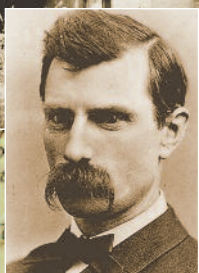
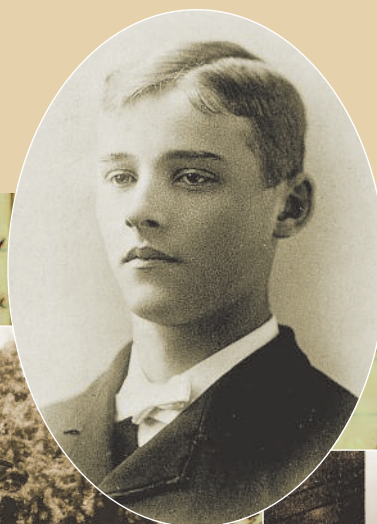


A NATIONAL HISTORIC
CHEMICAL LANDMARK

PRODUCTION OF ALUMINUM METAL BY ELECTROCHEMISTRY

OBERLIN, OHIO
SEPTEMBER 17, 1997



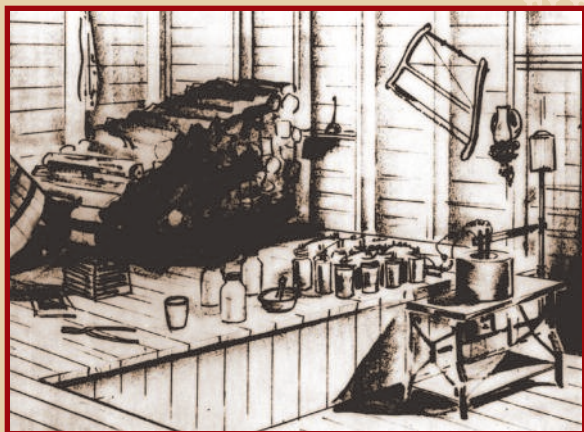
AMERICAN CHEMICAL SOCIETY
Division of the History of Chemistry and
The Office of Public Outreach

(No Model.)

C. M. HALL.
PROCESS OF REDUCING ALUMINIUM FROM ITS FLUORIDE SALTS BY
ELECTROLYSIS.

Patented Apr. 2, 1889.

Fig 1.



Sketch of the woodshed laboratory by Julia Severance, made while Hall was alive.

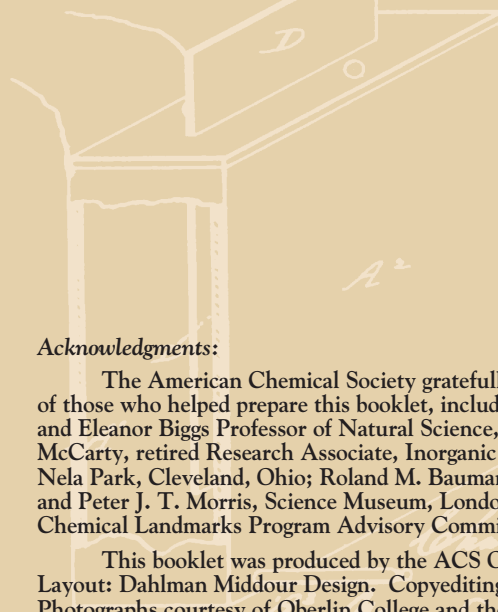
This booklet commemorates the designation of the production of aluminum metal by electrochemistry as a National Historic Chemical Landmark. The designation was conferred by the American Chemical Society, a nonprofit scientific and educational organization of more than 152,000 chemists and chemical engineers.

A plaque marking the designation was presented to Oberlin College on September 17, 1997. The inscription reads: "On February 23, 1886, in his woodshed laboratory at the family home on East College Street, Charles Martin Hall succeeded in producing aluminum metal by passing an electric current through a solution of aluminum oxide in molten cryolite. Aluminum was a semiprecious metal before Hall's discovery of this economical method to release it from its ore. His invention, which made this light, lustrous, and nonrusting metal readily available, was the basis of the aluminum industry in North America."

Fig 2.



Fig 3



Acknowledgments:

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On the Cover: (Clockwise) C. M. Hall, 1885; Hall reading *American Chemical Journal*, about 1905; F.F. Jewett, Hall's mentor; Hall family home and woodshed. Background: Letter from Hall to his brother February 24, 1886.

Background (this page): Diagram from C.M. Hall's patent.

