The History of Iodine From Discovery to Commodity

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The discovery of iodine by accident and the turning of this event into its industrial manufacturing constitutes a fascinating chapter in the development of chemical technology. We see in it how political and economical events brought drastic changes in the raw materials used and the production technologies. From a strictly European activity it turned into an important economic commodity for Chile and Japan.

Since the discovery of iodine in 1811 and its identification as a new element, many studies have been devoted to the study of its properties, preparation of derivatives, and possible applications. In 1819 it was discovered that potassium iodide was effective in the treatment of goiter. In 1820 it was found that iodine dissolved in alcohol (iodine tincture) and iodoform (CHI₃) had excellent antiseptic properties, and these preparations began to be used as disinfectants. In 1830 Louis-Jacques Daguerre (1787-1851) used iodine to prepare photographic plates by treating silver plates with iodine vapours. Later, it was found that potassium iodide was also an excellent reagent for certain quantitative chemical analysis.

Today, iodine has a wide range of uses in the chemical and allied industries. A high percentage of the initial use of iodine lies in the production of intermediates, which are frequently marketed as such. A breakdown of world iodine consumption for 1999 suggests that 45% was used in sanitizers (iodophors), 27% in the manufacture of animal feed, 10% to manufacture pharmaceuticals, 8% for catalysts, and 5% for heat stabilizers. Other smaller uses included inks and colorants, photographic chemicals, laboratory reagents, motor fuels, and lubricants. Photography represents one of the oldest industrial uses of iodide. The sensitive silver salt in rapid negative emulsions contains up to 7% or more silver iodide. Some dyes like Rose Bengal, erythrosin, and members of the cyanine group, contain iodine. Iodine and its compounds are very active catalysts for many reactions. The principal use is in the production of synthetic rubber through de Ziegler-Natta catalyst systems. About 75% of the iodine consumed in catalysts is used for polybutadiene and polyisoprene polymerization. Iodine and iodine preparations are employed extensively in medicine as antiseptics, as therapeutic agents in various thyroid abnormalities, and as drugs administered for the prophylaxis and treatment of many diseases. Iodophors are used as disinfectants in dairies, laboratories, and food processing plants.

A very attractive possibility for future growth is the use of methyl iodide as a pest control agent. This derivative has been tested by the U.S. Department of Agriculture and found to be an effective fumigant for controlling four species of fungi, one species of nematode, and seven species of weeds. Methyl iodide seems to be more effective than methyl bromide, in addition it has an ozone depletion potential of 0.016 compared to 0.65 for the bromide. It is more expensive than methyl bromide, but it can be used with the same fumigating equipment.

Iodine is an essential ingredient for the synthesis of the hormone thyroxin by the thyroid gland. A lack of iodine during infancy may cause a condition known as cretinism, in which the mental and physical development is seriously impaired. In adults and children, iodine deficiency leads to goiter and myxedema. Simple or endemic goiter, enlargement of the thyroid gland, is the most common manifestation of iodine deficiency. Today, iodine is normally added to table salt to diminish the incidence of this defect.

The earliest record of goiter troubling humans appear in Chinese medical writings. Endemic goiter has troubled man since immemorial and the earliest known remedy was a concoction of burnt sponge, with or without the addition of burnt seaweed. By 1819, the Geneva physician, Jean François Coindet

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(1774-1834) showed that iodine was the active therapeutic agent against goiter common to seaweed and burnt sponge.

In the fifty-year period between 1815 and 1865 iodine production was restricted to Europe alone, using seaweeds as raw material. The largest European production facilities were located in Glasgow, Scotland. In 1866, George Smith began to extract it from the caliche deposits present in the northern part of Chile. Around 1925 iodine began also to be extracted from oil wells. These two new sources brought an end to iodine manufacture from seaweeds. From 1874, and almost for one century the British monopoly of the commodity. The world production of iodine in the year 2000 was about 19,000 ton/year, the largest producers being Chile (from salitre) and Japan (from oil brine wells).

