Chemical of the Week

ALUMINUM

Aluminum is the most abundant metal and the third most abundant element in the earth's crust, after oxygen and silicon. It makes up about 8% by weight of the earth's solid surface. Aluminum is too reactive chemically to occur naturally as the free metal. Instead, it is found combined in over 270 different minerals. The chief ore of aluminum is bauxite, a mixture of hydrated aluminum oxide $(Al_2O_3 \cdot xH_2O)$ and hydrated iron oxide $(Fe_2O_3 \cdot xH_2O)$. Another mineral important in the production of aluminum metal is cryolite (Na_3AlF_6) . However, cryolite is not used as an ore; the aluminum is not extracted from it.

Metallic aluminum was first prepared by Hans Oersted, a Danish chemist, in 1825. He obtained the metal by heating dry aluminum chloride with potassium metal.

$$AlCl_2 + 3 K \longrightarrow Al + 3 KCl$$

Robert Bunsen prepared aluminum metal in the 1850s by passing an electric current though molten sodium aluminum chloride. However, because both potassium metal and electricity were quite expensive, aluminum remained a laboratory chemical and a curiosity until after the invention of the mechanical electrical generator. In 1886, Charles Martin Hall of Oberlin, Ohio, and Paul Héroult of France, who were both 22 years old at the time, independently discovered and patented the process in which aluminum oxide is dissolved in molten cryolite and decomposed electrolytically. The Hall-Héroult process remains the only method by which aluminum metal is produced commercially.

The first step in the commercial production of aluminum is the separation of aluminum oxide from the iron oxide in bauxite. This is accomplished by dissolving the aluminum oxide in a concentrated sodium hydroxide solution. Aluminum ions form a soluble complex ion with hydroxide ions, while iron ions do not.

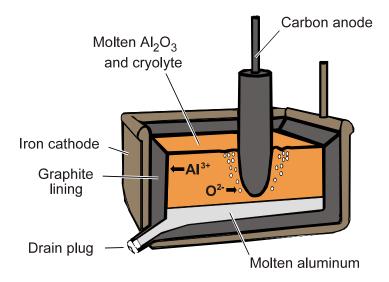
$$Al_2O_3$$
: $xH_2O(s) + 2OH^-(aq) \rightleftharpoons 2Al(OH)_4^-(aq) + (x-3)H_2O(1)$

After the insoluble iron oxide is filtered from the solution, $Al(OH)_3$ is precipitated from the solution by adding acid to lower the pH to about 6. Then the precipitate is heated to produce dry Al_2O_3 (alumina).

$$2 \text{ Al(OH)}_3(s) \xrightarrow{\text{heat}} \text{Al}_2\text{O}_3(s) + 3 \text{ H}_2\text{O}(g)$$

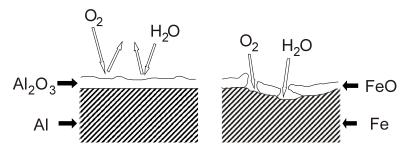
In the Hall-Héroult process, aluminum metal is obtained by electrolytic reduction of alumina. Pure alumina melts at over 2000 °C. To produce an electrolyte at lower temperature, alumina is dissolved in molten cryolite at 1000 °C. The electrolyte is placed in an iron vat lined with graphite. The vat serves as the cathode. Carbon anodes are inserted into the electrolyte from the top. The oxygen produced at the anodes reacts with them, forming carbon dioxide and carbon monoxide. Therefore, the anodes are consumed and need to be replaced periodically. Molten aluminum metal is produced at the cathode, and it sinks to the bottom of the vat. The principal cell reactions are

At intervals, a plug is removed from the vat and the molten aluminum is drained. The heat required to keep the mixture molten is provided by resistive heating of the electrolyte by the current passing through the cell. Typical cells use a potential of 4 to 5 volts and a current of 100,000 amperes.



Aluminum is a silvery-white metal with many valuable properties. It is light (density 2.70 g/cm³), non-toxic, and can be easily machined or cast. With an electrical conductivity 60% that of copper and a much lower density, it is used extensively for electrical transmission lines. Pure aluminum is soft and brittle, but can be strengthened by alloying with small amounts of copper, magnesium, and silicon.

Based on its chemical reactivity, aluminum should not be very useful at all. Its standard reduction potential is -1.66 volts, indicating that it is a very good reducing agent. It is far more active than iron, which has a reduction potential of -0.44 volt. Aluminum weathers far better than iron, however, because the product of its corrosion, Al_2O_3 , adheres strongly to the metal's surface, protecting it from further reaction. This is quite different from the behavior of iron's corrosion product, rust. Rust flakes off the surface of iron, exposing the surface to further corrosion. The protective oxide coating on aluminum is frequently enhanced by the process of anodization. Aluminum metal is made the anode in an electrolytic cell, where aluminum metal is oxidized, and its protective oxide coating is thickened. The oxide coating on aluminum renders it impervious to most acids. However, any chemicals that form a strong complex with aluminum ions, e.g., OH^- and Cl^- ions, will react with the oxide coating. Therefore, aluminum will dissolve in hydrochloric acid and sodium hydroxide solutions.



Recycling of aluminum saves considerable energy. Because the aluminum is already in the metallic state, all of the energy spent in purifying the ore and reducing it to the metal is saved when aluminum is recycled. The aluminum needs only to be melted to be reused. Aluminum has a rather low melting point, 660° C, and requires only 26 kJ/mol to melt. To reduce a mole of Al from Al_2O_3 requires over 780 kJ.

