Two Hundred Years Electric Current. The Impact on Metallurgy

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Introduction

In the year 2000 the world will be celebrating the 200th anniversary of the discovery of electric current. It can be fairly said that the electron is the basis of our modern civilization. This small particle that travels at the speed of light is used to turn huge machines, transmit messages thousands of kilometres away in a fraction of a second, to control almost every aspect of our lives, from the grocery store to a metallurgical plant. The electron itself was discovered a hundred years ago, but the origins of this discovery is much older. It was Alessandro Volta who, in 1800, constructed the first “pile” of metals from which he was able to generate an electric current.

The electric current from the pile was immediately used to liberate sodium and potassium from their salts, and these metals, in turn, were used to liberate aluminium from its compounds. Once aluminium was available it was used to liberate other metals that were not possible to obtain by the known methods, from their oxides.

Early Observations

The ancient Greek philosophers noted that amber, when rubbed with a woolen material, would attract bits of straw, feathers, and other light objects. Later, the same phenomenon was observed with many other objects like rubber, glass, and sulphur. They also noted that a certain kind of a naturally occurring rock near the village Magnesia in Asia Minor (near Izmir) had the power of attracting iron dust and small fragments of the same rock; it was called “magnetite.” These two phenomena were thought to be the same until in the sixteenth century when they were made distinct by William Gilbert (Fig. 1), Queen Elizabeth I’s physician who published the first scientific treatise on electricity. The first phenomenon was called electric after elektron, the Greek word for amber, while the second was called magnetic after “magnetite.” He also considered gravity to be of the same nature as magnetic forces.

Static Electricity

In the middle of the seventeenth century, scientists throughout Europe were beginning to perform electrical experiments. Rubbing two objects together was a slow way of making electricity. Otto von Guericke (Fig. 2) created a device that not only made electricity much more conveniently, but in appreciable quantities as well. In 1663, he made an electrical-friction machine. He made a sphere of sulphur about 10 cm in diameter, inserted an iron axle through the midpoint, and attached a wooden crank. By rubbing the sulphur with his hand as he cranked, von...
Guericke showed that the sphere became electrified, that he could transfer the charge to other balls of sulphur, and for the first time repulsion of two charged spheres was observed. Many other "friction machines" followed, including one built by Isaac Newton (1642-1727) in 1706, that used a rotating glass globe with a rubbing chain to collect the charge.

In 1745, a device called the Leyden jar was made that could store considerable charges for long periods of time. It could be "filled with electricity," carried around and discharged at will. It became a valuable experimental tool. Credited with this invention is the Dutch physicist Pieter van Musschenbroek (1692-1761), who had experimented with wrapping metal foil around a glass bottle at the University of Leyden. After he charged his creation with electricity from a friction machine, van Musschenbroek found that the jar could store electricity when he touched the top of the jar and received a severe shock. The Wimshurst machine, still used in schools for static electricity demonstrations, was invented by the British engineer James Wimshurst (1832-1903), in 1878.

The Nature of Lightning

Benjamin Franklin (Fig. 3), in the United States, attempted to find an explanation for the Leyden jar. He believed that electricity was an element common to all bodies, and rubbing merely transferred electricity from the rod to the cloth or vice versa, i.e., if a body had more electricity than another, it had a surplus of charge. He called this type of charge plus or positive. If one body had less charge than another, it had a deficiency of electricity and was a minus or negative. Therefore, electricity would flow from plus (a surplus) to minus (a deficiency), like water flowing from a higher to a lower level. His kite experiment, of 1752, showed that the electricity from lightning is the same kind of electricity as that from friction machines.

Franklin mounted a small metal rod atop a kite. To the kite string he attached a door key. Between the key and his hand was a piece of silk ribbon to protect himself from the charge because he knew that silk is a poor conductor of electricity. On a stormy day he flew his kite near a thundercloud then noticed that a spark jumped between the key and his hand. He collected some of the electricity from the string in a Leyden jar and later showed that it behaved in the same way as other electricity. Thus, the great friction in the clouds builds up electric charges that produce lightning. In Franklin's time, three sources of electricity were known: frictional as in the Leyden jar; atmospheric as in lightning; and animal as in certain types of fish.

