THE HISTORY OF THE CHEMICALS FROM SEAWEED INDUSTRY IN IRELAND

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Introduction

The collection and burning of seaweed for turning into kelp, used first as a source of alkali for bleaching and other industries and then as a source of iodine, was a major industry on the West and Northern Coast of Ireland in the 18th. and 19th. centuries and up until the mid-20th century. Kelp was the name given to the burnt ash of seaweed, rather than of the giant seaweeds as today. The Scottish Highlands and Islands were also heavily involved in kelp production, and it seems that the industry was imported from Ireland. Warren (1980) in his history of the alkali industry states "the industry seems to have begun in Ireland, but soon became important in Scotland" (1). Robert Jameson, writing in 1800, confirms this (2):

> It will not then surprise us, when we learn, that its first introduction was about the year 1730, into the island of Uist, by a Highland gentleman, of the name of McLeod, who brought the art from Ireland, where it had been carried on many years before.

The Channel Islands, the Scillies, France (particularly Brittany), Spain and Norway have also had long-established industries based on seaweed gathering and kelp production. This article will focus mainly on Ireland.

The word *kelp* (or *kilp*) referring to seaweed ash derives from an Old English word *culp(e)*, in Irish and Scots Gaelic *ceilp*, and probably meant ashes, and is referred to in French as *varec(h)* and in the Channel Islands as *vraic*. These came from Old French *wrach*, which became in English *wreck* or *wrack*, an alternative name for seaweed. Seaweed is called *ware* in Scotland, which comes from an Old English word, probably from the Dutch for seaweed. Seaweed is sometimes referred to as ore. Kelp is now used to refer to a large type of seaweed, known as giant kelp. In this article it will be used in its 19th-century meaning of burnt seaweed slag.

The history of the utilization of seaweed in Ireland is an interesting and unfinished story, going back three centuries. It has been celebrated by various writers including J. M. Synge, Tomás O'Flaherty, Pat Mullen, Seamus Mac an Iomaire and Tim Robinson amongst others, and by artists such as Aloysius O'Kelly, Sean Keating, Samuel Lover, Jack Yeats and others. However, it is today largely a forgotten industry, whose fortunes have waxed and waned over the years, although seaweed is still collected in Connemara and Donegal for the production of seaweed meal. This is used mostly for export to produce alginates in Scotland, though there is a growing use in small indigenous industries.

In this introduction I will give an overview of the industry before looking in more detail at each of its three temporal phases, each of around 140+ years:

1) kelp as a source of alkali—from ~1700 to ~1840;

2) kelp as a source of iodine—from 1811 to ~1950;

3) seaweed as a source of alginates—from ~1880 to the present.

The dates are approximate and production of alkali and iodine from kelp declined slowly rather than coming to an abrupt stop when alternative sources of these chemicals were found, e.g. iodine in Chile and potash in Germany.

Kelp burning goes back at least three centuries in Ireland and survived until just after World War II, so that there are still living memories of what was once a familiar sight in the summer along Ireland's west coast: rolling white clouds of smoke by day and the twinkle of the kelp fires at night.

> At the end of summer and the beginning of Autumn the coast of Connemara is alight. There are hundreds of kilns to be seen. Aren't they a lovely sight, their smoke rising slowly skywards in the quiet of the evening … The smell from the same smoke is healthy fragrance. (3)

Unlike the parallel Scottish industry, very little has been written about the Irish kelp industry, the exception being the chapters in Robinson's book *Stones of Aran: Pilgrimage* (4) and chapters in a recently republished book *The Shores of Connemara* (5), written in the mid-1920s by a native of Connemara. A new archaeological survey of Strangford Lough (6) has a chapter on the kelp industry, as many of the remains around the Lough are due to kelp burning. A survey of the early Irish chemical industry by Childs (1998) mentioned the iodine from kelp industry (7). The best older sources for the use of kelp as a source of chemicals are the series of articles by Booth (1977-1979) (8), the book on *Seaweeds and their Uses* by Chapman (1970) (9), the chapter on kelp in Scotland in Archibald and Nan Clow's book on *The Chemical Revolution* (1952) (10) and their earlier article on kelp (11), and articles written in the 19th century such as those by Glassford (12) and Stanford (13), among others.

