

## 2. THE MANUFACTURE OF METALLIC SODIUM

Metallic sodium can be prepared from a number of sodium compounds in a number of ways. The compound most commonly employed in early processes was sodium hydroxide, but modern manufacture is based almost entirely on sodium chloride. The most important techniques for the reduction of these salts to sodium metal have been the thermochemical method (using carbon or carbon compounds as the reducing agents) and electrolytic reduction.

A critical review of the development of the metallic sodium industry up to 1922 has been published by Batsford<sup>21, 22</sup>. Another review of the industry from 1855 to 1920 appears in Regelsberger's book, "Chemische Technologie der Leichtmetalle"<sup>23</sup>. Other reviews are those by Becker<sup>24</sup> and by Moltke-hansen and Eger<sup>25</sup>. The manufacture of sodium in Germany is reviewed by Schermack<sup>26</sup>. An early historical review of the processes for production of metallic sodium is that by Carrier<sup>27</sup>. Another review on the manufacture of sodium and of sodium compounds is by Achille<sup>4</sup>. A recent review of sodium manufacture is that by Hardie<sup>107a</sup>.

### THERMOCHEMICAL REDUCTION PROCESSES

Sodium can be obtained from any of a number of sodium compounds by high-temperature reduction, as reviewed by Meyer in Gmelin's Handbuch<sup>108</sup>.

Sodium carbonate can be reduced with carbon in the form of charcoal or coke, finely-divided iron, sulfur, aluminum, or magnesium as the reducing agent.

Aluminum, magnesium, calcium, calcium hydride, calcium silicide or calcium carbide will reduce sodium chloride to sodium at elevated temperatures.

Finely-divided iron, ferrosilicon, calcium carbide or coke yield sodium from fused sodium hydroxide.

Sodium silicate, sulfide, sulfate, and cyanide can also be reduced to sodium at high temperatures, according to Gmelin.

High-frequency induction furnace reduction of sodium compounds to sodium by granular graphite have been covered by Blackwell and Turner<sup>28</sup>.

Calcium carbide has also been proposed as a reducing agent<sup>109</sup>, as will be discussed more fully in the sections to follow.

Even though electrolytic processes for sodium manufacture had largely supplanted thermal reduction processes in industry by 1890, some new thermal processes were patented; among them are those by Wolfram<sup>29</sup>, Parker<sup>30</sup>, and Specketer and Weber<sup>31</sup>.

Some work has also been done on the production of sodium by electro-thermic reduction in furnaces similar to carbide furnaces as discussed by Cowles<sup>32, 33, 34, 35</sup>.

### Processes Using Sodium Carbonate

Sodium carbonate can be reduced to metallic sodium with aluminum powder, according to Gmelin<sup>109</sup> and Regelsberger<sup>23</sup>. Friend<sup>36</sup> states that iron can also be used as a reducing agent. However, magnesium is not suitable for the reduction of sodium carbonate because explosions occur on heating the mixture<sup>109, 231</sup>.

The commercially important reduction process for sodium from sodium carbonate has been that using carbon as the reducing agent. The over-all reaction is:



and the reduction presumably occurs in three stages:



The general conduct of such a process has been described by Gmelin<sup>109</sup>, by Batsford<sup>22</sup>, by Friend<sup>36</sup> and by Regelsberger<sup>23</sup>. The separation of the molten sodium carbonate from the carbon on heating is prevented by the addition of chalk to keep the material pasty, as discussed by Gmelin<sup>109</sup>, Mellor<sup>32</sup> and Thorpe<sup>33</sup>. Gmelin also states<sup>109</sup> that external heating of the reaction vessel may be avoided by conducting hot water-gas through the reaction mixture.

Contact of soda ash with carbon dissolved in molten iron causes reduction to sodium, according to Gmelin<sup>109</sup> and Mehner<sup>37</sup>.

A mixture of sodium carbonate, ferric oxide and calcium hydroxide can be reduced to sodium with wood charcoal, as stated by Gmelin<sup>109</sup>, Batsford<sup>22</sup> and Blackmore<sup>38</sup>. Sodium carbonate alone can be reduced with pure carbon prepared from alkali-soluble cellulose, according to Jacobs<sup>104</sup>.

Swan and Kendall have obtained British patents<sup>249, 250</sup> on process modifications for the reduction of sodium carbonate or hydroxide with carbon. One<sup>249</sup> provides for condensation of sodium vapor from the process in a

fused salt, such as sodium cyanide. Another<sup>250</sup> describes a column for reacting incandescent carbon with molten sodium hydroxide or carbonate.

Ylla-Conte has described a process for the manufacture of sodium by the reduction of the carbonate or hydroxide with carbon. The process is conducted under reduced pressure with vacuum pumps following a product condenser<sup>272, 273, 274</sup>. This process is illustrated in Figure 2.1.

The reduction of sodium carbonate with carbon at 1100°C should preferably be followed by a quick quench of the resulting sodium vapors to a temperature below 700°C, according to Lacy<sup>164</sup>.

The reduction of sodium carbonate with ferrophosphorus ( $\text{Fe}_2\text{P}$ ) has been described by Bowe<sup>61</sup>. Powdered iron, ferric oxide pigment and trisodium phosphate are co-products of the reaction.

**The Deville Process.** The Deville process for the manufacture of so-

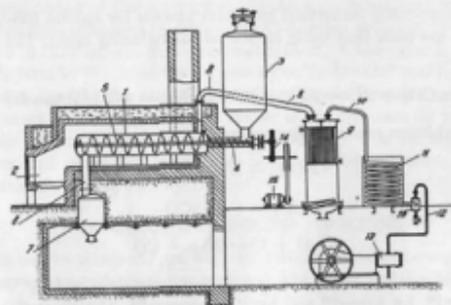


FIG. 2.1. Ylla-Conte Apparatus for Reduction of Sodium Compounds with Carbon

- 1—Reaction vessel
- 2—Hearth
- 3—Feeder vessel
- 4—Feed screw
- 5—Reaction conveyor screw
- 6—Exit tube for reaction residue
- 7—Storage vessel for reaction residue
- 8—Alkali metal vapor pipe
- 9—Condenser
- 10—Residual gas pipe
- 11—Secondary condenser
- 12—Non-condensable gas pipe
- 13—Vacuum pumps
- 14—Transmission gear
- 15—Motor
- 16—Liquid Receiver

dium is described by the inventor<sup>266, 267</sup>. A mixture of sodium carbonate, charcoal, and lime was heated to a high temperature and the sodium condensed in iron equipment. The efficiency of the process was low and the life of the equipment short due to the high-temperature operation.

However, the Deville process was in use for 30 years<sup>268</sup>, and it reached an annual production of 5,000 to 6,000 kilograms of sodium.

**The Dow Process.** A process for producing sodium by distillation of a mixture of carbon and sodium carbonate fused in an arc furnace has been patented by McConica, MacPhail and Kirk of Dow Chemical Company<sup>171</sup>. The furnace is operated at 1200°C and the sodium vapor is condensed by rapid chilling in a lead alloy, containing 5 to 15% sodium, at 375 to 400°C. A portion of this condensing liquid is continuously withdrawn to a still operating at 600°C in which sodium is removed. The process is illustrated in Figure 2.2.

The apparatus and techniques involved in the condensation and distillation recovery process are further described by Griswold and McConica<sup>120, 121</sup>.

The economics of producing sodium by distillation of a fused mixture of carbon and sodium carbonate have been discussed by Oettel<sup>211</sup>.

The recovery of sodium from a gaseous mixture with carbon monoxide may be accomplished by contacting the mixture with molten tin, according to patents by Deyrup<sup>212</sup> and by Deyrup and Knox<sup>213</sup>. These patents both refer specifically to treatment of the product mixture from the carbon reduction of sodium carbonate.

### Processes Using Sodium Hydroxide

The manufacture of sodium by the thermal reduction of sodium hydroxide with chemical agents has been described by various investigators. Thus, Netto<sup>266, 267, 268</sup> describes a process for sodium production whereby molten caustic was trickled over coke or wood charcoal as shown in Figure 2.3. Thowless<sup>262</sup> covers contact of preheated caustic with preheated carbonaceous or other reducing material to produce sodium vapor which is then condensed. He also describes the apparatus for this process<sup>262</sup>.

The production of sodium-lead alloy by the reduction of sodium hydroxide with carbon in the presence of lead is outlined by Rossiter<sup>218</sup>.

However, the major work on thermochemical reduction of caustic was that of Castner.

**The Castner (Iron Carbide) Process.** In the latter 1800's, Hamilton Y. Castner became interested in the manufacture of aluminum, then selling for about ten dollars per pound, as recounted by Fleck<sup>98</sup>.

Castner first worked out an improvement of the Deville process<sup>99</sup> designed to improve contact between the reactants, sodium carbonate and

charcoal. He substituted sodium hydroxide for sodium carbonate, a mixture of iron and carbon for the carbon alone. The improved process featured better contact between reactants, permitting a lower process temperature. It followed the reaction:



The process was put into operation on a commercial scale at Oldbury, England, in 1888. The sodium plant was located adjacent to an aluminum plant and the aluminum thus produced dropped from ten dollars to five dollars per pound. Over 100 tons of aluminum were produced in this plant over a two-year period.

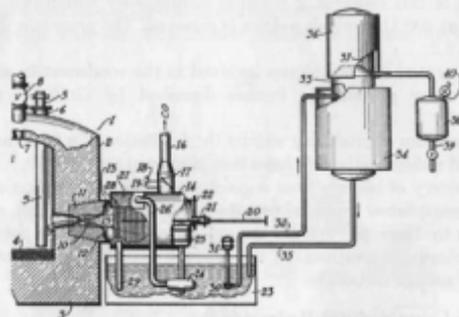


FIG. 22. Dow Thermochemical Process Apparatus

- |                        |                          |
|------------------------|--------------------------|
| 1—Arc furnace          | 21—Gland                 |
| 2—Steel shell          | 22—Cover flange          |
| 3—Brick lining         | 23—Lead reservoir        |
| 4—Hearth               | 24—Pump                  |
| 5—Electrodes           | 25—Motor                 |
| 6—Gas-tight glands     | 26—Insulated line        |
| 7—Solids inlet         | 27—Distributor box       |
| 8—Rotary lock          | 28—Transverse slots      |
| 9—Expansion orifice    | 29—Insulated drain       |
| 10—Bushing             | 30—Pump                  |
| 11—Thrust block        | 31—Motor                 |
| 12—Steel backing ring  | 32—Transfer line         |
| 13—Conduit             | 33—Still                 |
| 14—Quench chamber      | 34—Furnace               |
| 15—Molten lead streams | 35—Drain line            |
| 16—Gas exhaust         | 36—Cooling jacket        |
| 17—Damper              | 37—Sodium collector ring |
| 18—Controller          | 38—Product receiver      |
| 19—Gage line           | 39—Sodium outlet         |
| 20—Reamer rod          | 40—Vacuum connection     |

Then Hall's electrolytic method for aluminum appeared<sup>124</sup>. Almost simultaneously, Heroult developed an electrolytic process for making aluminum from bauxite and the principal use for metallic sodium was eliminated.

Castner continued to work on process improvements for sodium manufacture, however, and in 1891 he patented an electrolytic process using sodium hydroxide—a modification of the method by which Sir Humphry Davy first isolated sodium metal. The process is described in detail later in this chapter.

According to Gmelin<sup>102</sup> and Regelsberger<sup>231</sup>, iron carbide (obtained by heating tar with finely-divided iron at 1000°C) reduced sodium hydroxide to sodium according to the equation:



A patent by the Societe D'Electro-Chimie<sup>125</sup> also covers a process for the thermochemical reduction of sodium hydroxide to sodium.