**Discovery of iodine**

Iodine was discovered in 1811 by Bernard Courtois (1777-1838), a Parisian manufacturer or saltpetre. Courtois observed that when the copper vessels he used for concentrating the potassium carbonate were washed with hot sulphuric acid they became pitted and that a violet vapour appeared that condensed forming bright crystalline scales, having the colour and lustre or graphite. A more detailed check verified his assumption that corrosion was due to a new body contained in the ashes. The violet vapours were easily produced just by adding excess sulphuric acid to the mother liquors. Courtois was very busy with this commercial enterprise and did not have time to investigate the matter further, although he did communicate his discovery to Nicolás Clément (1779-1842) and Charles-Bernard Desormes (1778-1862)\(^1\). Clément reported the phenomena observed during a session of the Institute de France, held on November 29, 1813. Afterwards, Joseph-Louis Gay-Lussac (1778-1856) investigated this new substance (that was named "X") and brought to the attention the analogy that existed between its chemical behaviour and that of chlorine. Gay-Lussac declared that the body was a new chemical element that he named *iodine*, because of the violet colour of its vapour\(^2\). Almost simultaneously, other chemists like Humphry Davy (1778-1819) and Louis Nicolas Vauquelin (1763-1829), added information about the new element, reporting new and easier procedures for detecting its presence, and preparing derivatives.

The answer to the question who was the first to realize that iodine was a new element has been the subject of an impassioned debate. Some say it was Gay-Lussac and others claim that it was Humphry Davy (1778-1819). According to Crosland, the most extreme view is the one held by Davy's first biographer, John Ayrton Paris\(^7\), who considered the discovery of iodine "a good example of the ignorance of the French chemists". According to Paris "if Davy had not visited Paris, iodine would have remained at the end of 1814, as it had been for two preceding years, the unknown X". On December 10, 1813, Davy wrote a letter to the Royal Society of London, which was read on the session held on January 20, 1814, under the title "Some Experiments and Observations on a New Substance Which Becomes a Violet-Coloured Gas by Heat"\(^8\). In this communication he summarized the discovery of compound X by Courtois. He wrote that the name *ione* had been proposed in France for this compound, because of the violet colour of its vapours (Gay-Lussac proposed *iode*). Also, the name *hydroionic* had been suggested for the compound it formed with hydrogen. According to Davy these names would lead to confusion because the derivatives of *ione* would be called *ionics*. On the other hand, this confusion could be easily eliminated by calling the compound *iodine* from the week word for violet. Not only that, the name iodine would fit very well with *chlorine* and *fluorine*. Interesting enough, Davy's letter does not mention the name of Gay-Lussac but it neither attributes to Davy the discovery of the element.

Crosland believes although there was a strong rivalry between Davy and Gay-Lussac, it is clear that Gay-Lussac began his research quite independently of Davy's visit to France. The reader interested in more details about the dispute between Davy and Gay-Lussac should read Fullmer's paper on the subject\(^9\).

Courtois is also considered to be the first industrial manufacturer of iodine. During the British blockade of France (Napoleonic wars) he used his facilities not only to produce the saltpetre required for gunpowder, but also for manufacturing iodine from the residues. Aided by Clément and Desormes he developed a small industrial process to extract it by treating the mother liquors with chlorine, in earthenware vessels. At the end of the war,
Courtois' facilities were unable to compete with the cheap saltpetre that began to be imported from India and with other people who were producing iodine in larger scale. This brought the closure of Courtois' industry and his economical ruin. Anyhow, his discovery did not go unnoticed: In 1831 he received the Montyon prize, awarded to those who had improved the art of curing.

The many applications that were rapidly found for iodine and its compounds resulted in a large increase in demand that could not be satisfied by production from seaweed. This created the pressure for seeking new sources for the element, more economical, and more abundant. The first hints for solution were provided by Charles Robert Darwin (1809-1882) and John H. Blake. Blake informed that bread crumbs that fell in the mother liquor of Chilean salitre would turn violet. Darwin visited Chile during his mission on the Beagle and collected samples of caliche that contained 0.006% wt. sodium iodate.

