

CHARLES M. HALL'S PERSISTENT QUEST OF PATENTS FOR REFINING ALUMINUM METAL BY ELECTROLYSIS

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Introduction

In a single day, April 2, 1889, Charles M. Hall was awarded five patents for his discovery of the electrolysis process for extracting aluminum metal from aluminum oxide. To celebrate Hall's breakthrough achievement—ultimately, the commercial production of aluminum—under the Citation for Chemical Breakthrough (CCB) program of the Division of the History of Chemistry of the American Chemical Society, it was necessary to select the most important patent for display on the plaque (1). All five patents were carefully reviewed, as were the circumstances of the applications for the patents. As part of this evaluation, several fundamental questions were examined: Why were five patents issued and how do they differ from each other? Was more at stake than an inventor attempting to make the patent claims as broad as possible? The evidence brought out in this paper reveals that problems with the original process propelled Hall's determined investigation of alternative formulations of electrolyte baths and different cell designs.

Helpful reviews of the Hall patents are in the papers of Seabury C. Mastick (2) and Lloyd Van Doren (3), who were patent attorneys. For a full account of Hall's life and his work on aluminum metallurgy see the writings of Holmes, Edwards, and Craig (4-6).

Demonstrating the Hall Process

To give substance to Hall's original small-scale process and to make tangible the problems he encountered, a modern story helps. For a lecture demonstration celebrating the 100th anniversary of Hall's discovery, which had occurred on February 23, 1886, I began practicing the original tabletop process in early January 1986. The process involved electrolysis of alumina (Al_2O_3) dissolved in molten cryolite (Na_3AlF_6) (7). The (+) anode was a graphite (carbon) rod, and a graphite crucible served as the (-) cathode. I had confidently offered to do this presentation because of having helped my 9-year-old daughter, Julie, do the process for a school project in 1970. Soon it was apparent that aluminum metal was not being produced. Furthermore, upon reexamination, the shiny bits that Julie had harvested in 1970 proved not to be aluminum metal. Lowering the temperature below the 1000°C melting point of the cryolite solvent, which was also the upper limit of the available electric pot furnace, seemed a possible remedy. A phase diagram for the aluminum fluoride/sodium fluoride system showed that additional aluminum fluoride lowered the melting point of the solvent without compromising the solubility of aluminum oxide (8). Adding aluminum fluoride to the mix solved the problem of making aluminum metal for the centennial lecture demonstration. Figure 1 shows a small graphite crucible, after sawing it in half, of the type used in the lecture demonstration and by Hall. Shiny halves of small pellets of aluminum metal are in

the bottom of the crucible. Telling the story about having to rediscover the extra, unpublicized ingredient helped make the centennial lecture demonstration contemporary and fully engaging for the audience. (At the time, I had not studied the patents.)



Figure 1. A graphite crucible cut in half following a modern demonstration run on the small scale. Halves of shiny aluminum globules are in the bottom of the crucible.

Although the lecture demonstration was rescued for February 1986, I learned in subsequent presentations of this demonstration that I had been lucky and that the small-scale process was far from being dependable. With much help from Dr. Lewis V. McCarty in the late 1990s, many experiments were performed in an attempt to identify the problems with the small-scale process. We had limited success in doing so.

Working on the Small Scale

How does the account of doing lecture demonstrations of the Hall process relate to Hall's path to the patents that became the foundation of Alcoa and the whole aluminum industry? My troubled experience with the small-scale process confirmed the unpredictability that dogged Hall's work in refining the method and helped explain why a series of modifications of the original patent application were submitted separately. Hall worked tirelessly for two and one-half years to improve his original process and to convince investors to support him. When Hall began work at the nascent Pittsburgh Reduction Company (later Alcoa) in the late summer of 1888, he moved immediately to a larger scale. Once he scaled up the process, the difficulties largely vanished. It is also likely that changing within a few months from the use of the original method of external heating to only internal resistive heating helped solve the problems.

Hall's first financial support for developing the process came from Judge Henry Baldwin and a Mr. Brown of Alston, MA, located across the Charles River from Cambridge. These "Boston backers" were recruited by Charles Hall's brother, George, but they did not sustain their support beyond the fall of 1886 because of problems with the method.

