

Prospects for Chlorine Metallurgy of Aluminum

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Abstract

Brief analysis of the state of affairs in aluminum industry of Russia is presented. A selective chloridation procedure using minerals from the sillimanite group is described as an example. Possibilities for expanding the production of alumina and primary aluminum are suggested based on the chlorine pyrometallurgy processes. The benefits of a technology of this kind over traditional electrolysis in cryolite-alumina melts are: lower electric energy consumption, lower production cost of aluminum, no highly toxic emissions to the atmosphere, and no solid and liquid wastes.

In his work dealing with utilization of large resources of sillimanite ores in the national economy of Russia, G. G. Lepezin discussed prospects for Russian aluminum industry. Several points of contention are considered in the present contribution.

The author's pessimistic forecasts concerning prospects for Russian aluminum companies provoke objections. After September, 2001, aluminum industry abroad has been living through difficult times because of the setback in American aerospace industry, sweeping market penetration by Chinese aluminum producers, and price rise for alumina. Soaring prices for power supplies and electric energy make some manufacturers reduce the output of aluminum. Nevertheless, Russian companies exhibited steady growth in primary aluminum production and associated alumina production at their plants in 2003. The modernization project launched at the Nikolaev Alumina Plant and measures to increase the efficiency of current facilities at the Achinsk Alumina Refinery resulted in further growth of alumina production by RUSAL group manufacturers. The total amount of mined bauxites produced by SUAL group manufacturers was 3.28 million tons during nine

months of 2003, the increment being 19.1 % over the same period of 2002 [1].

Aluminum industry in Russia and abroad has adequately responded to the alumina price rise by reactivating previously suspended facilities in China, USA, Bosnia, and Romania [2]. Thus Russian and foreign aluminum manufacturers have not yet sought new sources of raw materials; they merely expanded alumina production from traditional raw materials.

G. G. Lepezin's idea to use electrothermics or, more precisely, carbothermal reduction (CTR) of aluminosilicate to silumin in ore heat-treating electric furnaces for processing sillimanites neglected the disadvantages of the process and disregarded the market. Aluminum and silicon differ strongly in their affinity to oxygen and carbon. The product mixtures obtained by co-reduction contain many carbides and oxycarbides, which leads to unproductive losses of raw material (up to 20 %). With 10–13 % silicon present in silumins of common grades, one has to add electrolytic aluminum to the alloy or to remove excess silicon from it to obtain a marketable product. As a consequence, according to reference [3] cited by G. G. Lepezin, the production cost of 1 t of an

alloy obtained by CTR decreases by no more than 20 % compared to the production cost of silumin obtained by fusion of electrolytic aluminum and silicon. Therefore, complicated metallurgical treatments are required.

Today's level of primary silumin consumption in Russia is dozens of thousands of tons, while sillimanite ores amount to billions of tons. It was shown [4] that high-silicon silumin can find wide use, for example, for manufacturing light framework structures in building industry. However, the price for silumin profiles equal in strength should not exceed \$500/t, *i. e.*, the double cost of rolled steel. For this, today's price of aluminum and its alloys should be reduced threefold. There is no way to reach this by using electrothermics or electrolysis in cryolite-alumina melts.

The more promising lead and monochloride [5] methods for refining aluminum alloys are not much better than electrothermics. Carbothermal reduction of aluminosilicates, as well as electrolysis in cryolite-alumina melts, actively developed as industrial procedures since the 1930s. These are well-studied processes, whose technical and economic characteristics can be compared. For large-tonnage production of primary aluminum, CTR is not recommendable.

Russian manufacturers are dependent on alumina supplies, which is a matter of concern for owners of these plants. As they expanded aluminum production and built new plants, they have repeatedly figured out all versions of development. As soon as alumina import becomes unprofitable, alternative sources for its supply will be found. The cancel of tolling, which actually came into force on January 1, 2004, will possibly alleviate this problem. The strategy of Russian and foreign producers of aluminum is ingenuous: to manufacture the maximally expensive product with the minimum production cost. According to informal expert evidence, the profit of the Russian producers in 2003 was over \$500/t of aluminum. However, this strategy hinders the development of scientific and technological progress not only in Russia, but all over the world, since the huge demand of engineering and building industry for low-cost aluminum is not satisfied. Therefore, this is not a matter

of their own business for aluminum companies any more.

While the ratio of aluminum to iron and titanium in the earth's crust is 15.6 : 7 : 1 (based on their oxides) [6], the ratio of construction costs for rolled metal products obtained from them is 5 : 1 : 50. The high prices of aluminum and titanium restrict the use of titanium and titanium-aluminum alloys in chemical industry, aerospace engineering, and manufacturing of expensive sports equipment. The wide application of these alloys in automobile industry, shipbuilding, and railway transport is ruled out, although their consumer properties exceed the properties of steel.

