The History of Saltpeter Production with a Bit of Pyrotechnics and Lavoisier

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Abstract: The early development of saltpeter (potassium nitrate) production is intimately related to the invention of pyrotechnics and gunpowder. The evolution of the industry in France was closely tied to the political events that took place during the period before and after the French Revolution. Lavoisier transformed it from a losing operation to a successful enterprise and in so doing set the beginning of industrial chemistry as we know it today. The DuPont Company was founded as a result of these activities.

The history surrounding the development of the large-scale production of saltpeter, the main ingredient in gunpowder, is important because it is at the root of the development of industrial chemistry as we know it today. Many critical events, taking place in different periods of history and in different countries, converged in the hands of Lavoisier, the father of modern chemistry. This convergence lead to the development of saltpeter production as a successful technological enterprise, which played a crucial role in the shaping of European history. We will trace the development of this enterprise by analyzing the different events that contributed to its establishment.

Gunpowder

Gunpowder is thought to have been invented by Chinese alchemists of the 9th century during their preparation of mixtures of sulfur, charcoal, and saltpeter for use as an elixir for immortality. A Taoist book warned that mixing three specific elixir ingredients was too dangerous for experiment: "some have heated together the saltpeter, sulfur, and carbon of charcoal with honey; smoke and flames result, so that their hands and faces have been burnt, and even the whole house burnt down."

The use of gunpowder for military purposes was first recorded in 919, and the first detailed description of using a "firing cannon" in warfare was in connection with a battle fought in 1126 when the Song army used it against the invading Nuchens. The Chinese invention of gunpowder never went much beyond its crudest form, and it was abandoned as a military weapon shortly afterwards. It reached Japan, Islam, and then Europe in the 13th century, and the Arabs improved gunpowder for military use. Rockets appear in Arab literature in 1258 as a description of their use by Mongol invaders' on February 15 to capture the city of Baghdad. The Arabs adopted the rocket during the seventh Crusade and used it against the French army of King Louis IX in 1268. By the year 1300, rockets had found their way into European arsenals, reaching Italy by the year 1500, Germany shortly afterwards, and later, England. French records from 1429 show rockets being used at the siege of Orléans during the Hundred Years War against the English. The English philosopher Roger Bacon (1246–1294) in his book "De Secretis Operibus Artis et Naturæ" recorded the early account of gunpowder in Europe. By the year 1350, gunpowder had become an effective weapon on the battlefield; its use revolutionized warfare and ultimately played a large part in changing European patterns of living up until modern times. Gunpowder was the only explosive in wide use until the mid-19th century, when it was superseded by nitroglycerin-based explosives.

Gunpowder Developments

Gunpowder (black powder) is a mixture of true saltpeter or niter (potassium nitrate), charcoal, and sulfur in approximate proportions of 75% saltpeter, 12.5% charcoal, and 12.5% sulfur by weight. The mixture explodes on ignition because charcoal and sulfur are completely combustible and potassium nitrate is an active oxidizing agent. Historically, the relative amounts of the components have varied as knowledge and technology have advanced and particularly after it was found that an increase in the percentage of saltpeter (potassium nitrate) increased the speed of combustion. Originally, the components were just blended, and the mixture was used as such until the 15th century when it was found that addition of a small amount of water to the mixture induced caking and that grinding of the caked product resulted in a powder superior to blended gunpowder. Water caused the basic ingredients to cling together, thereby insuring a proper combination of ingredients, which would burn thoroughly. Moreover, it was found that the powder could be stored for long periods without fear that the ingredients would settle out. Because, in its new shape, gunpowder took on the consistency of grain, it was called "corned" powder, and in this form it eventually became the standard. The new formula and the new production technique were more expensive than the old and more dangerous, because milling the cake into powder could generate sufficient heat to set off the powder. Still, the new powder was so superior to the old that it was worth the extra expense and risk.