On the other hand, Crozier claims that the most probable discoverers of iodine in the caliche deposits were actually William Bollaeert and George Smith who, at the request of the local government authorities, prepared a comprehensive ethnographic, geographical, and geological description of the northern provinces of Chile.

**Iodine sources**

Although not abundant in quantity, iodine is distributed in rocks, soils, waters, plants, animal tissues, and foodstuff. Iodine is never free in nature; it is always combined with other elements. Wherever it occurs, the quantities of iodine are very small. Only a few substances such as seaweeds, sponges, and corals, contain it in relatively large quantities. It is also present in the underground waters from certain deep oil-well brines and mineral springs and most particularly of all, in the vast natural deposits of sodium nitrate (caliche) ore found in the northern part of Chile. Even in these, however, the proportion of iodine is small, rarely exceeding one part in five hundred.

Like other substances, iodine is part of a natural cycle involving the atmosphere, the oceans and the ground, with most iodine in nature being present in the ocean. At the beginning it is probable that the primitive soil contained iodine salts, which because of their solubility were little by little carried by rivers, rains, and floods into the sea. Iodide ions are oxidized by sunlight to elemental iodine so that every year some 400,000 tons of iodine escape from the surface of the sea. The concentration of iodide in seawater is about 50 microgram/L; in the air it is about 0.7 microgram/m³. The principal source of atmospheric iodine is methyl bromide produced in large quantities by marine biota like macroalgae (seaweed) and plankton. Methyl iodide, like methyl chloride and bromide, is insoluble in water and is thus not frozen out at the tropopause (the top of the troposphere); however, it has a much shorter atmospheric lifetime so that only a small fraction survives long enough to reach the stratosphere. Iodide in the atmosphere is returned to the soil by rain, which has concentrations in the range of 1.8 to 8.5 microgram/L. The iodine-containing gases cross the sea-air interface and enter the atmosphere where their iodine is released into the so-called reactive iodine pool by the action of sunlight. Similar to fluorine and chlorine, the chemistry of iodine in the atmosphere is extremely complex and plays a part in the destruction of ozone.

The return of atmospheric iodide returned to the surface of the earth is slow and small in compared with the original loss, and subsequently, repeated flooding results in a steady depletion in the amount of iodine contained in the soil. There is no natural correction so that iodine deficiency will persist in the soil indefinitely and all crops grown in it will be iodine deficient. As a result, human and animal populations, which are totally dependent on food grown in such soil, will become iodine deficient.

The sources of the raw material for manufacturing iodine will now be discussed according to the historical development of its production.

**Seaweeds—**Iodine is produced from several seaweeds that contain different amounts of the material (iodine as % of dry weight), for example:

<table>
<thead>
<tr>
<th>Seaweed</th>
<th>Iodine (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laminaria digitata</td>
<td>0.13-0.49</td>
</tr>
<tr>
<td>Laminaria saccharina</td>
<td>0.20-0.28</td>
</tr>
<tr>
<td>Fucus serratus</td>
<td>0.04-0.18</td>
</tr>
<tr>
<td>Fucus nodosus</td>
<td>0.057</td>
</tr>
<tr>
<td>Fucus vesiculosus</td>
<td>0.02-0.03</td>
</tr>
<tr>
<td>Ascophyllum</td>
<td>0.04-0.86</td>
</tr>
</tbody>
</table>

Many of the seaweeds and some of the fucoids exhibit the phenomenon known as iodovolatilization, or the liberation of free iodine. This is the basis of their value for iodide extraction. The iodine is produced in the epidermal cells and basal portion of the blade and is associated with meristematic activity. The amount of iodine varies from season to season, and is also affected by immersion cutting, exposure,
wave action, and variations of temperature. The northern the location the higher the iodine content. Iodine escape supposed to occur by the action of iodide-oxidases acting in the presence of oxygen.