Hall's second financial backers were the brothers Eugene and Alfred Cowles of Cleveland, OH (9). They were making a copper-aluminum *alloy* with the process of electrothermy by putting a large electric current through a mixture of aluminum oxide, copper, and graphite. Their company was named the Cowles Electric Smelting Company. They agreed to support Hall's work on developing the electrolysis process to extract pure aluminum and assigned him to their plant at Lockport, NY, where waterpower generated large electric currents. Hall worked at Lockport for a year until the Cowles terminated the agreement in July 1888 (10). They concluded that Hall's uncertain process to make pure aluminum was not competitive with electrothermy for making alloys. The next month Hall joined Alfred Hunt and his fellow investors in Pittsburgh in forming a new company.

Applications for Patents

Hall submitted his first application for a patent on July 9, 1886, four and one-half months after making his original discovery. In a report from the patent examiner in October 1886, Hall learned that Paul L. T. Héroult had received a patent in France on April 23, 1886, for a comparable invention and had applied for a US patent on May 22, 1886. US patent law gave precedence to an American inventor who could prove that he had reduced his process to practice within a two-year period prior to the date of application of the foreigner for a US patent. Hall established precedence for his February 23 discovery through a patent interference proceeding. This demonstration was made with two postmarked technical letters he had mailed to his brother, George, on February 23 and 24, 1886, immediately after his first successful production of aluminum metal and through testimony of Hall and four witnesses on October 24, 1887 (11). One of the witnesses was Professor Frank F. Jewett, Hall's mentor at Oberlin College. Included in Hall's testimony was the phrase, "and I added some aluminum fluoride." This ingredient was not reported in any of the secondary accounts of Hall's original discovery. However, see the discussion of the patents below. I first saw the record of the patent interference testimony in early February 1986

after independently finding the beneficial effect of adding aluminum fluoride to the cryolite solvent.

The Five Patents

Hall's applications for the first two patents, a division of the original patent, were overseen by Robert L. Fenwick of the Washington, D.C., law firm of Mason, Fenwick, and Lawrence. Financial support for the initial patent application came from the Boston backers in the summer of 1886. Familiar signatures on the other patents show that the same law firm represented Hall's interests throughout the patent process.

For each patent the following summaries contain the patent number, the filing date and associated serial number, the number of figures, the title of the patent, and the principal claims for each patent (12). The patents use "aluminium," as "aluminum" was still called in the United States in the 1880s. All five patents refer to the method of external heating in a gasoline-fired oven. In the commercial process in the spring of 1889, Hall replaced external heating entirely with internal resistive heating by a large electric current. His use of internal heating became the basis for legal disputes with the Cowles brothers in the 1890s and early 1900s. They claimed internal heating was an application of their process of electrothermy, learned by Hall in Lockport. Because the patent No. 400,766 is the basic patent, it is put first in the list. This patent contained the substance of the first patent filed and was closest to the method employed in industrial practice. It was used on the CCB plaque. All five patents were issued on April 2, 1889.

It is unclear who bore the cost of the three patents filed in 1888. However, the dates are such that Alfred Hunt of the Pittsburgh Reduction Company probably paid for them. It is also unclear who paid any added cost for the submission of the divided patent No. 400,664 in February 1887. At that time, Hall did not have secure financial backers.

No. 400,766. July 9, 1886, Serial No. 207,601. Two figures. "Process of Reducing Aluminium by Electrolysis." **Basic Patent.**

Figure 2 is a reproduction of the page with the two figures accompanying this patent. The top figure shows two separate electrode rods in the melt and the gasoline-fired burner used to heat the pot. Crucibles in both figures were made from iron shells lined with graphite. The bottom figure anticipates the commercial process by having a graphite liner of the pot serve as the negative cathode.

Under the figures are the signatures of George E. Hall, Hall's brother, and Robert L. Fenwick, the lawyer, as witnesses. The name of the Mason, Fenwick, and Lawrence law firm appears below Hall's signature.

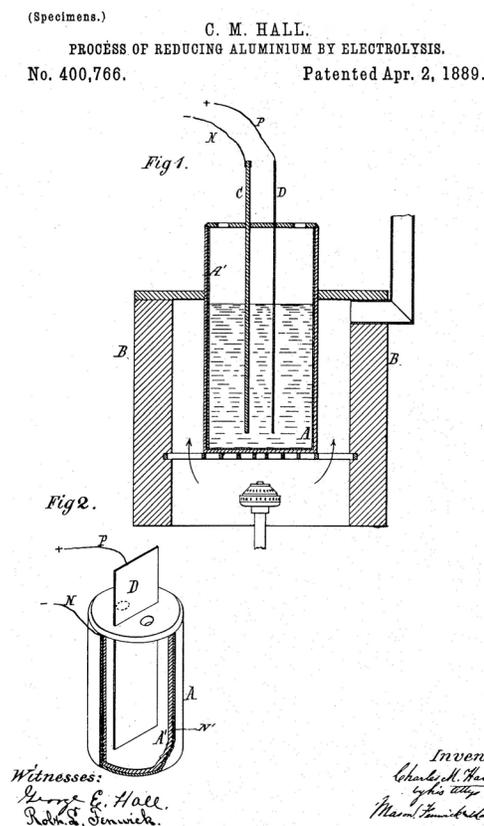


Figure 2. Two figures in patent No. 400,766.

