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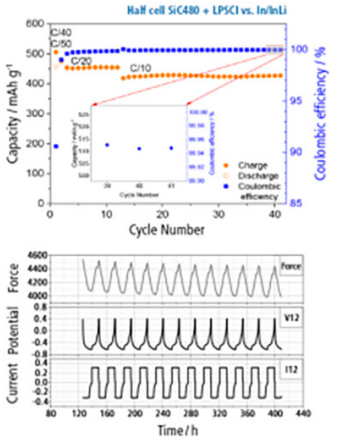
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Electrosynthesis of Chlorate in the Nineteenth Century

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ABSTRACT

A critical review is given of the origins of the electrosynthesis of chlorate in 1802 to the beginning of industrial chlorate manufacture toward the end of the century. The contemporary efforts to establish the fundamentals of a theory of electrochemical chlorate formation are also discussed.

The Origin of Chlorate Electrosynthesis

The first chlorate produced by electrosynthesis dates back to 1802, earlier than currently written in historical reviews. This fact gives rise to the need for a critical review of the origins of the electrosynthesis of chlorate and on the development of technology and theory in the first 100 years, at the same time correcting a number of misconceptions.

Volta's famous letter to the Royal Society in London in 1800 prompted scientists all over Europe to study the effect of the electric current on chemical reactions. It was this interest in the new matter that induced Wilhelm von Hisinger together with Jöns Jakob Berzelius to run "experiments relating to the effect of the electrical pile on salts and their bases" (1). Neither men were professionals: Hisinger was a mine owner and Berzelius had become doctor of medicine and was at that time an unpaid assistant to a professor of medicine and pharmacy at the School of Surgery in Stockholm (2). The studies on the electrolytic decomposition of salts, dissolved in water, took several months in the autumn and winter of 1802 and were more than only cursory hobby activities. Runs with several solutions and various electrode materials showed an amazingly systematic manner.

In one of the series, sodium chloride solution was electrolyzed between silver wires, serving as electrodes in a U-type cell. After the anolyte had been evaporated and cooled down, sodium chloride precipitated. The remaining clear solution was found to contain sodium chloride and silver chloride and "perhaps, hyperoxygenized muriatic sodium and a formerly unknown silver salt" (1d).[1] The latter one was immediately identified by Gehlen (1a) with the "hyperoxygenized muriatic silver" which Chevenix had obtained through a chemical way (3). In fact, the salts were sodium chlorate and silver chlorate. A definite proof of the formation of chlorate through electrolysis of chloride solutions was given much later by Kolbe in 1847 (4).

A report on the joint studies of Hisinger and Berzelius was written in Swedish by Berzelius and published in German in February 1803 (1a). It was further published in French two years later (1b), in Swedish (1806) (1c), and once more in German (1807) (1d). "This treatise contains the fundaments of those laws which the electrochemical theory later was based upon," Berzelius recapitulated with self-confidence many years later in his autobiography (5). However, "the unknown names of the authors attracted no special attention." Indeed, in the chlorate literature of our century, the first preparation by electrosynthesis is erroneously dated throughout as of 1808 and attributed to Berzelius only.

Hisinger and Berzelius were not the first to prepare chlorate, which had already been prepared by Glauber in 1657 by chemical means (6, 7) and rediscovered and identified by Berthollet (8) in 1786—nor were they the first who applied electrolysis to prepare it. It must be guessed that earlier electrolyses of chloride (9, 10) would have led to chlorate, but they were the first who recognized having prepared chlorate.

Industrial Chlorate Production

Few years after Kolbe's observation, in 1851, a remarkable attempt at industrial application is reported. The chemist Charles Watt in Kensington, London, received a patent for the electrochemical decomposition of salt and other substances and separation into their components (11), Fig. 1. It is surprising that some features of modern chlorate process are anticipated in this first chlorate cell patent: the omission of a diaphragm, the relevance of high temperature to favor the chlorate formation, the separation of chlorate by crystallization, and the recycling of the mother liquor and its electrolysis after resaturation. Some of these characteristics were not realized with the first

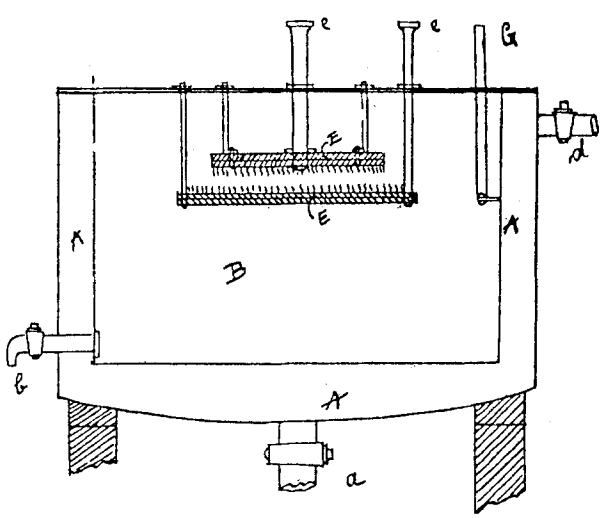


Fig. 1. Chlorate cell of the 1851 patent of C. Watt. The electrolyte vessel is surrounded by a steam-heated jacket.