**Processes Using Other Reducing Agents.** A number of reducing agents can be used to produce sodium metal from sodium hydroxide.

Calcium carbide can be used to reduce sodium hydroxide—alone, or in mixtures with sodium chloride. The caustic must be dry to avoid explo-

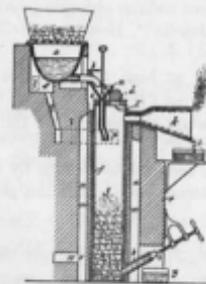


FIG. 23. Netto Reduction Process Apparatus

- |                     |                        |
|---------------------|------------------------|
| a—Caustic reservoir | m—Insulating jacket    |
| b—Valve             | n—Heating flue         |
| c—Charging funnel   | o—Hot gas inlet        |
| d—Iron plug         | p—Flue gas outlet      |
| e—Lid               | q—Flue gas duct        |
| f—Retort            | r—Flue gas duct        |
| g—Coal              | s—Caustic heating duct |
| h—Tap pipe          | t—Vent to chimney      |
| i—Valve             | u—Charging valve       |
| k—Vapor outlet      | w—Hot gases            |
| l—Sodium reservoir  | y—Soda receiver        |

sions of acetylene generated from the carbide and moisture. This process is described by Batsford<sup>12</sup> and by Wolfram<sup>98</sup>.

Calcium hydride may be employed, as pointed out by Gmelin<sup>102</sup>.

Carbon may be used according to the reaction:



which is conducted at red heat. At white heat, the sodium carbonate is reduced as well. The process is described by Ylla-Conte<sup>21</sup> and also in another reference<sup>16</sup>.

Batsford indicates<sup>12</sup> that coal gas or other reducing gases passed into molten sodium hydroxide cause sodium to distill over. Ferrosilicon may be employed, according to Gmelin<sup>102</sup>.

### Processes Using Sodium Chloride and Other Halides

Sodium chloride can be thermochemically reduced by a number of agents. Thus, aluminum will reduce NaCl on heating, but the yield is low, according to Mellor<sup>25</sup>. Gmelin states that<sup>102</sup> calcium hydride or silicide can be used to produce sodium from NaCl at high temperatures. The reduction of sodium chloride by a mixture of silicon metal and calcium oxide is covered by Kroll<sup>102</sup>.

Magnesium easily reduces sodium chloride to sodium in a hydrogen atmosphere, according to Gmelin<sup>102</sup>. However, Mellor indicated that<sup>25</sup> the reduction is incomplete.

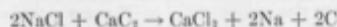
Sodium chloride heated at high temperatures with molybdenum, or tungsten, and hydrogen, forms sodium molybdate or sodium tungstate and HCl. The sodium compounds are reduced to the metal by heating with carbon at 1200 to 1300°C<sup>102, 221</sup>.

Sodium fluoride can be reduced to sodium by aluminum; the reaction occurs with explosive violence when aluminum powder is used. The reaction:



is described by Batsford<sup>12</sup> and by Specketer<sup>214</sup>. The reduction of alkali fluorides by aluminum is also covered by Specketer and Weber<sup>206</sup>.

**Reduction by Calcium Carbide.** Calcium carbide reduces sodium chloride to sodium at high temperatures according to the equation:



Methods of carrying out this reaction are described in Gmelin<sup>102</sup>, by Batsford<sup>12</sup>, by Hackspill and Staehling<sup>122</sup>, and by Regelsberger<sup>211</sup>. Sodium fluoride behaves similarly, as described by Mooser and Eidman<sup>105</sup>. According to the patent by Hackspill and Staehling<sup>122</sup>, lampblack of superior

quality is produced as a by-product. However, Gmelin<sup>102</sup> states that only traces of sodium are produced unless sodium carbonate is added to the NaCl.

Freeman<sup>97</sup> covers production of sodium by heating a finely-divided mixture of NaCl and CaC<sub>2</sub> to 1200 to 1300°C, obtaining CaCl<sub>2</sub>, sodium and carbon as reaction products. The sodium is volatilized and condensed.

Free-energy and equilibrium data for the reaction:



have been published by Kawahara<sup>104</sup>. Other publications by Kawahara<sup>101, 107, 102</sup> report the effects of various added substances, such as magnesium chloride, calcium oxide and calcium fluoride, on the reaction.

Other publications on the production of sodium by reduction of sodium chloride with calcium carbide include those by Gel'd, Mikulinskii, Polyakova and Selyanskii<sup>103</sup> and that by Specketer<sup>214</sup>. Specketer goes on to point out that thermal reduction processes are also applicable to potassium production, but not to lithium, due to its high boiling point.

Sodium fluosilicide can be reduced to sodium by the action of calcium carbide, according to Gmelin<sup>102</sup> and to Mellor<sup>102</sup>.

**Reduction by Carbon.** Sodium can be produced by reducing NaCl with carbon in the presence of CaO or Ca(OH)<sub>2</sub>



as stated by Barth<sup>20</sup>, Gmelin<sup>102</sup>, Regelsberger<sup>211</sup>, and Wood<sup>210</sup>. The melting point of the reaction mixture may be lowered by the addition of zinc chloride, calcium chloride, sodium fluoride, or barium chloride<sup>206</sup>.

**Reduction by Lead.** Sodium can be obtained by reducing anhydrous NaCl with lead according to the reaction:



According to Vourmas<sup>200</sup>, 100 parts of NaCl and 200 parts of lead powder or fine lead shot are heated until homogeneous at a temperature below red heat. The sodium distills over and the lead is recovered.

**Reduction by Iron.** As pointed out by Hackspill and Grandadam<sup>122</sup> and by the Societie D'Electro-Chimie<sup>202</sup>, sodium can be obtained in good yields by the reduction of sodium fluoride with iron.

Heating in a vacuum with iron displaces sodium from a number of sodium compounds, such as the hydroxide, carbonate, cyanide, nitrate or sulfate. With sodium chloride, bromide, or iodide, however, the high volatility of the iron halides prevents successful reaction. The lesser volatility of iron fluoride permits successful reduction of sodium fluoride.

**Processes Using Sodium Tetraborate**

Borax can be reduced with finely-divided coke or charcoal according to the equation:



The mixture is first heated to 600°C to remove the water of crystallization from the borax and then to 1000°C to distill the sodium, according to Peacock<sup>214</sup>.

**Processes Using Sodium Sulfide and Sulfate**

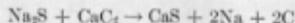
The production of sodium from its sulfate by heating with coke in a carbon-lined retort is described by Emanuel<sup>19, 48</sup>. Sodium sulfide is produced in an initial reaction. Lime and additional coke are then added and the temperature is raised from 600° to 850°C to distill over the sodium.



The same process may be adapted to sodium aluminate<sup>49</sup>.

Lavoisier<sup>186</sup> produced sodium by forming the sulfide in a first step and then heating it with carbon and a material which forms stable sulfides. The first step of Lavoisier's process can be carried out by heating sodium carbonate, oxide, chloride or fluoride with CS<sub>2</sub> vapors or with sulfur to give the sodium sulfide.

Specketer<sup>215</sup> describes a process for the reduction of sodium sulfide with calcium carbide according to the equation:



The same reaction is covered by Specketer and Hofmann<sup>216</sup> and in a patent by Chemische Fabrik Griesheim Elektron<sup>22</sup>.

**Processes Using Sodium Aluminate**

Sodium aluminate or mixtures of sodium aluminate and sodium carbonate can be reduced with carbon in an electric furnace. This process is described by Emanuel<sup>49</sup>, by Batsford<sup>52</sup>, by Regelsberger<sup>221</sup> and by Gmelin<sup>193</sup>.

**Processes Using Sodium Cyanides**

Sodium cyanide, ferrocyanide, or ferricyanide can be reduced to sodium by heating with finely-divided iron at about 1200°C



according to Bucher<sup>43, 44</sup>. Aluminum and magnesium may be used to replace the iron.

**Processes Using Sodium Peroxide**

The production of sodium from sodium peroxide is considered here, although the economics of such a process are certainly unattractive. However, sodium can be produced from its peroxide and some cyclic process might involve recovery of sodium from sodium peroxide.

Sodium peroxide is reduced to sodium on heating with powdered charcoal at 300 to 400°C, according to the equation:



A similar reaction, but one which proceeds with explosive violence is that with calcium carbide



as described by Thorpe<sup>222</sup>, Gmelin<sup>193</sup> and Friend<sup>98</sup>.

**Processes Using Misc. Sodium Salts**

The report of DeBoer *et al.*<sup>78</sup> states that sodium chromate is reduced by zirconium. The reaction begins at about 740°C and a yield of 70% sodium and 30% sodium oxide is reported. The same authors report that sodium dichromate heated with zirconium in a ratio of 1:10 evolved sodium at 250°C and that yields of 50% sodium and 25% sodium monoxide were obtained. This same report states that sodium molybdate can be effectively reduced with zirconium at about 550°C and that sodium tungstate can be reduced to sodium at 450°C.

The reduction of sodium nitrite with calcium carbide and a second sodium salt containing no oxygen is described by Danckwardt<sup>45</sup>. Some representative equations are:



Sodium silicate can be reduced to sodium with charcoal at 900 to 1300°C, according to Peacock<sup>213</sup>. The reduction of sodium silicate or ferrosilicate with iron in an electric furnace is described by Morrison<sup>199</sup>.

**SODIUM BY ELECTROLYSIS OF MOLTEN SODIUM SALTS**

The development of cells for the electrolysis of fused sodium salts has been described by Moltkehanzen and Eger<sup>198</sup>. The first patents on sodium manufacture are also discussed by them<sup>198</sup> and by Borchers in his handbook on electrometallurgy<sup>23</sup>.

A large number of salts and salt mixtures have been proposed for electrolysis to sodium. Some of these mixtures simply involve the addition of

a second salt to lower the melting point of the primary salt. Scholl<sup>283</sup> discusses a cell for the electrolysis of a melt of equal parts of NaOH and Na<sub>2</sub>S.

Reviews on the electrolytic manufacture of sodium include those by Davis<sup>28</sup>, Waeser<sup>286</sup>, Ryska<sup>285</sup>, Kirchrath<sup>186</sup> and Arndt<sup>11</sup>.

A summary of the types of cells proposed for the electrolytic production of sodium is that by Ryska<sup>285</sup>. Energy consumption in sodium manufacture in the years 1918, 1928, and 1938 has been tabulated by Walde<sup>287</sup>.

A variety of specific proposals have been made for cell construction for the electrolytic manufacture of sodium. Details of some early electrodes have been covered by Boelsterli<sup>28</sup>.

### Processes Using Sodium Hydroxide

Sodium was first prepared by electrolysis from sodium hydroxide. Sodium is formed at the cathode and the anode reaction is:



A secondary reaction occurs at the cathode when water diffuses through the bath and reacts with sodium:



This gives an over-all reaction:



and since water reacts with half the sodium produced, the yield can never be more than 50% of theoretical and other reactions in the cell may lower the yield even more. Thus, sodium may diffuse to the anode and react with oxygen to form Na<sub>2</sub>O<sub>2</sub>. This reacts with more sodium to give Na<sub>2</sub>O.

If commercial NaOH is used, the water is first electrolyzed to give oxygen at the anode and hydrogen at the cathode. Hydrogen production becomes more difficult until, at the decomposition voltage of fused NaOH, sodium appears. If no moisture is present, no hydrogen is evolved before the sodium appears.

