

THE LEBLANC SODA PROCESS

A Gothic Tale for Freshman Engineers

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What principles of chemical engineering can we teach freshmen, and how should those principles be taught? The traditional undergraduate curriculum demands extensive prerequisites before students begin the quantitative study of chemical processes, typically including two semesters of general chemistry, a semester of physics, and a year of calculus. The introductory chemical engineering course arrives only in the sophomore year, so students have no clear picture of the field until their first year has passed by.

In the College of Engineering at UMass, we have revised the freshman curriculum to include overview courses from each of our departments. In addition to helping the students understand the differences between engineering disciplines and the sciences, enabling them to make an informed choice of major, these courses have other important goals. They are intended to give the students an introduction to the relationship between design and manufacturing, experience in a team project, and instruction in oral and written presentation, computational skills, safety, and engineering ethics. This is a full plate of diverse topics, and the chemical engineering principles we teach in such a course must be linked to some strong, unifying thread lest they be perceived as disjointed and scattered scraps.

We decided to devote a module of lectures in our first-semester freshman course to tracing the history of one particular process, and to use this process to illustrate and explain basic engineering principles. We wanted to choose an old process, one born before the invention of chemical engineering, so we could point to the many sad consequences of ignorance and discuss their remedies. We also wanted a process that had struggled to maturity despite innate limitations, but that ultimately died at the hands of a better-designed and more efficient successor.

The best case study of this kind that we have found is the

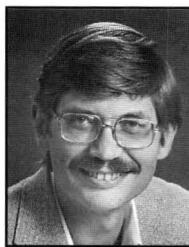
Leblanc soda process. For the eighty years between 1820 and 1900, the Leblanc process was a pillar of the CPI; but it was so completely supplanted by the Solvay process after World War I that it is almost forgotten by modern chemical engineers. Because of its former importance, however, it has been extensively described by historians of technology, and a number of excellent accounts are available in the literature.^[1-9]

In the following four sections of this article, we tell the story of the rise and fall of the Leblanc process and emphasize the lessons to be learned from its story. The final section describes how the material is integrated into our freshman course.

BEGINNINGS

During the eighteenth century, the production of chemicals and materials across Europe began to increase steadily under the pressures of increasing population growth and trade, urbanization, a rising standard of living, and the accumulation of capital. As demand increased, natural sources of raw materials began to fall into short supply. Among the most heavily stressed resources were soda ash (Na_2CO_3) and potash (K_2CO_3), known collectively as alkali.

Alkali was essential to three rapidly growing industries: it was used in textile processing as an alkaline scour in the



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bleaching of linen and cotton cloth; it was used in glassmaking as a fluxing ingredient to lower the melting point of soda-lime glass compositions; and in soapmaking, alkali was treated on-site with lime to produce caustic (NaOH or KOH) for the saponification of fats and oils to hard or soft soap.

The traditional source of natural alkali was the ash that remained after burning plant matter. Seashore plants were used where soda rather than potash was required, since these have the highest ratio of sodium-to-potassium content. Most popular were kelp from Scotland and barilla (saltwort) from Spain. The soda content of these ashes was comparatively small (10 to 30%) and was very variable; more seriously, supply was prone to sudden interruption by wars, tariff barriers, and acts of God.

The importance of an artificial source of soda became apparent early, and between 1730 and 1790 a dozen such processes were proposed, including a 1769 effort by the unexpected team of James Watt and Joseph Black.^[1]

Half a dozen of these processes were brought to small-scale production, typically to make captive soda for an adjoining glassworks or soap works, but none proved to be competitive with natural sources. In 1783, the French Academy of Sciences offered one of its celebrated prizes for a viable process to produce soda from common salt, but that prize was never awarded.

It was in France, however, that the first truly economic process for artificial soda was born.^[2] Its inventor was Nicolas Leblanc, an amateur chemist who was the personal surgeon to the Duc D'Orléans. In 1789, Leblanc conceived a two-step reaction pathway to convert common salt to soda. Leblanc left no clear record of his reasoning, although there is evidence that he might have been inspired by a false analogy with the smelting of iron from its ore. A simple block flowsheet is shown in Figure 1.

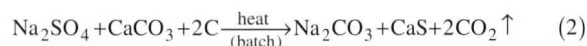
The first reaction step



was well known long before Leblanc. It was the second reaction step, the production of soda from saltcake

(Na_2SO_4) that was novel.

