BAYER'S PROCESS FOR ALUMINA PRODUCTION: A HISTORICAL PERSPECTIVE

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The Bayer Process (for alumina) as we know it today involves two steps:

- The pressure leaching of bauxite with NaOH solution to obtain sodium aluminate solution.
- The precipitation of pure aluminum hydroxide from this solution by seeding with fine crystals of $Al(OH)_3$.

The leaching step was invented five years after the precipitation step (Table 1), and the precipitation step was an improvement to the Le Chatelier Process (1), namely replacing CO_2 by the seed (Fig. 1).

In 1888 a British Patent entitled "A Process for the Production of Aluminum Hydroxide" was issued to the Austrian chemist Karl Josef Bayer (Fig 2, 3) who, at that time, was living in Saint Petersburg in Russia (known as Leningrad from 1924 to 1991)(Table 1). The process immediately achieved industrial success, displacing the thermal process known as the Le Chatelier process that had been used until that time to produce alumina from bauxite. The thermal route was invented by Louis Le Chatelier (1815-1873), the Chief Inspector of Mines in France, whose son the chemist Henri Le Chatelier (1850-1936) is best known for the thermodynamic principle which bears his name.

Table: Bayer's Patents

Contents	Country Granted	Number	Year
Precipitation of pure $Al(OH)_3$	Britain	10,093	1888
from sodium aluminate solution	USA	382,505	1888
by seeding	Germany	43,977	1888
The pressure leaching of bauxite	Britain	5,296	1892
with NaOH to obtain sodium	USA	515,895	1892
aluminate solution	Germany	65,604	1892

Bayer (2) was born in Bielitz, a few kilometers southwest of Cracow in Silesia, at that time a Province of the Austrian Empire, now in Poland. The map of Europe at that time was quite different from what we know it today. It was the age of empires: the British, French, German, Russian, Ottoman, and Austrian empires. The Austrian Empire was composed of a vast territory encompassing the present day Austria, northern Italy, Bohemia, and Moravia which are parts of present-day Czechoslovakia, Hungary, Transylvania (a part of present-day Romania), Croatia, Dalmatia and Bosnia Herzegovenia (parts of present-day Yugoslavia), and Silesia and Galicia in southern Poland. While the official language was German, many other languages were spoken, e.g., Hungarian, Romanian, Czech, Polish, Ruthenian (an old name for Ukranian), Slovak, Slovenian, Serbo-Croatian, and Italian. The multitude of nationalities and languages caused many revolts and political unrest, but music and the arts were fluorishing. This was the time of Johann Strauss and his waltzes and