Decomposition voltages, according to Mellor<sup>297</sup>, are as follows:

- 1.3 volts; water present in NaOH
- 2.2 volts; sodium in fused NaOH
- 3.1 volts; calculated from Thomson's rule
- 4.4 volts; calculated from heat of formation.

Labhardt<sup>263</sup> describes removal of NaOH which has absorbed water and replacement with anhydrous alkali in cell operation in manufacturing sodium from caustic.

Other observations on the decomposition voltage of NaOH are to be found in a book by Billiter<sup>28</sup> and in an article by Baur<sup>28</sup>.

The electrode reactions in the electrolysis of sodium hydroxide have been discussed by Ashcroft<sup>14</sup>, Carrier<sup>17</sup>, and Neumann and Giertsen<sup>289</sup>.

**The Castner Process.** The Castner electrolytic process has been described by the inventor<sup>21</sup>. Castner's life and personal notes on the development of the Castner process have been presented by Fleck<sup>28</sup>.

Commercial practice of the Castner process at the Vadheim Electrochemical Works in Sogn, Norway, and at the Fredrikstad Electrochemical Plant in Fredrikstad is described by Moltkehanzen<sup>290</sup>. Detailed plant investment and operating costs for Castner process plants are available in Moltkehanzen and Eger<sup>289</sup>.

The Castner cell as shown in Figure 2.4 consists of an iron container surrounded by brickwork so that the exterior of the cell body can be heated with gas flames. The cathode (iron, copper, or nickel) enters from a bottom well, as described by Wallace<sup>267a</sup>.

A cylindrical sodium collector is supported directly above the cathode. Below this collector is a cylinder of iron-wire gauze which surrounds the upper position of the cathode and serves as a diaphragm. This gauze cylinder is enclosed in turn by the iron or nickel anode which may consist of a cylinder or a series of bars suspended from the cover of the cell.

Some sodium particles pass through the screen to the anode where they react with atmospheric or anodic oxygen, causing small explosions and some yield loss. If a very fine mesh screen is used, it will act as a bipolar

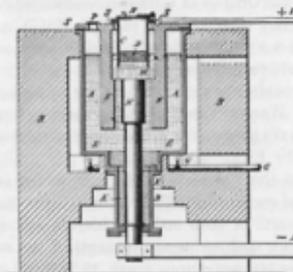


FIG. 2.4. Cross-Section of Castner Electrolytic Cell

- |                           |                        |
|---------------------------|------------------------|
| A—Iron cell body          | I—Anode connection     |
| B—Base pipe               | K—Molten caustic       |
| C—Sodium collector vessel | L—Cathode connection   |
| D—Sodium metal            | M—Iron gauze cylinder  |
| E—Molten caustic          | N—Lid                  |
| F—Anode                   | P—Gas escape port      |
| G—Gas burners             | R—Brickwork receptacle |
| H—Cathode                 | S—Asbestos insulation  |

electrode. Nonconducting screens of alumina or similar material have been proposed but, according to Koehler<sup>105</sup>, do not appear to be practicable.

The commercial Castner cells are about 18 inches in diameter and 24 inches deep and each hold about 250 pounds of molten caustic. The caustic used has to be pure and dry; dryness is insured by the addition of metallic sodium where necessary.

These cells are connected in series. The voltage across each cell is 4.5 to 5.0 volts. The anode current density is 150 amps per sq dm and the cathode density 200 amps per sq dm. A 1250-ampere cell holding 150 pounds of caustic averages 10 kg sodium per day. The current efficiency averages 36% for long periods. Taking the decomposition potential of NaOH as 2.25 volts at 340°C, the energy efficiency of such a cell is about 18%, according to Allmand and Ellingham<sup>3</sup>.

The variation in current efficiency with composition has been determined for NaOH-Na<sub>2</sub>CO<sub>3</sub> mixtures<sup>31</sup>.

% Na <sub>2</sub> CO <sub>3</sub>	Current Efficiency
2	25
17	63.03
27	40

The current yields of sodium for NaOH-NaCl mixtures are lower than for NaOH alone. Only 39% was obtained in the best run. No chlorine was generated from the electrolysis of mixtures containing 25 to 50% NaCl.

Asheroff<sup>104</sup> points out that addition of 30% NaCN and seven parts of NaCl or Na<sub>2</sub>CO<sub>3</sub> to a sodium hydroxide bath gives a mixture melting at 250°C which does not readily form crusts.

The sodium hydroxide was premelted before introduction to the cell in the Castner process. Waeser<sup>106</sup> describes this aspect in some detail.

A porous alumina diaphragm for use in the electrolysis of molten caustic has been described by Ewan<sup>90, 91</sup>.

The electrolyte in the Castner cell contains added sodium chloride to improve its electrical conductivity<sup>106</sup>. In addition, the caustic raw material contains small amounts of both sodium chloride and sodium carbonate. Therefore, the chloride and carbonate contents of the cell increase during operation. When the concentrations reach 18% NaCl and 8% Na<sub>2</sub>CO<sub>3</sub>, the bath is discarded and operation is started with a fresh charge. The caustic is recovered from this discarded bath by dissolving it in water, removing the chloride and carbonate, and reconcentrating the caustic. Koehler<sup>105</sup> states, however, that the presence of sodium chloride was objectionable because it attacked the iron parts of the cell and fouled the electrolyte. He therefore recommends mercury-cell caustic as a preferable charge material for Castner sodium cells.

Hydrogen can be collected from the anode compartment if desired.

Originally sodium was removed by hand from the cathode chamber with a perforated ladle that retained the sodium and allowed the molten caustic to flow back into the cell. However, mechanical means were later developed for separation and removal of the sodium.

The most favorable operating temperature for the Castner cell is 320 to 330°C<sup>104</sup>. An outside source of heat is needed to maintain this temperature in small cells but the combination of heat of reaction and heat produced by the current make external heating unnecessary in large cells. However, the operating temperature of the cell should not be much above the melting point of caustic (318°C for pure NaOH, 300°C for material containing impurities) or excessive diffusion will occur, reducing sodium production<sup>104</sup>. Thus, operation at 25°C above the melting point will cause the rate of recombination of the sodium to equal the rate of decomposition of the hydroxide and production will be zero. On the other hand, a theoretical yield of sodium can be obtained at a temperature 5°C above the melting point of the bath. Operation at low current density also reduces convection currents.

From the development of Castner's cell for the electrolysis of caustic in 1891 until about 1920, this was the only sodium process of practical importance. Sodium metal production was about 15,000 tons per year during this period.

The Castner cell is described by Mantell<sup>107</sup>.

The advantages of the Castner cell are simplicity of construction and low temperature operation. However, because pure sodium hydroxide is a relatively expensive chemical raw material, the Castner process has been superseded by the Downs process based on sodium chloride.

**Other Modifications.** A larger cell for the electrolysis of caustic was developed by T. Kolkin, the technical director of the Vadheim Works in Norway<sup>109, 106</sup>. The Kolkin cell overcame diaphragm troubles encountered in the Castner cells at the Vadheim works.

Another modification of the basic Castner cell is credited to Becker<sup>24, 25</sup>. Work on the Becker process by LeBlanc and Carrier has been published<sup>108, 107, 105</sup>.

The Hulin cell<sup>102, 104, 102</sup> differs from the original Castner cell mainly in electrode-mounting details. Another patent by Hulin<sup>107</sup> is also directed toward a clean cathode—in this case by periodic current reversal.

A development described by Rathenau and Suter<sup>103</sup> features a contact cathode that is immersed only a few millimeters in the electrolyte, thereby preventing loss of sodium through side reactions with the bath.

Neumann and Giertsen<sup>100</sup> described another modified cathode form for a Castner cell.

According to Kirk and Othmer<sup>104</sup>, a Castner-Krebs cell with a hollow cathode has been operated in Japan.

### Processes Using Sodium Chloride

In industry research emphasis was on the development of a practical cell for the manufacture of sodium from sodium chloride. Even Faraday<sup>28</sup> conducted experiments in 1833 with the object of obtaining sodium by the electrolysis of sodium chloride. An early patents on chloride electrolysis are those by Rogers<sup>226</sup>, Grabau<sup>127</sup>, Acker<sup>2</sup>, Ashcroft<sup>13</sup>, and R. J. McNitt who patented a design in 1917<sup>273</sup>.

However, the cell which finally achieved success was the Downs cell<sup>10</sup>. The Downs cell benefits from the advantages of using sodium chloride as opposed to sodium hydroxide as a source of sodium, as follows:

1. Sodium chloride is cheaper.
2. Sodium chloride is more easily available.
3. Chlorine is produced as a valuable by-product. (It must be pointed out, however, that chlorine is also produced as a by-product in the manufacture of the caustic later used for electrolysis in the Castner process.)
4. Increased current efficiencies are possible.

Furthermore, the Downs cell has successfully conquered the disadvantages of employing sodium chloride which include:

1. The corrosive effect of NaCl on refractory surfaces.
2. The need for special handling equipment for the chlorine evolved.
3. The higher cell temperature which must be maintained since NaCl

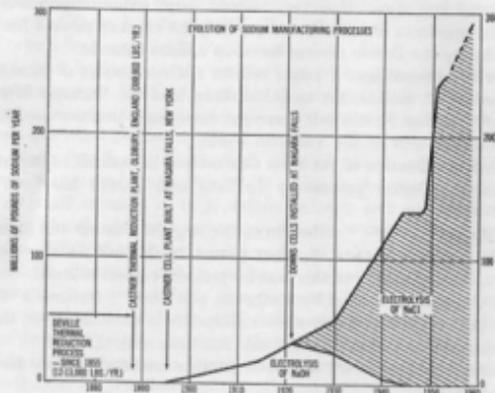


FIG. 2.5. Historical Trends in Sodium Manufacturing Processes

melts at 800°C as compared with 300°C for NaOH. (At 800°C, the vapor pressure of sodium is almost half an atmosphere and sodium becomes soluble in NaCl.)

However, Thorpe states<sup>251</sup> that the high working temperature (600°C) and the high operating voltage of the Downs cell imply substantial maintenance costs and a theoretically poor energy efficiency. Thus, many other salt mixtures have been investigated, as described by Danee<sup>16</sup>. The ascension of the sodium chloride process is illustrated in Figure 2.5.

According to Danee<sup>16</sup>, the decomposition voltage of NaCl is 4.2 volts. Among the salts proposed for addition to NaCl to lower its melting point in sodium cell operation are the following:

Material	References
CaCl <sub>2</sub>	192
	31
	193
KCl and an alkaline earth chloride	193
	251
KCl and Na <sub>2</sub> CO <sub>3</sub>	98
	103
KCl and NaF	193
	65
KF	192
	98
NaF	193
	31
NaF and an alkaline earth chloride	193
	193

The questions of melting points and decomposition voltages of sodium chloride and salt mixtures containing sodium chloride are discussed in detail in Engelhardt's "Handbuch der Technischen Elektrochemie". Volume III of this series is entitled "Die Technische Elektrolyse im Schmelzfluss" and the initial section by von Steinwehr<sup>262</sup> deals with the theoretical aspects of the electrolysis of melts. The second section by Moltkehanen and Eger<sup>198</sup> deals with production of the alkali metals.

The addition of aluminum to a fused chloride bath for sodium manufacture is covered by Grebe and Boundy<sup>115</sup>. An oxide in the bath is thus precipitated as sodium aluminate.

