Jason Taylor

The Impact of Alkali Production on the Emergence of Chemical Engineering

Alkali chemicals have been used to produce glass, dyes, soaps, detergents, bleach, and paper for hundreds of years. Before and during the 1700s, the main source of alkali in Western Europe was potash, also known as potassium carbonate, obtained from wood ashes of burned trees. Near the end of the eighteenth century, Western Europe was undergoing an industrial revolution sparked by increasing demands for glass, dyes, soaps, detergents, bleach, and paper. Heavy deforestation in Western Europe required that alkali demands be met by importing potash from Russia, Scandinavia, and North America. With supplies not plentiful, the need for imports raised costs. An alternative source of alkali was necessary to satisfy rising demand for glass, dye, soap, detergent, bleach, and paper. This challenge created a need for new applied chemistry on an industrial scale. The following discussion explains how the industrial demand for alkali was met, how the resulting industrial-scale procedures helped to trigger the emergence of chemical engineering as a recognized profession, and the impact that it has had on culture.

In an effort to implement a new source of alkali, in 1783 King Louis XVI of France ordered the French Academy of Sciences to offer a reward of 200,000 livres to the first French scientist who could develop a practical process to produce alkali from sea salt. After 7 years of research, a French chemist and physician, Nicolas LeBlanc, patented a two-step batch process to produce soda ash, also known as sodium carbonate, which is another source of alkali. The first step of the LeBlanc Process had been discovered in 1772 by a Swedish-German scientist, Carl Wilhelm Scheele, and the second step was discovered in 1791 by LeBlanc himself. The LeBlanc batch process can be summarized by two reactions:

(1) $2NaCl_{(s)} + H_2SO_{4(aq)} \rightarrow Na_2SO_{4(aq)} + 2HCl_{(g)}$

(2) $Na_2SO_{4(aq)} + CaCO_{3(s)} + 2C_{(s)} \rightarrow Na_2CO_{3(s)} + CaS_{(s)} + 2CO_{2(g)}$

Based on his new process, LeBlanc built a plant that was able to produce 320 tons of soda ash per year, significantly greater than the rate of production from organic sources such as trees. Unfortunately for LeBlanc, by 1794 the French Revolution required alkali to produce munitions for the French army. In time of war the French Army seized LeBlanc’s plant to produce alkali for military means, and outsourced LeBlanc’s patented process. In 1801 Napoleon returned the plant to LeBlanc, but by this time most of the industrial equipment had been confiscated, and that which remained had not been properly maintained for many years. Lacking the necessary funds to rebuild a fully functional plant that could compete with competitors, LeBlanc fell into depression and eventually committed suicide in 1806.

Despite the tragic demise of Nicolas LeBlanc, his process lived on and immediate global alkali needs were easily satisfied until the middle of the nineteenth century. Although alkali production was able to meet global demands, some major issues arose concerning the safety of the process. Reaction (1) produced hydrogen chloride gas that was vented into the environment, and reaction (2) produced solid calcium sulfide which liberated poisonous hydrogen sulfide gas. Both hydrogen chloride and hydrogen sulfide gases are toxic pollutants. For every 8 tons of soda ash, 5.5 tons of hydrogen chloride and 7 tons of calcium sulfide were produced. With no means of waste treatment or recycling at the time, the accumulating waste began to impact the health of the environment near the industrial plant. Prolonged exposure to the hazardous wastes scorched surrounding fields rendering them incapable for agriculture, caused the deterioration and death of local farm animals, tarnished furniture in neighboring homes, and caused chronic coughing and headaches in local inhabitants. The severity of the impact of chemical waste caused a large societal outcry. By 1863 the first of several laws to limit hazardous emissions was issued by the British Parliament. Although the LeBlanc process created a tremendous amount of hazardous waste, alkali was extremely important to the growth of industrialized nations. As a result, scientists began looking for alternative safe ways to produce sodium carbonate.

To respond to the need for safer living conditions, chemists and chemical engineers met the challenge of creating an alternative process for producing alkali. In 1811 French scientist Augustin Jean Fresnel discovered that soda ash precipitates when carbon dioxide is bubbled through brine that also contains ammonia. Unfortunately, he never published his discovery and it wasn’t until 1834 that Fresnel’s idea was patented by H.G. Dyan and J. Henning. With exclusive rights to Fresnel’s process, Dyan and Henning tried to scale-up the process to meet the production levels of the LeBlanc process. Despite numerous efforts, the two scientists were not able to scale-up their process.

A Belgian industrial chemist, Ernest Solvay, began working on the scale-up of Fresnel’s discovery. In conjunction with his brother Alfred, in 1864 Ernest Solvay constructed a plant that successfully scaled-up Fresnel's discovery to an industrial scale. The Solvay process is a continuous process that can be summarized in four steps:

(1) $NaCl_{(s)} + CO_{2(g)} + NH_{3(aq)} + H_2O_{(l)} \rightarrow NaHCO_{3(aq)} + NH_4Cl_{(aq)}$

(2) $CaCO_{3(s)} \rightarrow CO_{2(g)} + CaO_{(s)}$

(3) $2NH_4Cl_{(aq)} + CaO_{(s)} \rightarrow 2NH_{3(aq)} + CaCl_{2(s)} + H_2O_{(l)}$