In one sense kelp production was a cottage industry, as it was mostly done by whole families near their homes, along some of the most desolate shores in the country. The cash income obtained by selling kelp was a significant part of their annual income, anything from 25 -50% according to the sample family incomes produced by the Baseline Studies of the Congested Districts Board (14). The situation in Scotland was very similar to that in Ireland, and here the industry was concentrated in the islands.

Kelp produced from seaweed is also part of the history of the chemical industry, as kelp was an important raw material that was traded internationally. Kelp provided an early, indigenous source of alkali, for soap, glass, textiles, alum and paper, competing mainly with wood and plant ashes, which were often imported—wood ash (potashes) from North America and barilla (plant ashes) from Spain. Later kelp was the first source of iodine, together with potash salts, and finally it is still the only source of alginates and seaweed-derived organic chemicals. As well as these chemical uses of seaweed, it has also been used since time immemorial in coastal areas as a green manure (as it is rich in trace elements including potassium and iodine), and certain species have been and still are used as animal and human food. You can still buy edible seaweeds on the streets of Limerick and Galway today, and this year I saw a farmer collecting seaweed on a beach in Mayo. Seaweed baths are back in fashion and the green, natural image of seaweed as a sustainable resource has brought it back into fashion as a health supplement, as a liquid fertilizer, in cosmetics, etc.

Kelp-making was not a small industry, although it was located mainly in isolated coastal regions. These regions were in fact over-populated relative to their resources and were known as the Congested Districts. A recent book has republished some of the reports of the Congested Districts Board, many of which refer to kelp-making. The reports were written between 1892 and 1898 (15) and give a picture of an industry in decline. At its height at the end of the 18th and beginning of the 19th centuries, seaweed-gathering and kelp production employed tens of thousands of people in Ireland, and possibly up to 100,000 people in the Highlands and Islands of Scotland. In fact, almost every able-bodied person, young and old, in the coastal areas was involved in collecting, drying and burning seaweed to kelp, often at the expense of agriculture. Figure 1 shows the location of the iodine works in Ireland. In the Aran Islands off the coast of Galway and on the coast of Donegal, this lasted until after World War II, although it had died out in most other places before then. Major quantities were traded and transported, seashore leases (kelp shores) were actively traded, and the industry brought a measure of wealth and cash income to areas where subsistence was the norm. Some landowners in Scotland made a fortune at the end of the 18th. century and into the 19th century from kelp, although at the expense of their tenants.

The price of kelp went up and down with demand, especially with the price of iodine in Phase 2, but only reached a maximum of £9 per ton. In the 1860-70s between 450 and 750 tons kelp were exported per year from the Aran Islands, from around 6,000 tons of wet weed.

Figure 1. *Map showing the locations of iodine works in Ireland—in Donegal, Galway and Clare.*

Production revived in the 1890-1900s, when kelp made £4/ton, and finally ceased in 1948 (16). At the height of the industry in the late 1800s there were three kelp factories on Aran: *Teachan Smail*, The House of the Ash; *Port Chonnla*; and *An Teach Mor* at *Port Chorruch* (the largest one). The industry survived on the Aran Islands longer than in most places probably because it was the only source of cash income. For some of that period kelp was imported into Galway for processing into iodine, from ~1850 to 1877, revived briefly again around 1930 (see below).

Several contemporary accounts are available from the early 20th century, which describe the collection of seaweed and the burning of kelp on the Aran Islands and in Connemara. The process hadn't changed for at least 100 years by then. John Millington Synge's long account was published first in *The Manchester Guardian* (1905) (17) (later in his *Collected Works*) and a shorter piece in his book *The Aran Islands* (1907) (18). An extract from this contemporary account is given below:

> The people had taken advantage of this dry moment to begin the burning of the kelp, and all the islands are lying in a volume of grey smoke. There will not be a very large quantity this year, as the people are discouraged by the uncertainty of the market, and do not care to undertake the task of manufacture without a certainty of profit.
>
> The work needed to form a ton of kelp is considerable. The seaweed is collected from the rocks after the storms of autumn and winter, dried on fine days, and then made up into a rick, where it is left till the beginning of June.
>
> It is then burnt in low kilns on the shore, an affair that takes from twelve to twenty-four hours of continuous hard work, though I understand that the people here do not manage it well and spoil a portion of what they produce by burning it more than is required.
>
> The kiln holds about two tons of molten kelp, and when full it is loosely covered with stones, and left to cool. In a few days the substance is as hard as the limestone, and has to be broken with crowbars before it can be placed in curraghs for transport to Kilronan, where it is tested to determine the amount of iodine it contains, and paid for accordingly. In former years good kelp would bring seven pounds a ton, now four pounds are not always reached.
>
> In Aran even manufacture is of interest. The low flame-edged kiln, sending out dense clouds of creamy smoke, with a band of red and grey clothed workers moving in the haze, and usually some petticoated boys and women who come down with drink, forms a scene with as much variety and colour as any picture from the East.
>
> The men feel in a certain sense the distinction of their island, and show me their work with pride. One of them said to me yesterday, "I'm thinking you never saw the like of this work before this day?"
>
> "That is true," I answered, "I never did."
>
> "Bedad, then," he said, "Isn't it a great wonder that you've seen France, and Germany, and the Holy Father, and never seen a man making kelp till you come to Inishmaan."

Although written 200 years or so after the start of the industry, this account agrees with other descriptions of the process, in both the soda and the iodine ages, for example that in Muspratt (1860) (19), or accounts written in the early 1800s in Scotland. Other contemporary 20th-century accounts exist by Pat Mullen (1930) (20), Thomas O'Flaherty (21) and Seamus Mac an Iomaire (3). There are also a number of contemporary photographs, drawings and paintings showing the collection of seaweed and the burning of kelp, in Ireland and Scotland, so we can see the kelpers in action in both reality and in artistic imagining (e.g., Figure 2).

***Figure 2**: Burning seaweed on the Aran Islands 1922, Photo: A. W. Cutler. Image ID: BJT02T The Print Collector / Alamy Stock Photo.*

Phase 1: Alkali from Seaweed (~1700-1820)

Alkalis were traditionally made from imported plant ashes (e.g., barilla, largely obtained from Spain) and wood ashes (potash, mainly from North America and the Baltic states), as well as from mineral deposits (e.g., natron). The origin of the use of seaweed as a source of alkali is unknown, but it goes back at least to the 17th century. Selby refers to kelp-burning at Holy Island as early as the 13th century (22). Singer notes the use of kelp as well as urine in making alum in England around 1620 (23). Warren mentions that kelp was used in glass-making in Prestonpans in 1662 (24), and the earliest mention of kelp production in Scotland, according to Clow & Clow is in 1694 (25). It would appear to have been well-established in the 17th. century in Ireland as a source of alkali and probably goes back earlier than that. The technology was imported into Scotland from Ireland.

Kelp, the ash obtained by burning dry seaweed, is a mixture of salts and Walker (1799) (26) says "Kelp is a lixivial salt and is always mixed with other salts, sea salt, Glauber's salt, etc." Although the percentage of alkali was low (about 5-10%) the mixture of salts was not always a disadvantage. The salt was extracted as a by-product in soap making and used for salting out. Glassmakers skimmed off the salt that rose to the top of the melt and sold it off. The alkali content was the main factor for soap making but in glass manufacture the other salts helped the process. The alum makers used kelp for the potassium it contained (about 3% potassium chloride) and kelp was being used in alum making at Whitby as late as 1845. Estimating the quality of kelp was largely done empirically, for example, as Angus Beaton described it in 1799 (27):

> It is estimated to be of good quality when on breaking a piece, it is found to be hard, solid and resembling good indigo, that is, when it has some reddish and light blue shades running through it. When it has none of its peculiar salt taste it is unfit for making ley [*28*], though it may be of use to glass-makers.

Not a very reliable method of quality control! The first person to assess the alkali content of kelp chemically was the Irish chemist Richard Kirwan (1789) (29), again illustrating the importance of the industry in Ireland. At that time kelp was mainly used as an alkali in the linen industry. Joseph Black in Edinburgh devised a better method of analysis, which showed that there was no connection between the price paid and the chemical content: samples had the same selling price when one had over eight times the alkali content of the other. Chemical analysis also enabled the alkali content of kelp and barilla to be compared, showing the superiority of barilla (30). This problem of payment in relation to chemical content was a permanent problem of the industry until well into the iodine phase, and payment was largely by guesswork and prejudice and sometimes showmanship. Although accurate analysis was possible it was still being done by "rule of thumb" in the early 20th century.

