

2. BAYER PROCESS

This section includes five significant areas:

1. Bayer Process Design. This first area includes the fundamental principles of Bayer process design as well as the history of the development of the Bayer process. The basic process has not changed but the development of its application for more than a century is truly remarkable. What is even more remarkable is that significant further improvement is feasible.
2. Physical Data. Contains much of the materials and liquor data needed to prepare flow sheets and heat and material balances.
3. Calcium Chemistry. Included are papers that discuss the effects and use of lime in the process as well as using lime to re-causticize (react) sodium carbonate back to sodium hydroxide.
4. Silica Chemistry. These papers discuss the dissolution of bauxite silica during digestion and the subsequent reaction that forms solid sodium aluminum silicate (desilication product).
5. Organic Removal. These papers deal with the important subject of removing accumulated sodium organates (originating from organic carbon compounds in the bauxite) from Bayer liquor to enhance alumina product quality and to improve process productivity of alumina.

Equally good papers in the list of recommended readings could not be included as published papers because of the limitation on the size of the book.

Fred Williams

A HUNDRED YEARS OF THE BAYER PROCESS
FOR ALUMINA PRODUCTION*

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On August 3, 1888 German Patent No. 43977 entitled "A Process for the Production of Aluminum Hydroxide" was issued**. The discovery which led to the patent was made by the Austrian chemist Karl Josef Bayer (1847-1904) (Figure 1) who was at that time in Russia, and the process became known as the Bayer Process in his honour (1,2). The process immediately achieved industrial success, displacing the pyrometallurgical process that had been used until that time to produce alumina. The Bayer Process involved the pressure leaching of bauxite with NaOH solution to obtain sodium aluminate solution from which aluminum hydroxide was precipitated by seeding.

Today bauxite is not only the principal source of aluminum but also of gallium, both metals being effectively recovered by the Bayer Process. The purpose of this paper is to outline the historical background of this discovery and its importance to hydrometallurgy.

BACKGROUND

Bauxite was discovered in 1821 by the French chemist P. Berthier who called it alumine hydratée des Beaux after the village of Les Beaux near Arles in Southern France. The red color of the deposit had attracted Berthier's interest as a possible iron ore for the blast furnace in the district. However, he found it to contain too much Al_2O_3 to be of value for this purpose. The name was changed to beauxite in 1847, by A. Dufrenoy and to bauxite in 1861 by the French metallurgist Henri Sainte-Claire Deville⁽³⁾. Bauxite was first thought to contain alumina dihydrate, $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$; however, later it was shown by thermal analysis to contain a mixture of the hydroxides $\text{Al}(\text{OH})_3$ and AlOOH . Discoveries of bauxite were later reported in many parts of the

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Figure 1

Karl Josef Bayer (1847-1904). The Austrian-born chemist invented the process known by his name for the manufacture of aluminum hydroxide while working in a chemical factory in Saint Petersburg (now Leningrad) in 1888.

** This invention was made one year after another invention of equal importance to hydrometallurgy the so-called Cyanidation Process by John Steward MacArthur et al., entitled "A Process of Obtaining Gold and Silver from Ores", British Patent No. 14174 issued October 19, 1887. See F. Habashi, "One Hundred Years of Cyanidation", Bull. Can. Inst. Min. & Met. September, 1987.

world including Jamaica, Surinam, Guyana, Australia, USSR, USA, and Hungary. It now represents one of the highest tonnage mineral raw materials treated chemically — about 88 million tons annually world-wide (Figure 2).

Bayer's Process lies on three unrelated industries: The recently developed aluminum industry, the old textile industry, and the pressure technology of the rising synthetic dyestuffs industry.

The Aluminium Industry

After the 1854 discovery by Sainte-Claire Deville of a method for separating kilogram amounts of aluminum* from its oxide attempts were made to produce the metal on a large scale. To this end a plant was constructed at Salindres in France which combined two processes: The Le Chatelier Process for the production of aluminum oxide and The Sainte Claire Deville Process for the production of aluminum chloride and its reduction to the metal by metallic sodium. These processes are now described.