In the seventeenth century, French peasants began manufacturing soda, first from brown rockweeds and then from oarweeds, for use in the glazing of pottery and in glass manufacture. In the days of the iodine industry the oarweeds, known as goémon poussant en mer or goémon de fond, were cut by special workers known as goémonniers or soudiers, who had to obtain special licenses. The resulting ashes were called kelp in Scotland and varec, soude de varech, or varech in France. The word varech is said to be derived from the English word wrack and to have been introduced into France at the time of the Norman conquest of England. Several brown seaweeds were employed in the manufacture of kelp, the most common being the species of Laminaria and Saccorhiza polyschides, particularly in those places where storms deposit them in large amounts in the coast, for example, Western Ireland and Scotland. Other useful species were the Fucus (Fucus vesiculosus, Fucus serratum, and Ascophyllum), which grow on rocks and could be easily gathered and brought to the drying area. The Oarweeds were used in all three development stages of the industry: first they were collected for the soda they contained; then they were used for manufacturing iodine, and finally, for the manufacture of alginates. The brown rockweeds formed the principal source of supply of soda because they contain a higher percentage of this substance that the oarweeds. The kelp soda was a substitute for the expensive substance called barilla soda or salichord, which was prepared, especially in Spain, from certain coastal salt-rich plants. Later the burners turned almost wholly to drift-weed (Laminaria species) when iodine was required, because the oarweeds are much richer in this substance. Iodine is present in seawater in very small amounts (0.01 to 0.07 ppm), or but certain seaweeds, especially the oarweeds, have the capacity to accumulate it in their tissues, and hence their value as a source of this element. A rockweed such as Ascophyllum can concentrate the iodine up to 220 times that of seawater.

The production of kelp in Great Britain did not begin until about 1720. By the end of the eighteenth century Scotland was producing about 20,000 ton of kelp annually. The importation of barilla soda after the Napoleonic wars reduced the need for kelp in Great Britain, and by 1845 the industry was almost dead. The discovery of iodine in kelp by Courtois in 1811 and its subsequent use in medicine revived the industry. Using the best seaweeds properly burnt, the kelp contained 1.4% to 1.8% iodine, or 33 to 40 pounds per ton. With the discovery of the Chilean nitrate deposits the kelp industry in Scotland started its second decline. The third revival took place during the Second World War with the rise of the alginate industry.

The industry decreased dramatically with the development of the Le Blanc process for the manufacture of sodium carbonate, and further, when iodine started being produced as a by-product of the fabrication of salitre (sodium nitrate) in Chile and Peru.

It should be emphasized that although the chemical properties of iodine were not such as to make it a commodity of industrial significance comparable with chlorine, its production is not without importance, if for no other reason than it helped to retain kelp as a marketable commodity after the decline of its importance as a source of soda.

Japan entered the trade in 1900 and was producing large quantities of iodine as late as 1921.

Chilean salpetre present in the Atacama Desert in the North of Chile and their potential commercial value has been the subject of many investigations and argument. The deposits are very rich in sodium nitrate and a number of other unusual salts such as iodates, perchlorates, chromates, and dichromates, occur with the nitrates as well as the more familiar boron, sulfate, and chloride salts. The deposits have an exceptionally high iodine/bromine ratio of greater that 10 to 1, which is the reverse of the relative abundance of these elements in other saline deposits and in rock, water, and air.

The relative composition of the saline components vary largely from one place to the other. The average figures are 18.87% sodium sulfate, 7.6% sodium nitrate, 4.8% sodium chloride, 4.8% sodium chlorate, 2.15% calcium, 0.96% potassium, 0.63% magnesium, 0.35% sodium perborate, 0.037% iodine, and 0.06% potassium perchlorate. These constituents, which represent the water-soluble material, make-up an average of nearly a third of the nitrate ore, with the remainder being insoluble rock debris and saline minerals of low solubility.
Suggested potential sources of the nitrogen in the Atacama Desert deposits include bird guano, fixation of atmospheric nitrogen fixation during electrical storms and electrochemical and photochemical reactions in the atmosphere, leaching of Andean volcanic rocks, organic-rich sea spray, atmospheric fallout of marine-derived nitrate, microbial nitrogen fixation in the desert soils and playas, and ascending hydrothermal fluids.