Explosives and Explosions

When people talk about explosives, they are usually referring to highly exothermic combustion reactions that produce a large amount of gas in a short time. In a chemical explosion there are extremely rapid temperature and pressure

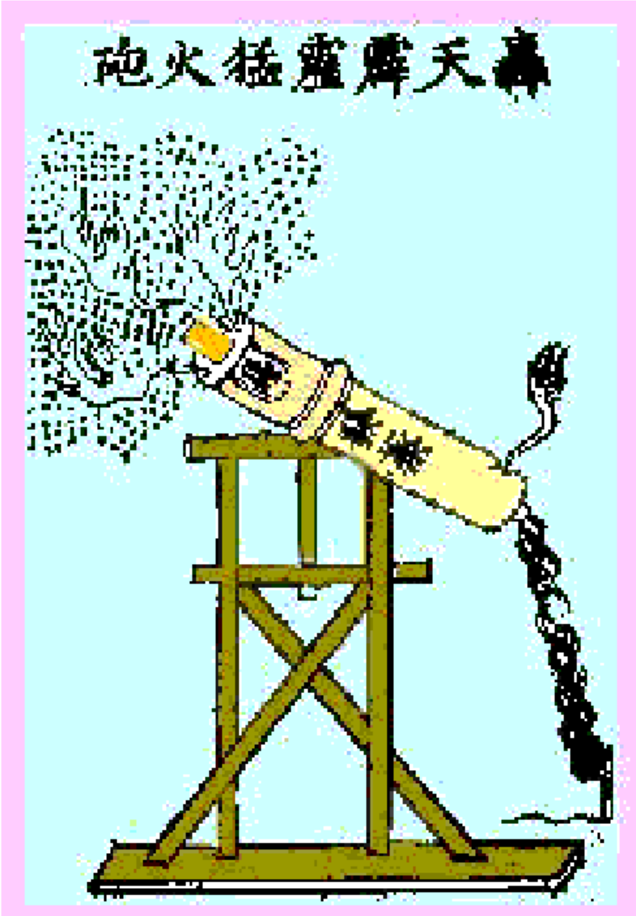

Figure 1. Chinese gun (Needham, J. *Science and Civilization in China*, vol 5, part 7, Cambridge University Press, 1986, reprinted by permission).

rises as some or all of the reactants are oxidized. The explosion comes from rapid overpressurization at the expanding shock-wave front. If the initial pressure is sufficiently high, the shock wave will travel at, but will not exceed, the speed of sound. This is the strict definition of an explosion. If the shock wave travels at a slower speed, the event is a deflagration.

In the explosion of a solid, because of mass-transfer limitations, usually only the oxygen present in the original mixture is involved in the reaction. In this case there may be a large number of partial oxidation stoichiometries possible. Consider, for example, the burning of charcoal and sulfur in air, according to the following reactions

$$C(s) + O_2(g) \rightarrow CO_2(g) \qquad (1)$$

(2)

These reactions release about 400 and 300 kJ mol^{-1} of energy, respectively, but they are not explosive because only the surface of the charcoal and sulfur burn, and fresh air must be blown in before the next layer of solid can burn. This problem can be solved by either grinding the solids into a fine powder so that as much surface area as possible is exposed or by mixing it with a solid oxidizing agent so that the burning charcoal and sulfur are provided in situ with the required oxygen. Many oxidizing agents could be used, but one of the best is a compound we will describe below: saltpeter or potassium nitrate. The train of chemical reactions occurring during the combustion of blackpowder is complex and still not fully understood. The oxidation processes primarily responsible for the explosion of ignited blackpowder, which occurs when potassium nitrate reacts with charcoal and sulfur, may be represented by the following two possible stoichiometries:

$$\begin{aligned} 20KNO_3(s)+32C(s)+5S(s) &\rightarrow 10N_2(g)+11CO_2(g)+16CO(g) \\ &+3K_2S(s)+5K_2CO_3(s)+K_2SO_4(s)+K_2SO_3(s) \end{aligned} \qquad (3)$$

$$\begin{aligned} 10KNO_3(s)+8C(s)+3S(s) &\rightarrow 2K_2CO_3(s)+3K_2SO_4(s) \\ &+6CO_2(g)+5N_2(g) \end{aligned} \qquad (4)$$

This shows that a large amount of gas may be produced. In practice, the rate of the reaction is more important than the stoichiometry.

Saltpeter

Potassium nitrate occurs naturally as crusts on the surface of the Earth, on walls and rocks, and in caves, and it forms in certain soils in Spain, Italy, Egypt, Iran, and India. The deposits in the great limestone caves of Kentucky, Virginia, and Indiana have probably been derived from the overlying soil and accumulated by percolating water. On the surface of such soil and in certain caves a white crust forms on the surface. Saltpeter (also spelled saltpetre) or niter (also spelled nitre) is the common name for potassium nitrate, and it has been the main ingredient of gunpowder since the time it was invented by the Chinese. In former times, the demand for saltpeter as an ingredient of gunpowder led to the formation of saltpeter plantations or nitriaries, which were common in France, Germany, and other countries; the natural conditions were simulated by exposing heaps of decaying organic matter mixed with alkalis (lime, etc.) to atmospheric action.