The Le Chatelier Process. Aluminum can be solubilized readily from bauxite by acids but on adding an alkali to the solution a basic salt, rather than a hydroxide is precipitated. Further more, since iron and titanium are also dissolved in acid the precipitate will be contaminated, creating a separation problem. As a result this route was never used to prepare pure Al₂O₃. The French mining engineer Louis Le Chatelier (1815-1873) whose son the chemist Henri Le Chatelier (1850-1936)* is best known for the thermodynamic principle which bears his name, obtained alumina from bauxite in 1855 by a thermal route in three steps:

1) An intimate mixture of powdered bauxite and sodium carbonate was heated in a reverberatory furnace to transform aluminum hydroxide into sodium aluminate:
 $2Al(OH)_3 + Na_2CO_3 \rightarrow 2NaAlO_2 + CO_2 + 3H_2O$.

2) Sodium aluminate was then leached from the insoluble ferric oxide with a dilute solution of aluminate from the preceding step.

* The metal was isolated in minute amounts for the first time in 1825 by the Danish physicist Hans Christian Oersted (1777-1851) by the reaction of AlCl₃ with potassium amalgam; he himself prepared AlCl₃ for the first time in the same year. The doubtful experiment was repeated in 1827 by the German chemist Friedrich Wohler (1800-1884) using metallic potassium instead of amalgam; by this technique he obtained small metallic particles of aluminum.

* Le Chatelier father was Chief Inspector of Mines in France, the son was professor in Ecole des Mines in Paris. The grandfather was an industrialist who operated lime kilns.

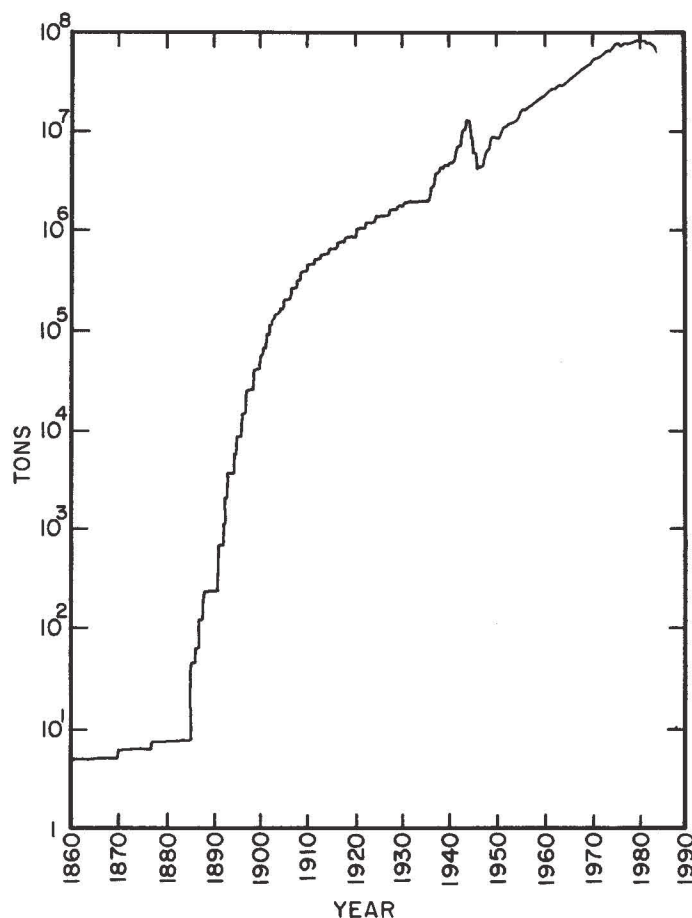


Figure 2 - Tonnage of bauxite treated annually.

3) The concentrated liquor was then treated with carbon dioxide to precipitate aluminum hydroxide analyzing typically 47.5% Al₂O₃, 50% H₂O, and 2.5% Na₂CO₃. Carbon dioxide was obtained from the furnace exit gases.

A drawback of this process was the excessive reagent consumption because any silica in the bauxite reacted with soda to form sodium aluminum silicate which represented a serious loss.

The Sainte-Claire Deville Process. Henri Sainte-Claire Deville (1818-1881), a professor of chemistry at Ecole Normale Superieure in Paris, laid the foundation of the aluminum industry in 1854 when he prepared the metal by making use of the reaction between metallic sodium and the double chloride of aluminum and sodium: AlCl₃ + 3Na → Al + 3NaCl, the sodium chloride acting as a protective flux. In 1856 a small plant constructed at Glacière near Paris produced about 25 kg of the metal. Aluminum chloride sodium chloride was prepared by heating Al₂O₃ with a mixture of NaCl and carbon in a stream of chlorine; the double chloride was then distilled off and condensed. Metallic sodium was produced by reducing Na₂CO₃ with carbon at high temperature and condensing the vapors.