Automobile construction industry makes use of only 4.6 % of the total output of aluminum, although its application lowers the weight of the car and reduces fuel consumption and CO₂ exhaust, making corrosion prevention treatment of the body unnecessary. European cars contain 120-130 kg of Al, this figure increasing by only 1 kg per year.

One hundred and seventeen years have passed since Heroult and Hall have discovered the procedure for the preparation of aluminum by electrolysis in a cryolite - alumina melt; the Crawl method of magnesium thermal reduction of titanium tetrachloride is about 70 years old. The industrial procedure of nickel recovery from sulfide and oxidized ores is approximately of the same age. Experts on nickel metallurgy have recognized that, according to experience gained in this field, no more than 5-10 % cuts of costs could be achieved by elaborating processes that have long been in use [7]. However, this is just the strategy that has been followed by large-tonnage non-ferrous and rare metallurgy within the last few decades. Short-term investments into improvement of old technologies result in a fast feedback with minimal risks. Now this strategy evidently no longer meets today's requirements, and looking for original technology concepts is necessary.

Among possible concepts is setup of new productions including the chlorine process. The use of chlorine even at the stage of ore processing enables almost complete recovery of metals from rocks and their conversion to the form convenient for further treatment. Previously,

prospects for enrichment of tin concentrates by chloridation were discussed [8]; prospects for selective extraction of titanium, iron, and aluminum with chlorine from rebellious ilmenite ores are validated in [9, 10]. Selective chloridation relies on the significant differences between the thermodynamic and kinetic characteristics of chlorination of silica and minerals containing metal oxides or sulfides. With a deficiency of chlorine in the system, metals (but not silica) are the first to be chloridated, and selectivity can be provided by simply varying the stoichiometry of the mixture for slow and batch pressure processes [9]. As shown by our experiments, silica does not react with chlorine during continuous fast chlorination of ores even if chlorine is present in excess. As a result, after chloridation the solid residue contains the same quantity of SiO_2 as the initial ore, and complete conversion of metals into chlorides takes 1 or 2 min at 900-1100 °C.

The physical properties of metal chlorides such as the melting and boiling points and electrochemical reduction potential differ widely. Due to this, they can readily be separated and reduced to metals without using chemical reagents.

For pilot production, selective chloridation of high-silicon aluminum raw material (kaolin clay) was performed by the Toth Aluminum Corporation (TAC, LA, USA). This gave aluminum chloride; subsequently, aluminum was obtained in an electrolytic cell with a melt of chloride salts with 1.5 times lower consumption of electric energy than for the best electrolyzers with cryolite-alumina melts. Dehydrated clay is treated with a chlorinating agent, SiCl_4 , according to the scheme



The advantage of this method of ore decomposition is that chlorine is not used for ore silica at any proportions, temperatures, and kinetic features of the process; aluminum chloride, whose sublimation temperature is 180 °C at atmospheric pressure, is readily removed from the reactor at the temperature of chlorination and purified from iron chloride (bp 320 °C), silicon tetrachloride (bp 57.45 °C), and titanium tetrachloride (bp 136.3 °C). Characteristically, the gas phase contains mostly alumi-

num chloride. This facilitates its trapping and purification from other volatile chlorides. Then AlCl_3 is dissolved in the melt of chlorides, in which it is subjected to electrolysis to yield production aluminum. Chlorine evolves at the anode and is recycled to silica chlorination.

In our opinion, this procedure has two limitations: 1) synthesis of silicon tetrachloride is needed, which involves certain difficulties for reasons stated above; moreover, excess solid silicon dioxide remains in the reactor and hinders the reaction; 2) the procedure involves the stage of electrolysis. Because of their low specific power, electrolytic cells with salt melts are large, which prevents their hermetic sealing, leads to significant heat losses, and requires large floor spaces. Today's daily output of a typical electrolyzer with fluorides is only 40 kg of aluminum per 1 m² of usable area. Heating an electrolyte is power-consuming. Therefore, we suggest that electrochemical reduction of aluminum chloride and the use of silicon tetrachloride in the process be rejected. From ecological and specific power viewpoints, electrolysis in salt melts is justifiable only for metal reduction from mixtures of high-boiling chlorides when other procedures for separating mixtures into pure chlorides are not readily feasible. In particular, for reduction of chlorides with high boiling points (Mn, Cu, REM, Ag, Na, K, Ca, Mg, *etc.*), it is possible to apply electrolysis of their mixed melts obtained after their separation from silica by leaching with water or weak hydrochloric acid solution and drying of the salt liquor. Most metals (Al, B, Fe, Ti, Zr, Hf, Nb, Ta, Ge, Ga, Sn, Hg, V, As, Se, Sb, Te, U, Zn, Ni, Co, Pb, Bi, Be, In, Th, Sc, Cd, Cr, Mo, W, *etc.*) form stable chlorides with boiling or sublimating points lower than the temperature in the chlorinator. These chlorides are liberated with the gas phase so that further chlorination is not hindered, and they can be fractionally condensed (desublimated) after the chlorinator. Further distillation for chlorides present in the liquid phase makes it possible to achieve very high degrees of purification.