In a solid-state batch reaction carried out in a furnace, Leblanc roasted 1 part saltcake by weight with 1 part chalk or crushed limestone and 1/2 part coal or charcoal. The chemistry of this reaction step was poorly understood for a century after its introduction into industrial practice, and there are certainly many side reactions. In simplest modern terms, however, the primary reaction can be thought of as



The product, a vile-smelling mass called "black ash," contained soda, CaS, byproducts, and unconverted reactants. The ash was broken up and extracted with hot water, or

"lixiviated"; the extract was evaporated to yield crude soda. The insoluble solids, or "tank waste," were discarded. If reactions (1) and (2) went to completion stoichiometrically without side reactions, 1 pound of soda could be produced from 3.2 pounds of reactants; but in practice, because of the excess of CaCO_3 and carbon, impurities in the reactants, the incompleteness of reaction, and the weakness of available H_2SO_4 , it could require as much as 10 to 12 pounds of reactants to make a single pound of soda.^[3]

Even so, Leblanc's process was better than its contemporary competitors. Leblanc was granted a fifteen-year patent by the French government in 1791, and in the same year he formed a company to produce artificial soda, bankrolled by his patron the Duke.

A small plant was built at St. Denis on the Seine near Paris. For two years the plant operated with some success (although well below its theoretical capacity), but in 1793, the economic and political climate turned sour. France executed Louis XVI and was soon at

war with the rest of Europe. All available supplies of sulfur and saltpeter (KNO_3) were requisitioned for the manufacture of gunpowder. Both of these chemicals were needed to produce sulfuric acid, and as the supply disappeared, Leblanc's plant shut down for lack of raw materials. Worse still, the Duc D'Orléans was guillotined in November, and his assets were confiscated, including the soda factory at St. Denis that he had capitalized.

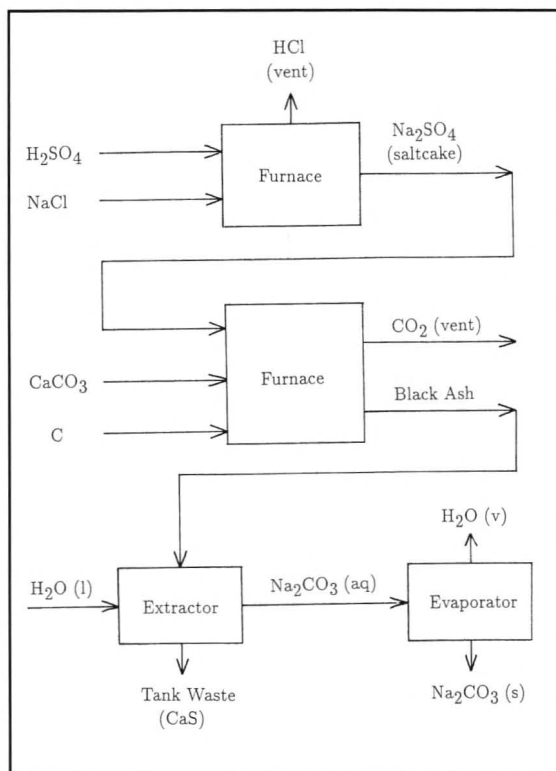


Figure 1. Simplified flowsheet of the basic Leblanc process; two solid-state, batch reaction steps followed by a separation. Flowsheets for Cl_2 recovery (Weldon or Deacon) or S recovery (Chance) can be added throughout the semester at the instructor's discretion

The revolutionary government was short of soda as well as every other industrial chemical, since its foreign sources had been cut off by the conflict. In order to stimulate production, in 1794 a government commission published and publicized a report on all available methods of making soda, including Leblanc's process. His patent, which had been closely held, became widely known and began to be used in a small way by others in France and abroad—without licensing fees. Leblanc spent nearly eight years suing for ownership of the idle plant and petitioning for reimbursement for his perceived loss of patent rights. He finally regained control of the plant in 1801, but he was unable to raise the money to operate it effectively. He went into debt, grew depressed, and committed suicide in 1806.

Soon afterward, France remitted its tax on salt and restricted the import of foreign barilla, and the Leblanc process became profitable on a significant scale.^[4] A number of Leblanc works were opened, primarily near Marseilles, the center of the French soap industry. The mature development of the process, however, took place across the Channel in Britain.

MATURITY

The Leblanc process had been worked in England in a minor way as early as 1802, but its expansion to a major industry had to wait for a drop in the price of its raw materials and the rise of a new class of chemical entrepreneurs. These factors came together in the early 1820s in three great seaports and industrial centers: Liverpool, on the Mersey; Newcastle, on the Tyne; and Glasgow, on the Clyde.

