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Ancient Roman technology of aluminum production: Process reconstruction

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Ancient sources indicate that aluminum was known at Ancient Rome. The article attempts to reconstruct the ancient technological process of production of metallic aluminum based on the currently available information about the properties of aluminum and modern production methods.

Keywords: *aluminum, Ancient Rome, fractional crystallization, pyrometallurgical processes, aluminothermy*

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Древнеримская технология получения алюминия: реконструкция процесса

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Античные источники свидетельствуют, что алюминий был известен еще в Древнем Риме. В статье делается попытка реконструировать древний технологический процесс производства металлического алюминия на основе имеющихся на настоящий момент сведений о свойствах алюминия и современных методах производства.

Ключевые слова: *алюминий, Древний Рим, фракционная кристаллизация, пирометаллургия, алюмотермия*

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The discovery and use of chemical elements are closely connected with the human history, and many mysteries are associated with them. In this article, we will try to unveil certain enigmas about aluminum, the 13th element of the Periodic Table.

Approximately in 25 AD, there existed an interesting story suggesting that aluminum was known by Romans already 2000 years ago [1]. This story is found in several ancient sources, and in a brief form in the works of Pliny the Elder [2]. The most comprehensive variant was written by Isidore of Seville who lived in the 7th century. In his book *Etymologiae*, volume 16, chapter 16, we read the following:

"They say that, during the reign of Tiberius, a worker invented a malleable and ductile glass alloy (*vitri temperamentum*). When he appeared before the Emperor, the worker showed him a chalice made of that material, and Tiberius threw it on the floor in indignation. The worker picked up the chalice, which was all bent as if it were a bronze vase, then took a hammer from his pocket and fixed the deformations. Then the Emperor asked, "Is there any other worker who knows the recipe of this glass?" When the worker swore that no one else knew the recipe, the Emperor ordered to behead him, fearing that the secret "would make gold not more precious than dirt, and other metals would lose value completely." Thus, the worker's secret remained unknown.

Based on the characteristics of the material mentioned in the text, such as its sheen and malleability, it must be aluminum, one of the most important metals in today's world. The indication that it was glass should be considered wrong, as there exists no such ductile glass [3].

Henri Étienne Sainte-Claire Deville recollected the story about the "silver made of clay" when he received a large subsidy from Napoleon III to build the first manufactory for aluminum production, and he spoke of generosity displayed toward him, thanking the emperor for being treated in a completely different way compared to the scientists of the Roman Empire.

Aluminum is one of the most widespread elements in nature, universally found in feldspar, mica and clay; it is the product of their weathering. Alum, the double sulfate of potassium and aluminum $KAl(SO_4)_2 \cdot 12H_2O$, according to Pliny the Elder, was known to Herodotus in the 5th century BC. Despite all this, metal aluminum was obtained much later, at the beginning of the 19th century.

Aluminum is a light metal of silvery color. Its density is 2.70 g/cm^3, the melting temperature is 660 °C, and the boiling temperature is 2270 °C. Aluminum has a face-centered cubic crystal structure. The thermal conductivity of aluminum at regular temperatures is 3 times higher than that of iron, and 2 times lower than that of copper. The electric conductivity of aluminum amounts to approximately 60% of that of copper. The heat capacity of aluminum is quite high, approximately 2.5 times higher than that of copper and 2 times higher than that of iron. The heat of fusion of aluminum is also rather high; that is why the metal, despite it having a lower melting temperature than copper, is more difficult to melt than copper. At the same time, melted aluminum remains liquid for longer than other metals.

The difficulties in production of metallic aluminum are determined by its extremely high affinity to oxygen. Aluminum oxide Al_2O_3 is naturally found in the form of corundum and emery, as well as gemstones – ruby and sapphire. A thin oxide layer covers the surface of the metal and prevents it from oxidation, even in a melted form. However, this protective layer is easily destroyed by mercury, which explains why mercury is banned from being carried onboard aircraft.