CHARLES MARTIN HALL SOLVES THE ALUMINUM CHALLENGE

From Semiprecious to Abundant

Before 1886, aluminum was a semiprecious metal comparable in price to silver. Although the element had been discovered in 1825 and had been investigated by many European scientists, the only way to prepare the metal was by the complex and difficult process that culminated in reacting metallic sodium with aluminum chloride. When the Washington Monument was completed in 1884, a 6-lb pyramid of this costly aluminum was placed as an ornament at the very top. It also served as the tip of the lightning rod system, a practical application of the high electrical conductivity and corrosion resistance of this remarkable metal. However, economical methods were needed to wrest aluminum from its abundant minerals, which Henri Sainte-Claire Deville, the great French chemist, observed “could be found in every clay bank.”

Two men with a common interest in aluminum metal met on the campus of Oberlin College near Cleveland, Ohio, in 1880. Frank Jewett was a world traveler and as well educated in chemical science as any American academic of his day. Charles Hall was a local youth, self-educated in science, who hoped to become a successful inventor and entrepreneur. Their association over the next five-and-one-half years led to the discovery of a practical process for making aluminum from its ore by an electric current. Within three more years, Hall was producing pure aluminum metal on an industrial scale. Aluminum, the curiosity, became a widely used material, and the younger man achieved his goal of a financially successful career in technology and industry.

Professor and Student

Frank Fanning Jewett received his undergraduate education and did some graduate work in chemistry and mineralogy at Yale University. From 1873 to 1875, he continued his chemistry studies at the University of Göttingen in Germany. There he



Frank Jewett at about 40 years of age when Hall made his discovery.

became well acquainted with current European science and became interested in the promise of aluminum. He met Professor Friedrich Wöhler, who had isolated aluminum as a metal in 1827 following H. C. Oersted's lead in 1825. Before Jewett returned to America in 1875 to become Oliver Wolcott Gibbs's private assistant at Harvard University, he obtained a sample of aluminum metal. In 1876, he was nominated by the president of Yale to teach science at the Imperial

University in Tokyo, where he was one of a small group of Westerners. In 1880 at the age of 36, Jewett became the professor of chemistry and mineralogy at Oberlin College.

Charles Martin Hall first learned chemistry as a serious-minded youth in the town of Oberlin by reading an 1840s textbook he found on the shelves of his minister father's study. He also carried on experiments at home, the beginning of a lifelong enthusiasm for experimental work. An avid reader in many fields, he eagerly followed the popular invention literature in *Scientific American*. Hall was already intrigued by the romance of aluminum when, as a 16-year-old freshman at Oberlin College in the fall of 1880, he went to the chemistry laboratory to obtain some items for his home laboratory. There he met Professor Jewett.



C. M. Hall at graduation from Oberlin College, 1885.

THE CHALLENGE

Hall took his first formal course in chemistry as a junior in college. Earlier, with Jewett's guidance and encouragement, he had worked on aluminum chemistry and other projects in Jewett's laboratory and in his own laboratory at home. He heard Jewett lecture on the chemistry of aluminum, display his sample of the metal, and predict the fortune that awaited the person who devised an economical method for winning aluminum from its oxide ore. To a fellow student, Hall declared that he intended to be that person.

After many unsuccessful experiments with chemical methods of reducing aluminum ores to the metal, Jewett and Hall turned to electric current to provide the powerful reducing conditions that were needed. To obtain electricity in a college town in the 1880s, one had to assemble batteries. Hall and Jewett used Bunsen–Grove cells, which consist of a large zinc metal electrode in a sulfuric acid solution that surrounds a porous ceramic cup containing a carbon rod immersed in concentrated nitric acid. Assembling enough of these cells to provide sufficient electrical energy for aluminum production was



Hall family home with attached woodshed.

a large undertaking. The eventual laboratory process used about 1 lb of zinc electrodes, hand cast by Hall, to obtain 1 oz of aluminum.

Hall did the first experiments with electricity in Jewett's laboratory during his senior year of 1884–85. He prepared aluminum fluoride from hazardous hydrofluoric acid in special lead vessels, and



Julia B. Hall in 1881. Julia helped her brother by preparing chemicals such as aluminum oxide. She had studied chemistry and followed his experiments closely. Through most of his life, Hall maintained a lively correspondence with his sister and other family members. Julia saved many of these letters and some of his notebooks, which provide an exceptional record of the day-to-day life of an inventor.

he passed a current through aluminum fluoride dissolved in water. Unfortunately, this system produced only unwanted hydrogen gas and aluminum hydroxide at the negative electrode.

After graduation, Hall continued the work in the woodshed behind his family's house. He experimented with molten fluoride salts as water-free solvents. He knew that the fluoride salts had the advantage over previously studied chloride salts of not absorb-

ing water from the air. Hall was aware of Richard Grätzel's success in obtaining magnesium metal by using an electric current in a magnesium chloride melt as reported in the *Scientific American* in 1885.