The many hypotheses on the origin of Chilean deposits have been discussed mainly by Goldschmidt and by Ericksen.

As intriguing as the nitrate source is, the iodate is even more unusual. People have speculated that it came from seaweed or marine organisms. Others have claimed it originated from seawater spray or atmospheric gases. Iodide accumulation presumably from kelp and other marine organisms has occurred in a few brine supplies (usually containing 100 ppm of iodine or less) associated with petroleum reserves.

The greater abundance of iodine over bromine suggests either a source enriched in iodine relative to bromine, such as organic films on the sea surface, concentration of iodine by the microorganisms in the playa lakes associated with the nitrate deposits, or photochemical oxidation to the relatively stable iodate, perhaps on soil surfaces in the nitrate fields, with bromine either not being oxidized and escaping as gaseous bromine and bromic acid, or oxidized to bromous oxide. According to McIntyre, the most likely sources of iodine are iodine-rich organic films on the sea surface, which are ejected in spray, or gases associated with Andean volcanism, part of which would be carried into the nitrate region in ground water and surface water. In both cases, the iodine would later be oxidized to iodate, probably by photochemical reactions in the atmosphere or at ground level in the nitrate fields. Bromine is at least one order of magnitude more abundant that iodine in nearly all inorganic materials, including the ocean and the thermal springs associated with the volcanism in the northern Chilean Andes, whereas it occurs only as traces (<0.01%) in the nitrate deposits. Inasmuch as iodine and bromine have similar chemical and physical properties, it would be expected that they become concentrated in the nitrate deposits in proportions similar to those of the source material.

Air-sea exchange may provide the mechanism by which iodine is transferred from the oceans to the atmosphere and land. This exchange occurs primarily by the emission of gases, such as methyl iodide, from the oceans. In the atmosphere methyl iodide is broken down to produce inorganic iodine. This breakdown may be an important control on ozone cycling in the remote atmosphere. The release from seaweed appears to be a response to stress, still unexplained, but probably related to the antibiotic properties of many iodine compounds. Once the methyl iodide is released to the atmosphere it has a lifetime of a few days before conversion to other forms of iodine associated with the smallest aerosol particles in the atmosphere. The iodine is eventually lost from the atmosphere through deposition in aerosol and rain.

However, the majority of reported δ¹⁵N values for marine nitrogen-bearing substance such as plankton, zoo plankton, dissolved ammonium, nitrate, and particulate organic nitrogen are significantly greater than 0%. It is not clear that these substances would be preferentially released from the ocean and transported to the continents.

Garrett has criticized the hypotheses of atmospheric fallout out of ocean spray pointing out some of the minerals in the nitrate deposits have been reported in atmospheric gases, but not all of them. According to Garrett the accumulation of iodates and perchlorates was caused by reactions driven by photocatalysis.

According to Garrett once the iodide was in the nitrate deposit, some unusual chemistry took place. The deposit is slightly basic and totally in an oxidized state (there is nitrate and no organic matter). This could have allowed following catalytic photochemical oxidation (well known in the laboratory) to take place:

\[ 2I^- + mhν \rightarrow I_2 \]

The iodine formed would immediately react with the alkaline solution to produce \( OI^- \)

\[ I_2 + 2OH^- \rightarrow OI^- + H_2O \]

The \( OI^- \) would in turn react with additional iodine to form iodate

\[ 2I_2 + 4OH^- + OI^- \rightarrow IO_5^- + 4I^- + 2H_2O \]

The iodide ion that was produced along with the iodate would remain in the deposit for additional photooxidation, and eventually all the iodide would be in the iodate form.

In the Chilean nitrate deposit there are no organics or other reducing agents, the solutions are basic, and therefore the iodate ions remain stable.
Oil well brines—Oil field brines contain variable amounts of iodine (present as iodide) depending on the location and strata tapped. For example, in California, the content may vary from 10 to 160 ppm. Analyses show that the bromine content of these brines is roughly twice that of iodine. This is in marked contrast with seawater that contains approximately 65 ppm bromine but less than 0.1 ppm iodine. The sodium chloride content is about the same as in seawater and appears to have no relationship to the iodine content.