Aluminothermy, a process of interaction between aluminum powder and oxides of other metals, is well known. A lot of heat is emitted during this reaction. That is why the mixture of aluminum with iron oxide (thermite) is used for generation of high temperatures. Even the crystal form of boron may be obtained through aluminothermy.

Today, the industrial production of aluminum is based on electrolysis of aluminum oxide dissolved in melted cryolite Na_3AlF_6. Graphite electrodes are used in this process. The contents of the electrolytic baths are maintained in a liquid form by the heat generated by the electric current. The temperature of the electrolytic baths should not exceed 1000 °C. Metallic aluminum obtained on the cathode sinks to the bottom, while in the liquid form. On the anode immersed into the bath, oxygen oxidizes graphite producing carbon monoxide, which is then oxidized into carbon dioxide. The latter is also produced directly on the anode [4].

"For the first time, aluminum oxide was produced from alum by Andreas Sigismund Marggraf in 1754, later it received the name of alumina. Humphry Davy attempted (in 1808–1810) to obtain the metal from Al_2O_3 by electrolysis, but his efforts were in vain. Hans Christian Ørsted managed to produce aluminum in 1825 by reduction of anhydrous aluminum chloride (discovered by him) by potassium amalgam upon heating. This method, not always reliable, was significantly improved by Friedrich Wöhler who used pure metallic potassium instead of the amalgam (1827). Wöhler also made the first rather accurate description of aluminum, and he is usually credited with purification of metallic aluminum, since Ørsted did not have proof that he had obtained a true pure metal" [4].

Henri Étienne Sainte-Claire Deville modified Wöhler's method in 1854 by using sodium instead of potassium. Thanks to this, the production cost became 10 times lower, industrial production of aluminum was launched, and visitors of the Exposition Universelle in Paris in 1855 could already see a large ingot of "silver made of clay." At that time, aluminum remained a very expensive metal [5, 6]. It was used for jewelry making (including some extraordinary pieces) and even for making dentures.

In the present work, we attempt to reconstruct the technology used by the ancient Roman metallurgist to produce metallic aluminum. Obviously, the technique was quite challenging at that time.

Electrolysis can be excluded from consideration. Although archaeological evidence from the Middle East suggests that a galvanic cell did exist then, there are two circumstances that make electrochemical production of aluminum unrealistic. First, we can see that the relevant knowledge has been lost. Second, the conditions of electrolysis, such as high voltage and temperature, the use of a special melt, the protection from immediate oxidation, seem unachievable for the technological level of that period.

Let us consider possible pyrometallurgical processes.

The use of charcoal as a reductant was well known in ancient Rome, for example in iron production. We can hypothesize that the following reactions could be used for aluminum:

$$Al_2O_3 + 3C = 2Al + 3CO\uparrow \quad (1)$$

$$2Al_2O_3 + 3C = 4Al + 3CO_2\uparrow \quad (2)$$

As a metallurgical furnace is an open system, it is possible that the equilibrium in the reactions (1) and (2) is shifted to favor the products, due to the removal of the gases from the system. However, these processes are not very well suited for production of metallic aluminum. This is due to the fact that aluminum carbide is formed easily in this case.