Figure 1 shows a fragment of our thermodynamic calculation for disintegration of a cyanite concentrate with tetrachloromethane according to the following reaction (coefficients

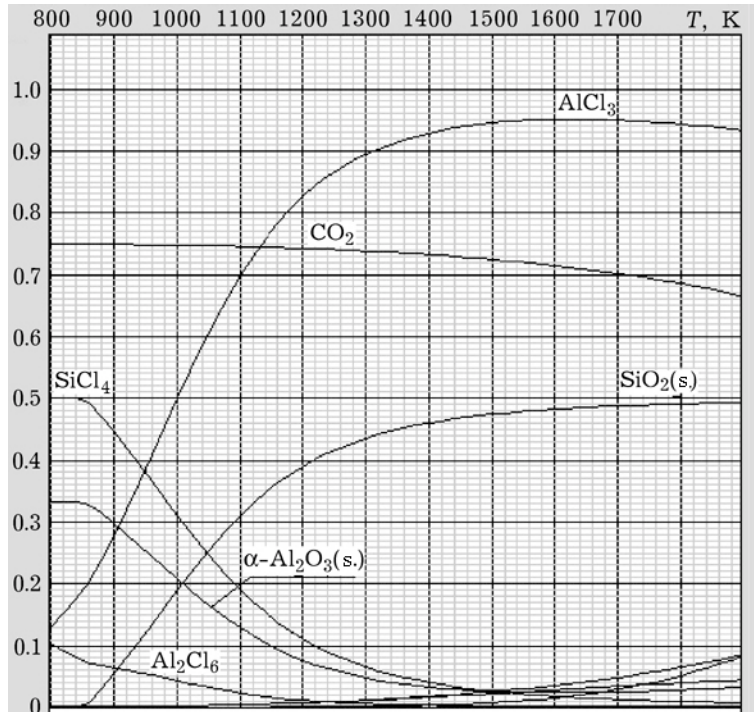
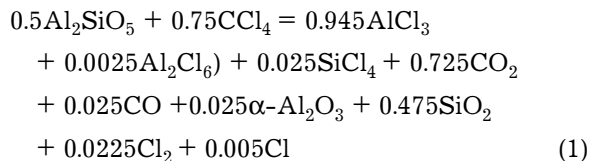


Fig. 1. Fragment of thermodynamic calculation of cyanite disintegration by tetrachloromethane according to eq. (1). Ordinate – content of components, mol. %. The following components are included in the calculation: C, C(solid)Carbon, Cl, Cl₂, CCl₄, CCl₃, CCl₂, CCl, SiCl₄, SiCl₃, SiCl₂, SiCl, SiO₂, SiO₂(liquid), SiO₂(solid), Si, Si(liquid), Si(solid), SiO, SiC, SiC(solid)Alpha, SiC(solid)Beta, SiC₂, Si₂C, Al, Al(liquid), Al(solid), Al₂, Al₂Cl₆, AlCl₃, Al₂O₃(solid), Al₂O₃(solid)Alpha, Al₂O, Al₂O₂, Al₄C₃(solid), AlC, CO, CO₂, AlCl₂, Al₂O₅Si(solid)Cyanite, AlCl, AlO₂, CClO, COCl₂, O, O₂. Mass balance maintained to an accuracy of 10⁻⁸ mol by the calculation program.

in the right part of the equation are given for $T = 1500$ K):



The fragment shown in Fig. 1 contains components with significant contents only. It is evident that 94.7 % of aluminum has passed into the gas phase in the form of a higher chloride, while 5.3 % remained in the form of alumina; 96.7 % of carbon is bound into dioxide, and 3.3 % of carbon is in monoxide form. After the solid residue has been isolated and subsequently chlorinated, the amount of alumina in the residue does not exceed 0.3 % of the initial content of alumina in the concentrate. Eventually, almost pure silica remains as a solid at the outlet of the chlorinator and may be buried or recycled as production wastes. The results of similar calculations for andalusite are practically the same as those for sillimanite,

but differ from cyanite data at $T = 1500$ K in the doubled quantity of aluminum in the solid residue because of the presence of undecomposed minerals.