Development of the production

Iodine occurs in nature as iodides and iodates. These compounds are very soluble in water so that their constant leaching by rain has resulted in very little iodine being found in the soil. This long-term process has resulted in iodine becoming accumulated in the oceans. It is estimated that the oceans contain at least $60 \times 10^9$ tons of iodine but in a concentration of less than 0.1 ppm. Some macrobiota like seaweeds are able to extract iodine from water, and over one hundred years ago they became the raw material for the first industrial production of the element.

As mentioned above, before the discovery of iodine in the Chilean nitrate beds, the world's supply of iodine was obtained largely from seaweed ashes by treating with sulphuric acid and manganese oxide or other oxidizing agent to liberate the free element, a process discovered by Ure in 1817. At present, most of the iodine produced in the world is obtained from Chilean saltpetre, which contains from 0.05 to 0.1% iodine as iodates of sodium and calcium, and oil well brines. The Chilean recovery process involves treating the saltpetre with sulphuric acid to yield iodic acid, which is then reduced with sulphuric acid. The resulting iodine is then purified by sublimation.

Table 1—Crude iodine: World production by country (tons/year)

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<tbody>
<tr>
<td>Azerbaijan</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Chile</td>
<td>5,514</td>
<td>7,154</td>
<td>12,618</td>
<td>9,720</td>
<td>9,800</td>
</tr>
<tr>
<td>China</td>
<td>500</td>
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<td>500</td>
<td>500</td>
</tr>
<tr>
<td>Indonesia</td>
<td>75</td>
<td>73</td>
<td>70</td>
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<td>70</td>
</tr>
<tr>
<td>Japan</td>
<td>6,178</td>
<td>6,036</td>
<td>6,000</td>
<td>6,750</td>
<td>6,760</td>
</tr>
<tr>
<td>Russia</td>
<td>150</td>
<td>150</td>
<td>120</td>
<td>120</td>
<td>120</td>
</tr>
<tr>
<td>Turkmenistan</td>
<td>255</td>
<td>250</td>
<td>250</td>
<td>150</td>
<td>150</td>
</tr>
<tr>
<td>United States</td>
<td>1,270</td>
<td>1,320</td>
<td>1,490</td>
<td>1,620</td>
<td>1,440</td>
</tr>
<tr>
<td>TOTAL</td>
<td>14,242</td>
<td>15,753</td>
<td>21,348</td>
<td>19,230</td>
<td>19,140</td>
</tr>
</tbody>
</table>
iodine, which was obtained in a dry crystalline form ready for the market. Iodine required in a pure state, especially for medicinal purposes, was sublimed in small earthenware pots.

In more modern times the process was carried out using the Shanks lixiviation process. The resulting concentrated solutions was either treated with lime in order to obtain the potash, or else sulphur was first removed by adding sulphuric acid, and then the ash was distilled with manganese dioxide when iodine volatilized off and could be collected. In France the iodine was obtained by the simple method of saturating the concentrated solution with chlorine, this caused iodine to be deposited and, after being washed, it was purified by distilling it in an iron kettle and collecting the fumes as they came off. Some factories used the Wollaston process in which the iodine was separated from the lixiviate by the addition of manganese dioxide and sulphuric acid.

The destructive distillation or char process, was suggested in 1862 by Stanford to decrease iodine losses. In the Stanford process the seaweed was collected, dried, cut up and packed into closed iron retorts with long outlet tubes. The retort was heated and the alga distilled at a low red heat. The material that vaporized was collected and separated into tar ammonia, and an illuminating gas. The charcoal left in the retort was broken up and water added to dissolve out the salts of soda and potash. The concentrated solution of the iodides was mixed with manganese dioxide and concentrated sulphuric acid and heated in cast-iron pots.

