HISTORY OF OZONE SYNTHESIS AND USE FOR WATER TREATMENT

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Summary

Unlike many other technologies, which started to be practiced by mankind much earlier than their regularities were scientifically understood, ozone synthesis and application to water treatment developed consistently on the basis of scientific findings. The way of ozone synthesis and application development passed through the highly desired route: discovery – study of properties – effective synthesis in amounts for full-scale implementation – application. The ozone implementation in water treatment presents a classical example of science meeting the growing requirements of the society based on increasing knowledge. This paper gives a historical sketch of the development of ozone studies in its synthesis and application to water treatment.

1. Ozone Generation

1. 1. 1839-1868

Ozone, first on March 13, 1839, reported to be a distinct chemical compound by Christian Friedrich Schönbein (1799-1868), Professor of Chemistry at the University of

Basel, was introduced to its applications after long years of studies of its properties in Chemistry laboratories. Therefore, the history of ozone synthesis at the laboratory scale machines starts long before the history of its applications. Among the processes excreting ozone at its discovery days, the contact of air with phosphorus and some other methods were not developed into the industrial scale procedures; "odour of electricity" introduced by Martin van Marum (1750-1837), Doctor of Philosophy and Medicine, working with his static electricity machine in Haarlem, Netherlands, remains an attribute of the contemporary ozone synthesis in gaseous discharge and electrolysis techniques.

The very first electric machine used purposely as ozone generator was, most probably, the Grove cell acquired by Schönbein by summer 1838 in Basel, although he reported the characteristic ozone odour produced not only by the electrolysis of water at the clean gold or platinum positive electrode, but also by an arc between electrodes separated by air. The Grove cell invented by about the same time (1839) was an early electric primary cell named after its inventor, British chemist William Robert Grove (1811-1896), and consisted of a zinc anode in dilute sulphuric acid and a platinum cathode in concentrated nitric acid, the two separated by a porous ceramic pot. The Grove cell was the favoured power source of the early American telegraph system in the period 1840 – 1860 and was replaced in use by other sources due to discharged poisonous nitric acid gas and unstable voltage.

The three methods described by Schönbein, arcing air or oxygen, electrolysing aqueous acid solutions, and exposing phosphorus to moist air, were all used by researchers in the early days of ozone studies. The most convenient of these at early days was the phosphorus reaction. Thus, Jean Charles Galissard de Marignac (1817-1894), Professor of Chemistry at the Academy of Geneva, described a simple tubular continuous flow apparatus filled with pieces of white phosphorus in which air was passed through. The resulting gas was washed with water and dried before use. Otto Linné Erdmann (1804-1869), Professor at the University of Leipzig, used the gas resulting from the flask containing water with pieces of white phosphorus directly for discolouration of indigo aqueous solution without washing and drying. Richard Felix Marchand (1813-1850), Professor of Chemistry at the University of Halle obtained ozone from phosphorus in contact with dry oxygen, giving another proof of the allotropic nature of ozone.

Due to the limited capacity of ozone production, the use of phosphorus gradually declined: at best the phosphorus reaction produced ozone concentrations of much less than 1%. The electrochemical method, being intensively studied, appeared to provide much higher concentrations of ozone in oxygen than any other method by using specially designed equipment and carefully controlled conditions, such as low temperatures.

Some doubtful methods for ozone generation attributed to various chemical reactions were described, such as, for example, decomposition of permanganate and dichromate with sulphuric acid. This reaction was found to form a gas able to oxidise iodide to molecular iodine solely due to the presence of chloride impurities. The confirmation of ozone emission by the reaction of barium peroxide with acids was also lacking; the fog containing hydrogen peroxide appeared to be the reason for iodine extraction in starch-

iodide method of analysis: hydrogen peroxide was found to pass through water traps. Formation of ozone in air passing over hot platinum wire was claimed based on odour and starch-iodide tests, but these results were later attributed to nitrogen oxides.