Vannoccio Biringuccio (1480–1539?), a famous Italian metallurgist and armament maker, describes in Book X of his masterwork, De la Pirotechnia [1], the composition of saltpeter and how to extract it. According to Biringuccio, saltpeter is “a mixture composed of many substances extracted with fire and water from arid and manurial soils, from that growth which exudes from new walls or from that loosened soil that is found in tombs or uninhabited caves where the rain cannot enter. It is my belief that it is engendered in these soils from an airy moisture that is drunk in and absorbed by the earthy dryness.…” Biringuccio goes on to describe a process for extracting saltpeter from this “manurial soil,” that is, soil that has formed from human or animal manure. A tub is filled with a mixture of saltpeter, quicklime, and oak ashes, and then water is run through the mixture. The water will carry with it the “substance and virtue of the saltpeter that was in the earth.” The solution should be recycled as many times as necessary until it tastes very salty. The resultant liquor is partly evaporated on a copper kettle, then left to cool and crystallize; subsequently, the crystals are separated and left to dry. The mother liquor is recycled to dissolve more saltpeter. According to Biringuccio, the amount of crystals obtained will depend on “the virtue present in the water or in the earth.” Furthermore, he recommends that the salt be recrystallized if it is needed in a purer state [1].

As we understand the process today, it is important that the soil carry organic material that contains nitrogen, chiefly proteins and their decomposition product, urea. Bacteria in the soil oxidize these nitrogen compounds to a family of nitrate salts: sodium nitrate, potassium nitrate, and calcium nitrate, depending on the other minerals present in the soil. These nitrate compounds are among the most soluble of all compounds. The solubilities of sodium, calcium, and potassium nitrate in boiling water are 952, 376, and 247 g/100 mL, respectively. Boiling water will dissolve more than nine times its own weight of sodium nitrate. The soluble part of wood ash is mostly potassium carbonate and potassium hydroxide, and the soluble part of the manurial soils is mostly mixed nitrates. Thus, the beginning of primitive saltpeter production is to collect this white crust while leaving behind as much as possible of the underlying soil. Of the three nitrates present, potassium nitrate is the one needed for gunpowder. To extract it, the metathesis reaction is used:

$$Ca(NO_3)_2(aq) + K_2CO_3(aq) \rightarrow CaCO_3(s) + 2KNO_3(aq) \quad (5)$$

This reaction removes all the calcium as insoluble calcium carbonate, leaving mostly potassium nitrate and a little sodium and potassium carbonate, which can be further separated by repeated recrystallization.

Eventually, it was found that potassium nitrate crystals were far superior to calcium or sodium nitrate crystals because they are nondeliquescent (do not take up moisture from the air) and, hence, do not make the gunpowder wet and unusable. The nitrate crystals thus obtained had to be further refined and purified. This purification procedure was mostly done at the refinery where the final gunpowder was made.

Development of the Saltpeter Industry in France

In eighteenth-century France, domestic provision of saltpeter was the monopoly of a guild, the Salpêtries du Roi, to whom the crown had granted exploitation rights when weapons based on gunpowder began to be employed in the fifteenth century. In France from the XIVth century onwards, the manufacture and sale of gunpowder came under state monopoly and was administered by the gunpowder and saltpeter authority. In 1664, because of the poor performance of this institution, King Louis XIV and Jean-Baptiste Colbert, his comptroller general, decided to delegate the royal monopoly to a gunpowder “farm.” These were private entrepreneurs, who operated the arsenals for their own profit in return for providing the state with agreed amounts of gunpowder and controlling the supply of saltpeter. The monopoly bought its raw material from saltpetermen. The saltpetermen constituted another closed-knit guild, whose members would ramble through the city and villages armed with their right to enter any place where they thought they could find the raw material.

The word itself, sal-petrae, was of genetic rather than chemical significance, and the method of harvesting the salt differed in Paris and the provinces according to the mode of its occurrence. The most accessible saltpeter formed on limestone in the course of the nitrogen cycle, an efflorescence mainly of calcium nitrate. The scale penetrated into the porous walls of cellars and the lower masonry of buildings where surfaces were exposed to a damp circulation laden with exhalations of animals, men, and organic refuse [2].