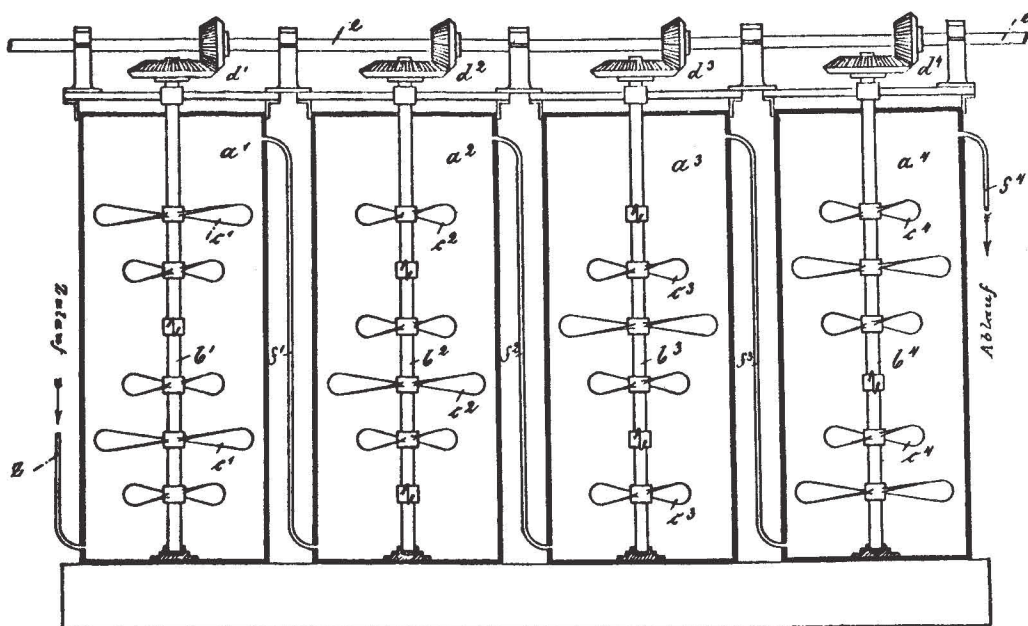


Figure 3 - Precipitator for seeded aluminum hydroxide described by Bayer in his patent.

Hamilton Y. Castner (1859-1899) of Columbia University in New York was responsible for reducing the cost of aluminum by his invention of two cheap methods for producing sodium from molten NaOH, the first in 1886 by reduction with an iron-carbon mixture, and the second in 1890 by electrolysis. However, this was too late for the Sainte-Claire Deville Process. Beginning in 1886 the Sainte-Claire Deville Process for the manufacture of aluminum was rapidly displaced by a new process invented simultaneously by Paul Heroult (1863-1914) in France and Charles Martin Hall (1863-1914) in the USA. The new process was based on the electrolytic reduction of Al_2O_3 dissolved in fused cryolite (Na_3AlF_6) found in Greenland⁽⁴⁾.

The Textile Industry

In 1885 the Austrian-born chemist Bayer emigrated to Russia to work in the Tentelev chemical Plant in Saint Petersburg (now known as Red Chemist). Russia at that time was open to all foreigners with technical and artistic skills. This plant using the Le Chatelier Process to produce aluminum hydroxide which was used as a mordant* for dyeing cotton, wool, and silk. The textiles to be dyed were soaked in a solution of the hydroxide dissolved in a weak acid, then squeezed, dried and

steamed where upon 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.

* Mordant dyeing was described by Pliny in 80 A.D.; at that time naturally occurring alum (aluminum sulfate) was used.

During this period, with the aluminium industry in its infancy, the chemistry of aluminum hydroxide was under intensive investigation. Early investigators were aware of two types of aluminum hydroxide: The gelatinous and the crystalline forms. The gelatinous hydroxide was formed by rapid precipitation from aluminate solution for example, by CO_2 and it was soluble in dilute acid. The crystalline hydroxide was formed by slow precipitation and was slightly soluble in acid. The gelatinous hydroxide was insoluble in ammonium hydroxide but soluble in sodium hydroxide. It was also known that if a saturated solution of the gelatinous hydroxide in NaOH was kept in a closed vessel for many days, a crystalline hydroxide was deposited. Bayer assumed that a solution saturated with the gelatinous hydroxide must be supersaturated with respect to the crystalline form. Consequently, if the solution of the gelatinous hydroxide were seeded with the crystalline form, precipitation of the crystalline hydroxide should slowly occur. Bayer succeeded in precipitating the crystalline $Al(OH)_3$ using the agitated tanks shown in Figure 3; precipitation took place in 2-3 days.