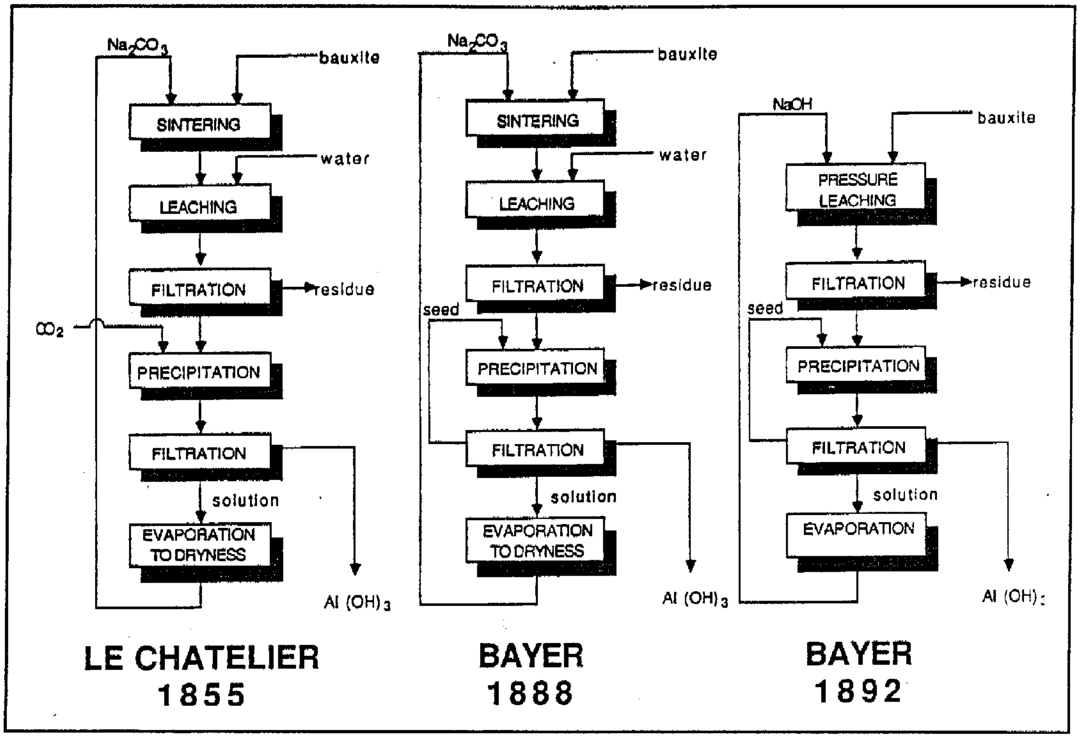

Figure 1 The development of Bayer's process for alumina production

Gustav Mahler and his symphonies. Bayer attended school in his home town and at the wish of his father, who was an architect, started to study architecture.

Later Bayer switched over to science and went to Wiesbaden in Germany to work in the laboratory of the famous chemist Remigius Fresenius (1818-1897), then in a steel factory in Charleroi, Belgium. In 1869 he enrolled at the University of Heidelberg where he worked under Professor Robert Bunsen (1811-1879) for three years. At that time Bunsen's laboratory was visited by many chemists who became famous later on. Among those were Dimitri Mendeleev, Friedrich Beilstein, Henry Roscoe, Auer von Welsbach, Lothar Meyer, Victor Meyer, and many others. Bunsen's reputation stems from his discovery, together with the physicist Gustav Kirchhof (1824-1887), of the spectroscopic method of analysis and the discovery of the two metals rubidium and cesium by this new tool in 1860-61. Bunsen is also famous for the burner known by his name and now found in every chemical labortory. In Heidelberg, Bayer earned the doctorate at the age of 24 after submitting a thesis entitled, "A Contribution to the Chemistry of Indium." Indium had been discovered few years earlier by the two German chemists, Ferdinand Reich (1790-1882) and Theodor Richter (1824-1989) utilizing Bunsen's spectroscope.

In the same year Bayer obtained his doctorate, Europe was undergoing tremendous changes. There was the war between France and Prussia; the French were defeated at Sedan, Napoleon the Third surrendered, and the Republic was proclaimed. Also, Germany was proclaimed a united empire: the victorious Prussian King Wilhelm the First was named Emperor of Germany at Versaille, near the defeated French capital. Italy, like Germany, also became one nation in the hands of Garibaldi.

After obtaining his doctorate, Bayer returned to his home country Austria where he was appointed a lecturer at the University of Technology at Brunn, a few kilometers northeast of Vienna in the Moravian Province of the empire (now in Czechslovakia). He left the University in 1873 to establish a research and consulting laboratory in Brunn.

However, he later gave up this venture and moved in 1885 to St. Petersburg, the capital of Russia. Russia at that time was open to all foreigners with technical and artistic skills but was suffering from the reign of terror of Alexander the Third after the assassination of his father, Alexander the Second, in 1881. In Russia, Bayer grew his beard the way the Russians did (Fig. 2). He was a contemporary to such famous personalities as

