Karl Josef Bayer and his time*—Part 1

On the occasion of the hundredth anniversary of his death

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Karl Josef Bayer (1847-1904), an Austrian citizen, studied for a short time under Remingius Fresenius in Wiesbaden and then under Robert Bunsen in Heidelberg from 1868 to 1871. After a short period of independent work in Brno in Moravia, he worked at the Tentelev Chemical Plant in Saint Petersburg, Russia, and then went to Yelbuga. It was there that he invented his process for the production of pure alumina from bauxite. In 1894, he returned to Austria but died suddenly at the age of 57. Details about Bayer and his time will be outlined.

Introduction

The aluminum ore known as bauxite was discovered in 1821 by Pierre Berthier (1782-1861), a professor at the School of Mines in Paris, while prospecting for iron ores in southern France. He called it "Terre d'alumine des Beaux" after the village of Les Beaux near Marseille where he made his discovery. The red colour of the deposit had interested him as a possible source of iron ore for the blast furnace in the district. However, it was found to contain too much Al_2O_3. The name was later changed to "beauxite" and then to "bauxite." Bauxite was first thought to contain alumina dihydrate, $Al_2O_3.2H_2O$, however, it was later shown by thermal analysis to contain a mixture of the hydroxides $Al(OH)_3$ and AlOOH. When the need arose to produce alumina, methods were developed to treat bauxite. Aluminum can be solubilized readily from bauxite by acids, but on adding an alkali to the solution, a gelatinous basic salt, rather than a crystalline hydroxide, is precipitated. The gelatinous precipitate is difficult to filter and wash. Furthermore, since iron and titanium are also partially dissolved in acid, the precipitate will be contaminated, creating a separation problem. As a result, the acid-leaching route was never used to prepare Al_2O_3; it is used only on a small scale to prepare aluminum sulphate for water treatment. A postage stamp issued in 1987 by France commemorated the discovery of bauxite in "Les Baux de Provence" (Fig. 1).

In 1855, Louis Le Chatelier (1815-1873; Fig. 2), the Chief Inspector of Mines in France, invented a process for the recovery of alumina from bauxite. His son, chemist Henri Le Chatelier (1850-1936), is best known for the thermodynamic principle which bears his name. The process involved heating bauxite with sodium carbonate at about 1000°C to form sodium aluminate and then leaching it with water. Aluminum hydroxide is then precipitated from this solution by bubbling CO_2 gas generated during the calcination step (Fig. 3a).

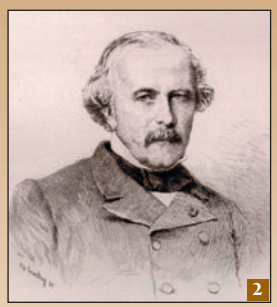

Fig. 1. A postage stamp issued in 1987 by France commemorated the discovery of bauxite in Les Baux de Provence.
Fig. 2. Louis Le Chatelier (1815-1873).