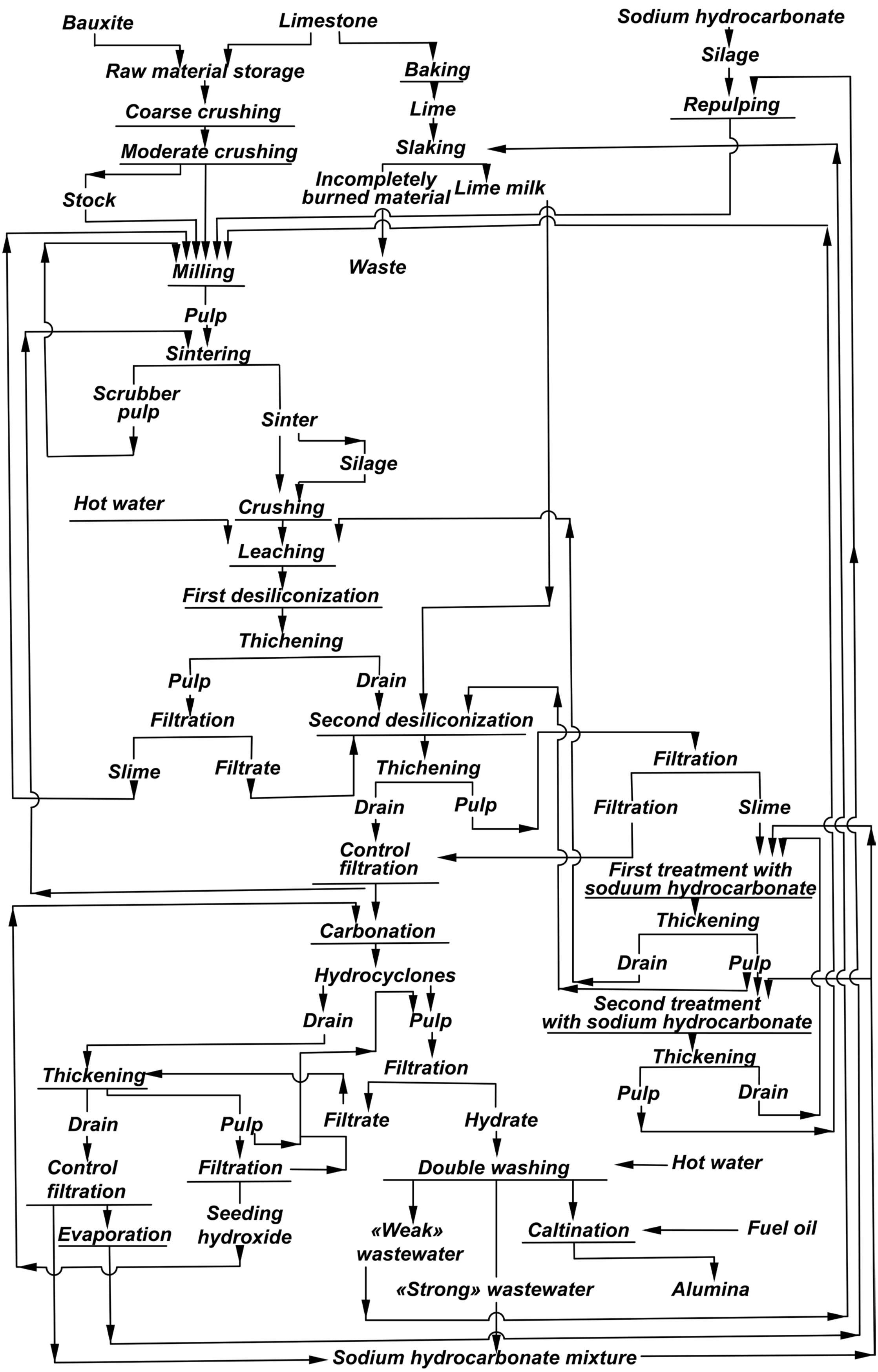
"All the attempts to replace electrolysis of a melt with thermal reduction of aluminum oxide have not been really successful so far. When carbon is used as a reductant, aluminum carbide Al_4C_3 is obtained, and this cannot be prevented" [4]. Still, it has been shown [7] that carbide formation can be minimized if the reaction is performed very quickly, and the oxide is mixed with just the exact amount of carbon. This method has been used to obtain aluminum in laboratory conditions with 93% purity. In the 19th century, there were successful attempts where alumina was reduced by carbon into metal with the use of fluxes, such as sodium chloride or borax [1].

So, in principle, carbothermal reduction of aluminum oxide into metal could be performed in ancient Rome. Let us consider now how alumina could be obtained from clay.