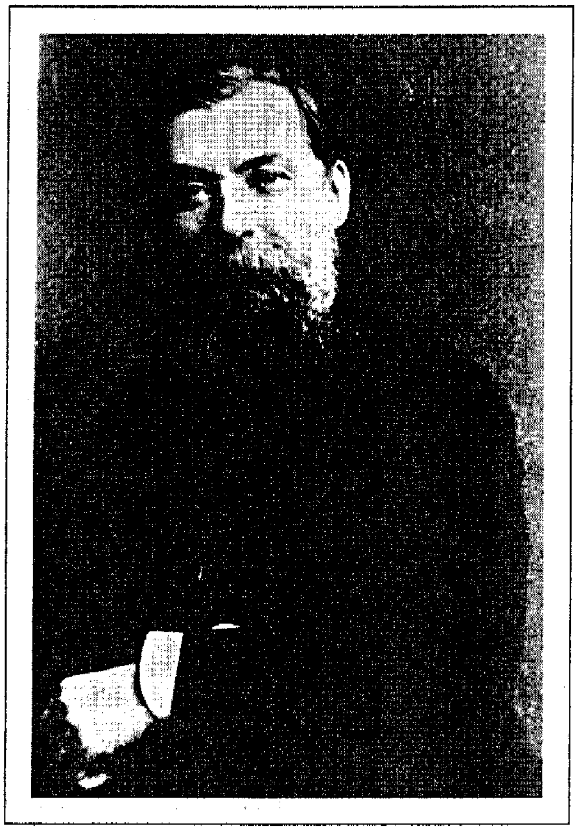

Figure 2 Bayer in Saint Petersburg, Russia

Tchaikovsky, Rimsky- Korsakov, Pavlov, and Mendeleev.

Bayer's years in Russia were his most fruitful and creative years. He joined the Tentelev Chemical Plant near Saint Petersburg to work on problems of production of pure aluminum hydroxide for the dyeing of fabrics. The plant, presently known as "Red Chemist Plant," was using the Le Chatelier Process to produce aluminum hydroxide which was used as a mordant for dyeing cotton, wool, and silk. Mordant dyeing was described by Pliny in Roman times when naturally occurring alum (aluminum sulfate) had been used. The textiles to be dyed were soaked in a solution of the hydroxide dissolved in a weak acid, then squeezed, dried and steamed whereupon the hydroxide precipitated on the fibers. Thus treated, the textiles could be immersed in a dye solution to form a colored "lake." This was a standard method of dyeing at that time. For example, Turkey red, a popular red color, was prepared by dyeing with alizarine on aluminum hydroxide mordant.

While in Tentelev Bayer, at the age of 41, made the discovery that aluminum hydroxide could be precipitated from sodium aluminate solution if a seed of a freshly precipitated aluminum hydroxide were agitated vigorously in the cold solution. The pure product could be collected by filtration and washed. The process was soon adopted by the Tentelev Plant. This was the subject of his first British Patent of 1887 and the German Patent of 1888 (Table 1). Four years later he made his second discovery that alumina contained in bauxite could be dissolved selectively by heating with a solution of sodium hydroxide under pressure in an autoclave to form sodium aluminate solution. He found also that the alkaline mother liquor obtained after the precipitation of aluminum hydroxide could be used.

At the age of 45, after firmly establishing his professional career and his social status, Bayer married the niece of the Russian statesman, Count Sergei von Witte, who was of German origin and who served briefly as prime minister after the 1905 Revolution during the reign of the last Russian Tsar Nicolai the Second.

After seven years in Saint Petersburg, Bayer then moved to another chemical plant at Yelabuga on the Kama River, 200 kilometers east of Kazan in the Tatar region not far from Urals, to build the second plant for alumina manufacture by his process. Coloring matters were used by man from ancient times, but these were all naturally occurring: for example, indigo and alizarine were mainly extracted from plants and insects and were imported to Europe from distant countries. At Bayer's time synthetic dyestuffs were produced for the first time on a commercial scale, and it was in this industry that high pressure reactors were first applied. Organic intermediates which were needed to manufacture the synthetic dyestuffs were produced in heated agitated reactors that were able to withstand the pressure required for reactions such as sulfonation, nitration, reduction, etc.

Bayer remained only two years in Yelabuga. During this period he received numerous contracts from foreign countries to build alumina factories. The aluminum industry in Russia started only many years after the revolution; bauxite was first mined there in 1926 at a location called Bocksitogorsk (which means bauxite city) and is 150 kilometers east of Saint Petersburg. The reduction plant was constructed in 1932 at Volkhov not far from the deposits.

Bayer then returned to Austria, apparently with the intention of developing the aluminum industry in his own country. He settled in Rietzdorf in southern Styria and devoted some time to scientific research (Fig 3). During this period he developed a method for the manufacture of synthetic cryolite which is used as an electrolyte in the aluminum industry. He then developed the first bauxite deposit in Austria and built a plant to produce Al_2O_3 by his process. However, he was unable to

Figure 3 Bayer in Rietzdorf, Austria

raise enough capital, and thus his plans failed. Bayer, although an average scientist, was an inventor and had a great sense of enterprise. He published only one paper entitled "Studies on the Winning of Pure Aluminum Oxide" but his patents were of great importance. He died suddenly at the age of 57; his widow survived to the age of 94. The foreign companies (except two) who were applying his patents stopped paying royalties after his death. It was difficult at that time to sue them, and consequently his house and laboratory had to pay for his debts. In 1906 his family moved to Graz.

