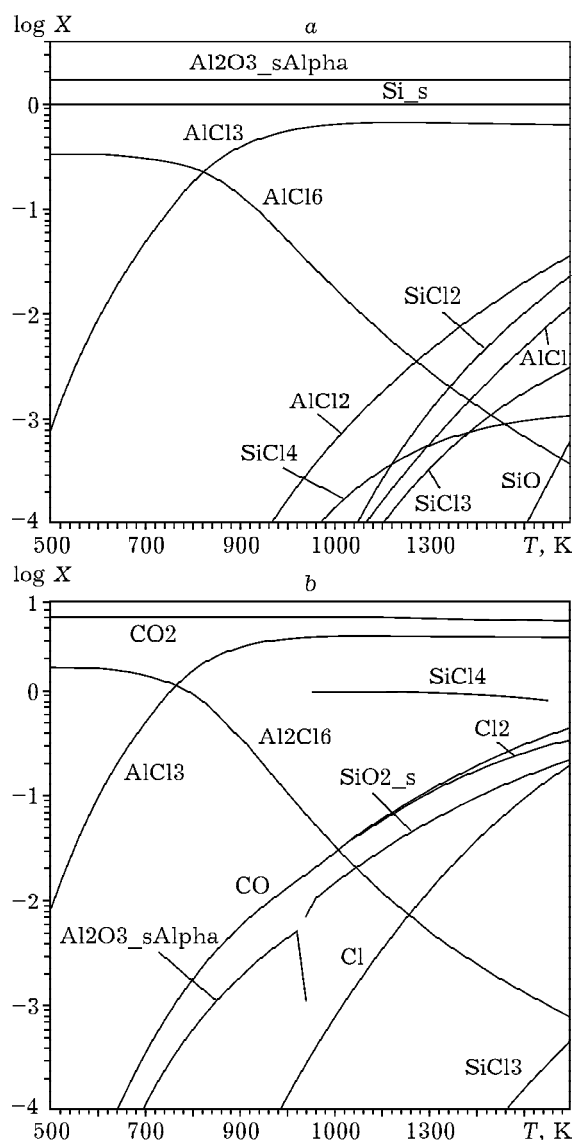


Fig. 1. Equilibrium composition of reaction products in the starting mixture  $\text{Al}_2\text{SiO}_5_{\text{s}} + 2\text{AlCl}$  (a) and mixture  $\frac{5}{3}\text{Al}_2\text{O}_3_{\text{s}} + \text{Si}_{\text{s}} + 5\text{CO} + 7\text{Cl}_2$  (b).  $P = 0.1$  MPa. Index “s” is related to solid phase; X is molar concentration.

minium chloride is just the process that has need for direct expenditure of electric energy. The preparation of 2 t of aluminium and ~1 t of silicon from kyanite calls for 1.33 t of aluminium, that is, 13.3 MW · h or 10 MW · h/t Al [2], which averages ~4 MW · h per ton of the product. This added direct energy expenditure is absent in the traditional technology of aluminium production. However this expenditure in the case of silicon chloride preparation is less as opposed to the expenditure of traditional tech-

TABLE 1

Direct expenditure of electric energy on the preparation of commercial products with the use of kyanite concentrate, traditional source material and technology, MW · h /t

Product	Alumina	Quartzite	Kyanite
Al	15	–	14.5
$\text{SiCl}_4$	–	12–18	4.5

nology of metallurgical silicon or ferrosilicon chlorination (12–18 MW · h/t). Consequently, the energy expenditure for aluminium preparation in the case of kyanite balanced production of metallic aluminium and silicon tetrachloride for solar energetics is to be correlated with the expenditure in the use of traditional and expensive stock (alumina) and 3–4 times smaller than that is in the use of quartzites in  $\text{SiCl}_4$  production (Table 1).

The proposed method is adaptable to the chlorination of fuel ashes wherein a considerable amount of mullite, which is derived from high-temperature burning of coal, is present.

## CONCLUSION

Minerals of sillimanite tribe are characterized by great-proved reserves and low content of admixtures [5], which is why they present an ideal source material for subchloride aluminium metallurgy and silicon tetrachloride. Both of these products can be obtained from one mineral with the use of one intermediate – aluminium subchloride.

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