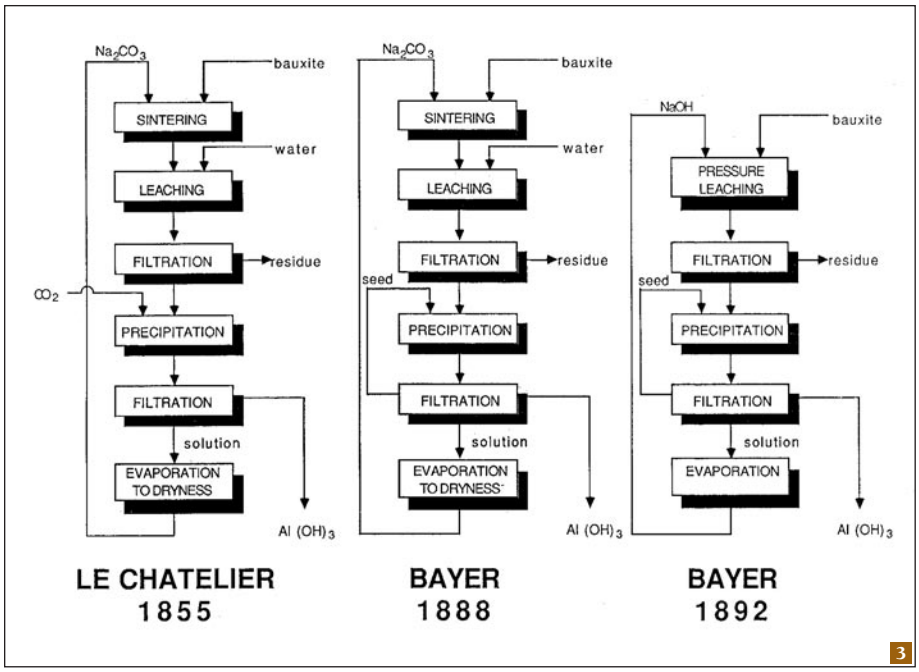

Fig. 3. The shift from the thermal route (Le Chatelier process) to the hydrometallurgical route (Bayer process) for the production of alumina.

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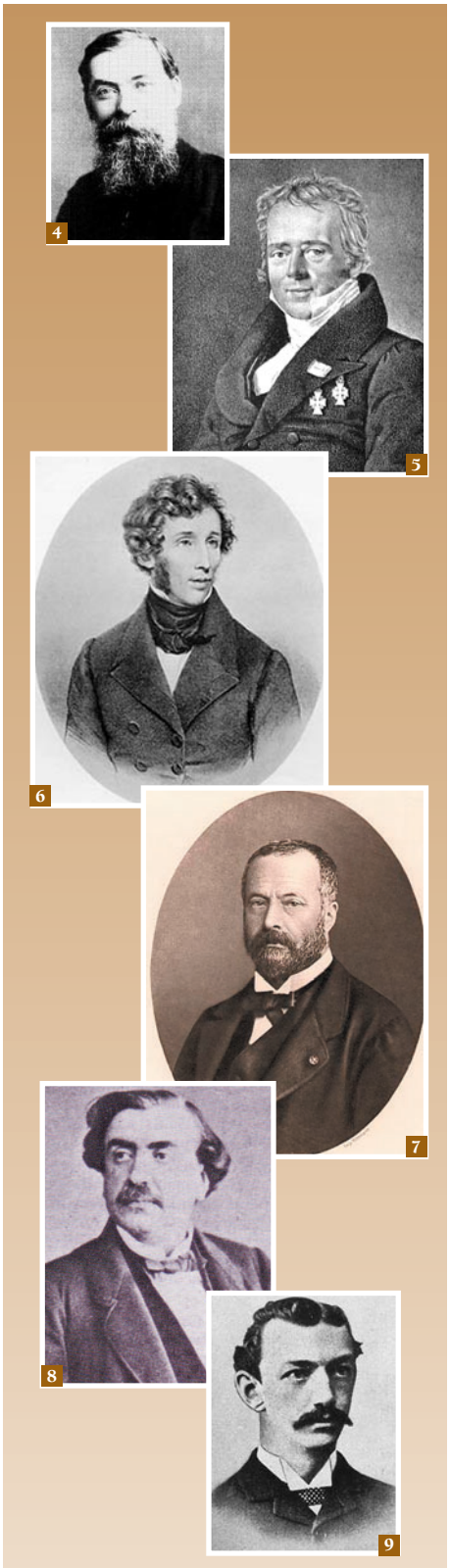

Fig. 4. Karl Josef Bayer (1847-1904).
Fig. 5. Hans Christian Oersted (1777-1851).
Fig. 6. Friedrich Wöhler (1800-1884).
Fig. 7. Henri Sainte-Claire Deville (1818-1881).
Fig. 8. Henry Merle (1825-1877).
Fig. 9. Hamilton Castner (1859-1890).

The process was modified by Karl Josef Bayer (1847-1904; Fig. 4) in two stages. In 1888, he replaced CO_2 by a seed of aluminum hydroxide on which precipitation took place by vigorous agitation (Fig. 3b). In 1892, he introduced the pressure leaching step which transformed the process into a fully hydrometallurgical process. This marked the beginning of pressure hydrometallurgy (Fig. 3c). The process, based on his two German patents, became known as the Bayer process.[1] The process received immediate recognition and is used today in practically the same way as described in the original patents.