The main reaction is

$$2NaI + MnO_2 + 3H_2SO_4 = 2NaHSO_4 + MnSO_4 + 2H_2O + I_2$$

The iodine was then washed, dried, and purified by sublimation.

The company that Stanford founded to exploit his process dominated the seaweed industry from 1863 until his death in 1899 and continued to be the major producer of iodine in Britain until it ceased production in 1934.

*From salitre* 11

Iodine manufacture in Chile started well after the salitre industry had become a flourishing industry. The birth of the iodine industry in Chile may be considered June 1853, when the Peruvian government granted to Pedro Gamboni a privilege to extract iodine from the mother liquors present in his salitre manufacturing facilities, named Sebastopol, in the desert of Tarapacá, and using a procedure of his invention. Gamboni's method reduced the production costs, allowed the opening of the European markets, and with not too many variations it is the method presently used by the Chilean industry.

It is not known how Gamboni came to know that iodine is present as sodium iodate in the caliche (the iodate remains in solution after the sodium nitrate has been separated). Gamboni's method was based on the reduction of sodium iodate using sodium bisulphite:

$$2NaI0_3 + 5NaHSO_3 \rightarrow 3NaHSO_4 + 2Na_2SO_4 + H_2O + I_2$$

The recovery from the mother liquor was about 75%, and some of the loss was due to the solubility of the iodine in the liquors, and the rest was lost in the form of vapours.

After precipitation iodine was separated by filtration, pressed, and purified by sublimation.

In 1868 the Société Nitríre de Tarapacá produced iodine by a process introduced by Thiercelin where the mother liquor was treated with sodium bisulphite containing free $SO_2$, in a stoneware vessel having a sand layer in the bottom. The following reactions took place.

$$3SO_2 + I_2 \rightarrow 3SO_2 + I_2$$

After the iodine was precipitated, it was transferred into a gypsum plaster receptacle to help remove the moisture.

In the first year of operation, 1868, the Société Nitríre already produced about 1,500 kg de iodine using Thiercelin's method. Thiercelin also tried to precipitate iodine using nitrous acid, but the procedure was no implemented because of technical difficulties.

Another method for recovering iodine was to add sufficient bisulphite to convert all the iodate to iodide and then precipitate it as copper iodide with copper sulphate, which was obtained from the nearby mines of Chuquicamata, Calama. The resulting product presented advantages for shipping and for conversion to potassium iodide, but eventually the process was discontinued.

In 1882 it was proposed to modify the process by utilizing calcium sulphide, prepared by the reaction
between gypsum and carbon was proposed. Addition of calcium sulphide to the leaching tanks would result in the reduction of iodates to iodides, which would then concentrate in greater quantities in the mother liquor owing to their greater solubility, and could then be removed by precipitation with copper sulphate. This modification was not implemented for the simple reason that the inefficient processes in use were yielding more iodine than the world's consumption. Moreover, the process released obnoxious fumes of H₂S from the leaching tanks. Another modification discarded was the possibility of replacing acid sodium bisulphite (which was purchased) by producing it in situ by the reaction between sodium thiosulphate and sulphuric acid. It turned out that buying the raw materials for the reaction was more expensive than buying the bisulphite.

The development of iodine as a by-product has very considerably benefited the industry owing to the large margin of profit which it has been sold. This is because it is comparatively easy to extract the iodine from the nitrate mother liquors, whereas the other sources of iodine are kelp and oil well brines, which involves a long and costly processes.

In 2000 Chile produced about 9,800 tons of iodine, corresponding to about 51% of the total world production.