Key words: electrosynthesis, electrochemical chlorate formation.

[1] The passage cited is given after (1d); the first edition (1a) uses the expression "oxygenirt-salzsaures Natron" instead of überoxygenirt-salzsaures Natron" (1d).

industrial chlorate cells coming on stream and had to be rediscovered gradually.

A practical use of the patent is not reported and cannot be expected owing to the absence of powerful energy sources at that time. The only method of manufacture was the chemical process developed by Liebig. Chlorine was introduced into solutions of caustic potash or calcium carbonate to make chlorate (12).

After the dynamo machine was invented and improved for industrial use, the prerequisite for industrial electrosynthesis of chlorate was given. But even in 1888, the conviction was declared that electrochemical processes would have no future in the alkali industry (13). That happened two years after H. Gall and A. de Montlaur had started in 1886 the first plant in Villers-St. Sépulcre in Switzerland, where chlorate was electrochemically produced under industrial conditions.[2] The cell cases were reported to be made of wood and equipped with a diaphragm (14). The cells were operated at elevated temperatures. The concentration of chlorate in cell liquid was raised until crystals precipitated which were removed manually using enameled iron scoops. Cell voltage was 5V and a current was used of 1000A. Energy consumption per kg of potassium chlorate is reported to 24 hp (14) or 17.7 kW-hr/kg $KClO_3$, corresponding to a total current efficiency of 37%. The plant served as a prototype and was shut down in 1891, when the new bigger factory in Vallorbe (Switzerland) was ready to start (15). In 1896, the Société d'électrochimie started a second factory in St. Michel de Maurienne (France) (14).

The company was not the only electrochemical chlorate producer for long. In Sweden, the Superfosfat Fabriks AB started the manufacture in 1894 in Mansboe and in 1899 at Alby fall in Ljungan using the process of O. Carlson (16).

A big factory was started in Chedde (France) in 1896, which used the process of Corbin and Lederlin with bipolar electrodes. A description in detail was given by Kershaw (14).

At nearly the same time, electrochemical chlorate manufacture started in the U.S.A. (14). In 1896 and, 1897, the Chemical Construction Company operated a chlorate factory at Niagara Falls, New York, using the process of Blumenberg. The cell was equipped with a diaphragm and differs from contemporary types by the fact that chlorine gas was transported through a special pipe into the cathode compartment to mix with the catholyte remote from the cathode, but inside the cathode compartment. Owing to the cathodic reduction losses the process was not successful and production was finished in 1898 or 1899. As early as in 1905 the opinion was uttered (14) that Blumenberg would have had better results if he had carried out the reaction between chlorine and alkali in a vessel completely separated from the cell, an important process feature which was much later patented (17) and has come into industrial use since about 1970.

In 1894, Franchot and Gibbs started a test plant in Buckingham, Quebec. After the foundation of the National Electric Company an industrial plant was constructed in 1897 and started in 1898 at Niagara Falls. The cells had no diaphragm and were equipped with some kind of bipolar electrodes with pre-electrode and an electrode distance of only 1.5 to 3.0 mm (14).

In 1898, the North American Chemical Company, a subsidiary of the United Alkali Company of Liverpool was founded. Production started a little later in Bay City, Michigan, using a process of Brock with cells arranged in terraces (18).

In 1899, Oldbury Electro-Chemical Company started manufacturing potassium chlorate at Niagara Falls. The chlorate manufacture in the United States and Canada from that time on was reported in detail by Wallace (19).

[2] The year 1866 is sometimes erroneously reported in literature.

At the turn of the century, chlorate factories were operated in Switzerland (Vallorbe and Turgi), in France (St. Michel de Maurienne and Chedde), in the U.S.A. (Niagara Falls and Bay City), and in Sweden (Mansboe and Alby) (14, 19). Chlorate was not manufactured by electrosynthesis in Germany where the commercial electrochemical chlorate production started not before 1915, after first attempts at industrial scale, executed in 1887 in Leopoldshall, had failed. This situation is surprising since Germany, at that time, was the center of chlorate research.