Remarkably, the multistage scheme of sublimation described above is a one-pot process with countercurrents of gas and solid reagents. The gas streams entrain the sublimates out of the reactor, and the unchanged metal oxides are continuously washed by fresh portions of chlorine and reducing agent. As a consequence, all metals completely transform into chlorides in a single pass through the chlorinator. This makes it possible to reduce the chlorination temperature to 1200–1300 K. The amount of silica in the ore has no effect on the chemistry of the chloridation process and manifests itself only in the amount of heat losses. Good results were obtained in experiment with initial mass ratio in the ore $\text{SiO}_2 : \text{SMeO}_x = 9 : 1$.

The results are similar to the above theoretical data on the composition of solid end products when tetrachloromethane is replaced by a CO + Cl₂ mixture. This replacement is of

great interest from practical viewpoint as it enables one to reject synthesis of tetrachloromethane from chlorine and natural gas and to make use of the available procedures for the preparation of carbon oxide (II) from oxygen and solid organic fuel, the product being free from polycyclic hydrocarbons. On the other hand, using a reducing agent in the form of carbon oxide (II) instead of carbon increases the amount of gaseous sublimates and material expenses. Additional 0.96 kg of oxygen is needed for synthesis of CO, which is necessary for extracting (in the form of chloride) 1 kg of aluminum contained in cyanite at a temperature of 1500 K.

Thus at the first stage, the problem of large-tonnage manufacturing of commercial products from sillimanites may be solved by producing marketable alumina by burning (in oxygen) decontaminated aluminum chloride and selling it to aluminum manufacturers working with alumina. Chloridation of ores is an exothermic process, which does not require additional heat. The stage of combustion in oxygen that follows AlCl_3 decontamination also occurs with heat evolution. A similar process for the preparation of titanium dioxide from its tetrachloride is well known [11]. Chlorine released in the process is recycled to chloridation.

The procedure suggested for the preparation of alumina is universal from the viewpoint of raw materials and may be used for processing not only sillimanites, but also low-quality bauxites, kaolins, and other aluminum-containing raw materials. Unlike Baeyer process used to produce ~95 % of world's output of alumina, it does not require large quantities of reagents and is not accompanied by the same amount of liquid and solid wastes having adverse effects on the environment.

Unlike alumina and other commercial metal oxides, pure metals are much more difficult to obtain from their chlorides without using electrolyzers, but using apparatuses with high specific power and with lower (compared to electrolyzers) expenses of electric energy.

We are developing several procedures for the production of aluminum from its chloride, both with direct consumption of electric energy and without it. Direct consumption of electric energy for a single-stage plasma chemical pro-

cess does not exceed 5.2 kW h/kg of Al, which is appreciably less than current figures, for example, at the Krasnoyarsk Aluminum Smelter (~15 kW h/kg of Al).

At present, power expenses at Russian smelters using low-cost energy produced by hydroelectric power stations do not exceed 20 % of the production cost of aluminum. Therefore, even significant reduction of electric energy consumption will not result in a desirable decrease in its production cost. What is important is that aluminum smelters can now be located arbitrarily with respect to sources of low-cost electric energy, but close to sources of raw material or organic fuel. Moreover, with rational organization of technological process as offered, for example, in [12] for power-chemical processing of natural and associated gas to yield engine fuel, aluminum smelters working with the new process can provide themselves with electric energy. Natural organic fuel, namely, coal or natural gas is a power basis for the power-chemical process of metal extraction from ores and concentrates which is now being developed. Gas seems to be preferable because of the less expensive procedure for the preparation of a reducing agent (purified from aromatic hydrocarbons) for chloridation of the oxidized ore, which precludes formation of polycyclic organochlorine compounds at subsequent stages. The off-heat is concentrated and high-enthalpy in almost all versions of the process, and can be easily utilized with current electric energy generation technology, for example, using steam turbines.

The cost of alumina accounts for more than 55 % of the production cost of primary aluminum of the Russian smelters. Rejection of alumina is the main reserve for reduction of production costs. With the cost of cyanite ore of less than \$100 per ton of Al_2O_3 , the production cost of commercial aluminum obtained by our technology can be reduced twice. It is noteworthy that electrolysis of aluminum chloride in a melt was first tried out by the world's largest manufacturer of aluminum – American company Alcoa (~4 million tons of Al per year). However, this attempt was a failure since expensive alumina served as a raw material for aluminum chloride [5]. TAC found a better solution to this problem than the aluminum giant did.