The breakthrough in ozone preparation was achieved by Ernst Werner von Siemens (1816-1892), the founder of Siemens & Halske, predecessor of the famous Siemens AG. Siemens applied the high voltage transformer developed by Heinrich Daniel Rühmkorff (1803-1877), who invented in 1851 the Rühmkorff's induction coil able to produce sparks more than 30 cm in length. This coil was used in the first radio transmitters, X-ray generators and some other electrical and electronic devices. In a paper on electrostatic induction published in 1857 Siemens described a silent discharge apparatus for preparing ozone from air or oxygen. In his later years Siemens considered his discharge configuration for the generation of ozone as one of his most important inventions. It is interesting to note, that he never applied for a patent for this configuration, although he received many patents on other subjects. A few years after Siemens' original publication, Thomas Andrews and P. G. Tait in 1859 proposed in their "Second Note on Ozone" published in Proceedings of the Royal Society of London the name "silent discharge", which still is frequently used together with corona discharge. In such equipment it became routinely possible to achieve ozone concentrations in oxygen on the order of 5%, and commercial equipment for generating ozone utilizing Siemens' discovery eventually became available. By the end of the 19th century, the silent discharge had displaced other procedures in laboratory practices. Siemens and Halske, as well as other companies supplied laboratory and industrial equipment for generating ozone, and the Berthelot tube had become the device of choice in ozone generation instruments. The Ullmann's encyclopaedia issued in 1920 indicates Siemens & Halske ozone generators' design as the predominant on the ozone generation market.

1. 2. 1869-1900

The idea that ozone was formed by combination of an atom of oxygen with a neutral oxygen molecule was first published by C. Than in 1870 in "Journal für Praktische Chemie" and gained wide acceptance even without direct evidence:

$O + O_2 \rightarrow O_3$

1. 2. 1. Electrical Discharge for Ozone Production

By the time under discussion the silent discharge method for preparing ozone became preferable for laboratory and industrial use. A number of papers and patents appeared describing variations in the design and operation of such equipment, summarized later by encyclopaedia and review articles in the end of 19th century.

The quintessence of any ozone generator is the silent discharge tube through which oxygen or air flows with application of high voltage alternating current as a dielectric-barrier discharge (DBD) maintained in a narrow annular gap between two coaxial glass tubes by an alternating electric field of sufficient amplitude. The novel feature of this discharge apparatus was that the electrodes were positioned outside the discharge

chamber and were not in contact with the plasma.

The actual discharge was established in 1880s to be necessary for formation of ozone, not only the applied high potential. Such tubes have been described as "Berthelot tubes" due to, most probably, its detailed description with drawings and instructions for construction and operation in 1877 by Marcellin Pierre Eugène Berthelot (1827-1907), the Professor of Organic Chemistry of the Collège de France in Paris.

During the second half of 19th century the ozone synthesis in silent discharge cells was intensively studied. In fact, ozone synthesis was the first application of silent discharge in history, others,such as abatement of gaseous emissions and treatment of surfaces, were offered much later. The use of oxygen rather than air was preferred for higher yields of ozone and avoidance of nitrogen oxides. Both dry and moist oxygen could be used but the best results were obtained using dry oxygen. Temperature was found to play a critical role in determining the yield: the production of ozone doubled if the operation temperature was reduced from 20 to -20-70 ºC. The increased frequency of alternating current was found to regularly improve the yield of ozone up to 175 mg L^{-1} (about 9% vol.). Voltages applied for industrial ozone production ranged from 6 kV to as high as 100 kV. The Siemens version of ozone silent discharge generator was found by the end of 19th century to be much superior both in terms of yield of ozone and reliability of operation as compared to Babo and Claus's, Houzeau's, Wright's, Boillot's and Wills's options.

1. 2. 2. Electrolysis of Aqueous Solutions

The electrolysis of aqueous solutions of acids led to Schönbein's discovery of ozone and was used by some of the early workers in the field for ozone preparation. It has the potential for giving higher concentrations of ozone than any of the other conventional methods: Herbert McLeod (1841-1923), Professor of Chemistry and Physics at Royal Indian Engineering College at Surrey, UK, described concentrations of ozone as high as 16 % vol. Electrolysis was rarely used, however, probably due to the convenience of the silent discharge method. From the other side, the aqueous solutions, from which ozone and oxygen had been liberated, had considerable oxidizing power on their own, containing persulphuric acid and hydrogen peroxide found in the aqueous solution after electrolysis.