Bayer and his wife raised five sons and a daughter. His home in Rietzdorf was a meeting center for many famous industrialists, among whom were Paul Heroult (1863-1914), and Charles Martin Hall (1863-1914) the discoverers of the electrolytic process for aluminum. He loved music and the arts; he himself was a talented artist. He spoke six languages: German, French, English, Russian, Italian, and Slovac. He had an excellent collection of minerals which he displayed at the Chicago exhibition in 1890.

Bayer's process involving both pressure leaching and precipitation by seeding is used today in practically the same way as when it was discovered one hundred years ago. However, marked improvements in the engineering aspects have taken place and these are responsible for decreasing the cost. The economy in energy is due to two factors: an increased heat recovery and the use of large autoclaves. Heat exchangers and flash tanks are now extensively used to economize energy. Flash tanks serve the additional purpose of the evaporation of solutions. The larger the reactor the less will be the heat losses. Construction of such equipment that can be used reliably is due to improvements in engineering design and manufacturing. Along with autoclaves, precipitation tanks have increased in size correspondingly. Furthermore, steam is now used for heating and agitation and autoclaves are connected in series to permit continuous operation. This allows automation and decreasing manpower.

The use of tube or pipeline autoclaves began simultaneously in Germany and in Czechoslovakia in 1967 for the leaching of bauxite by a modified Bayer Process. In this process a temperature of 300°C is used, resulting in a vapor pressure in the system of about 13000 kPa. Because of the high temperature, a reaction time of only 2-3 minutes instead of 4-6 hours is sufficient to extract the aluminum. The continuous process has a high thermal efficiency because of the effective heat exchange system.

A new importance was given to the Bayer Process when gallium was needed by the semiconducting industry and its recovery from process solution became desirable. Gallium was first discovered in zinc blende and its first production was from this source. When it was discovered in bauxite in 1896, however, this new source

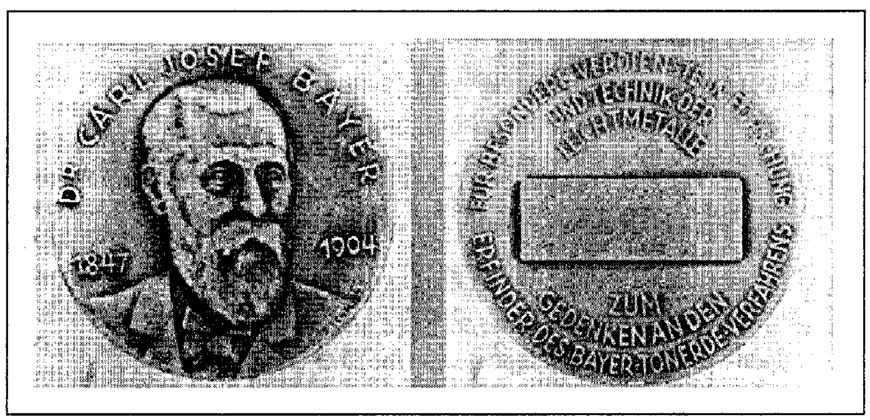

Figure 4 Medal in honor of Bayer awarded at the International Light Metals Congress

became the major supplier although its average concentration is less than 0.01%. Alusuisse, a major aluminum manufacturer in Switzerland, commenced industrial production of gallium from bauxite in 1955. Gallium follows aluminum in the Bayer Process being recovered from the aluminate solution. The present world production of gallium is about 50 tons/years.

Bayer is honored in his native country Austria by the medal bearing his name and awarded every six years to a distinguished researcher in the field of aluminum. (Fig. 4) The award ceremony takes place during the International Light Metals Congress, which is held in Leoben and in Vienna. Bayer's first name appears in the Germanized spelling as "Karl" in his patents but in the Latin form as "Carl" on his medal (Fig. 4).