Currently, electrolytic production of aluminum uses alumina which is mainly obtained from bauxite. The latter is purified to remove silicon oxides, iron, titanium, etc. The process of bauxite extraction was developed by Carl Josef Bayer and is still used today. The method involves autoclaving of ore in the presence of hot sodium hydroxide solution. Since, quite obviously, there were no autoclaves in ancient Rome, we should not consider this approach as a possible one. At the same time, it is interesting to look at the technique developed by Henry Louis Le Chatelier in 1858, that is, the dry sintering of bauxite with sodium hydrocarbonate. According to a later version of the method, sintering is performed by adding limestone and spent liquor into the fusion mixture (wet sintering, Scheme 1) [8]. The sinter is leached with water and spent liquor. The aluminate solution, after desiliconization with lime milk, is saturated with carbon dioxide, and aluminum hydroxide is precipitated.

Feldspar and clay are not used in production of alumina any more. The major disadvantage of these sources is the presence of large amounts of silicates, which hamper the generation of pure alumina and produce a lot of waste. However, there is a method of nepheline (aluminosilicate of sodium and potassium) processing, developed by Alexander Fersman in the 1930s on the Kola peninsula. This technology is quite unique because it produces almost no waste. Nepheline processing involves wet sintering with limestone (see Scheme 2) [8, 9]. The process resembles the Le Chatelier method (see Scheme 1). The temperature of the sintering is in the range of 1000–1150 °C. The key chemical reaction occurring here is the following one:

$$NaKAl_2Si_2O_8 + 4CaCO_3 + 4H_2O = NaAl(OH)_4 + KAl(OH)_4 + 2Ca_2SiO_4\downarrow \quad (3)$$



Scheme 1. Le Chatelier's scheme.