The solvent mixture was specified as $\text{Na}_2\text{Al}_2\text{F}_8$ or $2\text{NaF} \cdot 2\text{AlF}_3$ (13), which can be re-expressed as two moles of AlF_3 for each mole of Na_3AlF_6 (cryolite). Thus, this patent called for a substantial excess of aluminum fluoride. Aluminum oxide was dissolved in the molten solvent mixture and added as consumed in the electrolysis. The negative electrode (C in Figure 2) was made of graphite unless an alloy was intended to form with a metal electrode. When electrodes such as copper were used as the positive electrode (D in Figure 2), oxygen gas was released at the anode. When carbon was used as the positive electrode, the electrode was gradually consumed by production of "carbonic [acid] oxide (CO_2)."

The option of using lithium fluoride, or fluorides of other metals more electropositive than aluminum, in place of some of the sodium fluoride to lower the melting point

of the solvent was included. The source of electricity was a “dynamo-electric machine or other suitable source” giving a voltage of 4-6 V and a high current. Liquid aluminum, being denser than the solvent, sank to the bottom of the pot, where it was protected from reoxidation.

The final content of this patent differed substantially from the original submission. After 30 written communications between the Patent Office and Hall, the final formulation of the patent was reached.

No. 400,664. July 9, 1886, Serial No. 207,601. Divided and the new application filed February 2, 1887, Serial No. 226,206. Three figures. “Process of Reducing Aluminium from its Fluoride Salts by Electrolysis.”

The same initial serial number, 207,601, and the “divided” descriptor confirm that this patent was part of the original submission. The essential difference from patent No. 400,766 was use of potassium fluoride and aluminum fluoride with the composition of $K_2Al_2F_8$ instead of sodium fluoride and aluminum fluoride for the solvent. Replacing some of the potassium fluoride component with lithium fluoride made the bath lower melting and a better solvent for aluminum oxide. The first two figures for this patent were similar to those in No. 400,766. The third figure included a tube at the bottom of the crucible for drawing off molten aluminum metal. Cells in all three figures had graphite liners in crucibles made of iron or another metal. The graphite liners in the second and third figures served as the negative electrode. Use of non-carbonaceous anodes (+) was emphasized.

No. 400,665. August 17, 1888, Serial No. 282,954. One figure. “Manufacture of Aluminium.”

This patent concerned new developments beyond the original application. The cell design, as shown in Figure 3, differed significantly from the other patents in having a cover and a barrier made of graphite dividing one electrode area from the other near the surface of the melt. The divider was needed because liquid aluminum floated on the dense electrolyte composed of the alkaline earth metal fluoride solvents, as specified in this patent. The cover prevented rapid reoxidation of the aluminum metal by atmospheric oxygen, and the divider prevented reoxidation of the aluminum by contact with the anode. The principal claim in this patent was for electrolytes that avoided the formation of a “black substance” with its concomitant increase in resistance and voltage during

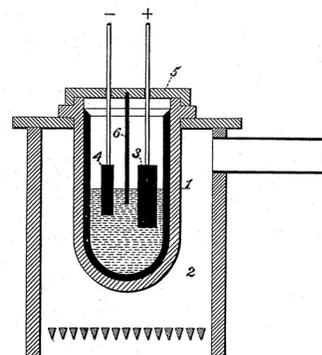
extended electrolysis. With sodium- or potassium-based electrolytes, the solvent system had to be renewed periodically. New electrolytes included $CaAl_2F_8$, which involved an excess of AlF_3 , as well as $SrAl_2F_8$ and $BaAl_2F_8$ and stoichiometrically balanced $Ca_3Al_2F_{12}$. All of these solvents had the advantage of being lower melting than the cryolite-based solvents and of making continuous operation possible. When alloys were made with a metallic cathode (-), the alloys were dense enough to sink to the bottom. If two-thirds of the weight of the solvent was replaced with $K_2Al_2F_8$, the solvent had a low enough density for molten aluminum to sink to the bottom. The barrier and cover were no longer necessary.