Animal Electricity and the Electric Pile

In 1790, Luigi Galvani (Fig. 4), a professor of anatomy at the University of Bologna in Italy, had for some time studied the effect of electric discharges from electric machines on frogs. On one occasion while dissecting a frog, he noticed that the legs of the frog attached to a copper hook moved suddenly as if alive when he touched them with an iron object. He attributed this to "animal electricity," similar to the electricity in torpedo fish studied by John Hunter (1728-1793) in England in 1773. In 1794, Alessandro Volta (Fig. 5), also in Italy, rejected Galvani's claim and asserted that the frog legs twitched because two different metals were brought into contact via a liquid producing electricity, and that the frogs were not essential. In 1800, he constructed the first "pile" in which discs of different metals were separated from one another by a moistened paper. He was able to generate electricity from this pile without frogs. He also showed that metals could be arranged in an "electromotive series" so that each became positive when placed in contact with the one below it in the series.

Although Galvani's interpretation of his observation about animal electricity was wrong, his name is preserved in a number of expressions. For example: galvanic electricity (the flow of electricity); galvanic cell — an electrochemical cell; galvanized iron — iron with a thin layer of zinc to protect it against corrosion; and galvanometer — an instrument used for detecting and measuring current.

Shortly after the discovery of the voltaic pile, William Nicholson (1753-1815), in England, demonstrated the chemical effects of the pile. He found that hydrogen and oxygen were evolved at the surface of gold and platinum wires if they were connected with the terminals of a pile and dipped in water.

Electrochemistry and the Electron

From this time on, the nature of electricity simultaneously became an intensive topic of study by physicists and chemists alike, the physicists examining the passage of electricity in gases and the chemists its passage in solutions. This eventually led to the development of physical chemistry — a new discipline in science that makes quantitative measurements of physical parameters for chemical substances. When electric current was introduced in the studies, electrochemistry emerged as a specialized branch of physical chemistry.

Electrolytic Conductance

It was soon observed that during what we now term 'electrolysis' there are chemical reactions at the two electrodes, whereas the liquid between the electrodes remains unaltered. An explanation which satisfied the scientific world for many decades was advanced by Theodor Grothuss (1785-1822) in 1805. He believed that chains of
Fig. 5. Alessandro Volta (1745-1827) with his pile (top), most distinguished Italian physicist shown on current Italian paper money. gave a description of the new electrical machines in two treatises published in 1769 and 1771. In 1774 he became rector of the gymnasium in his home town Como and professor of physics. In 1779 he was transferred to Pavia to fill the chair of natural philosophy in the university. Bottom: His museum in Como.

Fig. 6. Michael Faraday (1791-1867), British scientist at the Royal Institution, the first to formulate the laws of electrochemistry, discovered electromagnetic induction, laid the foundation of the electrical generator. Author of Experimental Researches in Electricity.

Svante Arrhenius (1859-1927) postulated, in 1887, that salts in aqueous solutions are largely dissociated into free ions. The theory was based on the fact that solutions that showed abnormally high osmotic pressures were conductors of electricity. At first, the theory of electrolytic dissociation was not enthusiastically received by the majority of chemists, who could not understand, for example, how sodium and chloride could be contained in a solution of common salt. Arrhenius was able to show that the degree of ionization calculated from the electrical conductivity, the equivalent conductivity at infinite dilution (when there is complete ionization), was approximately the same as that calculated from the deviations from Raoult's law in the case of freezing point measurements. These are two independent methods and the substantial correctness of the theory was thus established.

Electric Current

The magnetic effects of the electric current were discovered, in 1819, by Danish physicist Hans Christian Oersted (Fig. 7), thus again relating the two phenomena that became the basis of our modern civilization — electricity and magnetism. This was followed by the interpretation of the electromagnetic nature of light by the Scottish physicist James Clerk Maxwell (1831-1879). A few years later important observations were made:

- In 1875, Sir William Crookes (1832-1919), while studying the conduction of electricity through vacuum tubes, was able to deflect the cathode corpuscles with a magnet, thus confirming
the magnetic nature of the negatively charged particles.