The growth of the lead-chamber process for the production of sulfuric acid in the previous three decades had dropped the price of acid from £35/ton in 1790 to £3/ton in the 1820s.^[5] Salt also became much cheaper because of changes in tax policy. In the aftermath of the Napoleonic wars, the impoverished British government had imposed a crushing £30/ton tax on salt to raise its revenues; this was finally lifted after 1823.^[6] That same year, the Anglo-Irish entrepreneur James Muspratt opened a Leblanc soda works in Liverpool, followed by additional plants in smaller towns farther up the Mersey.

Muspratt chose his site carefully in that era of expensive transportation. Transport on the roads of the time was slow, expensive, and uncertain, particularly in the wet weather of winter and spring, and the railroad would not come to the region for another decade. The only affordable transportation for raw materials was by water; this was provided by the Mersey itself, its navigable tributaries, and the network of canals that had been dug since 1757. Merseyside plants had access to coal from South Lancashire and salt and limestone from Cheshire, within twenty miles; limestone was also often carried into port as ships' ballast and sold off cheaply at the quay.

Muspratt's markets, like his raw materials, were nearby. Liverpool was already a center of glassworks and soap manufacture. The new soda was marketed aggressively, and the plant was soon a thriving concern. Other plants opened in Britain, primarily at the three great northern seaports, and Leblanc soda began to capture the soda market away

from natural sources. By 1862, the industry employed 10,000 men directly and another 20,000 indirectly in mining and transportation; that year it consumed 250,000 tons of salt and produced £2,500,000 worth of products.^[1]

In histories of the chemical industry, the Leblanc process is sometimes called a "nearly perfect" process that changed very little except for "mechanical" improvements over its history.^[7] A glance at Eqs. (1) and (2) shows that this is nonsense. Apart from the fact that the Leblanc process did produce soda, it was a recipe for turning raw materials into toxic waste. All the potentially valuable chlorine liberated from salt was vented as HCl; the sulfur that had been expensively converted to sulfuric acid was entirely lost as insoluble sulfide. These wastes caused serious problems for both the community and the manufacturers.

The first Leblanc plants were surrounded closely by residential areas, agricultural land, and rural estates. As production increased, HCl emissions from the plants burned the vegetation of the surrounding countryside and damaged stone buildings.

Scolding letters appeared in the newspapers as early as 1827, and in 1831, Muspratt was served with the first of many civil lawsuits claiming damages. This was a serious matter; the copper smelters in Liverpool had already been declared a public nuisance and had been forced out of town because of their SO₂ emissions.

The first solution tried by the soda manufacturers was to discharge the HCl through a taller stack, relying on greater dilution of the exhaust plume before it contacted the ground (the solution to pollution is dilution). The record height appears to have been 454 feet.^[1] Often, however, the result

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of taller stacks was simply drawing lawsuits from acid rain damage further downwind.

Tall stacks also did not improve the condition of workers in the plant. The HCl fumes reportedly burned their clothes and rotted their teeth, and it was not unusual for workers to faint and be dragged outside to revive.^[3] Bronchitis and lung disease were endemic. Workers over forty years old were past their prime and were often moved out of the plant to lighter work in the yard.

The CaS waste was also a problem. Landfilling was not possible since there was no heavy earth-moving equipment at that time. Tank waste was simply piled on surrounding land, in heaps as high as 50 feet tall, many acres in extent. Four and a half million tons of tank waste had been laid

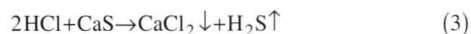
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down by 1885 in Lancashire alone.^[6] When the land had to be leased from other owners, the cost could run as high as £1500/acre; this was thirty times a workingman's annual wage.

Tank waste contained a spectrum of byproducts and unconverted reactants that continued to react outdoors as the waste was weathered by wind and rain. Sometimes the

waste formed a hard, impermeable crust; occasionally it burst into flame; and it regularly leached out a yellow-brown liquor into local watercourses.^[8]

In the acid environment surrounding the plants, the waste piles and waterways became inadvertent chemical reactors, producing hydrogen sulfide gas from the reaction



The stench was shocking, even to the robust noses of the Victorians.

Over the long history of the Leblanc process, as basic chemical engineering principles were slowly formulated and implemented, these serious economic and environmental problems were ameliorated or eliminated, one by one.

In 1836, William Gossage, an energetic inventor and owner of a Leblanc works, devised a solution to the problem of HCl emissions. He owned a derelict windmill near his plant; he packed the mill with brush and twigs, piped in water at the top from a nearby brook, and absorbed the HCl into solution.^[4] This was the first use of a scrubbing tower in the CPI.