The major argument against chlorine metallurgy of aluminum is the potentially high hazard of environmental pollution by superecotoxicants. However, the modern electrolysis process with fluorine salts has the same limitation. The presence of even minor residue of chloride salts in cryolite-alumina melts of electrolyzers results in release of chlorine at the anode. This chlorine interacts with petroleum coke and coal tar pitch inherent in the bulk of the anode to form polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), and biphenyls (PCBs), whose harmful action on the human immunoenzyme system and that of animals and plants is well-studied. Foreign aluminum manufacturers release to the environment an average of $1.3 \cdot 10^{-4}$ g of dioxins per ton of aluminum according to the international dioxin scale [13] (this dioxin factor is 100 times smaller in the rest of metallurgical processes). Comparable data were obtained by the Ecology Ltd. Company (Krasnoyarsk) who investigated atmospheric release from the Krasnoyarsk Aluminum Smelter ($2.18 \cdot 10^{-4}$ g/t of Al) [14, 15]. In 2003, KrAZ (Krasnoyarsk Aluminum Smelter) discharged 0.197 kg of dioxins into the atmosphere. For comparison, in 1995 (later data are not available), 2.98 kg of dioxins appeared in the atmosphere in Russia due to aluminum and steel melting and organic fuel combustion, including 0.87 kg on the European territory of Russia (ETR) [13]. Presumably, dioxin emissions did not increase during recent years on the ETR. In 2003 the emission of PCDDs and PCDFs to the atmosphere of Krasnoyarsk from the aluminum smelter alone was more than 20 % of the annual value for the whole ETR, these compounds being stable organic contaminants characterized by high toxicity, high stability, and capability of accumulating in the environment. Application of cermet anodes might be a good solution to the problem, but this requires large capital investments and is accompanied by increased power consumption during electrolysis.

Chlorine pyrometallurgy processes are used by the majority of titanium metallurgy plants in the world. In our case, application of apparatuses with a high specific power would enable complete hermetic sealing of a reaction chamber (sealing is about 90 % for self-baking

anode electrolyzers). Using specially prepared reducing agents (CCl_4 , CO) would completely rule out the contact of chlorine to complex organic substances. The oxidized ore should be prepared by calcination to the temperature of 1250°C in the presence of oxygen. For sulfide ores, this is a less acute problem since their chloridation occurs vigorously without a carbon-bearing reducer, through simple replacement of sulfur by chlorine. At reduced temperatures, sulfur precipitates as a condensed phase and is discharged from the reactor in the form of a commercial product.

Apart from the potential dioxin hazard, all other ecological characteristics of chlorine production of aluminum win in comparison to traditional electrolysis. Thus the presence of F_2 and HF in the atmosphere and the presence of fluoride salts in the soil in the neighbourhood of smelters are much more dangerous than the presence of gaseous, liquid, and solid inorganic compounds of chlorine. Moreover, fluororganic compounds are present in great amounts in the atmosphere around smelters. It is yet to be proved that they are harmless to the environment or that they possess substantially lower toxicity than organochlorine compounds. Here lies the second most important (next to improvement of economic factors) advantage of chlorine metallurgy of aluminum. Ecology is a weak point of current aluminum and alumina productions.

Aluminum is non-ferrous metal No. 1 in the world, and it accounts for 38 % of the world's total output of non-ferrous and rare metals and for 24.4 % of all sales [1]. Expansion of existing smelters and creating new plants in Russia noted by analysts bear witness to the large capacity of the market, which will multiply increase after price cuts for aluminum and will shift accents in the development strategy of engineering and building industry. A promising line of development may be, for example, widespread acceptance of low-cost aluminum in iron, non-ferrous, and rare metallurgy as a reducing metal for both oxides (now in use for obtaining only expensive metals) and halides of practically all metals widely employed in industry, except alkaline and alkaline earth metals. This scenario will be feasible if chlorine technology is used for process-

ing alternative and low-cost aluminum raw materials, which are primarily sillimanite minerals because of the low content of impurities.

The conclusions can be briefly formulated as follows:

1. Sillimanite minerals can outperform bauxites and nephelines in the proportion between aluminum and impurities (other than silicon). These are ideal raw materials to produce aluminum chloride by selective chloridation and to subsequently transform it into alumina or metal.

2. The problem of large-tonnage processing of sillimanite ores is directly related to the problem of change-over of aluminum manufacturers to chlorine metallurgy or of building new plants. This will essentially reduce the production cost of products and eliminate a number of environmental problems at Russian alumina plants and smelters.

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