- J.J. Thomson (1822-1892) pursued the work of Crookes and confirmed that those corpuscles emitted at the cathode are electrons whose mass was 1/1840 that of a hydrogen atom.
- Robert A. Millikan (1868-1953) determined the charge of the electron.

The electron is one of the fundamental particles of which all matter is composed. In modern terms, a direct current of electricity passing along a copper wire is a flow of electrons along the wire. In a metal or a similar conductor of electricity, there are electrons that have considerable freedom of motion, and that move along between the atoms of the metal when an electric potential difference is applied. Magnetism, on the other hand, is due to the orbital motion and axial spin of electrons in an atom. In most atoms these nearly cancel each other, except in iron, nickel, and cobalt. In these elements, the number and the position of the d electrons in the atoms, within certain crystalline structures, produce external magnetic effects.

Modern investigation has modified Arrhenius’ theory in some respects, because strong acids, bases, and salts are now supposed to be almost completely ionized in dilute solutions. The deviations from the results for complete ionization is ascribed to interaction between the ions of opposite charge, which causes a reduction in the mobilities of the ions as shown by Peter Debye and Erich Hückel in 1923. Early and important workers in the ionic theory were Jacobus Henricus van’t Hoff (1852-1911) who laid the foundation for the thermodynamic theory of solutions, and Wilhelm Ostwald (1853-1932) who was an influential investigator, writer, and editor.

In 1889, Walther Nernst (1864-1941), former assistant to Ostwald and then professor in Berlin, showed that the production of electromotive force in galvanic cells could be explained in terms of a “solution pressure” of the metal electrodes, tending to throw off charged ions into the solution, a tendency that is balanced by the osmotic pressure of the dissolved ions. In some metals, electrons are given up more easily than in other metals. Zinc, for example, gives up its electrons freely, while copper retains its electrons more firmly. When copper and zinc are placed in contact, electrons pass from zinc to copper. Copper builds up a negative charge; it has an excess of electrons. Zinc acquires a positive charge; it has a shortage of electrons. The activity is very small in dry metals, but if a strip of zinc and a strip of copper were dipped into a container filled with a salt solution (an electrolyte) more electrons would move. Any two dissimilar metals will produce a similar effect.

Direct Versus Alternating Current

For a long time, alternating current was considered only of academic interest. It was thought that it could not be put to work in the same way as direct current, and that it could not run a DC motor, the only kind known at that time.

Thomas A. Edison (Fig. 8) constructed the first three power stations in 1882, two of which were driven by steam engines and the third by a water turbine. Electricity was furnished to light his recently invented incandescent lamps. It soon became obvious, however, that using 110-volt direct current generators presented a basic problem—two kilometres away from the generating station, the power was too low to light the lamps properly because of the resistance of the transmission lines. To use heavy wires to decrease the resistance or to build many small plants near the consumer would be uneconomical. To increase the voltage at the station to maintain 110 volts at the end of the line would burn the lamps of the customers near the station.

Georges Westinghouse (1846-1914) solved this problem, in 1886, by building the first alternating current transmission and distribution system. The power was transmitted at high voltage and the customers were receiving their electricity at low voltage, regardless of their distance, with the use of transformers. Thus, the controversy between direct and alternating currents was resolved as an indirect result of the application of the electric light. The value of alternating current was enhanced, in 1888, when Nikola Tesla (1856-1943) invented the induction motor (also known as squirrel cage motor) that would operate from alternating current.

Growth of the Industry

The electrical engineering industry consolidated and grew rapidly. The Edison Electric Light Company, organized in 1878, absorbed other companies and became Edison General Electric Company in Schenectady, New York. In 1892, it incorporated Thomson-Houston Company and became General Electric of today.

One of the major changes that the twentieth century has witnessed has been the replacement of the reciprocating steam engine by steam turbine, with electricity becoming abundant. But transmission of
Fig. 9. Humphry Davy (1778-1829), British chemist, studied medicine and pharmacology, the first to be appointed at the Royal Philosophical Institution in London. There, in 1807, he succeeded in isolating the alkali metals electrically and, in the same year, published Some Chemical Agencies of Electricity.