In 1785, a stamping mill had been devised and laborers would shovel the gritty materials brought in daily into water barrels for leaching out the salt. Potash (potassium carbonate) was added to the barrels, sometimes in the form of wooden ashes, to convert the raw material to true saltpeter. The mixture was put in large copper kettles to cook out the main impurities, among them common salt. As the concentration increased, a dose of Flanders paste (alumina) was added to clarify the product. On additional evaporation, the brew precipitated muddy, yellow crystals of crude saltpeter (first cut).

The saltpetermen were allowed to process the raw material only up to the first-cut stage, lest they be in a position to sell it privately. According to their privilege, they were obliged to deliver a certain annual amount of the crude saltpeter to the Arsenal of Paris or to other royal magazines. There, it was refined by means of two further crystallizations, after which came out a solution, white as flour, to be dried into loaves and shipped to powder mills for corning, together with sulfur and charcoal, into gunpowder. The saltpetermen were paid a fixed price for their crude product, regardless of its quality. There were no reliable means for estimating the percentage of saltpeter in the yellow lumps, although different subjective tests were used for this purpose. The economic impact of this trivial fact would eventually lead to the technical developments permitting the extraction of saltpeter by all civic hands in the year II of the Republic [2, 3].

At the end of the 18th century, the gunpowder-farmer system began to create social problems, because the people were becoming increasingly intolerant at having their premises and living quarters searched by saltpeter manufacturers, and they preferred to avoid this by paying a secret tax [2]. In addition, production was insufficient to satisfy the national demand, and the remainder had to be imported from the Indies. The powder farmers of the reign of Louis XV took no interest in technology. They preferred to contract out to local entrepreneurs the fabrication of much of the powder that they were required to supply, and they allowed the powder magazines and refineries to fall into neglect. They were under no obligation to furnish more than the powder stipulated in their contract. If war came, the crown might find additional supplies wherever it could. One of the explanations given by the French military to justify its defeat in the Seven Year war was the dependence on saltpeter from overseas. The maritime powers drew their saltpeter from India and the land powers from national manufacture. In Sweden and Prussia the state had commissioned construction of nitrification plants that composted wastes to the order of the armed forces [2].

In 1774, Anne-Robert-Jacques Turgot (1727–1781), comptroller general of finance under Louis XVI (1754–1793), the last king of France, instituted a crash program to develop the saltpeter industry and engaged the help of the Académie des Sciences to achieve its objectives. He revoked the contracts of the powder farmers and replaced them by a new administration, “Régie Royale des Poudres et Saltpêtres” (Royal Gunpowder and Saltpeter Company). The regulations stated that the régisseurs would be bondsmen who furnished the capital and were paid royalties upon production. The mandate of the Régis was triple: (a) profit made from exploitation of saltpeter and fabrication of gunpowder belonged to the crown; (b) production was to be increased to make France self-sufficient in munitions of war; and (c) property owners would no longer be harassed by the right to search of the saltpeter corps.

Four régisseurs were appointed to manage the operation: Le Faucheux and Barbault de Glatigny, who were experienced in industry, and Clouet and Lavoisier, who were experienced chemists. Concurrently, in 1778, Turgot charged the Académie des Sciences to institute a saltpeter prize for the best essay on the most advantageous method of making saltpeter that could substitute for the one obtained by the traditional method. Sixty-six papers were presented to compete for the prize, and of these only forty-one were considered worth considering. Although the prize was awarded to the proposal of the Touvenal brothers, none of the proposals contributed much to the solution of the saltpeter problem [4]. The Académie was also ordered to draw up a detailed work program that included a literature survey on what was known about the formation of saltpeter and the experimental routines to follow in order to test the different ideas. At the same time, the Régie was given three years to turn the project into reality. Eventually, the project would fail, not because of chemistry, but because of incentives. The risks were too large for a single entrepreneur, the scale too large for the crown [2].

The leading part in reforming the munitions industry was played by Lavoisier. He made the munitions industry his main occupation and proceeded to revamp it by installing new administrative, technological, and research policies that would eventually turn it into a financial success. He constructed new factories, mills, refineries, and warehouses; reinforced the methods for checking the quality of production; and organized courses in physics, chemistry, and mathematics for the personnel. He also looked for the possibility of enlarging the production of saltpeter by building artificial nitrate works (nitrières). In addition, he published a manual giving potential investors very detailed instructions on how to look for soils containing saltpeter and how to extract, refine, evaporate, and crystallize the product. The incentives proved to be of no avail, and in the long run the only nitrate factories created were those belonging to the Gunpowder Administration.