To obtain good results in the electrolysis of fused NaCl,

1. The anode must be made of graphite
2. The anode space must permit the easy removal of chlorine
3. The cathode must be metallic, preferably iron
4. The cathode space must permit the sodium to be collected and removed without coming in contact with reducible substances.
5. Fire-resisting materials must be used for all parts of the cell

6. No metallic particles should be present in the melt between the poles.

In the electrolysis of mixtures of fused carnallite ( $MgCl_2$ ) with  $NaCl$ , very little sodium is found in the magnesium metal product until the  $MgCl_2$  concentration falls below one per cent, according to Shcherbakov and Yumanova<sup>128</sup>.

A unique type of cell construction for the electrolysis of sodium chloride to produce sodium is covered by Brode<sup>12</sup>. The cathodes come up through the cell floor and are surrounded by a dome-shaped partition, entirely below the surface of the melt. Sodium is withdrawn from underneath the top of this dome.

Improved current efficiencies are claimed for sodium cell operation at very high temperatures at which sodium is volatilized from the cell as it is formed. A patent by Grebe and Boundy<sup>129</sup> describes the apparatus for such a process.

**The Acker Cell.** The Acker cell<sup>1, 2, 4, 5, 3</sup> is of historic interest because it was the first cell to produce sodium from sodium chloride. The sodium was obtained as a sodium-lead alloy and was ultimately recovered in the form of  $NaOH$  by steam decomposition of the lead alloy.

A cross-section of an Acker cell is shown in Figure 2.6. The sodium produced in the cathode chamber alloys with a layer of molten lead in the bottom of the cell to give sodium-lead alloy. Steam decomposes the alloy and circulates the mixture of lead and caustic around the cell. As the mixture circulates, caustic and hydrogen are disengaged and removed, and the lead re-enters the cathode chamber to undergo further alloy formation.

The Acker cell operated at  $850^\circ C$  ( $1562^\circ F$ ) and this temperature was maintained entirely by the current. The cell required 6 to 7 volts and had an average current efficiency of about 94%.

**The Ashcroft Cell.** The Ashcroft cell, as described in the literature<sup>13, 14, 20, 21</sup>, has been operated on a large commercial scale in Norway.

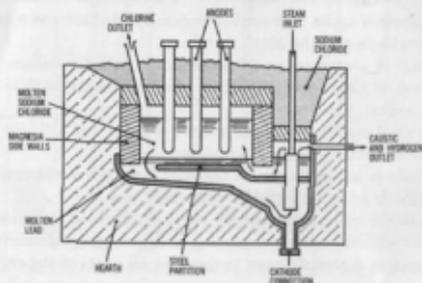


FIG. 2.6. Section of Acker Electrolytic Cell

As shown in Figure 2.7, the cell consists of two compartments: a decomposing compartment in which the primary electrolysis takes place—and the producing compartment in which a second electrolysis is carried out.

In the second compartment, fused sodium hydroxide is used as the electrolyte and sodium metal is deposited on a spherical nickel cathode. A hood above this cathode collects the sodium, which leaves the cell continuously through a riser pipe.

The operating temperature in the decomposing compartment of the Ashcroft cell is about  $770^\circ C$  ( $1418^\circ F$ ). The current density at the cathode is about 1860 amps per sq ft (200 amps per sq decimeter). The temperature in the producing compartment is  $330^\circ C$  ( $626^\circ F$ ).

The pipe connecting the two chambers has a partition along its entire length. The hot lead-sodium alloy passes through one side of the pipe and the denuded lead alloy through the other, the partition acting as a heat-exchange surface.

The  $NaCl$  compartment takes about 7 volts, the  $NaOH$  compartment 2 volts. The current is about 2000 amps.

**The McNitt Cell.** In the McNitt cell<sup>172, 178, 179</sup> shown in Figure 2.8, the cathode is in the middle of the cell surrounded by an annular anode. The hood over the cathode collects the metallic sodium. The cell is rather tall with the object of increasing the hydrostatic pressure in the electrolyzing zone and thus raising the boiling point of the sodium formed. The structure of the McNitt cell is thus similar to that of the Downs cell, except that the McNitt cell has the cathode in the central position.

In a variation of the basic McNitt cell<sup>180</sup>, the molten electrolyte is flowed through a number of cells in the same electrical circuit.

In recent years, R. J. McNitt has been granted a number of patents on specific equipment modifications for sodium cells, but not for the central-cathode cell which is referred to above as the McNitt cell. Rather, they involve modifications of Downs type cells. They include:

A technique for feeding salt to cells<sup>181</sup>

An instrument for the detection of cell diaphragm failure<sup>184</sup>

A sodium collector hood design<sup>185</sup>

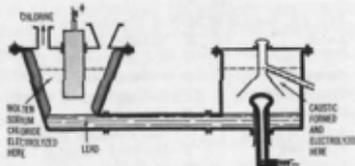


FIG. 2.7. Section of Ashcroft Electrolytic Cell

Recovery of light metal from a fused bath<sup>186</sup>

Electrolyte circulation for heat transfer<sup>187</sup>

Current regulation for increased cell efficiency<sup>188</sup>

Auxiliary purifying electrodes for removal of oxides from the bath<sup>189</sup>

Heat regulation for improved cell efficiency<sup>190</sup>

**The Daneel-Lonza Cell.** Three other cells for the electrolysis of fused NaCl have been operated on a commercial scale. The Daneel-Lonza cell described by Daneel<sup>14, 45, 46, 47</sup> and by Arndt<sup>12</sup> was the first of these and employed ceramic walls or "salt curtains" to confine the sodium to the cathode area; no diaphragms were used. The name of this cell is derived from the fact that the cell invented by Daneel was used by the firm of Elektrizitätswerk Lonza.

**The Seward Cell.** The Seward cell, using the contact-electrode principle with the cathode immersed only a few millimeters in the electrolyte, was used by the Virginia Electrolytic Company.

The Seward cell has been described by von Kugelgen and Seward<sup>191, 192</sup>,

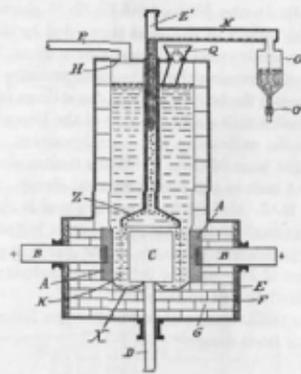


FIG. 2.8. Section of McNitt Electrolytic Cell

A—Anode	K—Metallic diaphragm
B—Conductor	N—Sodium overflow pipe
C—Cathode	O—Sodium receiver
D—Conductor	O'—Sodium drawoff valve
E—Steel vessel	P—Chlorine duct
F—Asbestos lining	Q—Salt charging port
G—Fire brick	Z—Inverted collector bell
H—Cover	Z'—Riser pipe

by Seward, von Kugelgen and von Bidder<sup>193</sup> and by von Kugelgen, von Ridder and Seward<sup>194</sup> and by von Bidder<sup>194</sup>.

Seward and von Kugelgen<sup>194</sup> covered an electrolyte composition containing sodium fluoride and an alkaline earth metal chloride. Another patent<sup>195</sup> by von Kugelgen and Seward was quite similar.

Von Kugelgen and Seward<sup>197</sup> also covered a cell using a molten metal anode of silver or copper such that the chlorine liberated formed a chloride of one of these metals.

**The Giba Cell.** The Giba cell was an adaptation of the Castner cell for the electrolysis of caustic to sodium chloride. A mixture of sodium chloride and other chlorides which were molten at 620°C were electrolyzed in rectangular or oval cells heated only by the current.

The Giba cell was developed by L. Lhuib and E. Steinbuch of Ges. für Chem. Ind., Basle (Soc. Anon pour L'Ind. Chim. à Basle) and patented by them<sup>193, 240, 241, 242</sup>. Another modification of the Giba design was patented by Steinbuch<sup>240</sup>.

**The Downs Cell-Arrangement.** The Downs electrolytic process and cell are described by Downs<sup>99, 229</sup>. The essential characteristic of the Downs cell was the provision of a central anode and a surrounding cathode defining an annular electrolysis zone.

The Downs cell consists of a steel shell lined with refractory and insulating brick as shown in Figure 2.9. The graphite anode projects upward from the bottom of the cell and is attached to the electrical connections<sup>200</sup>. The cathode is a cast-steel cylindrical ring, supported by projecting iron arms which extend through the cell walls to the electrical connections.

Over the anode and submerged in the electrolyte is a conical collector bell for chlorine gas, made of iron or refractory material. Cornell<sup>17</sup> describes a baffle to lessen splashing and deposition of salt in this dome.

Around the lower edge of the bell is an inverted annular launder or trough, also submerged, for collecting the sodium. There are screens extending downward from this bell assembly between the electrodes which serve to prevent the sodium from recombining with the chlorine. A riser pipe attached to the top of the launder permits the sodium to flow continuously into an external receiver. The riser pipe extends far enough above the bath level so that the sodium (sp gr 0.88) can overflow but the bath (sp gr 2.1) cannot. The riser pipe and receiver also permit the sodium to cool before it passes to the filter where calcium is removed.

The electrolyte contains an added salt, calcium chloride, which depresses the melting point of pure NaCl which is 800°C to 505°C for the eutectic mixture containing 66.8% CaCl<sub>2</sub>. In commercial Downs cell operation, however, 58 to 59% CaCl<sub>2</sub> is used at a permissible operating temperature of 575 to 585°C, which simplifies cell construction and the choice

of materials of construction. The salt is purified and dried before being fed to the cell through openings in the cell covers.

The sodium produced in the cell is pure, except for dissolved calcium (except, of course, for traces of various impurities, usually arising from the salt from which the sodium is made—see Chapter 8 for detailed analyses). The solubility of calcium in sodium is as follows:

°C	%
600	5.5
(eutectic) 505	—
400	4
200	2
(m.p. of Na) 97.5	0.01

During cooling in the riser pipe, an appreciable amount of calcium crystallizes out and, because of its higher density, falls back into the electrolyte

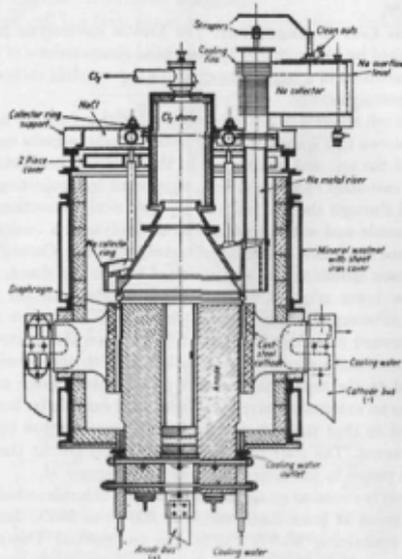


Fig. 2.9. Section of Downs Electrolytic Cell (from C. L. Mantell, "Industrial Electrochemistry").

and reacts with it. The operation of such a riser pipe is described by Hulse<sup>142</sup> and the construction of the tickler in the riser pipe is described by Hulse and Hardy<sup>144</sup>.

The crude sodium issuing from the receiver following the riser pipe is filtered at 105 to 110°C to reduce the calcium content below 0.04% and to separate small amounts of bath and oxides. The purity of the sodium is 99.9% and the chlorine as produced is pure enough to be liquefied and marketed.

The cell operates at about 7 volts, according to Mantell<sup>107</sup>, and at a current efficiency of 80 to 85%. This corresponds to an energy consumption of 5 KWH of AC power per pound of sodium, allowing for a 6 to 8% loss in converting AC to DC power.

Electrode manufacture has been covered in a number of patents. Gilbert<sup>104</sup> covers the manufacture of graphite anodes. Attachment of the anode to the bottom plate of the Downs cell to eliminate heat losses at that point is covered by Smith and Williams<sup>203</sup>. Anode sealing and retaining means have also been discussed by Carlisle<sup>65</sup>. Minor improvements on cathode structure have been detailed by Williams<sup>205</sup>.