The first medal was awarded at the Fourth Congress in 1961 to the Swiss metallurgist Prof. Alfred von Zeerleder of the Eidgenössische Hochschule in Zürich for his work on aluminum alloys. The second medal was awarded at the Fifth Congress in 1968 to the German Chemist Professor Hans Ginsberg of the Technische Hochschule in Clausthal for his two volume book on "Bauxite and Aluminum." The third medal was awarded to the Austrian metallurgist Professor Roland Mitsche of the Montan Universität in Leoben for organizing the Light Metals Congresses and for his book "Angewandte Metallographie." In 1981 two medals were awarded: one to the German chemist Dieter Altempohl, Head of Research Department at Alusuisse in Switzerland and author of "Aluminum and Aluminum Alloys;" the other to the American chemist Allen Russell, Vice-President of Alcoa who developed the Alcoa Chloride Process.

In 1987 two medals were again awarded: one to the German chemist Dr. Klaus Bielfeldt, Director of Research of Vereinigte Aluminiumwerke in Bonn where he developed the pipeline reactor for bauxite digestion and the fluidized bed aluminium hydroxide calciner; the other to the Norwegian chemist Professor Kai Grjotheim of Oslo University, who contributed extensively to the chemistry of fused salts and particularly aluminum production. He coauthored "Aluminum Electrolysis. Fundamentals of the Hall-Heroult Process" and "Aluminum Smelter Technology. A Pure and Applied Approach."

Bayer's invention to satisfy the need of the Russian textile manufacturers soon turned out to become the most important invention for supplying the need of the growing electrolytic aluminum industry that was discovered four years earlier by Hall and Heroult. The Hungarian aluminum industry issued in 1987 a medal in Bayer's honor to commemorate the hundred years's anniversary of depositing his first patent.

REFERENCES AND NOTES

1. J. D. Edwards, F. C. Frary, and Z. Jeffries, aluminum and Its Production, McGraw Hill, New York, 1930.
2. *Wiener Zeitung*, July 16, 1932; *Berg und Hüttenmännisches Jahrbuch*, 82(3), 83 (1934); and *Österr. Biographie Lexikon*, 1815-1950, Vol. 1, p.59 (1957). There has been practically nothing written about Karl Josef Bayer himself in historial metallurgy books, technical encyclopedias, or books on aluminum either old or new except for the following. In 1969 while the writer was working at Anaconda's Research Department in Tucson, Arizona, an old Austrian friend, Professor Franz Pawlek, who had just retired from the Technische Universität in Berlin, visited him. When the writer raised this question with him he was told that he knew only that Bayer, although so famous for his process, had died a poor man, and that he was Austrian and not German. The writer then took the matter to the Austrian Chemical Society in Vienna; through the efforts of its secretary, Professor Anton Maschka whom the writer knew well, he was able to get the home address of Professor Fritz Bayer, the inventor's son. Professor Fritz Bayer was the writer's examiner in electrochemistry at the Technische Hochschule in Vienna (now known as Technische Universität) when he was a graduate student there from 1956 to 1959. Professor Bayer retired from teaching at the age of 70 in 1959, the same year the writer graduated. He was kind enough to send the writer a comprehensive biography and a photograph of his father. The writer immediately sent the photograph to be included in Volume Two of his book, *Principles of Extractive Metallurgy*, which was at that time (1969) in press (4). A summary of the biographical data was published in Volume One of the newly founded series, *Progress in Extractive Metallurgy*, in 1973 (5). This included also other photographs of Bayer that were kindly supplied to the writer by another old Austrian friend from Leoben, Professor Erich Schwarz von Bergkampf, who retired from teaching at the Montanistische Hochschule (now Montan Universität) in 1962. The article in *Progress* included the German text of the two patents by Bayer. His letter to the writer dated November 10, 1969, authorizing publication of this information and requesting a copy of the paper when published, was no doubt typed by Prof. Bayer as can be judged from the numerous typographical errors it included; at that time he was 80 years old.
3. K. J. Bayer, "Beiträge zur Kenntnis des Indiums," Dissertation, Heidelberg Universität, 1871.
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5. F. Habashi, Ed., *Progress in Extractive Metallurgy*, Vol. 1, Gordon & Breach Science Publishers, New York, 1973.