Fig. 10. Robert Bunsen (1811-1899), German professor of chemistry in Heidelberg, discovered spectral analysis with Kirchoff, and the elements cesium and rubidium, inventor of the burner known by his name. The first to prepare metallic magnesium by electrolysis of molten MgCl₂.

Electrometallurgy

The Beginnings

The first application of Volta's pile in metallurgy was in 1807 when Humphry Davy (Fig. 9), in London, built a large battery and was able to decompose caustic potash and caustic soda and identify potassium and sodium as metals for the first time. The next year, this same technique was used to liberate barium, calcium, magnesium, and strontium. Michael Faraday, who was Davy's assistant, continued this research and, in the early 1830s, found the relationships between current used and quantity of metal deposited. He was the first to have clear ideas concerning the quantity and intensity of electricity, i.e., the quantities now measured in terms of amperes and volts. Faraday introduced the terms ion, cation, anion, electrode, electrolyte, etc., in common use today. During the same period, electroluting of silver was commercialized by George Richard Elkington (1801-1865) and Henry Elkington (1810-1852) in Birmingham, England.

Davy's liberation of sodium, potassium, and calcium from their salts had a great impact on metallurgy because sodium was used, in 1841, by Henri Sainte-Claire Deville (1818-1881) in Paris to liberate aluminum from aluminum chloride. Once aluminum became available, it was used to liberate other metals that were difficult to free from their oxides by known methods.

Fused Salts Electrolysis

The first use of electric current to deposit a metal from its fused salt was clearly demonstrated by Robert Bunsen (Fig. 10) in Heidelberg. In 1852, he prepared magnesium from MgCl₂ and, in 1858, lithium from LiCl. The carbon cathode was cut so as to form pockets inside which the metal was deposited. Unless this precaution was taken, the metal, being lighter than the fused chloride, rose to the surface and burned. The fused salt method was later adopted for preparation of other reactive metals such as beryllium, niobium, tantalum, and others.

The Production of Sodium

The production of sodium played an important role in the early aluminum-making process. It was made by electrolysis of molten NaOH in Castner cell, in 1886. The cell, named after its inventor, American chemist Hamilton Young Castner (1859-1899), was composed of a cylindrical nickel anode surrounding the copper cathode concentrically. The process is now obsolete for the following reasons:

- The Castner process yields sodium, hydrogen, and oxygen:
  \[ \text{Na}^+ + e^- \rightarrow \text{Na}_{\text{(cathode)}} \]
  \[ 2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2e^-_{\text{(anode)}} \]
  \[ \text{H}_2\text{O} + \text{Na} \rightarrow \text{NaOH} + \frac{1}{2}\text{H}_2 \]

Overall reaction:

\[ \text{NaOH} \rightarrow \text{Na} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{O}_2 \]

Thus the current efficiency cannot exceed 50% because of the loss of half of the sodium by reaction with water produced as a by-product. In practice, current efficiencies of < 45% were achieved.

- Before sodium can be produced by this method, sodium hydroxide must first be obtained (e.g., by electrolysis of aqueous sodium chloride).

A process was, therefore, sought to produce sodium by direct electrolysis of sodium chloride to by-pass the production of NaOH. This resulted in the invention of Downs cell, in 1924, so named after its American inventor, chemist J.C. Downs, which rapidly displaced the Castner cell.

If NaOH in the Castner cell is replaced by a molten salt containing NaCl, the collection and containment of the chlorine evolved causes problems that are solved only when the positions of the anode and cathode are reversed, as in the Downs cell in which the anode is surrounded concentrically by the cathode. It consists of a lined steel vessel in which the graphite anodes pass through the floor, and the two electrical conductors connected to the cathodes pass through the walls. The anode is surrounded by the cylindrical iron cathode. The diaphragm prevents the sodium droplets formed at the cathodes from reacting with the chlorine bubbles formed at the anodes.