(No Model.)

C. M. HALL.
MANUFACTURE OF ALUMINIUM.

No. 400,665.

Patented Apr. 2, 1889.



WITNESSES:
C. Hewell.
F. C. Kauter.

INVENTOR,
Charles M. Hall
by Saml. b. Wolcott
ATTY.

Figure 3. The figure in patent No. 400,665.

This patent described the “artificial” preparation of aluminum fluoride from hydrated alumina and hydrofluoric acid, which is nasty chemistry because of the hazardous nature of hydrofluoric acid. The aluminum oxide was also described as being “artificially” prepared, presumably from alum $[KAl(SO_4)_2]$.

No. 400,666. August 17, 1888 Serial No. 282,955. One figure. "Process of Electrolyzing Crude Salts of Aluminium."

This patent, a companion to 400,665, described further improvements for avoiding the formation of the black substance accompanied by an increase in resistance that occurred with sodium- and potassium-based solvents. The variation was a solvent composed of $\text{Na}_2\text{Al}_2\text{F}_8$ + CaAl_2F_8 , which was sufficiently low in density to allow molten aluminum to sink to the bottom of the crucible. No cover or barrier between the electrodes was needed. In addition, a few percent of calcium chloride was added, which, due to volatility, had to be resupplied periodically. Continuous operation was affirmed.

No. 400,667. September 21, 1888, Serial No. 286,034. No figure. "Process of Electrolyzing Fused Salts of Aluminium."

Little difference exists between this patent and Nos. 400,665 and 400,666, filed a month earlier. As in the previous two, the emphasis was on achieving continuous operation without replacing the solvent. Tests were described for when to supply additional calcium chloride. These tests were observing a rise in voltage and an increase in the CO/CO_2 ratio. No method for determining this ratio was supplied. Absorption of CO_2 gas in base, leaving CO gas to be measured volumetrically, would have sufficed.

Had I studied the patents before doing the lecture demonstration, I would have known from the outset to add aluminum fluoride to the cryolite solvent.

The account of the essentials of the multiple patents shows that Hall was preoccupied with overcoming various difficulties by changing solvent composition and cell construction before he had the resources to run the process on a larger scale. This interpretation of the goal of Hall's intense work during the 1886-1888 development period and the multiplicity of patents concerned with improving the reliability of the process was confirmed in the detailed prospectus that Hall wrote on July 10, 1888 (14) and by Van Doren (3). This prospectus was written to convince Alfred Hunt to found a company that was soon named Pittsburgh Reduction Company. Most of the additional methods described in the patents were not needed because when the process was scaled up the difficulties largely disappeared. Switching over

to internal resistive heating by a strong electric current also simplified the process, managing the contents of the cell, and prolonging the life of the cell.

The industrial process is substantially the same as that described in patent No. 400,766, the patent with the earliest filing date. Thus, *despite it having the higher number*, this patent was the appropriate one to honor by a CCB award. This plaque honoring Charles Hall and his achievement is shown in Figure 4 (15). The figure on the plaque is a slight rearrangement of the figure (Figure 2) that was on patent No. 400,766.

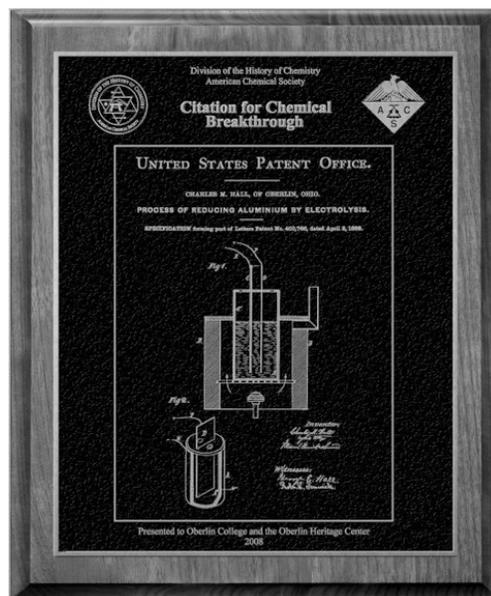


Figure 4. The display on the plaques presented to Oberlin College and the Oberlin Heritage Center for the Citation for Chemical Breakthrough.