A report by Gardiner<sup>100</sup> describes the Downs cell as it was operated at Knapsack, Germany. It consisted of a steel shell, five feet in diameter and six feet high, set into the operating floor so that half of it protruded. The shell was internally-lined with acid-resisting brick and externally lagged to conserve heat. A composite cylindrical graphite anode entered through the base of the shell and was surrounded by a cast-steel cathode. The cathode rested on lugs fastened to the lower half of the sides of the cell. The one-and a half inch annulus between anode and cathode had a 16-mesh iron gauze diaphragm centered therein. This gauze was suspended from an inverted circular trough which collected the sodium rising on the cathode side of the diaphragm. Chlorine evolved at the anode passed up through a central nickel dome within the sodium collector. The chlorine contained  $\text{SiCl}_4$  and was therefore washed with water in stoneware towers and then dried with sulfuric acid in similar towers prior to use.

Since the cells operated at 7 to 8 volts, they were commonly arranged as 24 cells connected in series and arranged in two parallel rows.

A cell at Knapsack was started by packing it with a dry mixture of 58%  $\text{CaCl}_2$  and 42%  $\text{NaCl}$  up to the top of the anode. Graphite wedges were placed in the annulus between anode and cathode and a current of 24 kiloamperes passed to melt the salt mixture around the wedges. The wedges were then withdrawn and the cell filled to the top. When all the salt had melted, the diaphragm, sodium collector ring, and chlorine dome were lowered into the cell.

In operation, sodium passed up the riser pipe into a collector tank and

thence to a scale tank from which it was discharged under nitrogen into a filtering vessel held at 120°C. Most of the calcium metal and sodium oxides were removed in the filter. Some calcium metal which deposited on the walls of the riser pipe was scraped back periodically into the collector channel.

The Knapsack cells had a life of several hundred days, determined by the rate of corrosion of the graphite anode. Diaphragms required more frequent renewal, however. A battery of 24 Downs cells operating at 24,000 amperes current produced 250 metric tons of sodium metal per month and 385 metric tons of chlorine. According to Neubauer and Deutseh<sup>100</sup>, the Knapsack plant contained 65 Downs cells operating at 25,000 amperes and producing 650 tons of sodium per month. Energy consumption was 1 KWH per 90 to 95 grams of sodium. Labor requirements at Knapsack were given as 3.45 man-hours per 100 kg sodium, including both process and repair work.

Details of cells similar to the Downs cell are given by McNitt<sup>102, 103</sup>, by du Pont<sup>84, 86</sup> and by Gilbert<sup>100</sup>.

Circulation of the electrolyte or bath in the annular space defined by the anode and cathode of a Downs cell has been the subject of a number of patents. Two techniques are described by Gilbert<sup>100, 101</sup>. One simply involves the use of a perforated cathode and the other involves the use of a gas lift within the cell. Hardy and Hulse<sup>104</sup> describe a perforated anode for improved circulation.

**The Downs Cell Over-All Process.** Some interesting figures on Downs cell operations in the Degussa plant in Germany are presented by MacMullin<sup>100</sup> and a comparison with amalgam cell operation is given in Table 2.1.

The over-all process flow sheet for a modern Downs cell plant is shown in Figure 2.10. It shows the salt purification system and other facilities attendant to the manufacture of sodium.

TABLE 2.1. RAW MATERIAL CONSUMPTION FIGURES FOR DOWNS VS. AMALGAM CELLS (PER POUND OF SODIUM)

	Downs Cell	Amalgam Cell	Reference
Graphite consumed, lbs.	0.0160	0.0007	169
Power consumed, kw-h.	5.91	4.55	169
Chlorine produced, lbs.	1.54	1.88	169
Salt consumed, lbs.	2.83	3.22	169
Mercury consumed, lbs.	—	0.001	169
Calcium chloride consumed, lbs.	0.004	—	100
Calcium metal consumed in purification step, lbs.	—	0.006	69

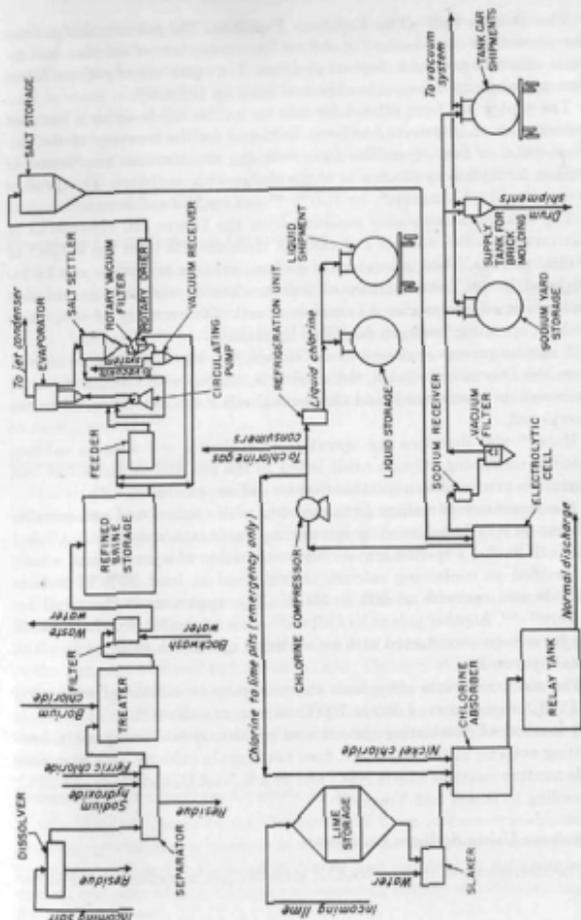


Fig. 2.10. Process flow sheet of modern electrolytic sodium plant (Courtesy of U. S. Industrial Chemicals Company)

**The Downs Cell—The Calcium Problem.** The calcium sludge from the electrolytic manufacture of sodium from a mixture of calcium and sodium chlorides present a disposal problem. The operation of sodium filtration and of sludge removal has been outlined by Gilbert<sup>106</sup>.

The sludge has been offered for sale on an "as is" basis as a low-cost reducing agent. A process has been developed for the recovery of the calcium metal in fine, crystalline form with the simultaneous production of sodium methylate by treatment of the sludge with methanol. This process is described by Calingaert<sup>15</sup>, by Hill<sup>129, 130</sup> and by Hill and Soroos<sup>131</sup>.

The sodium-calcium alloy resulting from the Downs cell electrolysis of mixtures of molten sodium and calcium chlorides has been the subject of several patents. Thus, a mixture of sodium, calcium and oxide can be introduced into a fused mixture of sodium chloride and calcium chloride undergoing electrolysis in a Downs-type cell. The recovery of sodium in such an operation has been described by Hulse<sup>145</sup>.

A similar process is described by Gilbert<sup>130</sup>, wherein sodium is filtered from the Downs cell sludge, the residue is reacted with sodium chloride, more sodium is separated, and the residual salt mixture is returned to the Downs cell.

Hulse<sup>145</sup> also describes the operation of a similar cell wherein calcium chloride containing calcium oxide is fed to the cell and an oxide-free salt mixture is produced as a suitable feed for sodium-producing cells.

The separation of sodium from mixtures with calcium and non-metallic substances may be achieved by introducing the impure sodium into a fused salt bath having a specific gravity higher than that of sodium. Such a bath is specified as containing calcium chloride and at least 30% of sodium chloride and operates at 600 to 800°C. The apparatus is described by Gilbert<sup>107, 113</sup>. Another patent by Gilbert<sup>108</sup> covers a similar process in which impure sodium is contacted with an oxidizing agent such as air or an alkali metal hydroxide.

The sodium-calcium alloy from the cells may be contacted with solid NaCl at temperatures of 500 to 700°C to recover sodium<sup>146</sup>.

A method of eliminating the calcium problem would be to use a low-melting eutectic in the cell which does not contain calcium. One such possible mixture contains 35.6% NaCl and 64.4% Na<sub>2</sub>CO<sub>3</sub> and melts at 600°C, according to Smith and Veazey<sup>207, 208</sup>.

### Processes Using Sodium Carbonate

The electrolysis of molten Na<sub>2</sub>CO<sub>3</sub> gives sodium according to the equation:



Sodium chloride may be added to lower the melting point of sodium carbonate and even when a mixture of 55% Na<sub>2</sub>CO<sub>3</sub> and 45% NaCl is electrolyzed at high current density, chlorine is evolved. Metal anodes cannot be used because of oxidizing conditions in the melt and even carbon anodes are attacked by oxygen with the formation of CO<sub>2</sub><sup>105</sup>.

The electrolysis of sodium carbonate to sodium is covered by a patent by Dickson<sup>147</sup> and a number of patents by Chemische Fabrik Von Heyden<sup>148, 149, 150</sup>; one patent<sup>149</sup> covers the electrolysis of a molten mixture of sodium carbonate and sodium chloride.

### Processes Using Sodium Tetraborate

Metallic sodium can be obtained by electrolyzing borax at about 800°C in a carbon crucible with an internally-cooled cathode. The cathode deposit consists of pure sodium inside, a layer of sodium and boron, and an outside layer of pure boron covered with solid electrolyte.

The addition of Al<sub>2</sub>O<sub>3</sub> and BeO almost completely prevents reduction of the electrolyte by sodium. On the other hand, sodium production is decreased and boron production increased at high temperatures, according to Austin and Lee<sup>79</sup>.

### Processes Using Sodium Nitrate

Molten sodium nitrate can be electrolyzed to give sodium metal. Graphite or carbon anodes are used and NO<sub>2</sub> and O<sub>2</sub> are evolved at the anode.

J. D. Darling first reduced sodium nitrate electrolytically to sodium nitrite in 1889 as described in a series of patents<sup>21, 22, 23, 24, 25, 26, 27</sup> and articles<sup>68, 69, 70</sup>.

Other work on the electrolysis of alkali nitrates has been reported by Muller<sup>203, 205, 206, 204</sup>.

The electrolysis of molten sodium nitrate is advantageously carried out in the presence of fused sodium carbonate. The second salt serves to suppress the migration of the nitrate anion, fixing the nitrate ion in the anode chamber as carbon dioxide, and forming more sodium nitrate<sup>206</sup>. This prevents migration of nitrate ion to the cathode where it could react with the sodium metal.

### Processes Using Sodium Cyanide

According to Thorpe<sup>201</sup>, the electrolysis of fused sodium cyanide, using graphite anodes and a nickel-wire cathode has also been proposed. The cyanogen produced is absorbed in NaOH and returned to the process. A current efficiency of 90 to 95% and an operating voltage of 6 volts is claimed for such a process.

Acker has been granted patents<sup>6, 7</sup> covering sodium cyanide baths for the electrolytic production of sodium.

Bucher<sup>15</sup> prescribes molten sodium cyanide as the electrolyte in a patented process.

Ashcroft<sup>17</sup> covers sodium manufacture by electrolysis of a mixture of sodium hydroxide and sodium cyanide. The sodium is recovered as sodium-lead alloy.

### Processes Using Sodium Sulfide and Sulfate

The recovery of sodium and sulfuric acid from sodium sulfate by electrolysis is covered at Aten<sup>18</sup>. According to Rogers<sup>22</sup>, sodium can be obtained by the electrolysis of sodium sulfide.

### MANUFACTURE OF SODIUM IN ALLOY FORM

In so-called "double-cell" processes, a sodium alloy or sodium amalgam is produced at the cathode and is decomposed in a secondary cell with the reformation of the cathode metal and the production of a sodium compound.