Kelp production started in the Orkneys around 1720 and was sold to bottle-makers in Newcastle. In 1732 Richard Holden introduced bleaching with kelp into Scotland and the Board of Trustees for Manufactures, Fisheries and Improvements in Scotland helped him to set up a bleachfield at Pitkerro, near Dundee. Around 1730 kelp-burning began in the Hebrides and it was said to have been introduced from Ireland. Kelp-burning was well established in both Ireland and Scotland by the middle of the 18th century.

The earliest account of kelp burning may be that of Daniel Colwall, in his 1678 description of making alum (31):

> Kelp is made of Sea-weed. Being dryed, it will burn and run like Pitch. This is beaten into ashes, steeped in Water and the Lees drawn off.

There was regular trade in kelp in and out of Irish ports in the 18th and 19th centuries, as described by L'Amie (32). From 1764 to 1800 53,074 tons of kelp were exported through Irish ports (Figure 3), an average of 1,434 tons per year. This does not include kelp that was used within Ireland, and total kelp production would have much higher than the recorded exports. Producing 1 ton kelp required the collection from 20 tons upwards of wet seaweed. The exports of kelp over these 37 years involved the collection of over a million tons of seaweed. The maximum export in 1797 amounted to 3,561 tons, equivalent to at least 71,220 tons of wet seaweed.