To work with molten fluoride salts, he needed a furnace capable of producing and sustaining higher temperatures than the coal-fired furnace of his earlier experiments. For this purpose, Hall adapted a second-hand, gasoline-fired stove to heat the interior of a clay-lined iron tube. Despite the higher temperature of this furnace, he was unable to melt calcium, aluminum, or magnesium fluorides. Potassium and sodium fluorides melted but did not dissolve useful amounts of aluminum oxide.

Hall moved on to experiment with cryolite (sodium aluminum fluoride) as a solvent. He made cryolite, found that it would melt in his furnace, and showed that it would dissolve more than 25% by weight of aluminum oxide. The melting point of cryolite is 1000 °C, an exceptionally high temperature for electrochemistry. He did this crucial experiment early in February 1886 and repeated it the next day for his sister Julia to witness.

Six days later, Hall first attempted to prepare aluminum metal by passing an electric current

berium made in the same way
but lately some German
invented an electrolytic process
for magnesium from the
the process is said to be more
the old one and the compar

(No Model.)
C. M. HALL.
PROCESS OF REDUCING ALUMINUM FROM ITS FLUORIDE SALTS BY
ELECTROLYSIS.
No. 400,664. Patented Apr. 2, 1889.

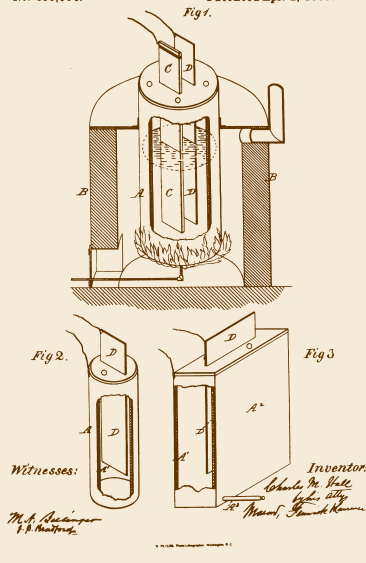


Diagram from patent No. 400,664.

through a solution of aluminum oxide in molten cryolite. He immersed graphite rod electrodes into the fiery solution in a clay crucible and let the current run for a while. In Julia's presence, he poured the melt into a frying pan and broke apart the cooled mass but found no aluminum. There was only a grayish deposit on the negative electrode, a deposit that did not have the shiny metallic appearance of aluminum. After repeating this process several times, Hall realized that this deposit was probably silicon from silicates dissolved out of the clay crucible. If he had not been acquainted with the appearance of metallic aluminum from seeing Jewett's sample, Hall might have been slower to interpret this false result.

Success

From a large graphite rod, Hall made a graphite crucible to line the clay crucible. He also lowered the melting point of the cryolite solution by adding aluminum fluoride. The first experiment with this new system was performed on February 23, 1886. The electric current ran for several hours, and once again he cooled the melt and broke it open in the presence of his three sisters and father. This time they found several small silvery globules, which he tested with hydrochloric acid. He took them to Jewett, who confirmed that they were aluminum.

On July 9, 1886, Hall applied for a patent. Meanwhile, Paul L.T. Héroult was granted a French patent on April 23, 1886, for a comparable process based on cryolite and aluminum oxide; he had also applied for a U.S. patent in May. This meant that Hall had to prove that he had made aluminum by the new method before the date of the French patent to obtain patent protection in the United States. Evidence from his family and Jewett, including two postmarked letters to his brother, George, helped to establish the priority of Hall's discovery in the United States in a ruling made by the Patent Examiner. Hall's patent rights were also upheld in two subsequent legal struggles with the Cowles Electric Smelting Co. of Cleveland, Ohio, which made copper-aluminum alloy.

now more about the...
I wrote and I will try and...
ten you further. You may ask...
now that enough Aluminium can...
made by this process to pay for...
electricity used. If you will...
article "Electrolysis" in the Ency...

Simultaneous Discoveries

Letter from C. M. Hall to his brother George written the day after the discovery.

How could it be that Paul Héroult in Paris, France, and Charles Hall in Oberlin, Ohio, made nearly simultaneous, yet independent discoveries of the same process of refining aluminum? Many factors seem to

have contributed. Finding an economical process for refining aluminum was widely recognized as a prime target for inventors. Electrochemistry had begun to mature as an applied science. Large electricity-generating dynamos were being developed commercially. Interest had been aroused in the chemistry of fluorine-containing substances. Although Hall was working in a small U.S. college town, he had access to the latest in scientific thought with Jewett as his mentor. Proximity to Cleveland and its emerging technical industries, such as Standard Oil for gasoline, Brush Electric for large graphite rods, and Grasselli for chemicals, was also a contributing factor.