In modern terms the precipitation of crystalline aluminum hydroxide from alkaline solution can be described as follows: The aluminate ion undergoes hydrolysis according to the equilibrium:



The function of the seed is twofold:

- 1) To shift the above equilibrium to the right by reaction with OH^- ions (a dissolution process), and
- 2) To provide a nucleus on which $Al(OH)_3$ can grow.

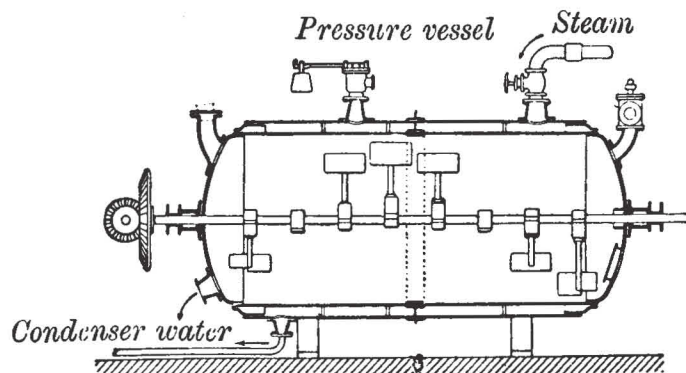


Figure 4 - Autoclave for leaching bauxite at the time of Bayer: it is 2 1/2 m long, 1 m diameter, withstands 300-400 kPa at 160-170°C and can treat 4000-5000 kg bauxite/day.

In today's practice, the seed is finely divided $\text{Al}(\text{OH})_3$ obtained from a previous precipitation batch by classification, i.e., allowing the coarse product to settle as a product and recycling the fines as a seed. The seed usually amounts to about one third of the product - - an appreciable amount.

Bayer then argued that if the mother liquor could be used to solubilize aluminum hydroxide in bauxite then such a process should be more economical than the Le Chatelier Process. The reaction of bauxite with NaOH was, however, very slow unless a high temperature was used so that it was necessary to use a reactor which was closed and able to withstand the high vapor pressure generated.

Pressure Technology

Coloring matters were used by man from ancient times, but these were all naturally occurring, for example, indigo, alizarine, etc., were mainly extracted from plants, and insects and were imported to Europe from far countries. In the 1870's synthetic dyestuffs were produced for the first time on 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 reasonable pressures required for reactions such as sulfonation, nitration, reduction, etc.

After discovering the precipitation method for obtaining crystalline aluminum hydroxide, Bayer found 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. A typical reactor of this period is shown in Figure 4.

RECENT TRENDS

Bayer's process involving both pressure leaching and controlled precipitation is used today in practically the same way as when it was discovered one hundred years ago. However, tremendous improvements in the engineering aspects have taken place and these are responsible for decreasing the cost. Furthermore, a new importance was given to the process when gallium became needed by the semiconducting industry and its recovery from process solution became desirable.

A problem of the Bayer Process, however, is the disposal of the so-called red mud-- the residue of the leaching step. This is mainly iron oxide with small amounts of rutile, ilmenite, quartz, and hydrated sodium aluminum silicates. Each ton of alumina produces about one ton of red mud (on a dry basis). With increased production of metallic aluminum world-wide, the amount of red mud produced has reached tremendous proportions - about 100 million tons each year. No use for this material has yet been found and each plant has large ponds to store its waste material.

Energy Economy

In the early days of the Bayer Process 1 ton of bauxite required 2.33 tons of coal for processing. Today it requires only 0.15 tons⁽⁵⁾. Thus in the early days the bauxite had to be transported to regions where coal was available, whereas now alumina plants are situated near the bauxite (Figure 5). The economy in energy is due to two factors:

- 1) An increased heat recovery. Heat exchangers and flash tanks are now extensively used to economize energy. Flash tanks serve an additional purpose: the evaporation of solutions (Figure 6).
- 2) The use of large autoclaves. The larger the reactor the less will be the heat losses. Construction of such equipment that can be used