**Oil well brines**—Production of iodine from brines started in the USA in 1926 when C. W. Jones located a brine containing iodine in Louisiana. This brine came from a well that was primarily an oil producer. The Dow Chemical Company became interested in this development and decided to produce iodine in Louisiana by a process developed by the company. The Dow process was based on blowing the iodine out of the acidified and oxidized brine using a current of air. A Californian petroleum company recovered the iodine using the silver process also developed by Dow. In this process the following reactions took place

\[ \text{NaNal} + \text{AgNO}_3 \rightarrow \text{Agl} + \text{NaNO}_3 \]
\[ 2\text{Agl} + \text{Fe} \rightarrow \text{FeI}_2 + 2\text{Ag} \]
\[ 2\text{FeI}_2 + 2\text{Cl}_2 \rightarrow 2\text{FeCl}_3 + 2\text{I}_2 \]

The skinned liquid is then treated with a ferric chloride solution to flocculate oil, silt, and other impurities. Afterwards, the clarified brine is treated with sulphuric acid to assure liberation of the iodine at the oxidation step. The acidified brine is treated with chlorine and then sent to the top of the blowing-out packed tower where it flows countercurrent to air. The air stream, loaded with iodine, is then led to the bottom of another packed tower to be washed by and aqueous solution of hydrogen iodide and sulphuric acid. Water and sulphur dioxide is added continuously to the washing solution to reduce the free iodine absorbed according to the following reaction

\[ \text{I}_2(\text{air}) + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{HI} + \text{H}_2\text{SO}_4 \]

The hydrogen iodide-sulphuric acid liquor bled off passes to a precipitating tank where iodine is precipitated with chlorine according to:

\[ 2\text{HI} + \text{Cl}_2 \rightarrow \text{I}_2 + 2\text{HCl} \]

The precipitated iodine is then filtered and treated with hot strong sulphuric acid to eliminate organic matter and water. Heating melts the iodine, the liquid is discharged, allowed to solidify, the solid is flaked or prilled and then packed in kegs. The final product contains about 99.8% iodine.

For brines having very low iodide concentrations, like some facilities in Japan and Russia, the activated carbon method of recovery is used. The method consists in treating the acidified brine with sodium nitrite, to separate the iodine, as follows:

\[ \text{NaI} + \text{H}_2\text{SO}_4 + \text{NaNO}_2 \rightarrow 0.5\text{I}_2 + \text{Na}_2\text{SO}_4 + \text{NO} + \text{H}_2\text{O} \]

The free iodine is recovered by adsorption on activated carbon and the residual brine is neutralized with lime or ammonia.

The iodine is liberated from the activated carbon using hot caustic soda to give a concentrated solution of iodide and iodate anions, according to the reaction

\[ 6\text{I}_2 + 6\text{NaOH} \rightarrow 5\text{NaI} + \text{NaIO}_3 + 3\text{H}_2\text{O} \]

This solution is treated with sulphuric acid and potassium dichromate, precipitating the iodine crystals and filtering them out. The iodine in the filtrate cake is purified either by sublimation or melting and flaking.

A new process uses ion-exchange resins on brines already oxidized to liberate iodine. The liberated
iodine in the form of polyiodide is adsorbed on Amberlite IRA-400, an anion-exchange resin. Iodine is eluted from saturated the resin is washed first with a caustic solution and then with aqueous sodium chloride. The eluant, rich in iodide and iodate ions, is acidified and oxidized to precipitate iodine. The crude iodine is then separated in a centrifuge and purified with hot sulphuric acid or refined by sublimation.

Japan is the world's second largest producer of iodine. In 2000 it manufactured about 6,760 tons from brine wells, corresponding to about 35% of the world's total. Chiba prefecture accounts for about 90% of all production in Japan.

Plants in the U.S.A. are basically iodine producers and must extract the solutions from deep wells. The depleted solutions are reinjected for environmental reasons and maintain the pressure of the exploitation area. In Japan, on the other hand, iodine is mainly a by-product of natural gas production, and the wells are less deep. Depleted solutions are often discarded into the ocean.

For the Chilean iodine, which is mainly associated with nitrate production, plant location is near the nitrate plants.

To understand the impact of the different sources we can say that in 1904 a total of 520 tons of iodine was produced, 370 (71.1%) from Chilean nitrate and the rest from seaweeds. In 2000, production had risen to 19,140 tons with 51.2% coming from Chile, and the rest from mineral springs (see Table 1). Estimated reserves for the countries that appear in the table are 27 million tons.

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