Hall, like Héroult, was a resourceful experimentalist, who not only devised a method of making aluminum metal, but made most of his apparatus and prepared many of his chemicals.



Paul L. T. Héroult, who discovered the same electrochemical process for refining aluminum metal in France. He was born the same year and died the same year as Charles Hall (1863–1914).

Like Héroult, Hall had a burning desire to be a successful inventor and industrialist. In recognition of the contribution these two young men made to the development of this electrochemical process on both sides of the Atlantic, it is now called the Hall-Héroult process.

COMMERCIALIZATION

In the summer of 1888, a group of investors organized by Captain Alfred Hunt, an MIT graduate involved in the metallurgical business in Pittsburgh, provided sustained support for Hall. He worked at the fledgling Pittsburgh Reduction Company, the predecessor of Alcoa, to bring his process from laboratory to commercial scale. By Thanksgiving day 1888, with the able assistance of Arthur Vining Davis, Hall was producing aluminum in a pilot plant on Smallman Street in Pittsburgh.



Sketch of the pot room at the original aluminum production facility on Smallman Street in Pittsburgh.

The process was soon simplified by using internal heating caused by electrical resistance in the reaction pots to achieve and maintain the molten state. Steam-driven Westinghouse dynamos provided the electricity. Further cost improvements resulted later from the use of hydroelectricity.

The Pittsburgh Reduction Company became the Aluminum Company of America (Alcoa) in 1907, just before the patent rights ran out. At first aluminum was a solution in search of a problem, but

gradually many uses were found for it, ranging from aircraft and other modes of transportation to power lines for long-distance transmission of electricity, construction, food storage, and decoration. The ready availability of this light, lustrous, and nonrusting metal has changed our lives.

Recognition

In 1911 Hall became the fifth recipient of the Perkin Medal, which was awarded for “valuable work in applied chemistry” by the Society of Chemical Industry (American Section) with the support of the Electrochemical Society and the American Chemical Society. Paul Héroult attended the award ceremony in New York and made a graceful contribution to the speeches. Hall responded with equal warmth.

Upon Hall’s death in late 1914, his holdings in Alcoa stock amounted to a sizeable fortune, most of which he bequeathed to educational institutions in this country and abroad.



Hall reading the *American Chemical Journal* on the porch of the new family home, which Hall had built.

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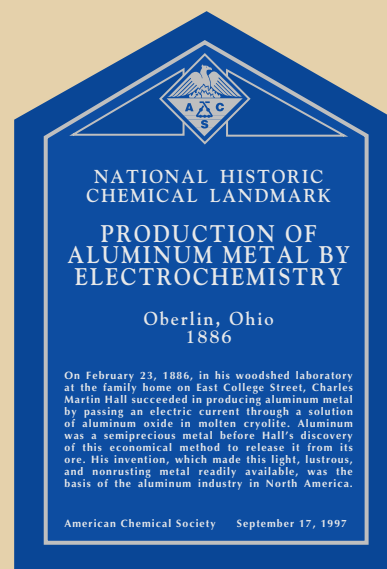
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THE NATIONAL HISTORIC CHEMICAL LANDMARKS PROGRAM OF THE AMERICAN CHEMICAL SOCIETY

The ACS National Historic Chemical Landmarks Program recognizes our scientific and technical heritage and encourages the preservation of historically important achievements and artifacts in chemistry, chemical engineering, and the chemical process industries. It provides an annotated roster to remind chemists, chemical engineers, students, educators, historians, and travelers of an inspiring heritage that illuminates where we have been and where we might go when traveling the diverse paths to discovery.

An ACS Historic Chemical Milestone designation marks a landmark step in the evolution of the chemical sciences and technologies. A site designation marks the location of an artifact, event, or other development of clear historical importance to chemists and chemical engineers. A historic collection designation marks the contributions of a number of objects with special significance to the historical development of chemistry and chemical engineering.

This program began in 1992, when the Division of the History of Chemistry of the ACS formed an international Advisory Committee. The committee, composed of chemists, chemical engineers, and historians of science and technology, works with the ACS Office of Public Outreach and is assisted by the Chemical Heritage Foundation. Together, these organizations provide a public service by examining, noting, recording, and acknowledging particularly significant achievements in chemistry and chemical engineering. For further information, please contact the ACS Office of Public Outreach, 1155 Sixteenth Street, N.W., Washington, DC 20036; 800-ACS-5558, ext. 6274.



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