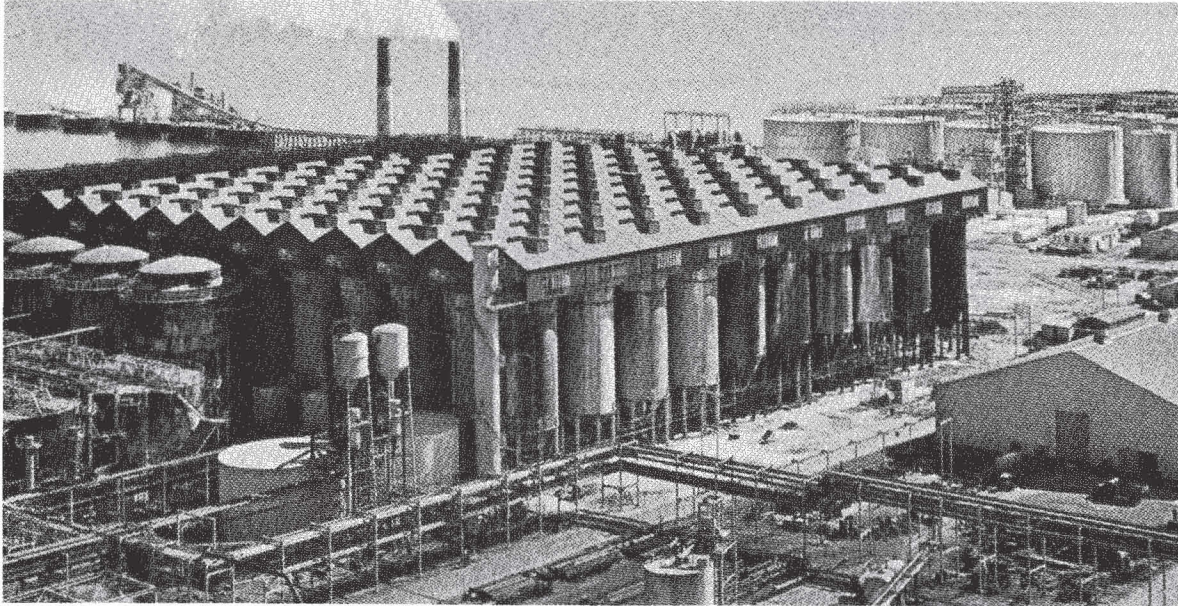


Figure 5 - Bayer Process bauxite treatment plant in Kwinana, near Perth in Australia producing 1,250,000 tons/year alumina. (Courtesy Alcoa).



Figure 6 - Heat economy systems in a sodium aluminate evaporation plant in Sardinia. Shown are three lines of 9 flash evaporators each with preheaters. Evaporation capacity of 3 x 90 tons/hour. (Courtesy Escher Wyss Co.).

reliably is due to improvements in engineering design and manufacturing. Along with autoclaves, precipitation tanks have increased in size correspondingly (about ten times the size of an autoclave, Table 1).

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. A typical modern autoclave is shown in Figure 7.

Tube Autoclaves

The use of tube autoclaves (Figure 8) began in Germany 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 13 000 kPa. Due to the high temperature, a reaction time of only 2-3 minutes instead of 4-6 hours is sufficient to extract the aluminum. The process is continuous and has a high thermal efficiency due to the effective heat exchange system.

Gallium Production

Gallium was discovered in 1875 in zinc blende and its first production was from this source. In 1896 it was discovered in bauxite by W.N. Hartley and H. Ramage⁽⁶⁾. Gallium is now produced mainly from this source although its average concentration is usually less than 0.01%. Gallium is also found in coal fly ash. Alusuisse, a major aluminum manufacturer in Switzerland, commenced industrial scale production of gallium from bauxite in 1955. Gallium follows aluminum in the Bayer Process, and is recovered from the aluminate solution either by electrodeposition on a mercury cathode, or by cementation using sodium amalgam, or by selective carbonation. After precipitation of Al(OH)₃ and recirculation of the caustic solution, gallium may be enriched to a concentration of about 0.2 g/l. The present Western world production of gallium is about 50 tons/year.

Gallium (Figure 9) is a vital material in the semiconductor industry which started in the 1960's. It is mainly used in form of arsenide and phosphide, GaAs and GaP, respectively. Both compounds show electroluminescence, and are used in the manufacture of light-emitting diodes. Gallium arsenide in combination with (Ga, Al) As-layers is a material used in solid-state lasers, especially in telecommunication systems with optical fibers. Gallium arsenide is also a promising material for solar cells and for computer memories.

