

## HISTORY OF THE CHLORINE INDUSTRY

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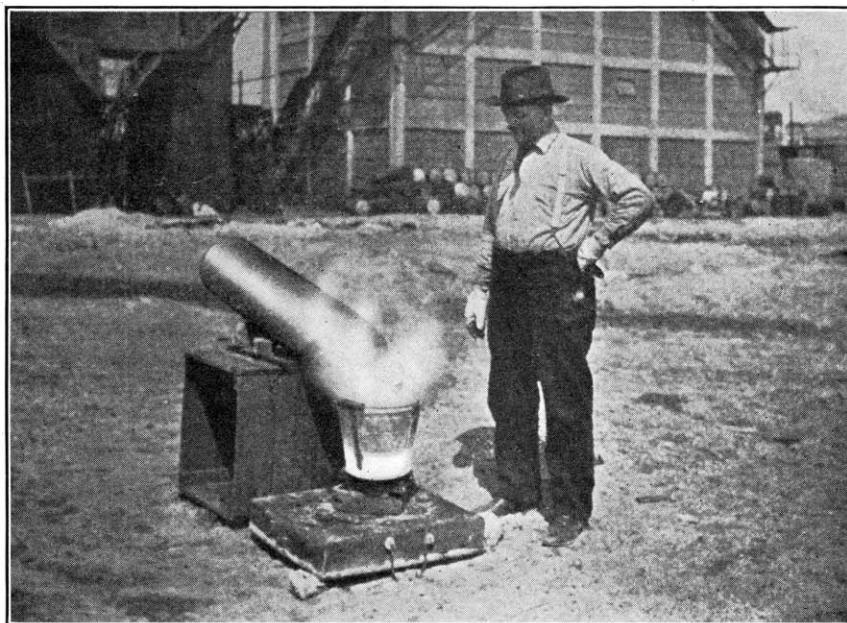
It is reasonable to suppose that chlorine gas was known to the alchemists, because their one solvent for gold, aqua regia, gave off on heating the fumes of chlorine. The discovery of chlorine, however, is attributed to the Swedish chemist, C. W. Scheele, in 1774. He discovered that on heating black oxide of manganese with hydrochloric acid he obtained fumes similar to those evolved when aqua regia is heated. Scheele called this gas dephlogisticated muriatic acid, on the basis of the then prevailing theory that the manganese had displaced phlogiston, as hydrogen was then called, from the hydrochloric acid. Scheele noticed that the gas was soluble in water, that it gave a permanent bleaching effect on paper and vegetables and flowers, and had action on metals and oxides of metals.

In 1785 Berthollet prepared a bleaching agent by dissolving Scheele's gas in water. In 1789 he improved this bleaching fluid by adding the gas to a solution of caustic potash at a French chemical plant on the Quai de Javelle, Paris, and this solution became known as *Eau de Javelle*. James Watt, inventor of the steam engine, and a chemist of standing, obtained the process of manufacture of *Eau de Javelle* from Berthollet and brought it to Scotland for Charles Tennant, founder of the great English chemical company of that name. Tennant in 1798 made still another bleaching agent, a chlorinated milk of lime, and in 1799 improved upon this substance by making a chlorinated hydrate of lime, a dry product, and known to commerce ever since as bleaching powder. It is also called "bleach" and "chloride of lime."

In the period 1774 to 1810, the nature of Scheele's gas was being investigated by such men as Berthollet, Lavoisier, Gay-Lussac, Berzelius, Thenard, and H. Davy. On July 12, 1810, H. Davy, before the Royal Society, London, said that the gas is an elementary body which, in muriatic acid, is combined with hydrogen. He proposed the name "chlorine" from the Greek "chloros" variously translated "green," "greenish," "greenish yellow," and "yellowish green" in allusion to the color of the gas. Davy's conclusions were generally accepted, although Berzelius did not adopt them for some years afterward.