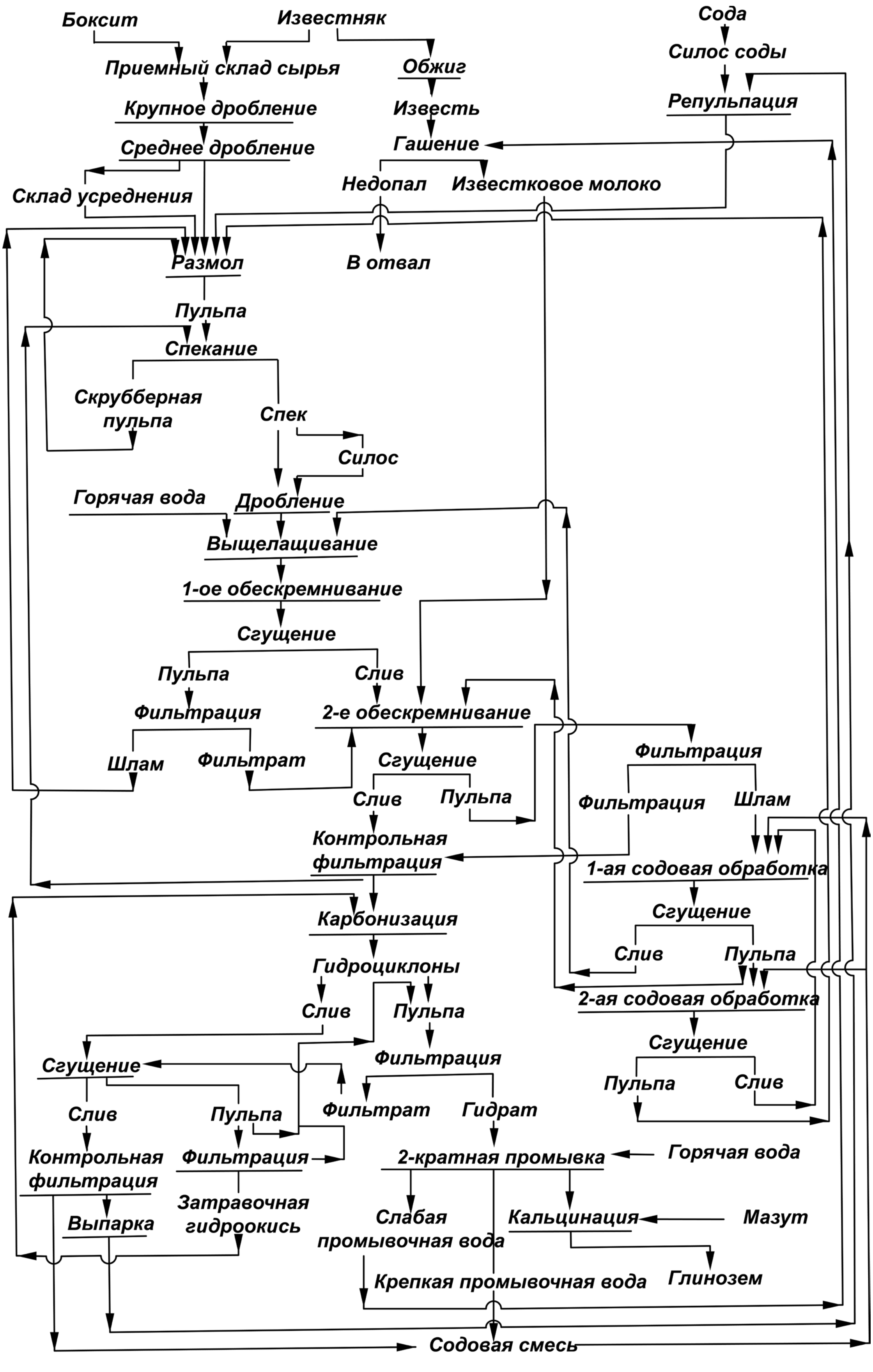
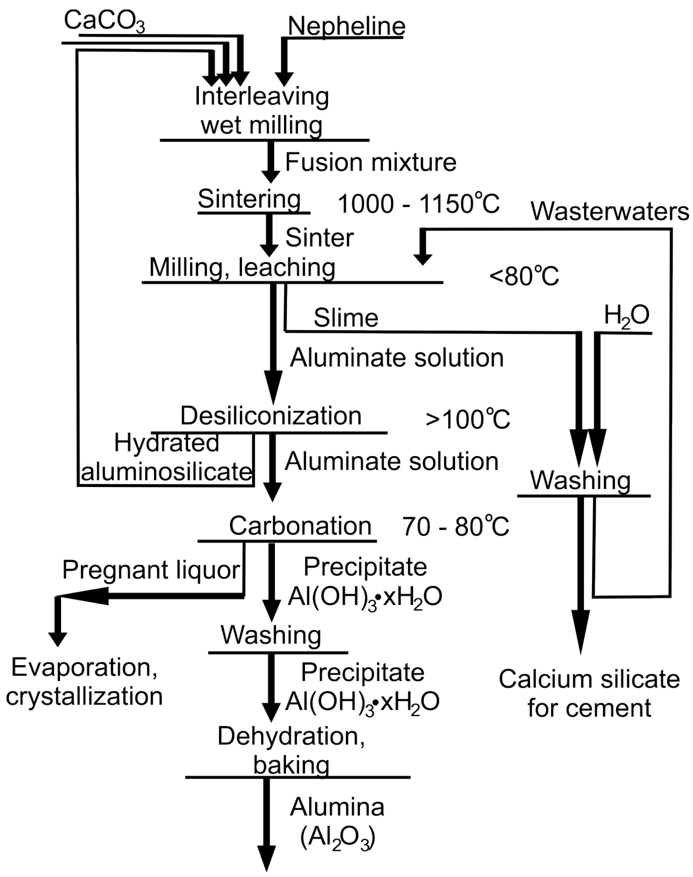


Схема 1. Схема Ле-Шателье.



Scheme 2. A.E. Fersman's scheme.