The Downs process used a mixture of 60% CaCl₂ and 40% NaCl at an operating temperature of 560°C to 585°C. This composition represents a compromise between the melting point of the salt mixture and the oxygen content of the sodium. The eutectic mixture, which contains 66.8% CaCl₂ and 33.2% NaCl, melts at about 505°C. Although increasing the CaCl₂ content reduces the melting point of the binary mixture, it also increases the concentration of calcium in the product due to the equilibrium:

\[ 2\text{Na} + \text{CaCl}_2 \leftrightarrow 2\text{NaCl} + \text{Ca} \]

Refining of Metals

The first patents for metal refining were for copper by James B. Elkington in 1865. In 1876, copper was refined electrolytically by the Norddeutsche Affinerie
in Hamburg, in Germany (Fig. 11), and two years later, in 1878, the first gold refinery was introduced by the same company using the Wohllwill process, named after chemist Emil Wohllwill (Fig. 12). The first copper refinery was built in Newark, New Jersey, by the Balbach Smelting and Refining Company, in 1883. Because high purity copper was essential to transmit the current, once refined copper became available, an expansion in the electrical industry took place.

In 1884, Bernhard Moebius (Fig. 13), in the United States, invented a process for silver refining. During the same period, silver was produced with the development of the Balbach-Thum cells. The first Betts refinery for the production of lead was established at Trail, British Columbia in 1902. In 1905, Victor Hybinette (Fig. 14) invented a method of refining which used a divided cell. This development enabled nickel to be refined electrolytically for the first time, and one of the first refineries was set up in Kristiansand, Norway in 1910.

The electrolytic refining of tin using acid electrolyte was developed in the United States at Perth Amboy, New Jersey during World War I. The initial electrolyte was a mixture of fluosilicic acid and sulphuric acid, but was later changed to sulphuric acid and cresyl sulphonic acid. However, production was discontinued in 1923. The electrolytic refining of tin using an alkaline electrolyte was established in England, in 1936, by Capper Pass to treat complex ores and secondary materials. In Germany, tin is refined using an alkaline sodium sulphide electrolyte by Berzelius Metallhütten at Duisburg.

Production of Aluminum

In 1886, Paul Héroult (1863-1914) in France and Charles Hall (1863-1914) in the United States discovered a new process for producing aluminum by electrolysis of fused bath containing Al₂O₃ dissolved in cryolite. The process was adopted on a commercial scale in 1887, and rapidly replaced Sainte-Claire Deville's chemical process by heating metallic sodium with an AlCl₃-NaCl mixture. This coincided with Karl Josef Bayer's (1847-1904) discovery of a process producing pure Al₂O₃ from bauxite. Both processes are used today, and practically unchanged.

Electrowinning

During 1912-1915 two important applications in electrometallurgy took place:
- the large scale copper electrowinning in Chile; and

Fig. 11. The first copper electrolysis tanks in which copper was refined electrolytically in the old works of the Norddeutsche Affinerie in Hamburg, in 1876.

Fig. 12. Emil Wohllwill (1835-1912), German chemist, studied under Bunsen, Wöhler, and Kirchhoff. While at Norddeutsche Affinerie in Hamburg, he developed the gold refining process known by his name.

Fig. 13. Bernhard Moebius (1852-1898), German metallurgist, worked in industry in Germany, Spain, and Mexico before emigrating to the United States. He developed the silver refining process known by his name.

Fig. 14. Victor Hybinette (1867-1937), Norwegian metallurgist, invented the diaphragm cell known by his name, used for electrowinning and electorefining of nickel.
In 1965, the first plant for recovering copper from low-grade ores by solvent extraction-electrowinning went into operation in Arizona, United States. This marked the beginning of a new technology that gradually displaced the cementation of copper by scrap iron.

Anodic Dissolution of Sulphides

In 1957, Louis Renzoni (1915-1994) and his co-workers at INCO developed the electorefining of nickel sulphide anodes and produced elemental sulphur. With engineering developments, the process was adapted at INCO's nickel refinery at Thompson, Manitoba, then used in Russia and Japan.

The Electric Furnace

William Siemens (Fig. 15), in 1878, was the first to employ the electric current to melt metals. At this early date, electric power was limited and expensive, and the development of the electric melting-furnace had to await the expansion of the electrical industry. In 1900, Paul Héroult produced the first successful commercial direct-arc steelmaking. Today, this technology is widely used, not only in steelmaking but also in ferroalloy production, copper smelting, and other applications.

References