In 1785, B. Pelletier and, 1786, Karsten had succeeded in obtaining yellow crystals of chlorine hydrate by cooling Scheele's gas in the presence of moisture, and inferred that Scheele's gas was not a simple substance. In 1805 Thomas Northmore liquefied chlorine gas. He called chlorine gas "oxygenated muriatic acid," having adopted the name given it by Berthollet who was convinced at this time that chlorine was a mixture of hydrochloric acid and oxygen. Northmore in describing the experiment says: "Upon the compression of oxygenated (oxygenated) muriatic acid gas in

a receiver two and a quarter inches capacity, it speedily became converted into a yellow fluid of such extreme volatility under the common pressure of the atmosphere that it instantly evaporates upon opening the screw of the receiver. I need not add that this fluid, so highly concentrated, is of a most insupportable pungency. When atmospheric air was pumped into the empty receiver it was speedily filled with dense white fumes. There was a trifling residue of a yellowish substance left after the evaporation, which probably arose from a small portion of the oil and grease used in the machine mixed with some of the concentrated gas;



*Reproduced from "Liquid Chlorine," Electro Bleaching Gas Co.*

Liquid Chlorine Being Poured into an Open Bucket. Note the frost on the bottom of the bucket, due to the evaporation of the liquid.

it yielded to sulphuric ether, and destroyed vegetable colours. This gas is very injurious to the machine, and on that account difficult to work."

In 1810 Davy proved that the yellow crystals of Pelletier and of Karsten could not be formed at  $-40^{\circ}$  Fahrenheit if dry chlorine gas was used. On March 5, 1823, Faraday, while working with chlorine hydrate in a sealed tube, was visited by Dr. J. A. Paris. The latter noticed some oily matter in the tube, and twitted Faraday for using dirty apparatus. Faraday thereupon started to open the tube, and it shattered, and the oily matter vanished. Faraday studied the accident and Dr. Paris on the following morning received a note—"Dear Sir: The oil you noticed yester-

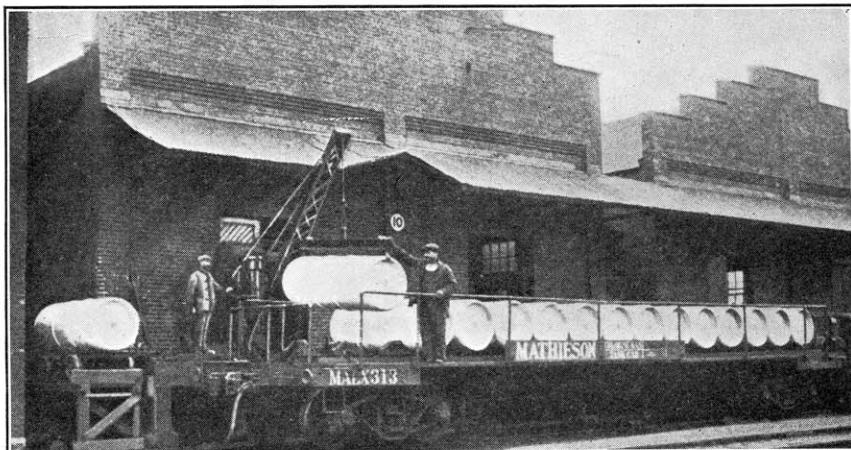
day turned out to be liquid chlorine. Yours faithfully, Michael Faraday." Liquid chlorine remained, from 1805 onward, a laboratory curiosity, and a dangerous one, in glass apparatus, until it was produced on a commercial scale by cooling and pressure and in suitable apparatus, by Knietsch in 1888.

The manufacture of bleaching powder, begun in 1799, grew rapidly, and until about 1836 the chlorine was obtained by Berthollet's method of heating sodium chloride, manganese, and sulfuric acid in lead stills. In 1836, Gossage invented his coke towers for the absorption of waste hydrochloric acid evolved in the LeBlanc soda process. With this cheap acid available, Scheele's method of obtaining chlorine by treating manganese dioxide with hydrochloric acid became largely the commercial method. In 1868 Deacon and Hurter patented the "Deacon" process of preparing chlorine by decomposing hydrochloric acid with oxygen. Again Scheele's method was largely abandoned and the "Deacon" process prevailed until the introduction of the electrolytic method of preparing chlorine in 1890 by the Elektron Co., Griesheim.