Early work on the production of sodium alloys and the recovery of sodium from these alloys was conducted by Rogers<sup>23</sup>. This work has also been described by Richards<sup>222, 223, 224</sup>.

Vautin was also an early worker in electrolysis of sodium salts with lead cathodes<sup>224, 225</sup>, and Hulin<sup>226</sup> was still another.

An interesting process patented by Ashcroft<sup>28</sup> covers the treatment of sodium-lead alloy with ammonia, thus recovering the sodium as sodium amide and regenerating the lead. A somewhat similar process is described by Chemische Fabrik Von Heyden<sup>26</sup>.

### Manufacture of Sodium as Sodium Amalgam

The electrolysis of sodium chloride or sodium hydroxide in a mercury cathode cell may be used to produce sodium in the form of sodium amalgam.

A typical cell may be 18 inches wide and 25 feet long. It has mercury seals at each end to keep the electrolyte in the cell. If sodium hydroxide is used as the electrolyte, practically pure oxygen is obtained as a by-product; if sodium chloride is the electrolyte, chlorine is obtained, of course.

The sodium amalgam produced may be used directly in chemical processing, as in the manufacture of sodium methylate, for example. See Figure 2.11.

The manufacture of sodium amalgam will be treated only briefly here since this Monograph is primarily concerned with the manufacture and uses of metallic sodium. However, the largest use of sodium amalgam has been in amalgam cells for the manufacture of caustic where the sodium metal is never isolated as such. Amalgam cells for caustic have been adequately reviewed by Mantell<sup>29</sup>.

An excellent review of the production of sodium amalgam, of the recovery of metallic sodium from such amalgams, and of the uses of sodium amalgam as a chemical intermediate has been presented by MacMullin<sup>19</sup>.

### Manufacture of Sodium as Sodium-Lead Alloy

The use of Pb-Na alloy in producing sodium by electrolysis is described by Carrier<sup>18, 20</sup>. The electrolysis of PbNa alloys to give sodium at the cathode and lead at the anode is discussed by Kremann, Kienzl and Markl<sup>20</sup>. Philipp and Foersterling<sup>224</sup> have described an apparatus for the electrolytic preparation of sodium-lead alloy. Schlotter has described<sup>222</sup> a lead cathode cell for sodium alloy manufacture.

The electrolysis of sodium hydroxide with a lead cathode to produce sodium-lead alloy is covered in a number of patents by Raschen<sup>229</sup> and Ashcroft<sup>18, 21, 24</sup>. A number of patents have also been granted to Ashcroft<sup>19, 22, 23, 27</sup>, Fievet<sup>26</sup>, Orlandi<sup>22</sup>, Hulin<sup>227, 228</sup>, and McNitt<sup>127, 223, 226, 227</sup> for the electrolysis of fused sodium chloride with molten lead cathodes.

The separation of sodium from lead offers a major problem when pure sodium is desired. Hulin has described his work on this problem<sup>229</sup> as has Jelinek and his co-workers<sup>227, 248, 249, 250</sup>.

The production of sodium-lead alloy in a cell using a thin stream of molten lead as the mobile cathode for the electrolysis of fused salt is a feature of a cell developed by Szechtman<sup>26</sup>.

### MANUFACTURE OF SODIUM BY ELECTROLYSIS IN SOLVENT MEDIA

The electrolysis of sodium salts in non-aqueous media is attractive from a research viewpoint in that it offers the possibility of a low-temperature electrolytic process for sodium. Although many organic media do not react with sodium, there remains the problem of picking a medium in which the salt is soluble, one which does not react with sodium, or with the coproduct of the electrolysis of a particular sodium salt.

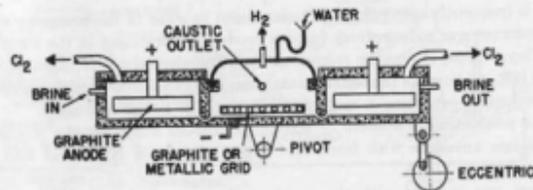


FIG. 2.11. Section of cell for sodium amalgam manufacture (from R. B. MacMullin, *Chem. Eng. Progress*, 46, 440 (1950)).



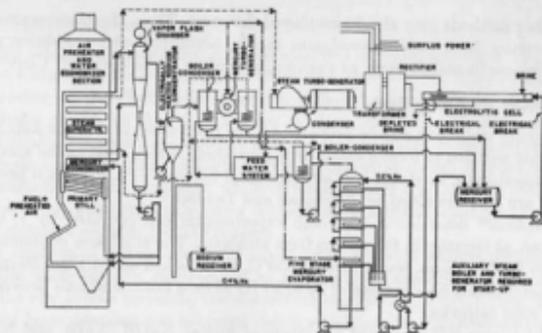


Fig. 2.13. Flow diagram of Moulton process for sodium from amalgam with power generation (from R. B. MacMullin, *Chem. Eng. Progress*, 46, 440 (1950)).

The production of sodium from an alloy with tin or other metals can be carried out by making such an alloy the anode in a fused alkali borate bath, according to Stalhane and Pyk<sup>97</sup>.

### Recovery by Distillation

A number of patents have been issued on the distillation of sodium alloys including one by McNitt<sup>174</sup> and one by Pidgeon<sup>177</sup> which covers an apparatus for the separation of sodium and magnesium by distillation.

A process for the recovery of metallic sodium from amalgam by distillation in a high-temperature binary-fluid steam generator has been proposed by Moulton<sup>180</sup> and by Crahan, Moulton and Seavey<sup>62</sup>. The process flow sheet, as presented by MacMullin<sup>180</sup> is shown in Figure 2.13.

### REFERENCES CITED IN CHAPTER 2

- Achille, P., *Atti V. Congr. nazl. chim. pure applicata*, Rome, 1935 (II), 607-15 (1936).
- Acker, C. E., *Trans. Am. Electrochem. Soc.*, **1**, 165 (1902).
- Acker, C. E., *Trans. Am. Electrochem. Soc.*, **9**, 137 (1906).
- Acker, C. E., U. S. Patent 623,691 (Apr. 25, 1899).
- Acker, C. E., U. S. Patent 623,692 (Apr. 25, 1899).
- Acker, C. E., U. S. Patent 1,116,865 (Nov. 10, 1914).
- Acker, C. E., U. S. Patent 1,142,220 (June 8, 1915).
- Acker, C. E., German Patent 110,548 (Mar. 29, 1898).
- Allmand, A. J. and Ellingham, H. J. T., "Principles of Applied Electrochemistry", 2nd Ed., London, Edward Arnold & Co. (1924).
- Anon, *Chem. Eng.*, **62**, No. 3, 101-102 (1955).
- Anon, *Eng. Mining J.*, **45**, No. 25, 449 (1888); *Abstr. J. Soc. Chem. Ind.*, **7**, 568.
- Arndt, K., *Z. ges. Eisenerei-Praxis: Das Metall*, **46**, 193-95 (1925).
- Arndt, K., "Technische Elektrochemie", Stuttgart, F. Enke (1929).
- Ashcroft, E. A., *Trans. Am. Electrochem. Soc.*, **9**, 123-26 (1906).
- Ashcroft, E. A., *Trans. Am. Electrochem. Soc.*, **9**, 394 (1906).
- Ashcroft, E. A., U. S. Patent 801,199 (Oct. 10, 1905).
- Ashcroft, E. A., U. S. Patent 1,106,384 (Aug. 11, 1914).
- Ashcroft, E. A., U. S. Patent 1,106,436 (Aug. 11, 1914).
- Ashcroft, E. A., U. S. Patent 1,161,585 (Nov. 23, 1915).
- Ashcroft, E. A., U. S. Patent 1,204,234 (Nov. 7, 1916).
- Ashcroft, E. A., British Patent 12,377 (May 30, 1903); *Abstr. J. Soc. Chem. Ind.*, **23**, 25.
- Ashcroft, E. A., British Patent 25,144 (Nov. 4, 1913).
- Ashcroft, E. A., British Patent 26,813 (Dec. 22, 1905).
- Ashcroft, E. A., French Patent 426,960 (Feb. 10, 1911).
- Ashcroft, E. A., French Patent 494,951 (Nov. 14, 1913).
- Ashcroft, E. A., German Patent 158,574 (Oct. 9, 1903).
- Ashcroft, E. A., German Patent 268,826 (Feb. 27, 1912).
- Ashcroft, E. A., German Patent 274,304 (Feb. 27, 1912).
- Aten, A. H. W., U. S. Patent 2,250,023 (Jan. 28, 1941).
- Auslin, L. W. and Lee, P. W., Canadian Patent 258,442 (Feb. 23, 1926).
- Barth, A., German Patent 258,353 (Feb. 27, 1912); *Abstr. J. Soc. Chem. Ind.*, **32**, 608.
- Batsford, H. E., *Chem. Met. Eng.*, **26**, 888-94 (1922).
- Batsford, H. E., *Chem. Met. Eng.*, **26**, 932-35 (1922).
- Baur, E., *Z. Elektrochem.*, **27**, 194 (1921).
- Becker, H., in V. Engelhardt, "Monographien über Angewandte Elektrochemie", **9**, Halle, W. Knapp (1903).
- Becker, H., German Patent 104,955 (Jan. 21, 1890).
- Bില്ലiter, J., "Technische Elektrochemie", **3**, Halle, W. Knapp (1932).
- Blackmore, H. S., U. S. Patent 391,110 (Oct. 16, 1888).
- Blackwell, H. A. and Turner, W. L., British Patent 486,930 (June 10, 1938).
- Boelsterli, J., U. S. Patent 589,523 (Sept. 7, 1897).
- Borchers, W., "Elektro-Metallurgie", Braunschweig, H. Bruhn (1896).
- Bowe, L. E., U. S. Patent 2,484,366 (Oct. 11, 1949).
- Brode, J., U. S. Patent 1,258,529 (Mar. 5, 1918).
- Bucher, J. E., U. S. Patent 1,079,974 (Dec. 2, 1913).
- Bucher, J. E., French Patent 453,086 (Jan. 13, 1913).
- Calingaert, G. (to Ethyl Corp.), U. S. Patent 2,543,399 (Feb. 27, 1951).
- Carlisle, J. W. (to Ethyl Corp.), U. S. Patent 2,648,631 (Aug. 11, 1953).
- Carrier, C. F., Jr., *Electrochem. Met. Ind.*, **4**, 442-46 (1906).
- Carrier, C. F., Jr., *Trans. Am. Electrochem. Soc.*, **9**, 363 (1906).
- Carrier, C. F., *Chem. Met. Eng.*, **8**, 255-57 (1910).
- Carrier, C. F. (to Elmira Electrochemical Co.), U. S. Patent 830,051 (Sept. 4, 1906).
- Castner, H. Y., U. S. Patent 342,897 (June 1, 1886).
- Castner, H. Y., U. S. Patent 452,030 (May 12, 1891).
- Chemische Fabrik Griesheim Elektron, French Patent 416,926 (June 9, 1910).
- Chemische Fabrik von Heyden, British Patent 25,957 (Nov. 12, 1913).
- Chemische Fabrik von Heyden, French Patent 464,661 (Nov. 8, 1913).
- Chemische Fabrik von Heyden, German Patent 269,712 (Nov. 19, 1912).
- Chemische Fabrik von Heyden, German Patent 273,256 (Nov. 5, 1911).