In 1775, at the beginning of the crash program, the gunpowder farmers were producing about 800 tons per year; whereas, 1600 tons were needed. In England, saltpeter production was no problem because virtually all the required supply was imported from India. Prussia produced 75 tons per year and Sweden between 90 and 300 tons. The measures taken by Lavoisier brought about a dramatic increase in gunpowder production. Production of saltpeter rose from 800 tons per year in 1775 to 1,000 tons per year in 1777 and 1750 tons in 1787. Simultaneously, the stocks of gunpowder rose to 2500 tons, enough to provide for two or three campaigns. Thanks to all the improvements achieved by Lavoisier, French gunpowder became the best in Europe. The tables were now reversed, and part of the production was exported to Holland and Spain as well as to America for use by the revolutionaries. In thirteen and a half years the Régie was a resounding financial success. It had paid the sums owned to the original powder farms under their contract, and on the eve of the revolution it had restored the French munitions industry, producing large profits and savings [2, 5].

During this period, Lavoisier continued with his theoretical work, which he published. He helped to improve the basic knowledge of the chemistry of saltpeter and gunpowder and brought a better understanding of the chemical and physicochemical phenomena governing the manufacture of saltpeter and the way gunpowder works. Several practical applications resulted from this, including a new procedure for refining unrefined saltpeter, both faster and cheaper, and the development of a new, safer type of gunpowder magazine. The research program that accompanied the enterprise encouraged the development of allied trades. For example, it was found that potash was superior to wood ashes for converting the earthy nitrates into crude saltpeter. The supply of potash depended on that of alkali. To liberate the former for munitions created incentives to develop an artificial procedure for the manufacture of soda. The Leblanc process, which became one of the foundations of the heavy chemical industry in the nineteenth century, developed out of that effort during the revolution. The profession of industrial chemistry may itself be traced in large part to the staff and suppliers of the Régie des Poudres [2].

In 1785, Claude-Louis Berthollet (1748–1822) proposed that saltpeter be replaced by superoxygenated potassium muriate (potassium chlorate). Berthollet had already become famous in 1785 when he discovered the bleaching properties of chlorine. While exploring the chemistry of chlorine, he also discovered potassium chlorate, a violently unstable material in the presence of reducing materials, particularly carbon and sulfur. This property made Berthollet think that it might perhaps replace saltpeter to fabricate a more powerful gunpowder. The idea was proposed to the Régie, who prepared an experimental and developmental program to test the idea. The first experimental run resulted in a fatal accident at the gunpowder factory at Essone. The wet mixture of the new composition had different rheological characteristics than standard gunpowder and the efforts of the workers to mix it properly caused it to explode. Two people were killed as a result of the explosion. By a twist of destiny, one of Lavoisier's young assistants, Eleuthère-Irénée Du Pont, was absent that day, and this probably saved his life. Eventually, after Lavoisier was sent to the guillotine, Irénée and his father Pierre would transport the gunpowder production technology developed by Lavoisier to America. There they bought land on the banks of the Brandywine River near Wilmington, Delaware and began making gunpowder for the military and for hunters. Pierre-Samuel Du Pont, a very close friend of Lavoisier, wanted to call the installation "Lavoisier Mills" and requested permission from the widow. Old financial disputes between Madame Lavoisier and Pierre-Samuel made agreement impossible, and the company would eventually be called DuPont de Nemours and Company. Notwithstanding, the DuPont Company awards the Lavoisier medal each year for technical achievement. This honors the fact that Lavoisier served as teacher and mentor to the company's founder [6]. The medal is presented to select individuals who have been instrumental in building DuPont into a world leader in technology. According to the rules of the prize, the purpose of the Lavoisier Medal is not only to highlight the great technical accomplishments of these individuals but also to present role models for current employees.

Epilogue

In 1791, the Gunpowder Company was brought under state control, and Lavoisier, now viewed as suspicious by the new political leadership, was separated from the Régis. When the Reign of Terror erupted in France, Lavoisier was sent to the guillotine (May 8, 1794), falling victim to its tyranny, France lost one of her greatest scientists.

Conclusions

The early development of saltpeter (potassium nitrate) production is intimately related to the invention of pyrotechnics and gunpowder. The evolution of the industry in France was closely tied to the political events that took place during the period before and after the French Revolution. Lavoisier transformed it from a losing operation to a successful enterprise, and, in doing so, not only set the beginning of industrial chemistry as we know it to day but also influenced the course of European history. The DuPont Company was founded as an offshoot of these activities.

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