(4) $2NaHCO_{3(aq)} \rightarrow Na_2CO_{3(s)} + H_2O_{(l)} + CO_{2(g)}$

Overall: $2NaCl_{(s)} + CaCO_{3(s)} \rightarrow Na_2CO_{3(s)} + CaCl_{2(s)}$

The Solvay process offers many advantages over the LeBlanc process with regard to lowering production costs and limiting environmental pollution. While the LeBlanc process requires coal, limestone, salt, and sulfuric acid to produce alkali, the Solvay process requires ammonia, limestone and salt. Because the ammonia can be recycled in the Solvay process, and because sulfuric acid and coal are the two most expensive raw materials in the LeBlanc process, the Solvay process leads to a substantial decrease in production costs. Furthermore, because the Solvay process doesn't use sulfuric acid, it generates neither hydrogen chloride nor calcium sulfide and subsequent hydrogen sulfide. Although the Solvay process was both less expensive and less polluting than the LeBlanc process, it never the less produced roughly 50% more waste than soda ash. To reduce the amount of waste stored in localized waste beds, calcium chloride was sold for use as road salt. Eventually the process was changed so that ammonium chloride was produced in place of calcium chloride. Ammonium chloride was preferred because it could be sold as fertilizer which had greater demand than road salt. Unfortunately, however, the Solvay process produces significant carbon dioxide emissions; in light of current concerns with greenhouse gases on global warming, scientists are now proposing changes in the process toward carbon dioxide sequestration.

Around the time that the Solvay process was emerging as a replacement for the LeBlanc process, Britain issued the Alkali Act of 1863, which appointed alkali inspectors to visit industrial production plants to monitor hazardous emissions. One alkali inspector, George Davis, visited a number of LeBlanc and Solvay plants and gained an appreciation for the roles that both LeBlanc and Solvay played in the industrial revolution. Seeing the integration of chemistry and industrial engineering utilized by LeBlanc and Solvay, Davis was convinced that growing industrial nations required a new type of engineer capable of applying both fields. In 1880 Davis attempted to form a “Society of Chemical Engineers.” Most industrial plants employed both chemists and mechanical engineers, and he felt that a new branch of engineering would not improve their current industrial capabilities. Lacking support in the scientific community, Davis’ “Society of Chemical Engineers” failed. Undaunted by initial skepticism, Davis continued to develop his understanding of chemical engineering; in 1887 he wrote a 12-lecture series on unit operations for chemical engineers. The lectures had a significant impact on the scientific community, and finally convinced many of the need for chemical engineering. In 1888 Professor Lewis Norton of the Massachusetts Institute of Technology created the first bachelor-degree program for chemical engineering. The American Institute for Chemical Engineers was formed in 1908.

Alkali production has a tremendous impact on our culture, as it is used to produce glass, dyes, soaps, detergents, and bleach. Table 1 gives a breakdown of total alkali use in the United States in 2001 by industry:

Category	% of U.S. Consumption
Glass	49.0
Chemicals (Including Dyes)	27.0
Soap/Detergents	11.0
Pulp/Paper	2.0
Miscellaneous	11.0

Table 1: Percentage of total alkali consumption in the U.S. in 2001 by industry.

When alkali is combined with silicon dioxide at high temperatures, glass is formed. Glass is used in a wide variety of applications including containers, auto-glass, windows, glass lasers, and all sorts of optics. Additionally, alkali is used to alter the pH of dyes to allow for binding of dyes to cellulose fiber. The fibers are activated by alkali which helps them bind to the dye molecules. Soap, detergents, and bleach are used in a variety of cleaning and disinfecting applications. Annual global production of alkali is estimated at approximately 44 million metric tons. Without the development of the Solvay process, which currently produces two-thirds of the alkali used around the world, alkali would be in huge demand. This would drive up the cost of alkali and make a number of current applications economically impractical. Imagine if glass production was so costly that windows used in buildings and automobiles were non-existent. Would business offices still have a wonderful view on a sunny day, and would driving still be considered safe? If another material, say plastic, were used in place of glass How about the impact it would have on dyes? Imagine walking into a department store to buy clothes that are nearly all the same color. Would wardrobe style still be important to the social status quo? What about soaps and detergents? Clothes would become ruined much more quickly because washing with water alone will make removing any non-polar compounds, such as oil and grease, nearly impossible. In addition, clothes wouldn't retain a pleasant scented fragrance which would make body odor much more noticeable than it is today. It is easy to see that we take a lot of these things for granted, and without early chemical engineers like LeBlanc and Solvay our lives would be drastically different than they are today.

References

1. Eggeman, T., 2001, Sodium Carbonate, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc, Hoboken, NJ.
2. Bide, M., 2004, Dyeing, *Kirk-Othmer Encyclopedia of Chemical Technology,* John Wiley and Sons, Inc, Hoboken, NJ.
3. Boyd, D.C., Brow, R.K., Danielson, P.S., Thompson, D.A., Velez, M., and Reis, S.T., 2004, Glass, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley and Sons, Inc, Hoboken, NJ.
4. Pafko, W., 2000, *History of Chemical Engineering,* http://www.pafko.com/history/index.html.
5. Burch, P.E., 1999, What's Soda Ash, and What's in it for Dyeing?, *Paula Burch's All About Hand Dyeing*, http://www.pburch.net/dyeing/FAQ/sodaash.shtml.