The Controversy on the Theory of Electrosynthesis of Chlorate

With the beginning of the electrochemical chlorate production on an industrial scale, an interest in the knowledge of the processes of chlorate formation developed. At that time, it was the general belief that the electrosynthesis of chlorate took place in complete agreement with the chemical formation. Thus, chlorine and hydroxide "primarily" generated at anode and cathode were thought to react with each other to form "secondarily" hypochlorite and chlorate (20, 21)

$$2KOH + Cl_2 \rightarrow KClO + KCl + H_2O$$

$$6KOH + 3Cl_2 \rightarrow KClO_3 + 5KCl + 3H_2O$$

Soon it became clear that these reactions did not comprehensively describe the processes in the cell.

In 1889, Fogh (22) had subjected a neutral solution of alkali chloride to electrolysis without diaphragm and had found from a gas analysis that oxygen was also evolved at the anode. One of the reasons for the loss of current efficiency was found, irrespective of the question whether oxygen is generated by decompostion of water or by any other way.

Oettel, in 1894 (23), interpreted the finding as follows. "Primarily" chloride is anodically oxidized to chlorine. Secondarily, hypochlorite forms at both sides of the diaphragm. In the cathode compartment the hypochlorite is reduced at the cathode. In the anode compartment, part of the hypochlorite is "tertiarily" oxidized to chlorate, while the rest, together with some "tertiarily" formed chlorate is electrolytically decomposed

$$2ClO^- + H_2O \rightarrow 2HClO + \tfrac{1}{2} O_2 + 2e^-$$

$$2ClO_3^- + H_2O \rightarrow 2HClO_3 + \tfrac{1}{2} O_2 + 2e^-$$

Additionally, an anodic discharge of hydroxyl is supposed. In any case, the formation of chlorate through anodic discharge of hypochlorite was unthinkable at that time. "The formation of oxygen compounds with chlorine is, therefore, attributed to purely chemical interaction between chlorine and potassium hydroxide," Oettel concluded (23).

The reaction scheme established by Oettel was questioned a few years later in connection with studies on the electrolysis of hydrochloric acid. In 1898, Haber and Grinberg (24) concluded that simultaneously with the secondary (chemical) formation of hypochlorite and chlorate a primary (anodic) formation takes place

$$Cl^- + 2\,OH^- \rightarrow ClO^- + H_2O + 2e^-$$

$$Cl^- + 6\,OH^- \rightarrow ClO_3^- + 3H_2O + 6e^-$$

With this interpretation, the old theory of an exclusively chemical formation of chlorate was fundamentally shaken, stimulating extensive research at various places. The activities resulted in a complete revision of the chlorate theory, accompanied by sometimes violent discussions. The results of these fertile years shortly before and after the turn of the century form the basis of a theory which nowadays is essentially considered valid.

Oettel (25) compared the conclusions of Haber and Grinberg with older considerations and gathered that in neutral electrolytes chlorate is preferably formed from hypochlorite partly by "secondary" reactions in bulk of the solution, partly "primarily" by oxidation at the anode. In alkaline electrolytes he surmised a formation of chlorate predominantly by direct combination of chlorine and oxygen set free at the anode.

In 1898, Wohlwill (26), stimulated by his teacher Nernst, carried out experiments on the subject. In agreement with the Haber-Grinberg hypothesis he also stated that chlorate is not exclusively formed "secondarily" (*i.e.*, by chemical reaction in bulk of the solution), but directly at the anode. From the observation that chlorate is never formed without the presence of hypochlorite he followed that chlorate is always generated from hypochlorite according to

$$2ClO^- + OH^- \rightarrow ClO_3^- + H^+ + Cl^- + 2e^-$$

while hypochlorite is formed "secondarily." From today's viewpoint the reaction cannot be considered valid since the concentration of OH^- in the bulk is usually small and its rate of diffusion toward the anode is negligible (27), but it is to Wohlwill's credit to have first given a formula for anodic discharge of hypochlorite to form chlorate and chloride.

This construction, possibly kindled by the rude style of the paper and the direct attacks on Oettel and Haber, prompted the arousal of controversy on the central question of whether chlorate is formed "primarily" or "secondarily." In his famous Göttingen lecture in 1899, Foerster (28) reported on his essential finding that the electrolyte has to be slightly acidic to give way to the autoxidation of hypochlorite ($ClO^- + HClO$) to chlorate (29) which was a real novelty and stood in marked contrast to theory and practice of that time. But at the same meeting he strictly denied that chlorate formation took place at the anode. He had found that always, even in alkaline electrolytes, the electrolyte in the vicinity of the anode was acidic, and so he excluded the possibility of any anion discharge.