BAYER AND HIS MEDAL

Bayer was born on March 4, 1847 in Bielitz in Silesia, at that time a Province of the Austrian Empire, now in Poland. The empire was composed of a vast territory encompassing the present-day Austria plus northern Italy, Bohemia and Moravia (parts of present-day Czechoslovakia), Hungary, Transylvania (part of present-day Rumania), Croatia, Dalmatia and Bosnia-Herzegovina (parts of present-day Yugoslavia), and Silesia and Galicia (southern Poland). While the official

Table 1 - Capacity of reactors used in the Bayer Process

Year	Autoclaves m ³	Precipitators m ³
1907	5	50
1916	12	170
1920	25	225
1963	150	1300
1970	250	3000
1982	420	4500

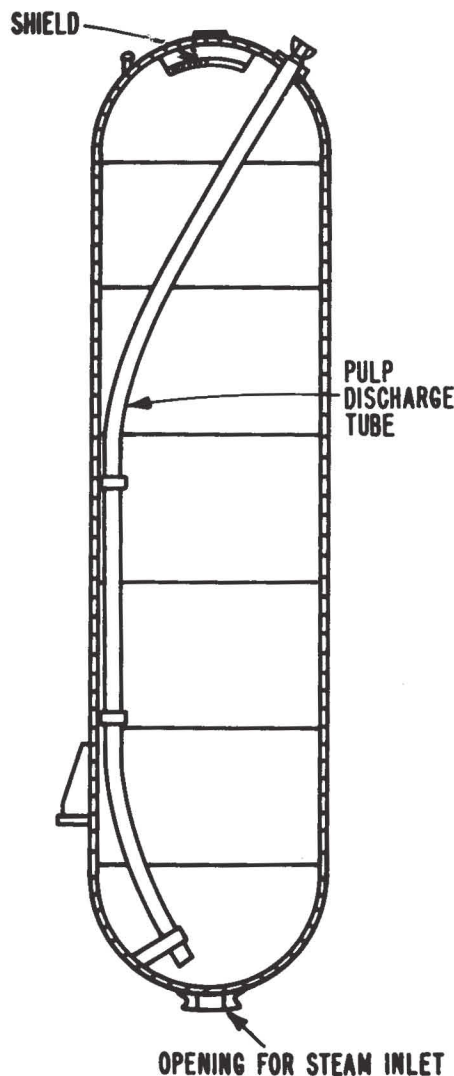


Figure 7 - A modern autoclave for leaching bauxite, about 30 m³ capacity.

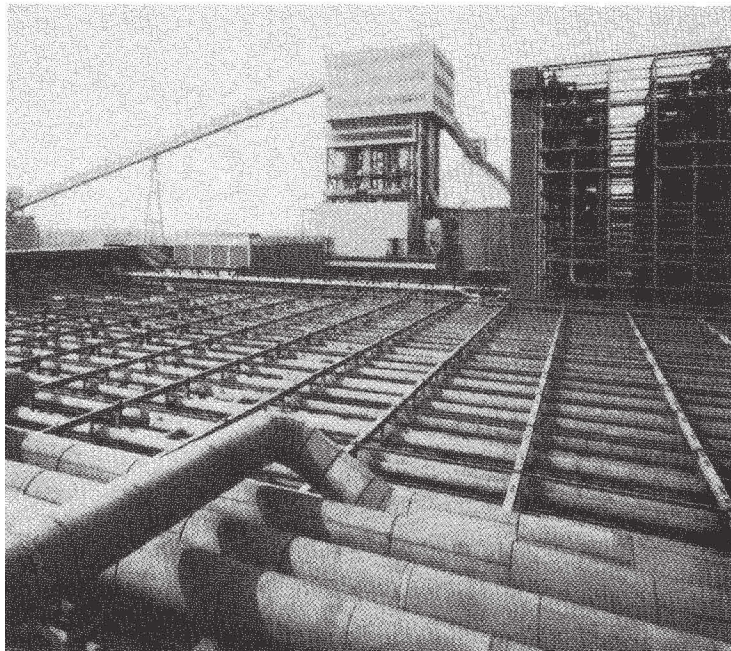


Figure 8

Tube autoclaves for digestion of bauxite at the Vereinigte Aluminium Werke in Germany.

language was German, many other languages were spoken, e.g., Hungarian, Rumanian, Czech, Polish, Ruchenian (Ukranian), Slovak, Slovenian, Serbo-Coratian, and Italian. The multitude of nationalities and languages caused many revolts and political agitation.