The Beginning of the Aluminum Industry

Aluminum was isolated in minute amounts for the first time in 1825 by Danish physicist Hans Christian Oersted (1777-1851; Fig. 5) by reacting $AlCl_3$ with potassium amalgam; he himself prepared $AlCl_3$ for the first time that same year by reacting chlorine with Al_2O_3. On his way home, after studying with Berzelius in Stockholm, German chemist Friedrich Wöhler (1800-1884; Fig. 6) stopped in Copenhagen to visit Oersted. In 1827, after settling in Berlin, he repeated Oersted's experiment using metallic potassium instead of amalgam; using this technique, he obtained small metallic particles of aluminum from which he was able to determine its density.

Henri Sainte-Claire Deville (1818-1881; Fig. 7), a professor of chemistry at École Normale Supérieure in Paris, laid the foundation for the aluminum industry; he prepared the metal on a large scale in 1854 at the Chemical Works Javel in a suburb of Paris, using a modified Oersted method. Bars of aluminum were displayed at the Paris Exhibition in 1855 as "silver from clay." In 1857, a new plant was installed at Nanterre near Paris, and in 1859, he wrote his book *De l'Aluminium, ses Propriétés, sa Fabrication et ses Applications*. Deville's process involved the following steps:

- preparation of a double chloride sodium and aluminum by reacting a mixture of bauxite, NaCl, and coal tar with gaseous chlorine in an iron retort;
- preparation of metallic sodium by heating a mixture of sodium carbonate, limestone, and coal in a retort; and
- reaction of metallic sodium with the double chloride $AlCl_3$.NaCl in a reverberatory furnace to get metallic aluminum and slag.

In 1882, one year after Deville's death, the process was used at Compagnie des Produits Chimiques d'Alais (Alès) et de la Camargue at the Salindres plant near Nimes. The plant belonged to Henry Merle (1825-1877; Fig. 8) who was fabricating sodium carbonate using the Leblanc process, H_2SO_4 by the chamber process, hydrochloric acid, and other chemicals. The plant manager was Alfred Pechiney who was put in charge of operations when Merle died suddenly in 1877 at the age of 52. Merle is considered to be the founder of the inorganic chemical industry in France and his plant as the origin of the Pechiney Company.

Hamilton Castner (1859-1890; Fig. 9), of Columbia University in New York, was responsible for reducing the cost of aluminum by his invention of a cheap method for producing sodium from molten NaOH by reduction with an iron-carbon mixture. However, this was too late for the Deville process, which was rapidly displaced by a new process invented simultaneously by Paul Héroult (1863-1914; Fig. 10) in France and Charles Martin Hall (1863-1914; Fig. 11) in the United States. The new process was based on the electrolytic reduction of Al_2O_3 dissolved in fused cryolite found in Greenland. The process is used worldwide today.

[1] Bayer's first invention coincides in the same year with MacArthur's invention of the cyanidation process for leaching gold ores. Both the cyanidation and Bayer's process are the largest hydrometallurgical processes today and thus the year 1888 marks the beginning of modern hydrometallurgy.

Alumina from Cryolite

Before the utilization of bauxite for alumina manufacture, cryolite (Na_3AlF_6), which was discovered in Ivigtut, in south Greenland, by a Danish whaler who brought a piece of it to Copenhagen, was used. The name of the mineral means "frost-stone" in Greek in reference to the snow-like appearance of the solid that melts easily. In 1854, one year before Le Chatelier invented his process, a process was developed by Julius Thomsen (1826-1909; Fig. 12), a professor at the Technical University of Copenhagen, which involved heating the cryolite with limestone, followed by water leaching, to extract sodium aluminate formed, leaving behind CaF_2 in the residue. Aluminum hydroxide was then precipitated from the aluminate solution by CO_2 leaving sodium carbonate in solution to be recovered as a by-product (Fig. 13).