In 1833, after years of experimentation, Faraday discovered and formulated the laws that govern the action of an electrical current in aqueous salt solutions. In 1851, Charles Watt obtained an English patent for the electrolytic manufactures, including chlorine, caustic soda, and sodium hypochlorite, but as there was no practicable dynamo for electric current available the patent was largely of academic interest. With the introduction of better dynamos in the seventies and the eighties, interest in electrochemistry was greatly stimulated, and as before stated, the commercial production of electrolytic chlorine was attained in Germany in 1890. The first American commercial production was at Rumford Falls, Maine, in 1893. The English began the electrolytic manufacture about the same time and within a decade there were numerous small electrolytic plants in Germany, England, and the United States of America. The first Canadian plant was established in 1912.

In Germany non-electrolytic chlorine had been liquefied on a commercial scale in 1888, as said before, and electrolytic chlorine was first liquefied on a commercial scale in America in 1909, and in England about 1912. From 1799 until 1888, bleaching powder was, excepting for small quantities of chlorine-containing solutions, such as *Eau de Javelle*, almost entirely used as the substance yielding chlorine for bleaching and other purposes. The English, and later the Germans, built up large export businesses in bleaching powder, and consumed great quantities in their home markets, especially in England where the bleaching of cotton textiles had been well established long before the advent of chemical bleaches. America, from about 1870 to 1893, was a very large consumer of English bleach. When the American plants got under way, the imports declined rapidly and have

since all but disappeared. Small shipments of liquid chlorine were exported from Germany to the United States of America from 1888 onward, but the business did not grow because shipments were restricted to cargo boats and were carried as deck loads and were subject to instant jettison in the event of cylinder leaks. Furthermore, there was a heavy American duty on the steel cylinders, and endless customs red tape in securing ear marking or drawback of duty. Industries requiring chlorine were using bleaching powder, and loath to try a new substance which might not always arrive in time for their needs. In Germany the dye and related synthetic organic chemical manufactures stimulated the use of liquid chlorine, thus replacing bleaching powder. As the English and Americans had no synthetic organic chemical industries of importance until after the



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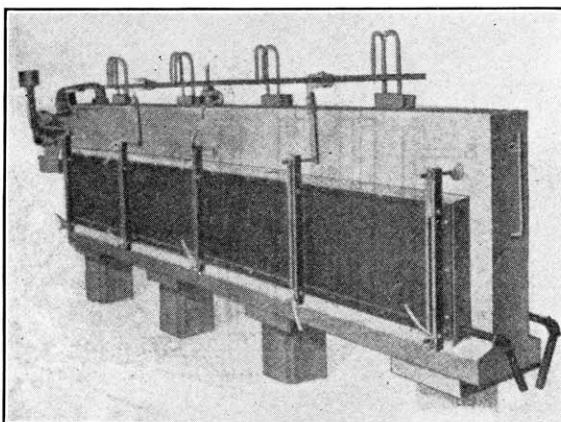
Shipping Liquid Chlorine in Large Quantities. Multiple-Unit Tank Car.

war started in 1914, liquid chlorine came but slowly into commercial importance in America and England. The first commercial American liquid chlorine manufactured was in 1909 and the chlorine was furnished in steel cylinders, of German manufacture, containing one hundred pounds. In this same year was started anew the work of interesting the users of bleaching powder in liquid chlorine. This business grew slowly but steadily, largely through the pioneer efforts of E. D. Kingsley who spared no effort to interest, first, the bleachers of cotton textiles and, a little later, municipal water works which had already, in a few cases, begun to treat potable water supplies with bleaching powder as a sterilizing agent.

In 1909 the first American fifteen-ton tank car for railroad transportation of liquid chlorine was put into service, the chlorine being used in the detinning of scrap tin. Cylinders containing one hundred and fifty

pounds came into use, and, in 1917, the United States Army Chemical Warfare Service used a one-ton container. Still later, a car holding fifteen of the one-ton tanks was put into service. In the American industry at this time over three hundred tank cars of both types and eighty thousand cylinders are in use. The transportation of liquid chlorine is regulated by law in Europe, England, Canada, and the United States of America. The regulations are elaborate, and are rigorously enforced, and great quantities of liquid chlorine are transported and handled yearly with almost complete absence of accident.