57. Corneil, E. R., U. S. Patent 2,218,021 (Dec. 15, 1940).  
 58. Cowles, A. H., *Electr. Ind.*, **2-3**, 384 (1904).  
 59. Cowles, A. H., *Z. Elektrochem.*, **8**, 187,208 (1902).  
 60. Cowles, A. H., U. S. Patent 673,761 (May 7, 1901).  
 61. Cowles, A. H., U. S. Patent 679,253 (July 23, 1901).  
 62. Crahan, P. F., Moulton, S. A. and Seavoy, G. E., U. S. Patent 1,961,135 (June 5, 1934).  
 63. Danekwardt, P., U. S. Patent 746,796 (Dec. 15, 1903).  
 64. Daneel, H., *Chem. App.*, **13**, 90-91 (1926).  
 65. Daneel, H., *Chem. Met. Eng.*, **30**, 144-47 (1925).  
 66. Daneel, H., *Z. Elektrochem.*, **30**, 145-57 (1924).  
 67. Daneel, H., German Patent 268,280 (Dec. 12, 1913).  
 68. Darling, J. D., *J. Franklin Inst.*, **153**, 65-67 (1902).  
 69. Darling, J. D., *J. Soc. Chem. Ind.*, **2**, 334 (1904).  
 70. Darling, J. D., *Z. Elektrochem.*, **8**, 150 (1902).  
 71. Darling, J. D., U. S. Patent 517,001 (Mar. 20, 1894).  
 72. Darling, J. D., U. S. Patent 590,826 (Sept. 28, 1907).  
 73. Darling, J. D., U. S. Patent 641,276 (Jan. 16, 1900).  
 74. Darling, J. D. and Forest, H. C., German Patent 83,097 (Mar. 20, 1894).  
 75. Darling, J. D. and Harrison, C. L., German Patent 97,166 (Sept. 29, 1897).  
 76. Darling, J. D. and Harrison, C. L., German Patent 115,746 (Nov. 29, 1899).  
 77. Darling, J. D. and Harrison, C. L., German Patent 118, 178 (Nov. 29, 1899).  
 78. Davis, F. J. H., *Naturwissenschaften*, **102**, 104-13 (1916).  
 79. DeBoer, J. H., Broos, J. and Emmens, H., *Z. anorg. allgem. Chem.*, **191**, 113-121 (1930).  
 80. Deville, H. St. C., *Compt. rend.*, **38**, 279 (1854).  
 81. Deville, H. St. C., *Compt. rend.*, **39**, 321 (1854).  
 81a. Deyrup, A. J. (to du Pont), U. S. Patent 2,685,505 (Aug. 3, 1954).  
 81b. Deyrup, A. J. and Knox, J. J. (to du Pont), U. S. Patent 2,685,346 (Aug. 3, 1954).  
 82. Dickson, J., British Patent Appl. No. 2,206 (Aug. 13, 1892).  
 83. Downs, J. C. (to du Pont), U. S. Patent 1,501,756 (July 15, 1924).  
 84. du Pont de Nemours & Co., E. I., British Patent 522,635 (June 24, 1940).  
 85. du Pont de Nemours & Co., E. I., British Patent 523,008 (July 3, 1940).  
 86. du Pont de Nemours & Co., E. I., German Patent 660,503 (May 30, 1938).  
 87. Emanuel, P. A., British Patent 29,046 (Aug. 27, 1910).  
 88. Emanuel, P. A., U. S. Patent 937,758 (May 10, 1910).  
 89. Emanuel, P. A., U. S. Patent 937,756 (May 10, 1910).  
 90. Ewan, T., *Electr. Ind.*, **2**, 34, 70 (1904).  
 91. Ewan, T., British Patent 218,606 (Apr. 3, 1923).  
 92. Ewan, T. (to Cassel Gold Extracting Co., Ltd.), U. S. Patent 745,958 (Dec. 1, 1903).  
 93. Farsday, M., Ostwald's Klassiker der exakten Wissenschaften, No. 86, Leipzig.  
 94. Fedot'ev, N. P. and Kinkul'skaya, R. N., "Proc. First All-Union Conf. on Non-Aqueous Solutions" (USSR), **1935**, 114-41.  
 95. Fievet, H. E. L., French Patent 608,893 (Feb. 3, 1909).  
 96. Fleck, A., *Chem. & Ind.*, **66**, 515-21 (1945).  
 97. Freeman, H., U. S. Patent 1,319,148 (Oct. 21, 1919).  
 98. Friend, J. N., "A Textbook of Inorganic Chemistry", II, Philadelphia, J. B. Lippincott & Co. (1924).  
 99. Gardiner, W. C., PB-44670 (FIAT Final Report 819) (May 16, 1946).

100. Gardiner, W. C., PB-44671 (FIAT Final Report 820) (June 20, 1946).  
 101. Gel'd, P. V., Mikulinskii, A. S., Polyakova, M. S., Selyanskii, A. P., *Zaur. Priklad. Khim.*, **20**, 800-08 (1947).  
 102. Gesellschaft fur. Chem. Ind., Basle, British Patent 18,300 (Aug. 2, 1910).  
 103. Gilbert, H. N. (to du Pont), German Patent 709,741 (July 17, 1941).  
 104. Gilbert, H. N. (to du Pont), U. S. Patent 1,714,165 (May 21, 1929).  
 105. Gilbert, H. N. (to du Pont), U. S. Patent 1,837,770 (Dec. 22, 1931).  
 106. Gilbert, H. N. (to du Pont), U. S. Patent 1,943,307 (Jan. 16, 1934).  
 107. Gilbert, H. N. (to du Pont), U. S. Patent 2,029,998 (Feb. 4, 1936).  
 108. Gilbert, H. N. (to du Pont), U. S. Patent 2,054,316 (Sept. 15, 1936).  
 109. Gilbert, H. N. (to du Pont), U. S. Patent 2,056,184 (Oct. 6, 1936).  
 110. Gilbert, H. N. (to du Pont), U. S. Patent 2,073,031 (Mar. 16, 1937).  
 111. Gilbert, H. N. (to du Pont), U. S. Patent 2,224,814 (Mar. 15, 1938).  
 112. Gilbert, H. N. (to du Pont), U. S. Patent 2,148,404 (Feb. 21, 1939).  
 113. Gilbert, H. N. (to du Pont), U. S. Patent 2,150,437 (Mar. 14, 1939).  
 114. Gilbert, H. N. (to du Pont), U. S. Patent 2,224,814 (Dec. 10, 1940).  
 115. Gilbert, H. N. (to du Pont), U. S. Patent 2,234,967 (Mar. 18, 1941).  
 116. Gilbert, H. N. and Clare, N. D. (to du Pont), U. S. Patent 2,124,565 (July 20, 1938).  
 117. Graham, L., U. S. Patent 464,697 (Dec. 1, 1891).  
 118. Grebe, J. J. and Boundy, R. H. (to Dow Chemical Co.), U. S. Patent 1,826,773 (Oct. 13, 1931).  
 119. Grebe, J. J. and Boundy, R. H. (to Dow Chemical Co.), U. S. Patent 1,839,756 (Jan. 5, 1932).  
 120. Griswold, T., Jr., and McConica, T. H. (to Dow Chemical Co.), U. S. Patent 2,416,235 (Feb. 18, 1947).  
 121. Griswold, T., Jr. and McConica, T. H. (to Dow Chemical Co.), U. S. Patent 2,416,992 (Mar. 4, 1947).  
 122. Hackspill, L. and Grandadam, R., *Compt. Rend.*, **180**, 68-70 (1925).  
 123. Hackspill, L. and Staehelin, C., U. S. Patent 1,828,824 (Mar. 10, 1925).  
 124. Hall, C. M., U. S. Patent 400,706 (Apr. 2, 1889).  
 125. Hars, R. and Abe, S., U. S. Patent 2,102,151 (Dec. 14, 1937).  
 126. Hars, R. and Abe, S., British Patent 441,753 (Jan. 24, 1936).  
 127. Hars, R. and Abe, S., French Patent 795,150 (Jan. 16, 1936).  
 127a. Hardie, D. W. F., *Ind. Chemist* **30**, 161-66 (1954).  
 128. Hardy, R. L. and Hulse, R. E. (to du Pont), U. S. Patent 2,194,443 (Mar. 19, 1940).  
 129. Hill, E. F. (to Ethyl Corp.), U. S. Patent 2,543,406 (Feb. 27, 1951).  
 130. Hill, E. F. (to Ethyl Corp.), U. S. Patent 2,561,862 (July 24, 1951).  
 131. Hill, E. F. and Sorocso, H. (to Ethyl Corp.), U. S. Patent 2,543,407 (Feb. 27, 1951).  
 132. Hulin, P. L., German Patent 79,435 (June 15, 1894).  
 133. Hulin, P. L., German Patent 224,853 (Aug. 3, 1910).  
 134. Hulin, P. L., German Patent 229,825 (Dec. 12, 1910).  
 135. Hulin, P. L., U. S. Patent 542,057 (July 2, 1895).  
 136. Hulin, P. L., U. S. Patent 971,198 (Sept. 27, 1910).  
 137. Hulin, P. L., U. S. Patent 1,835,716 (May 25, 1926).  
 138. Hulin, P. L., German Patent 79,435 (June 15, 1894).  
 139. Hulin, P. L., *Z. anorg. Chem.*, **11**, 159 (1898).  
 140. Hulse, R. E. (to du Pont), U. S. Patent 2,071,124 (Feb. 16, 1937).  
 141. Hulse, R. E. (to du Pont), U. S. Patent 2,091,179 (Aug. 24, 1937).