By the early 1860s, a large-scale soda and alumina production based on cryolite was in operation and was one of the largest industries in Denmark. The process was also implemented in other nearby countries as well as in the United States at the Pennsylvania Salt Company in Natrona, near Pittsburgh. However, in 1894, soda production from cryolite ceased in Copenhagen due to competition with the new Solvay process. In 1897, about 13 000 tons of the mineral were mined, the major part of which was delivered to the Pennsylvania company, but three years later, the process was also abandoned in the United States. Thomsen is best known for developing the principle that the heat of formation is a measure of chemical affinity, and for a four-volume work, *Thermochemische Untersuchungen* he published between 1882 and 1886.

Later, cryolite played an important role in the Hall-Héroult process when it was discovered by German chemist Martin Kiliani (1858-1895) that a cryolite sample had an exceptionally low melting point, and when analyzed, it was found to contain a small amount of Al_2O_3 as an impurity. Thus, he concluded that Al_2O_3 decreases the melting point of cryolite. This information was immediately utilized by Héroult and Hall to propose cryolite as a molten salt solvent for Al_2O_3. However, before this process was invented, German chemist Heinrich Rose, and, independently, British metallurgist Allan Dick devised a method for producing aluminum by reduction of cryolite with sodium. Henri Sainte-Claire Deville also considered using this method but abandoned the idea after a French expedition to Greenland in the summer of 1856 discovered that the cryolite deposit was of limited size. The French bauxite was considered to be a more suitable raw material for an expanding aluminum industry. In 1962, the Greenland operation was closed.

Early German Alumina Plants

Three plants producing Al_2O_3, alum, and aluminum sulphate using bauxite imported from France were erected in Germany:

- 1880 Chemische Fabrik Bergius in Goldschmieden near Berslau (now Worclaw in Poland);
- 1885 Giulini in Ludwigshaven; and
- 1914 Martinswerk in Bergheim near Cologne.

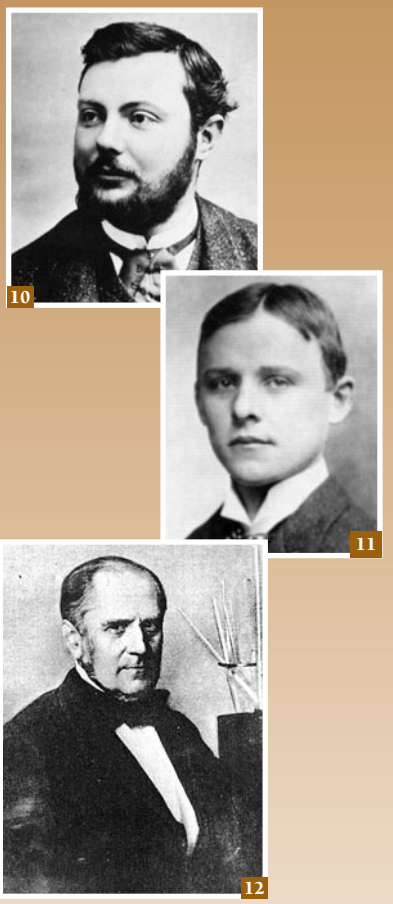

Fig. 10. Paul Héroult (1863-1914).
Fig. 11. Charles Martin Hall (1863-1914).
Fig. 12. Julius Thomsen (1826-1909).