Bayer went to school at his home town and at the wish of his father, who was an architect, started to study architecture. Later he switched over to science and went to Wiesbaden in Germany to study chemistry under the famous analytical chemist C. Remigius Fresenius (1818-1897). After a short period of interruption when he worked in a steel factory in Belgium, he went to Heidelberg to continue his chemistry studies at the University of Heidelberg. There, he became assistant to Professor Robert Bunsen (1811-1899) in the period 1869 to 1871. At that time Bunsen's laboratory was visited by many chemists who became famous later on. Among those was 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 Kirchhoff (1824-1887) of the spectroscopic method of analysis, and the discovery of the two metals rubidium and cesium by this new tool. Bunsen is also famous for the burner known by his name and now found in every chemical laboratory.

In Heidelberg Bayer got the doctorate after submitting a thesis entitled "A Contribution to the Chemistry of Indium". Indium had been discovered few years earlier (in 1863) by the two German chemists Ferdinand Reich (1790-1882) and Hieronymus Theodor Richter (1824-1898) utilizing Bunsen's spectroscope. Afterwards, Bayer returned to his home country Austria where he was

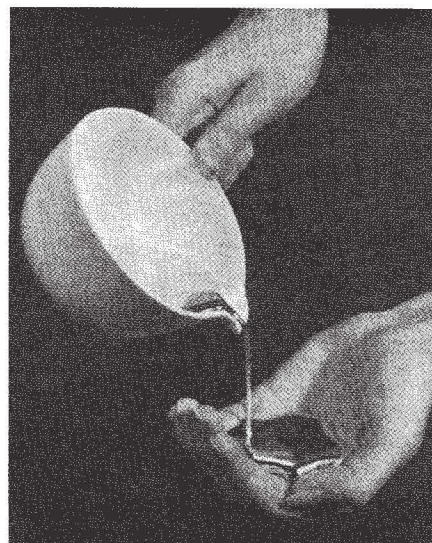
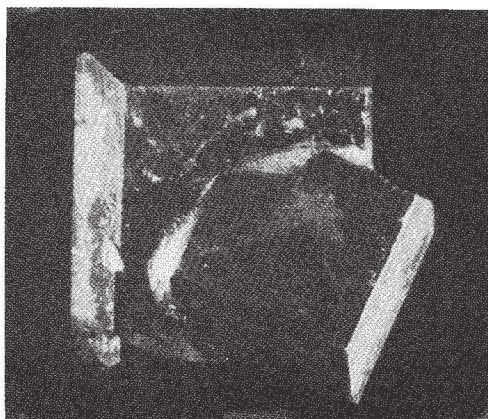


Figure 9 - Gallium from bauxite can be recovered by the Bayer Process. Metallic gallium is solid at room temperature and liquid at 29.78°C.

appointed a lecturer at the University of Technology at Brno in the Moravian Province of the empire now in Czechoslovakia). He remained there until 1873, when he left the University to establish a research laboratory in Brno. However, he later gave up this venture and in 1885 packed to St. Petersburg in Russia.

Bayer's years in Russia were the most fruitful and creative years. He joined the Tentelev Chemical Plant near St. Petersburg in 1887, to work on problems of production of pure aluminum hydroxide for the dyeing of cotton fabrics. There in 1888 he 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. Bayer mentioned that the product obtained by his process was purer than that obtained by CO_2 precipitation since no phosphates or SiO_2 precipitated. Further, the aluminum hydroxide precipitated was also crystalline and can be easily filtered and washed. The process was soon adopted by the Tentelev Plant.

Bayer's second discovery was in 1892 at the Elabuga Plant on Kama River (Tatar SSR). He found 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 by the seed, could be used.

While at Elabuga, he received numerous contracts from foreign countries to build alumina factories. Thus he built one in England for the British Aluminium Company in London, one in France for the Compagnie des Produits Chimiques et Electrometallurgiques in Froges, one in Italy for the Societa Italiana Elettrochimica in Bussi, one in USA for Merime Chemical Company in Boston, and one in Germany for Gebruder Giulini in Ludwigshafen. He was awarded the gold medal of the Academie Parisienne des Inventeurs industriels et exposants for his scientific and technical services.