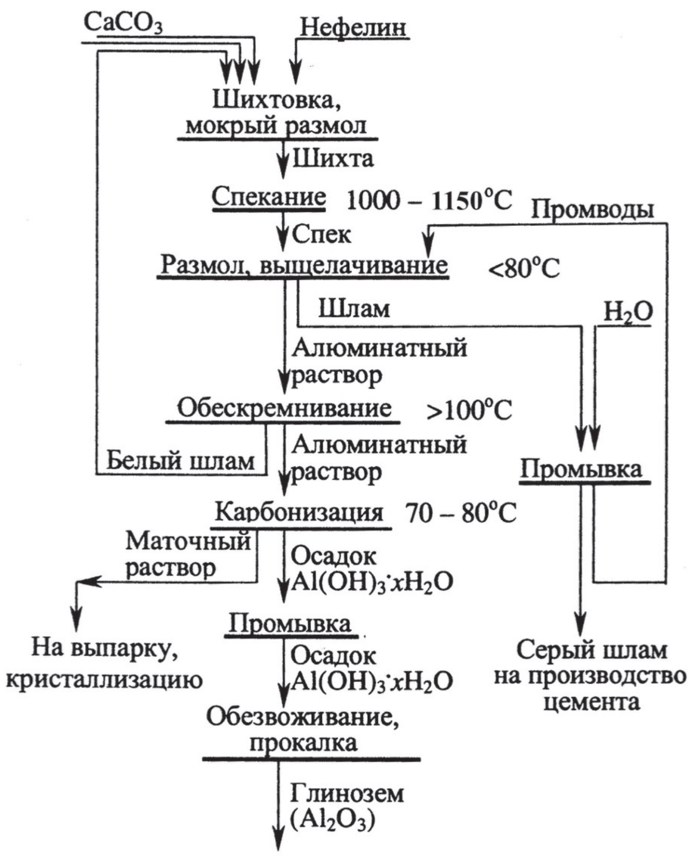


Схема 2. Схема А.Е. Ферсмана.

Calcium silicate is insoluble in water, and after washing it is used for cement production. The aluminates of alkaline metals are found in the alkaline solution. Desiliconization of the aluminate solution is carried out by heating it up to the boiling point. The hydrate of aluminosilicate, $Na(K)[AlSiO_4]xH_2O$, precipitates. The key stage of the process is precipitation of aluminum hydroxide. It is achieved by decreasing the pH of the solution through carbonation, just like in the Le Chatelier method. The chemistry of the process is the following:

$$2NaAl(OH)_4 + 2KAl(OH)_4 + 2CO_2 = Na_2CO_3 + K_2CO_3 + 4Al(OH)_3\downarrow + 2H_2O \quad (4)$$

Alumina is obtained by calcination of the precipitate.

However, the most probable source of the material used for the ancient aluminum production is clay. It is a family of minerals with complex composition and structure. One of clays is kaolin, or china clay, which is a water-containing aluminum silicate whose approximate composition is $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. Usually, there is almost twice more silica in clay than in nepheline. Other clays also contain alkaline metals [10].

Clay processing into alumina was a significant issue in Germany.

"In Germany, it is highly important to extract Al_2O_3 from local sources, namely the abundant clays. Due to the high silicates content in the clay, alkaline processing, such as the Bayer method, is not recommended. To reduce the dissolution of silicic acid, clay is processed with acids, and the technology aims to prevent the dissolution of iron oxides, since the following separation of iron from aluminum is challenging.

In the Buchner method, also called the Nuvalon process, separation of Al_2O_3 from SiO_2, Fe_2O_3 and TiO_2 is achieved through heating the clay in an autoclave with nitric acid, at a certain concentration. Aluminum nitrate is obtained in the solution, and the main admixtures are nitrates of alkaline and alkaline earth metals, which may be separated by fractional crystallization. Nitric acid is removed when aqueous aluminum nitrate is heated, and a very clean Al_2O_3 is produced.