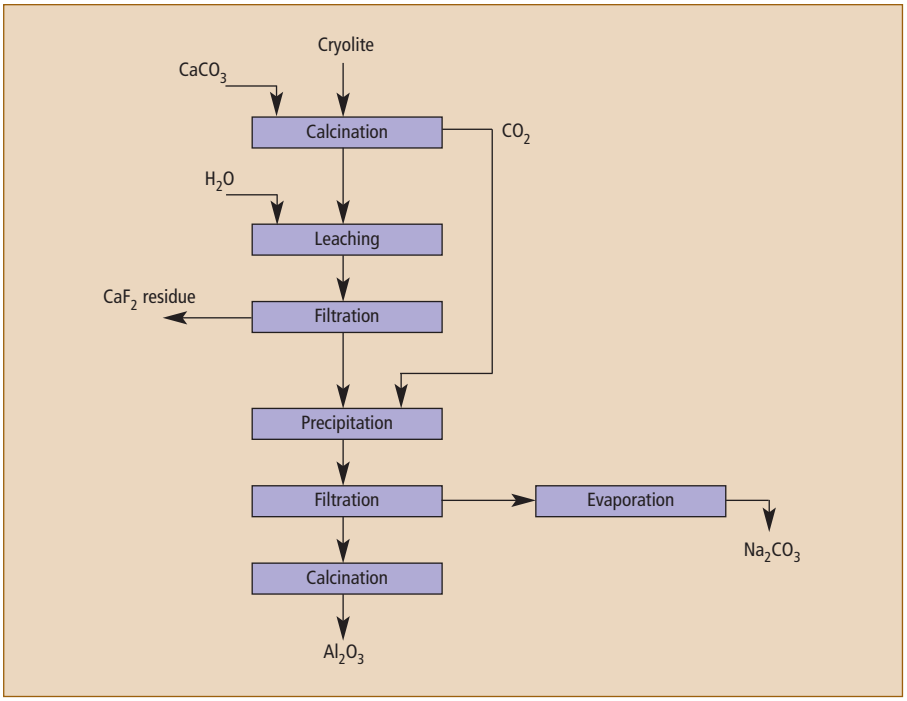

Fig. 13. Thomsen's process for the recovery of Al_2O_3 and Na_2CO_3 from cryolite.

While alum and aluminum sulphate were produced by acid leaching, Al_2O_3 was produced by the Le Chatelier process. During World War I, when the supply of French bauxite was cut off, the Vereinigte Aluminium Werke, a German state-run company undertook prospection for bauxite in 1917 and acquired interests in its mining in Istria, Italy, Croatia, and Hungary. Two more alumina plants were constructed and located in the lignite district that used the sodium carbonate calcination process to treat Hungarian bauxite and Bayer's seed precipitation method. The first plant near Lauta (the Lautawerk) and the second in Grevenbroich near Duisburg (the Erftwerk) were built in cooperation with the Giulini brothers.

Appendix: Important dates in the history of aluminum

1807	In England, Humphry Davy (1778-1829) attempted to produce aluminum by electrolyzing a fused mixture of alumina and potash.
1825	In Denmark, Hans Christian Oersted (1777-1851) produced aluminum by reducing aluminum chloride with potassium amalgam.
1827	In Germany, Frederich Wöhler (1800-1882) produced aluminum by reducing aluminum chloride with potassium.
1845	Wöhler made enough aluminum to determine its density and other important properties.
1854	In France, Henri Sainte-Claire Deville (1818-1881) reduced aluminum chloride with sodium and laid the foundation of the aluminum industry.
1854	In Germany, Robert Bunsen (1811-1899) and Sainte-Claire Deville produced the first aluminum by electrolysis, using fused sodium aluminum chloride as electrolyte.
1855	In France, Sainte-Claire Deville, Henri Debray (1827-1888), and others started aluminum works in Glacière, France.
1859	Sainte-Claire Deville published *De l'Aluminum, ses Propriétés, sa Fabrication, et ses Applications.*
1885	The Cowles brothers produced aluminum alloys by electrothermal reduction of alumina and carbon in the presence of copper and iron.
1886	In the United States, Hamilton Castner (1859-1899) invented a process for producing cheap sodium for reduction of aluminum chloride.
1886	In the United States, Charles Martin Hall (1863-1914) and in France, Paul Héroult (1863-1914) invented the first commercially successful electrolytic reduction process and founded the modern alumnum industry.
1887	In Russia, Karl Josef Bayer (1847-1904) invented his process for the production of Al_2O_3.
1888	The Pittsburgh Reduction Company (now Aluminum Company of Amrica) was founded.
1888	Aluminum Industrie, A.-G., Neuhausen, Switzerland, was founded.
1888	Société Électrométallurgique Française (Froges) started its first electrochemical plant for the production of aluminum in France.
1891	The last plant using the sodium reduction process for the production of aluminum was closed.
1894	The British Aluminum Company was founded.
1907	In Germany, Alfred Wilm invented duralumin.
1917	Vereinigte Aluminum-Werke, A-G., was formed in Germany.
1919	In the United States, William Hoopes perfected the electrolytic refining process.
1960	Aluminum production surpased that of copper and became the second metal after iron.
1986	The hundredth anniversary of aluminum production by the Hall-Héroult process was celebrated worldwide.

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