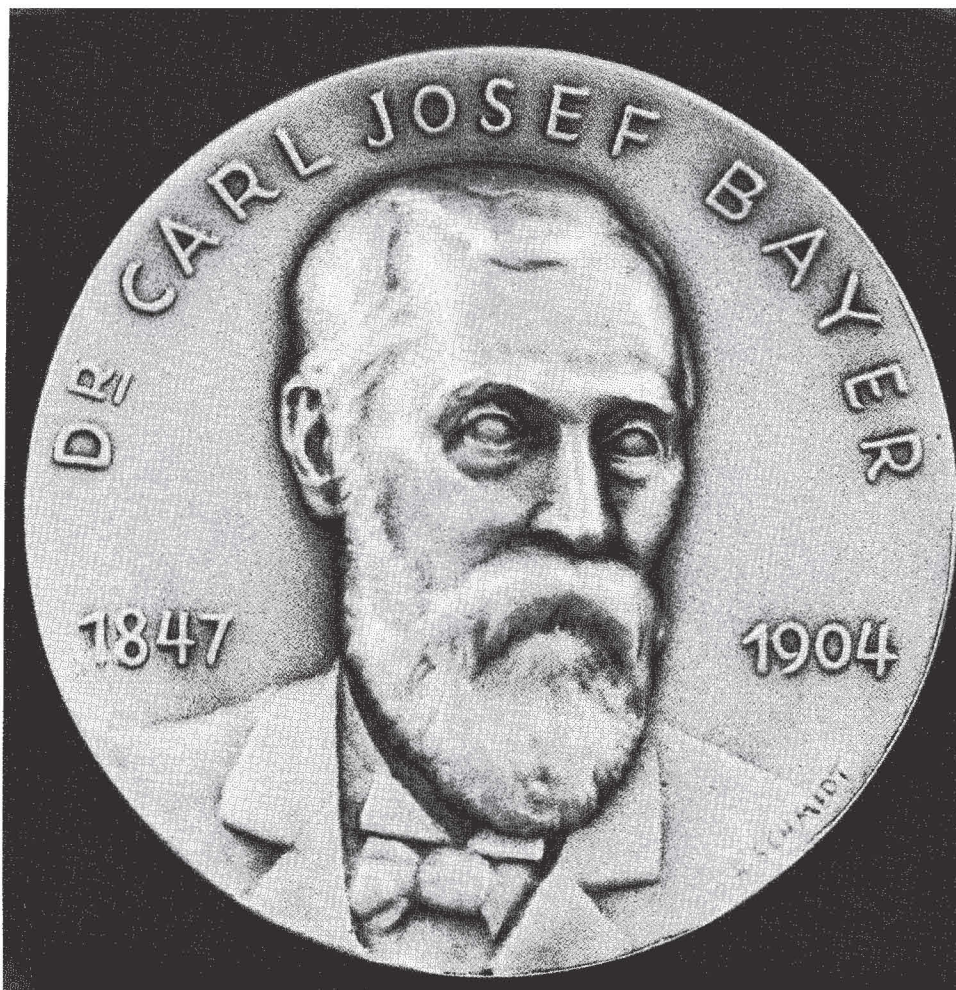


Figure 10- Medal in honour of Carl Josef Bayer awarded by the International Light Metals Conference in Leoben, Austria showing the inventor of the process at advanced age.

In 1894, Bayer returned to Austria and finally settled in Rietzdorf in southern Styria in order to devote himself to scientific research. During this period he developed a method for the manufacture of synthetic cryolite which is used as an electrolyte in the aluminum industry. While in Rietzdorf, he planned to build the aluminum industry in Austria. However, he was unable to raise the necessary capital, and thus his plans failed in his home country.

Bayer was married to Alma von Witte, a niece to the Russian prime minister Count von Witte. He raised five sons and a daughter. One of his sons, Fritz Bayer was professor of electrochemistry at the Technische Hochschule in Vienna (now known as Technische Universität Wien) until 1956 when he retired.

Bayer's home in Rietzdorf was a meeting center for many famous industrialists among whom were Héroult and Hall. He loved music and the arts; he himself was a talented artist. He spoke six languages: German, French, English, Russian, Italian and Slovak. He had an excellent collection of minerals which he displayed at the Chicago exhibition in 1890.

Bayer died suddenly on October 4, 1904 at the age of 57, and his widow died in 1962 at 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.

Bayer is honored in his native country Austria by the medal bearing his name (Figure 10)*, and awarded every three years to a distinguished researcher in the field of aluminum. The award ceremony takes place during the the International Light Metals Congress which is held in Leoben and in Vienna.

Thus, 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 Héroult.

ACKNOWLEDGEMENT

The writer acknowledges with thanks the biographical information about Bayer supplied in 1966 by his son Prof. Fritz Bayer.

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* Bayer's first name appears as "Karl" in his patents but as "Carl" on his medal