142. Hulse, R. E. (to du Pont), U. S. Patent 2,130,804 (Sept. 29, 1938).
143. Hulse, R. E. (to du Pont), U. S. Patent 2,224,820 (Dec. 10, 1940).
144. Hulse, R. E. and Hardy, R. L. (to du Pont), U. S. Patent 2,068,681 (Jan. 26, 1937).
145. Imperial Chemical Industries, Ltd., British Patent 491,880 (Sept. 12, 1938).
146. Jacobs, C. R., U. S. Patent 1,587,323 (June 1, 1926).
147. Jellinek, K., *Z. Elektrochem.*, **31**, 542-45 (1925).
148. Jellinek, K. and Czerwikinski, J., *Z. physik. Chem.*, **110**, 192-236 (1924).
149. Jellinek, K. and Tomoff, G., *Z. physik. Chem.*, **111**, 234-50 (1924).
150. Jellinek, K. and Wolff, J., *Z. anorg. allgem. Chem.*, **148**, 329-87 (1925).
151. Kawahara, H., *J. Soc. Chem. Ind. Japan*, **47**, 322-24 (1944).
152. Kawahara, H., *J. Soc. Chem. Ind. Japan*, **47**, 511-15 (1944).
153. Kawahara, H., *J. Soc. Chem. Ind. Japan*, **47**, 620-22 (1944).
154. Kawahara, H., *J. Soc. Chem. Ind. Japan*, **47**, 754-56 (1944).
155. Kirchuth, H., *Electrochem.*, **3**, 368-71 (1933).
156. Kirk, R. E. and Othmer, D. F., "Encyclopedia of Chemical Technology," New York, Interscience (1951).
157. Klocho, J., *Zhur. Priklad. Fiz.*, **9**, 420 (1936).
158. Koehler, W. A., "Applications of Electrochemistry," New York, John Wiley & Sons (1935).
159. Kolklin, T., German Patent 351,409 (Apr. 6, 1922).
160. Kolklin, T., U. S. Patent 1,449,008 (Mar. 20, 1923).
161. Kremann, R., Kienzl, H. and Markl, R., *Monatsh.*, **45**, 133-39 (1924).
162. Kroll, W. J., U. S. Patent 2,465,730 (Mar. 29, 1949).
163. Labhardt, H., U. S. Patent 1,191,799 (July 18, 1916).
164. Lacy, B. S., U. S. Patent 2,162,619 (June 13, 1939).
165. Lavoiner, H., French Patent 802,579 (Sept. 8, 1906).
166. LeBlanc, M. and Carrier, C. F., Jr., *Electr. Ind.*, **2**, 357-64 (1904).
167. LeBlanc, M. and Carrier, C. F., Jr., *J. Soc. Chem. Ind.*, **73**, 828 (1940).
168. LeBlanc, M. and Carrier, C. F., Jr., *Z. Elektrochem.*, **10**, 568 (1904).
169. MacMullin, R. B., *Chem. Eng. Progress*, **46**, 440-55 (1950).
170. Mantell, C. L., "Industrial Electrochemistry," 3rd Ed., New York, McGraw-Hill.
171. McConica, T. H., MacPhail, A. A. and Kirk, R. C. (to Dow Chemical Co.), U. S. Patent 2,391,728 (Dec. 25, 1945).
172. McNitt, R. J., *Chem. Met. Eng.*, **16**, 401 (1917).
173. McNitt, R. J., German Patent 240,367 (Sept. 7, 1910).
174. McNitt, R. J., U. S. Patent 959,785 (May 31, 1910).
175. McNitt, R. J., U. S. Patent 903,291 (May 30, 1911).
176. McNitt, R. J., U. S. Patent 985,476 (June 20, 1911).
177. McNitt, R. J., U. S. Patent 1,027,495 (May 28, 1912).
178. McNitt, R. J., U. S. Patent 1,107,137 (Sept. 5, 1916).
179. McNitt, R. J., U. S. Patent 1,214,808 (Feb. 6, 1917).
180. McNitt, R. J., U. S. Patent 1,324,298 (Jan. 27, 1925).
181. McNitt, R. J., U. S. Patent 2,263,181 (Nov. 18, 1941).
182. McNitt, R. J., U. S. Patent 2,291,644 (Aug. 4, 1942).
183. McNitt, R. J., U. S. Patent 2,315,843 (Mar. 30, 1945).
184. McNitt, R. J., U. S. Patent 2,374,762 (May 1, 1945).
185. McNitt, R. J., U. S. Patent 2,375,232 (May 8, 1945).
186. McNitt, R. J., U. S. Patent 2,382,434 (Aug. 14, 1945).
187. McNitt, R. J., U. S. Patent 2,390,114 (Dec. 4, 1945).
188. McNitt, R. J., U. S. Patent 2,390,548 (Dec. 11, 1945).
189. McNitt, R. J., U. S. Patent 2,414, 831 (Jan. 28, 1947).
190. McNitt, R. J., U. S. Patent 2,449,856 (Sept. 21, 1948).
191. Mehnert, H., U. S. Patent 1,616,758 (Feb. 6, 1912).
192. Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry" II, London, Longmans, Green & Co. (1946).
193. Meyer, R. J., Ed., "Gmelin's Handbuch der anorganischen Chemie," System-Nummer 21, Berlin, Verlag Chemie (1928).
194. Minnick, L. J. and Prosser, C. (to G. & W. H. Corson, Inc.), U. S. Patent 2,615,838 (Oct. 28, 1952).
195. Moesser, L. T. and Eldman, W. E., U. S. Patent 710,433 (Oct. 7, 1902).
196. Moltkehausen, I. J., U. S. Patent 2,150,289 (Mar. 14, 1939).
197. Moltkehausen, I. J., *Trans. Am. Electrochem. Soc.*, **C-2**, 85-87 (1927).
198. Moltkehausen, I. J. and Eger, G., in V. Engelhardt, "Handbuch der Technischen Electrochemie," **3**, Leipzig, Akademische Verlag (1934).
199. Morrison, W. L., U. S. Patent 1,265,360 (May 7, 1918).
200. Moulton, S. A., U. S. Patent, 1,961,160 (June 5, 1934).
201. Muller, E., *Ber. Deut. Chem. Ges.*, **38**, 1190 (1905).
202. Muller, E., *Z. anorg. Chem.*, **26**, 1 (1900).
203. Muller, E., *Z. Elektrochem.*, **9**, 955 (1903).
204. Muller, E., *Z. Elektrochem.*, **11**, 509 (1905).
205. National Distillers Chemical Corp., "Sodium", Nat. Dist. Chem. Corp. (1949).
206. Netto, C., U. S. Patent 460,985 (Oct. 13, 1891).
207. Netto, C., German Patent 45,105 (Nov. 5, 1887).
208. Netto, C., German Patent 52,558 (June 30, 1889).
209. Neubauer, J. and Deustsch, Z. G., FIAT Final Report 431 (PB-7747) (1945).
210. Neumann, B. and Giersten, S., *Z. anorg. Chem.*, **28**, 65 (1914).
211. Ortel, F., *Chem. Ztg.*, **61**, 155-56 (1937).
212. Orlandi, O., French Patent 561,110 (Jan. 17, 1923).
213. Parker, T., British Patent 19,196 (Sept. 5, 1903).
214. Peacock, S., U. S. Patent 1,493,126 (Mar. 6, 1924).
215. Peacock, S., U. S. Patent 1,531,623 (May 31, 1925).
216. Philipp, H. and Foersterling, H., U. S. Patent 1,240,821 (Dec. 11, 1917).
217. Pidgeon, L. M. (to Dominion Magnesium, Ltd.), Canadian Patent 415,764 (Oct. 12, 1943).
218. Plotnikov, V. A. and Yankelevich, Z. A., *Mem. Inst. Chem., Akad. Sci. Ukrain S.S.R.*, **5**, 30-45 (1938).
219. Raschen, J. and United Alkali Co., Ltd., British Patent 13,662 (July 4, 1901).
220. Rathenau, W. and Suter, C., German Patent 96,672 (Mar. 30, 1938).
221. Regelsberger, F., "Chemische Technologie der Leichtmetalle," Leipzig, Verlag Otto Spamer (1926).
222. Richards, J. W., *Z. angew. Chem.*, **20**, 528 (1894).
223. Richards, J. W., *J. Chem. Ind.*, **1894**, 448.
224. Richards, J. W., *Z. angew. Chem.*, **21**, 452 (1895).
225. Roessler & Hasselbacher Chemical Co., British Patent 238,956 (May 28, 1924).
226. Rogers, A. J., *J. Franklin Inst.*, **128**, 486 (1890).
227. Rogers, A. J., U. S. Patent 296,357 (Apr. 8, 1884).
228. Rossiter, E. C., U. S. Patent 1,673,523 (Sept. 16, 1913).
229. Ruban, J., *Zhur. Obshchei Khim.*, **7**, 1419 (1937).
230. Ryska, Z., *Chem. Obzor.*, **18**, 153-59 (1943).
231. Schermack, L., PB-37788 (FIAT Final Report 830) (Aug. 6, 1946).
232. Schlotter, M., British Patent 662,769 (Jan. 6, 1932).
233. Scholl, A. P., U. S. Patent 679,997 (Aug. 6, 1901).

234. Seward, G. O. and von Kugelgen, F., U. S. Patent 841,724 (Jan. 22, 1907).
235. Seward, G. O., von Kugelgen, F. and von Bidder, F., U. S. Patent 1,043,154 (Nov. 5, 1912).
236. Shcherbakov, I. G. and Yumanova, L. V., *Kolli (USSR)*, 1937, No. 3, 16-23.
237. Smith, A. W. and Venzey, W. R. (to Dow Chemical Co.), U. S. Patent 1,334,179 (Mar. 16, 1920).
238. Smith, A. W. and Venzey, W. R., U. S. Patent 1,375,330 (Apr. 19, 1921).
239. Smith, F. E. and Williams, H. B., U. S. Patent 2,592,483 (Apr. 8, 1952).
240. Soc. Anon. pour L'Ind. Chim. a Basle, British Patent 340,451 (Aug. 29, 1929).
241. Soc. Anon. pour L'Ind. Chim. a Basle, German Patent 236,804 (Dec. 23, 1909).
242. Soc. Anon. pour L'Ind. Chim. a Basle, Swiss Patent 142,518 (Aug. 23, 1929).
243. Soc. D'Electro-Chimie, D'Electro-Metallurgie et des Acieres Electriques D'Ugine, French Patent 603,825 (Dec. 27, 1924).
244. Specketer, H., *Nernst's Festschrift (Halle, 1912)*, 424-27.
245. Specketer, H. and Hofmann, W., U. S. Patent 1,034,320 (July 30, 1912).
246. Specketer, H. and Weber, O. H., U. S. Patent 730,979 (June 16, 1903).
247. Stalhane, J. B. and Pyk, S. C., Swedish Patent 72,878 (Oct. 13, 1931).
248. Steinbuch, E., U. S. Patent 1,074,988 (Oct. 7, 1913).
249. Swan, J. W. and Kendall, J. A., British Patent 7987 (Apr. 4, 1913).
250. Swan, J. W. and Kendall, J. A., British Patent 25,100 (Oct. 28, 1910).
251. Thorpe J. F., "Dictionary of Applied Chemistry", Fourth Ed., X, London, Longmans, Green & Co. (1950).
252. Thowless, O. M., U. S. Patent 380,775 (Apr. 10, 1888).
253. Thowless, O. M., U. S. Patent 380,776 (Apr. 10, 1888).
254. Vautin, C. T. J., German Patent 78,091 (Jan. 9, 1894).
255. Vautin, C. T. J., German Patent 81,710 (June 3, 1894).
256. von Bidder, F., U. S. Patent 1,002,178 (April 7, 1914).
257. von Kugelgen, F. and Seward, C. O., U. S. Patent 850,376 (Apr. 16, 1907).
258. von Kugelgen, F. and Seward, C. O., U. S. Patent 808,070 (Oct. 22, 1907).
259. von Kugelgen, F. and Seward, C. O., U. S. Patent 1,007,869 (Nov. 7, 1911).
260. von Kugelgen, F. and Seward, C. O., U. S. Patent 1,080,113 (Dec. 2, 1913).
261. von Kugelgen, F., von Bidder, F. and Seward, C. O., U. S. Patent 1,095,600 (May 5, 1914).
262. von Steinwehr, H., in Engelhardt "Handbuch der Technischen Elektrochemie," II, Leipzig, Akad. Verlag (1934).
263. Vourناسos, A. C., British Patent 23,689, *Abstr. J. Soc. Chem. Ind.*, 29, 151 (Nov. 5, 1908).
264. Wacker Alex. Ges. fur elektrochem. ind., Gmbh., French Patent 828,712 (May 27, 1938).
265. Wasser, B., "Alkalien und Erdalkalien," Dresden, T. Steinkopff (1931).
266. Wasser, B., *Edel-Erden u. Erze*, 4, 63-66 (1923).
267. Walde, H., *Chem. Tech.*, 18, 153-57 (1943).
- 267a. Wallace, T., *Chem. and Ind.*, 1943, 876-82.
- 267b. Williams, H. B. (to du Pont), U. S. Patent 2,621,155 (Dec. 9, 1952).
268. Wolfram, G., British Patent 18,604, *Abstr. J. Soc. Chem. Ind.*, 18, 832 (Aug. 30, 1898).
269. Wolfram, G., German Patent 101,374 (Mar. 23, 1898).
270. Wood, T., U. S. Patent 2,200,906 (May 14, 1940).
271. Ylla-Conte, J., *Z. anorg. Chem.*, 43, 99 (1930).
272. Ylla-Conte, J., British Patent 342,609 (Apr. 27, 1929).
273. Ylla-Conte, J., French Patent 694,587 (Apr. 26, 1930).
274. Ylla-Conte, J., U. S. Patent 1,837,935 (Dec. 22, 1931).