In the Goldschmidt method, another acid is used for the treatment of the starting material, sulfurous acid, which is significantly cheaper. However, considerable amounts of iron are found in the solution as a result. Iron forms a basic salt with aluminum that crystallizes well. Also, as long as there is not too much iron, it is possible to separate aluminum by fractional crystallization of the basic sulfite" [4].

These methods requiring acid treatment are unlikely to have been used in the ancient Roman times [6].

Let us consider another approach which employs an absolutely different strategy. It is the Haglund method; it is the most probable option to produce aluminum precursor from clay. The method was originally developed for Al_2O_3 extraction from bauxite, but later it was found to be applicable for clays, too. In this technique, oxide ore is heated with carbon and pyrite in an electric oven. Aluminum is partially transformed into its sulfide which forms a relatively fusible slag with Al_2O_3, containing, for example, 80% Al_2O_3 and 20% Al_2S_3. This slag, because of its low density, is easily removed from the iron–silicon alloy that is formed simultaneously. The solidified slag is treated with hydrochloric acid, producing H_2S that can be used for sulfur manufacturing. Besides, $AlCl_3$ and insoluble crystalline Al_2O_3 are obtained [4].

Pyrite FeS_2 is a very common mineral which was already known in the Antiquity [2]. For the purposes of our historical reconstruction, we can hypothesize that slag, obtained in a process similar to the Haglund method, could be subjected to a second reduction with charcoal. In strictly controlled conditions, this reaction would produce metallic aluminum. However, such a process would have been a challenging one in ancient Rome, since the classical Haglund method requires high temperatures that do not seem reachable for the technology of that time. The requirement comes from the fact that the components are hard to melt; the melting temperature for the iron–silicon alloy it exceeds 1200 °C.

We could suggest that the ancient Roman technology of aluminum production included the stage of clay processing, based on a method similar to Le Chatelier and Fersman processes. The technique would involve sintering with limestone and/or sodium hydrocarbonate. In ancient times, limestone was well known and it was used in cement production. Sodium hydrocarbonate was common, too [2]. The temperature of sintering, 1000–1150 °C, could be achieved in ancient Rome.

Carbonation might have been a problematic part of the process, since we can say with great confidence that carbon dioxide in pressure vessels could not exist in ancient Rome. At the same time, this gas is formed upon burning of charcoal. Even today, factories use purified emission gases for carbonation. Therefore, it is quite possible that the ancient Roman worker whose story we know thanks to Pliny the Elder and Isidore of Sevilleused carbon dioxide. As metallic aluminum is so ductile, a chalice could be made from it very easily.

However, we still cannot hypothesize what kind of equipment was actually used. The process would require a crusher, a mixer, different ovens, a sediment tank, some filtering equipment, gas supply and many more things, and we do not know what the technology of that time had to offer.

It has to be mentioned that chemistry did not quite exist as a science at the times we are discussing. This means that the worker, if he really existed, had to go into great lengths to solve very complex issues – without understanding the nature of what he was doing. Possibly, it could have caused the feeling of divine intent – quite in line with the habits of the Antiquity.

We can suggest that the place where the discovery was made was almost certainly an ironworks. Such an establishment would offer certain advantages for aluminum production. Steel was commonly used in Rome for making gladius swords. The quality of the steel was not great, but this disadvantage was compensated by low prices. Iron was obtained from ore with the help of charcoal that is required in reactions (1) and (2). The waste gases in the process contain carbon dioxide. The temperature in the shaft furnace and the finery (Scheme 2) could reach 1200 °C. We need to mention that for cast iron, the eutectic point in the iron–carbon system is 1140 °C. Experiments with clay sintering would have been natural for refractory making.

Thus, we speculate that components needed for aluminum production were plentiful in ancient Rome. However, it is not very probable that the metal was actually obtained, as it would have required great luck and talent to do so.

The authors declare no conflicts of interest.

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