The windmill was soon replaced by a patented tower of

tar-soaked stone, packed with coke or broken brick. The Gossage tower greatly reduced gaseous HCl emissions, although they were not completely eliminated. In particular, back-pressure from the tower reduced the rate of saltcake production, and since workers were paid bonuses according to output, there was a temptation to bypass the tower and vent HCl directly when nobody was looking^[3] (an early demonstration that it is a bad idea to give personnel an economic or psychological incentive to do the wrong thing). Many alkali works did not install Gossage towers at all, preferring to pay occasional damages in court rather than to invest in the capital costs.^[8]

In 1863, pressure from the rural gentry forced Parliament to pass the first Alkali Act, which mandated that plants must scrub 95% of the HCl from their stack gases. A network of inspectors was established to enforce the Act by regular visits and surprise inspections. One of the first alkali inspectors was George E. Davis; his experience inspecting chemical works led him to formulate the first comprehensive view of chemical engineering as a discipline, culminating in his *Handbook of Chemical Engineering* (1901 and 1904).

The weak HCl solution condensed by Gossage towers had little market at the time, so the first result of HCl scrubbing was to convert the gas-disposal problem into a liquid-disposal problem (illustrating the dictum that the chief cause of problems is solutions). Most of the liquid HCl was expelled into nearby canals and brooks. The Sankey Canal on Merseyside became so acidic that iron-bottomed barges were kept off it for fear of corrosion.^[6]

As the understanding of basic chemistry improved through the nineteenth century, auxiliary processes were gradually developed to convert the Leblanc wastes into saleable byproducts or recyclable raw materials. The most important were two processes that transformed the HCl from saltcake furnaces into Cl_2 ; Weldon's process (1867) used a reaction with manganese dioxide, while the Deacon-Hurter process (1872) used a copper chloride catalyst. The Cl_2 was absorbed onto slaked lime to produce a solid bleaching powder (a crude calcium hypochlorite), for sale to the textile and pulp and paper industries.

The bleaching powder works were hardly perfect by modern standards. The reaction was carried out batchwise in large chambers, and the finished powder was shoveled out manually by workers smeared with beef tallow, wearing goggles and dampened cloth masks called "muzzles."^[3] Nevertheless, this was one of the first major successes at converting an industrial waste into a valuable byproduct.

In 1887, Chance developed a process to recover sulfur from black-ash waste, and the solid-waste problem was also alleviated. From the 1840s onward, sulfur burning was replaced by the roasting of pyrite ores to produce H_2SO_4 for the saltcake process; the pyrite slags were processed to re-

cover iron and copper as further byproducts.^[5]

Several mechanical improvements were also made over the latter half of the century. Leblanc black-ash furnaces were originally mixed by hand throughout the course of the reaction, a labor-intensive and inefficient technique. In 1853, Elliott and Russell developed a revolving furnace that mixed the reacting solids much more effectively. These “revolvers” came into general use over the following fifteen years.

In 1861, James Shanks perfected a method for extracting the carbonate from black ash using an ingenious system of vats that reduced manual handling of the material, and this improvement was also generally adopted. Large Leblanc works often attempted to exploit economies of scale, but this was not always successful. Thermodynamics was in its infancy at the time, and there was no understanding of the principles of heat and mass transfer, so large furnaces and towers were often improperly sized or proportioned.^[1]

By the late 1880s, the Leblanc process had been modified to recover the bulk of its wastes and to operate far more efficiently than it had done originally. The process was finally mature; but it was also obsolete.

DECLINE

As early as 1811, it was known that sodium bicarbonate could be precipitated from a brine solution saturated with ammonia and CO_2 . The reaction was easy to carry out on the benchtop, but despite repeated efforts, no one was able to make it a viable industrial process. The sticking point was the loss of ammonia. In order to make an ammonia-soda process economical, almost all the ammonia had to be recovered and recycled, and the gas-handling systems of the day were not equal to the job.

Finally, in 1861, after a long period of R&D, Ernest Solvay constructed a practical plant. Solvay’s process was licensed in Britain by Ludwig Mond, who made further improvements, and Brunner, Mond & Co. began to produce soda by the Solvay process at Winnington, on the Merseyside, in 1874.

Leblanc soda was an inherently batch process, and it carried all the natural disadvantages of batchwise production in the manufacture of a large-volume commodity chemical. It required a lot of manual labor; uniform product quality was hard to maintain between batches; and there were few opportunities for thermal recycle, so a great deal of energy was wasted.