Today, the Hall-Héroult process, as it became known in the twentieth century, has been scaled up by orders of magnitude and is largely automated. Computer control of the current, of the distance between electrodes, of the addition of aluminum oxide, and of the addition of aluminum fluoride and some calcium fluoride gives maximum efficiency in the use of electric power and materials. Today, a representative composition of the solution (in mol) is 1.0 Na_3AlF_6 , 0.34 AlF_3 , 0.17 CaF_2 , and 0.13 Al_2O_3 . A modern smelter has hundreds of pots running in series for roughly a year's lifetime each. Figure 5 is a photograph of a small part of the massive pot line of the new Alcoa plant at the Fjardaál smelter in Iceland, where electricity from geothermal energy is abundant. The scale-up and continuity of operation are breathtaking in comparison with the original tabletop process. The robustness and

reliability of the industrial process is a long way from the uncertainties that Charles Hall faced during the period of development. For the most part the multiplicity of patents proved to be unnecessary.

Acknowledgment

I am grateful to Maurice Laparra, president of the Institute for the History of Aluminium in Paris for the information about the composition of today's electrolyte solution and for his hosting of a tour of the huge, new aluminum smelter at Dunkerque, France.



Figure 5. A small part of the pot line in the Alcoa aluminum smelter at Fjardaál, Iceland. 2008 photograph. Image used courtesy of Alcoa Inc.

References and Notes

1. Presentation of the CCB plaque by the Division of the History of Chemistry to Oberlin College and to the Oberlin Heritage Center citing Charles M. Hall's principal patent, February 23, 2009. For a broader introduction to the challenge "first" or "breakthrough" as this distinction relates to the CCB award program, see: J. I. Seeman, "HIST's Citation for Chemical Breakthrough Awards: The 'First' or the 'Breakthrough' Paper?" *Bull. Hist. Chem.*, **2013**, 38, 4-6.
2. S. C. Mastick, "Chemical Patents—II," *J. Ind. Eng. Chem.* **1915**, 7, 874-882; "Chemical Patents—III and IV," *J. Ind. Eng. Chem.* **1915**, 7, 984-991.
3. L. Van Doren, "Studies in Chemical Patent Procedure. I. Hall Patents for Aluminum Production," *Ind. Eng. Chem.* **1929**, 21, 120-124.
4. H. N. Holmes, "The Story of Aluminum," *J. Chem. Educ.* **1930**, 7, 232-244.
5. J. Edwards, *The Immortal Woodshed*, Dodd, Mead and Co., New York, 1955.
6. N. C. Craig, "Charles Martin Hall – The Young Man, His Mentor, and His Metal," *J. Chem. Educ.* **1986**, 63, 557-559.
7. J. Walker, "Retracing the Steps by which Aluminum Metal was Initially Purified back in 1886," *The Amateur Scientist, Sci. Am.*, August **1986**, 255(2), 116-119.
8. J. D. Edwards, F. S. Frary, and Z. Jeffries, *The Aluminum Industry*, Vol 1, *Aluminum and its Production*, McGraw-Hill, New York, 1930, p 287.
9. A. Cowles, *The True Story of Aluminum*, Henry Regnery, Chicago, 1958.
10. Ref. 5, p 78.
11. United States Patent Office Publication, including testimony on the interference between Charles M. Hall and P. L. V. [sic] Héroult, 1887. Oberlin College Archives.
12. Copies of these patents are available through the website of the US Patent Office or Oberlin College Archives.
13. The use of the formula $\text{Na}_2\text{Al}_2\text{F}_8$ and similar formulas in the other patents was puzzling. It is not the simplest formula, which is NaAlF_4 . In the prospectus (13) written for Hunt, Hall consistently used " Al_2 ." Thus, Hall must have regarded Al_2 as the fundamental unit of the element aluminum, as reflected in $\text{Na}_2\text{Al}_2\text{F}_8$.
14. C. M. Hall, Prospectus written for Alfred Hunt, July 10, 1888. Oberlin College Archives.
15. Identical plaques were presented to Oberlin College and the Oberlin Heritage Center. The college's plaque is located near the aluminum statue of Charles M. Hall in the Department of Chemistry and Biochemistry. The plaque at the Oberlin Heritage Center is in the woodshed attached to the Jewett House, where there is a recreation of Hall's workplace.

About the Author

Norman C. Craig is Emeritus Biggs Professor of Natural Science in the Department of Chemistry and Biochemistry at Oberlin College, Oberlin, OH 44074. He has been a student of the work of Charles M. Hall, a 1885 graduate of Oberlin College. Craig has written papers and has given a number of presentations on Hall's life and work. He has an article about Julia Hall, Hall's older sister, in *Chemical Heritage*. He has also written about the history of chemistry at Oberlin College in the *Bulletin*.