The use of bleaching powder has declined rapidly of late years in Germany, Canada, and the United States of America, and to a lesser extent in England. Liquid chlorine, properly packaged and stored in a cool spot, will keep indefinitely. The pressure on the cylinder walls is well within



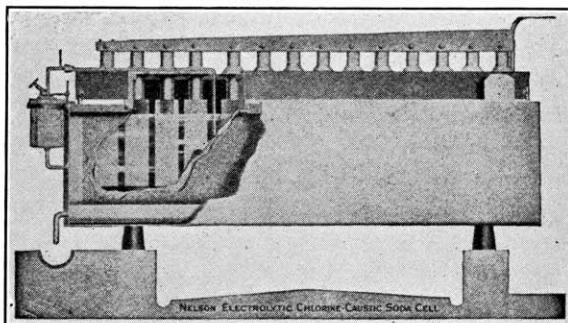
*Reproduced from Chemistry and Industry*

Allen-Moore Cell.

the safety limits at all ordinary temperatures, and liquid chlorine has no appreciable action on the steel of the container. On the other hand, bleaching powder and its packages, either wood or sheet iron, deteriorate quite rapidly. A remarkable technic in the application of gaseous or liquid chlorine, on release from the containers, has been built up by degrees. This gradual shift from bleaching powder, containing when fresh about thirty-five per cent available chlorine, to liquid chlorine, practically one hundred per cent chlorine, illustrates well the modern tendency in chemical industries to use elemental or simple substances in concentrated form.

In the rise of the practical electrolytic cell for chlorine from 1890 onward there have been many developments and great expenditures of time and money. The cell is still a far from perfect thing and requires skilled

attention. Three substances, chlorine, a noxious gas, hydrogen, a flammable gas, and caustic soda, a powerful alkali, are produced simultaneously. For economic reasons a chlorine plant is operated seven days weekly with three eight-hour shifts. In the earlier days of the industry abroad, it was thought that the electrolytic chlorine process would supplant the Solvay soda process, just as the latter had supplanted the LeBlanc soda process. That is to say, it was felt that caustic soda was now to be made in a comparatively simple operation as compared with the older processes, and that caustic soda could somewhat replace soda ash and that the introduction of carbon dioxide at the cathode cell compartment would produce cheap soda ash. These ideas, workable as they are, presupposed sufficient uses to balance the chlorine production. These chlorine uses did not exist then and do not exist now. Approximately, the commercial manufacture of one ton of electrolytic chlorine entails the manufacture of a little more



*Reproduced from an advertisement by H. R. Nelson in  
Chemical and Metallurgical Engineering*

Nelson Cell.

than a ton of caustic soda and about nine thousand cubic feet of hydrogen. The economic existence of the chlorine cell depends on the profitable utilization of this chlorine, with the caustic soda and the hydrogen as by-products. Chlorine in quantity cannot be passed into the air or the sewer with impurity. The caustic soda liquors, as they come from the cell, average from eight to twenty-five per cent of caustic soda depending on the type of cell. These liquors are concentrated in evaporators and pans to fused caustic soda, or with some evaporation to fairly strong solutions. These solutions are shipped in tank cars, but are obviously restricted to short hauls because of heavy freights on a low caustic soda content. In either case this caustic soda must compete with that made by causticizing ammonia soda process soda ash with lime. The hydrogen is very pure, and in the United States of America is now largely coupled with nitrogen in the synthesis of ammonia. It is also employed in the hydrogenation of oils, and in the synthesis of hydrochloric acid.

The productive capacity of the chlorine industry both in the United States of America and elsewhere had overtaken the demand before the World War. The war needs added to the capacity and since 1918 in England, France, Germany, Italy, and the United States of America the available capacity has far outstripped consumption. This has led to renewed searches for more uses. The noxious character of chlorine gas, its corrosive action in the presence of moisture, its readiness to attack nearly all known substances, and to unite with nearly all gases but the rarer ones, render its manufacture, handling, and use a very technical matter. Nevertheless, its manufacture, handling, and use in the industrial arts have been remarkably free from serious accidents.

Chlorine is indispensable today, and the measure of its use is an index of the comparative civilization of a country.

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