The Solvay process, on the other hand, was continuous. It emitted no HCl , and its solid waste was the chloride of calcium, much less objectionable environmentally than the sulfide. Solvay’s process also had a simpler separation step (filtration rather than extraction). Mond did not try to undercut the prices of Leblanc manufacturers since demand for soda was high and he could sell all his product without a

price war. Nevertheless, as the capacity of the industry grew, the price of soda slid from £4 10 s per ton in 1861 to £2 15 s in 1889.^[8] Solvay plants were still profitable at this price, but Leblanc manufacturers were soon selling their soda at a loss. They stayed afloat only through the profits from bleaching powder, which now became their principal product.

The Leblanc manufacturers formed a voluntary Bleaching Powder Association in 1883, a cartel that propped up the price of bleach artificially by limiting production (this was not illegal at the time, although it was frowned upon in many newspaper editorials). Inevitably, the cartel collapsed in 1889 through price undercutting by nonmembers and renegade member companies. During this period, chlorine was also beginning to be produced in quantity electrolytically, and the Leblanc monopoly on bleach was disappearing.

It became clear that a voluntary association would not be able to enforce prices and keep the industry viable. Finally, in 1890, the forty-five remaining Leblanc works in Britain merged to form United Alkali, a consolidated, publicly-held stock company. The new company closed the most inefficient plants, downsized the industry, and diversified its product lines.

The Leblanc process staggered on in Britain, in increasingly straitened circumstances, for another thirty years; but the last Leblanc works closed soon after World War I. United Alkali itself was swallowed up in the giant merger that created Imperial Chemical Industries in 1926.^[9]

LESSONS

By tracing the rise and fall of the Leblanc soda process, we can introduce a surprisingly large number of elementary chemical engineering principles at a level that doesn’t require much pre-existing background in chemistry and physics. For example:

- *The concepts of a process, its flowsheet, and the unit operations arise naturally in explaining how the reaction scheme of Eqs. (1) and (2) was translated into practice. Only a few simple inorganic reactions are necessary, and the students become more comfortable with these over the course of the semester as they concurrently study their first semester of college chemistry.*
- *The Leblanc process offers many concrete examples of how the economic potential of a process is affected by the supply of raw materials, the demand for product, transportation costs, plant-siting decisions, and government regulation and tax policy.*
- *The advantages and disadvantages of batch vs. continuous processes are illustrated by the final struggle of Leblanc’s process with Solvay’s.*
- *The health, safety, and environmental problems associated with the process give a backdrop for discussions of plant safety and engineering ethics later in the course.*

The Leblanc process offers such a rich context that an

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instructor who wants to stress different principles than we have done can easily find appropriate examples in its history.

COURSE FORMAT

Our freshman course consists of two fifty-minute lecture periods and one two-hour computer laboratory per week. The course is typically taught in two sections averaging thirty students each.

In the paragraphs above, we gave a condensed and sequential account of the Leblanc process. In practice, this material is spread across a four- to five-period block of lectures. At each opportunity to illustrate a new concept (classification of processes, economies of scale, etc.), we suspend the narrative and focus on a discussion of that concept, involving the students in as much back-and-forth interaction as possible. Then the narrative resumes.

Although we present a good deal of concrete detail and history in these lectures, the emphasis is not on memorization of detail, as it might have been in an old-style industrial chemistry course; instead, it is to illustrate and illuminate basic principles within one coherent story. The students apply these principles to other processes in weekly homework assignments and in the two examinations that are given during the semester.

At the beginning of the course, the students are organized into teams of three, with each team assigned a different commodity chemical process to research in the literature. During the semester, each team gives two oral presentations on its process to the class and produces a final written report. Our in-depth discussion of Leblanc soda helps the students organize a clear presentation of their own team's process and its flowsheet. By the end of the term, each student has actively participated in analyzing and presenting one simple chemical process and has seen analogous presentations on the nine or ten different processes studied by the other teams.

More details of the syllabus, structure, and lecture schedule of our freshman course can be found on the web at

<http://www.ecs.umass.edu/che/classroom.html>

This web site will be expanded and updated as the course evolves.

Does the strange, Gothic tale of Leblanc soda scare fresh-

men away from chemical engineering? Does it give them the impression that they are entering a demented and immoral profession? That hasn't been our experience at all. After recounting each of the inefficient or damaging aspects of the Leblanc process, we can turn to the class and ask, "Now, why did they have this terrible problem?" and the students quickly recognize that the correct answer is, "Because they had no chemical engineers." Students are eager to solve real problems, and the Leblanc history offers an abundance.

All too often, the first experience of chemical engineering students with the profession is a blind and headlong rush into the pages of a sophomore stoichiometry text, and they do not have a clear overview of the structure and aims of the field until their capstone senior design course. Our hope is that this semi-historical module in the freshman year will help to give students an accurate context for their education at its very beginning, rather than at its end.

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