1. 2. 3. Photochemical Formation of Ozone

The first report of photochemical formation of ozone was published in 1900 by Philipp Eduard Anton von Lénárd (1862 – 1947), the winner of the Nobel Prize for Physics in 1905 for his research on cathode rays, Professor of the University of Heidelberg. He described his experiments on the effect of ultraviolet light on a number of gases using a zinc arc as light source. While no reaction was observed if a piece of window glass were placed between the light source and a sample of air or oxygen (wet or dry), a very strong ozone odour and immediate coloration of starch-iodide paper were observed using a quartz window.

1. 2. 4. Miscellaneous Chemical Methods

The reaction of white phosphorus with oxygen became less and less important for preparation of ozone with the passage of time since it suffered mostly from low yields: even modified procedures using solutions of potassium dichromate and sulphuric acid instead of water did not increase ozone concentrations higher than 2.5 mg L^{-1} in air. The kinetic studies of the phosphorus-oxygen reaction were conducted in the mid-1890s in the laboratory under direction by Jacobus Henricus van 't Hoff (1852 – 1911), Professor of Chemistry, Mineralogy, and Geology at the University of Amsterdam, the first winner of the Nobel Prize in Chemistry in 1901. The reaction kinetics suggested that the kinetics supported the idea that oxygen molecules were cleaved into two oxygen atoms.

Another chemical reaction producing ozone beyond any doubt is the exothermic reaction of elemental fluorine with water. Ferdinand Frederick Henri Moissan (1852 – 1907), the winner of the Nobel Prize in Chemistry in1906, Professor of École superieure de pharmacie in Paris, reported concentrations of ozone as high as 14.4 % vol. by bubbling fluorine gas through water. This reaction was never in use for ozone synthesis to any extent.

Some other reactions were under the scope for ozone formation, although all of them were found the be misleading due to the presence of impurities (mostly chlorine) and imperfection of the analysis techniques, often limited to the odour and starch-iodide test. In addition to the reaction of sulphuric acid with potassium permanganate, dichromate or barium peroxide, crystallization of iodic acid was wrongly claimed to produce ozone. The list of claims of ozone formation occurred to be incorrect includes: waterfalls, salt evaporation installations, simultaneous formation of ozone and oxygen by growing plants, reaction of heated potassium chlorate with manganese dioxide, heating of a number of metal oxides, the passage of air over copper metal covered with aqueous alkali and reactions of variety of organic compounds with oxygen under light (photo-oxygenation). The latter error was due to formation of organic oxidising substances.

Considerable attention in the second half of 19th century was paid to the issue of thermal formation of ozone, whatever weird it sounds these days. Thermal instability was one of the first properties of ozone described by Schönbein and was repeatedly confirmed by others. Nonetheless, a number of reports of ozone formation in flames and over hot, up to 1600 ^{o}C, surfaces appeared. Interesting products such as hydrogen peroxide and ammonium nitrite were identified in the hydrogen flame in purified air, however, the quantities of ozone, if formed at all, were insufficient for methods of identification other than odour.

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Biographical Sketch

Sergei Preis was born in Tallinn, Estonia in 1959. Received degrees: Diploma in Chemical Engineering *Cum Laude*, Tallinn University of Technology (TUT), Tallinn, Estonia, 1981; Candidate of Technical Sciences of the USSR (equal to a Doctoral degree), Environmental Technology, TUT, Tallinn, Estonia, 1988; Doctor in Chemical Engineering, Lappeenranta University of Technology (LUT), Lappeenranta, Finland, 2002, Docent at LUT.

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Research interests: Advanced oxidation processes application in water treatment, photocatalytical oxidation of organic compounds in water and air; application of pulse DBD to water treatment