In an answer, Wohlwill (31) defended his construction against Foerster and uttered the opinion that in neutral or slightly acidic solutions chlorate is generated by primary as well as by secondary reactions. The aggressive mode of his comment on Foerster's theory provoked Foerster himself to a sneering answer (32) in which he insisted on his old conviction. The way this controversy was carried out obstructed the general acceptance of Wohlwill's theory, and probably was part of the phenomenon that Wohlwill's contribution to the chlorate theory is widely underesteemed.

One year later, Foerster published a study on the anodic processes (33) containing the untenable statement that oxygen is set free only to a very small extent and that chlorate is formed "anodically not in any appreciable extent." It was also in 1900 when Brochet (34) concluded from experiments that in alkaline solutions a primary chlorate formation does not occur.

The same year, Lorenz and Wehrlin summarized the existing views and published their voluminous experimental results (35). The authors concluded that primarily hypochlorite is formed and that under certain conditions chlorate is formed at the anode, thus confirming Wohlwill.

Foerster continued to deny any anodic chlorate formation (36), but soon Foerster and Müller (37, 38) came to the definite conclusion that apart from autoxidation of hypochlorite requiring a slightly acidic region chlorate formation occurs by discharge of hypochlorite at the anode

$$3ClO^- + 1.5H_2O + ClO_3^- + 2Cl^- + 3H^+ + 0.75\,O_2 + 3e^-$$

They coined the expression of "anodic chlorate formation" which is still in use.

The Problem of Hypochlorite Reduction

The other relevant problem that occupied the science in the chlorate field was the question whether and how it was possible to prevent reduction of hypochlorite at the cathode. The formation of chlorate is favored by intensive mixing of anodic and cathodic products. But it was just this mixing that caused hypochlorite reduction to such an extent that current efficiency was held down and the economy of the whole process severely affected. To allow industrial operation, a diaphragm was generally used to separate anolyte and catholyte (20). "It is self-evident that the electrolysis of chlorides of potassium or sodium must be carried out with use of a membrane" (23).

When in 1894 Oettel (21) studied the conditions of electrochemical chlorate formation with the intention to check the assumed reaction equations, he concluded that the process should run best in the case where the diaphragm is omitted. In an extended test with a single compartment cell he was able to show that the current efficiency could be maintained at 80-82% without tendency of significant decrease (21). He soon obtained an efficiency of 87% when he operated such a cell with a strongly alkaline solution of calcium chloride (39). Oettel erroneously interpreted this current efficiency to be caused by the absence of hypochlorite during electrolysis. He was so enthusiastic that he called electrolysis without diaphragm "one of the most elegant processes that electrochemistry presents" (39), a statement which must be seen before the background of the enormous technical difficulties of making suitable diaphragms.

Independent of this realization, that same year the first industrial chlorate cell without diaphragm was started. As early as in 1890, Oscar Carlson had taken a Swedish patent (40) for a single-compartment cell. The process was used in the Mansboe factory. An advanced technology was used: "In a vessel alkali chloride is dissolved and the solution is then electrolyzed between an anode made of carbon or other convenient material and a cathode preferably made of iron under omission of a partition" (40). However, when discussing the question of priority of diaphragmless cells, Watt's patent of 1851 (11) has to be considered. Carlson was the first who used carbonates of alkaline earths as additive to the solution. The text of the patent (40) reveals that Carlson did not have a clear idea of the effect of this step. He was of the opinion that the hydroxides of alkaline earths react directly with the chlorine, thus playing an active role in the formation of chlorate. The disadvantageous side effect was that the layer of alkaline earth hydroxide attaching to the cathode continued to increase in thickness during electrolysis, causing a corresponding increase in voltage drop.

In 1898, Bischoff and Foerster (41) gave an interpretation of the way of action which also today is roughly valid: calcium hydroxide, being less soluble than alkali hydroxide, forms a diaphragm at the cathode surface thus obstructing the reduction of hypochlorite.

It was another Swede, J. Landin, who gave a definitely practicable solution of the problem (16, 42). In 1897, he proposed to use additives of compounds of those metals which occur in various valencies, particularly chromic acid. In 1898, Imhoff was granted a German and an American patent (43) (which was transferred to the United Alkali Company, Limited) for the addition of chromate.

Obviously without knowledge of Landin's and Imhoff's patents, Müller (44, 45) used potassium chromate additive with the intention of accelerating the conversion of hypochlorite to chlorate, but found that the additive was suitable to extensively suppress the cath-

odic reduction. "The electrolysis with chromate represents one of the most ideal diaphragm processes one can imagine" (46). Contemporary experiments showed that current efficiencies of 80-92% were attainable (33). A means thoroughly satisfying in industrial electrosynthesis of chlorate had been found. In 1905, world production of chlorate amounted to 15,000 tons per year, 65% of which were already made by electrosynthesis (14).

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