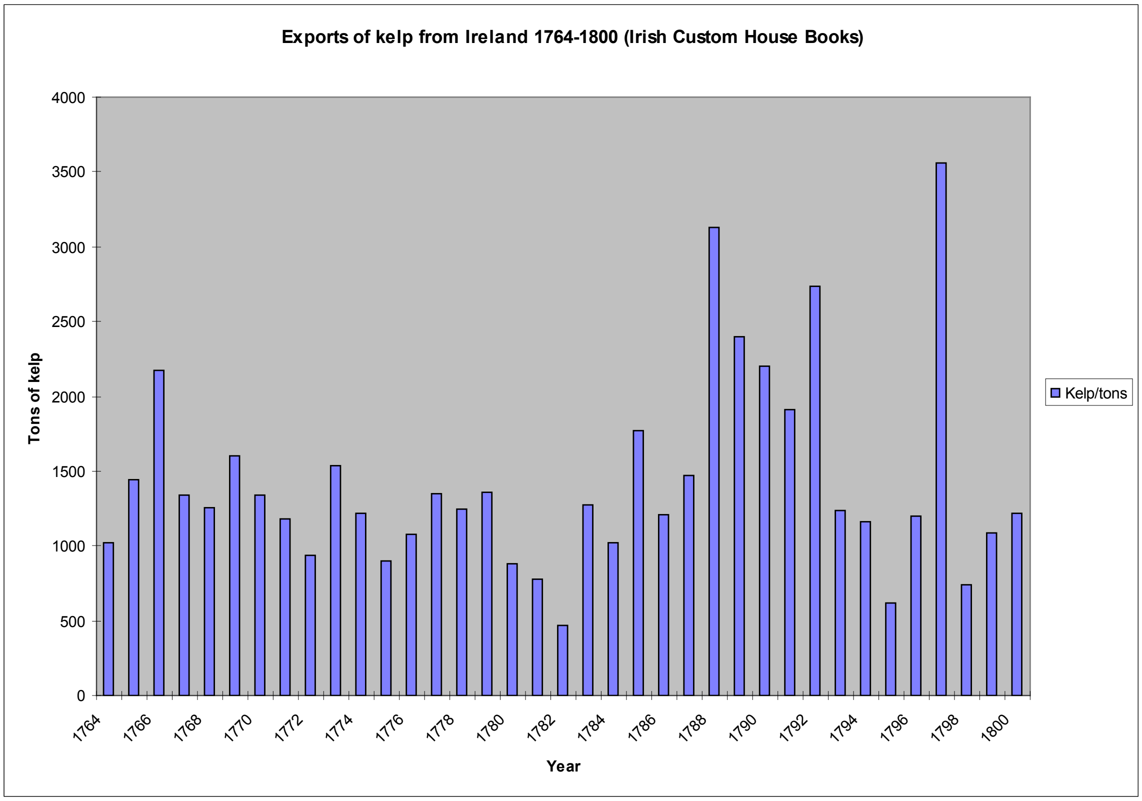

Figure 3. *Exports of Kelp from Ireland (1764-1800), based on data in Ref. 32.*

Figure 3 above shows only exports from Ireland at the end of the 18th century and does not include the large amounts consumed locally by the linen, soap and glass industries. Production and prices of kelp peaked in the early 1800s due to the shortage of imported barilla during the Napoleonic Wars, after an earlier peak during the American Revolution, which cut off supplies of potash. This period, from 1790 to 1815, was to be both the high point and the golden age of kelp burning in Ireland and Scotland. It also seemed it was to be the end-game of the Scottish and Irish kelp industries as prices fell from a high of £20 a ton in 1810 to £4 in 1820. The resumption of barilla supplies and repeal of taxes after the defeat of Napoleon and the introduction of synthetic soda processes from 1823 onwards, sounded the death-knell of the kelp industry as a source of alkali, although it struggled on into the middle of the century.

A viable process to produce synthetic soda made from salt had been patented by Nicholas LeBlanc in France in 1791, and small-scale production of soda was already underway in Scotland and England from the last decade of the 18th century (33). James Muspratt (1793-1885), an Irishman born in Dublin, who had started as a chemical manufacturer in Dublin, moved to England and started making synthetic soda on a large scale in Liverpool in 1823 (34). This date is usually taken as the foundation of the alkali industry in the United Kingdom, which was synonymous with the chemical industry until 1856. Although Muspratt initially had to give away his product to the soap boilers, eventually his superior product ousted barilla and kelp as the source of alkali. The synthetic product was purer, more concentrated, cheaper and more reliable in supply than the impure, dilute and seasonal soda from kelp and ashes. Fyfe (1820) writes of (35)

> a time when kelp manufacture is threatened with a total overthrow from the introduction of alkali matter made by the decomposition of sea salt.

There is much more information on the Scottish kelp industry than the Irish industry (10, 36) but in many respects they developed in the same way. However, it would seem that the Scottish kelp industry collapsed more completely than that in Ireland from 1820 and by 1860, when Stanford reported kelp production statistics for Scotland and Ireland (then used mainly for iodine production): annual production in the United Kingdom was around 10,000 tons with 60% being made in Ireland (37). Note that this nearly doubles the maximum amount exported in the 18th Century (shown in Figure 1), so the industry was far from dead. However, Scotland remained the major center for the processing of kelp, located mainly in Glasgow and surroundings, and eventually the Scottish industry absorbed the Irish kelp-processing industry and took most of its kelp exports, as it still does.

In County Down, Harris reports that 300 people were involved in the industry in 1744, giving the proprietors profits of over £1,000 per annum (38).

> This Peninsula produces large Quantities of Barley, and a kind of Oats, called the Light-Foot-Oats, as well from the Help of Marle abounding in the marshy grounds, as from Ore-Weed, which they have in great plenty, both from the Islands in the Lake, and the Eastern Shore. But this Vegetable is too precious to be used much as Manure; for they turn it to a better Account by burning it into Kelp, which they do in great Quantities, that they not only supply the linen manufacturers in this and neighbouring counties, but export it in abundance for the use of glass-houses in Dublin and Bristol, as appears in the custom-house books of Portaferry.

In his *History of Galway* Hardiman (1820) (39) reported export figures for Galway as: in 1808, 4,000 tons of kelp at an average cost of £16/ton; in 1820, 2,500 tons at £4/ton. These figures show both the collapse in the price of kelp in the early 1800s, and also the importance of the coast around Galway (which includes the Aran Islands) to the Irish kelp industry. The export figure for Galway in 1808 is greater than the maximum annual exports for the whole of Ireland from 1764 to 1800. On the Aran Islands alone there was an annual production of kelp of 120-200 tons/yr in the 1820s.

In the first phase of the seaweed industry kelp was used by many other industries as a cheap, indigenous source of alkali: for making glass, soap, paper, alum and in bleaching textiles, e.g. (40)

> Kelp is used by the Irish bleachers, and is made along the coasts of Clare, Galway, Mayo, Sligo and Donegal.

In fact, some end-users continued to prefer kelp into the 1830s and after, long after synthetic alkali had swept the market, as this quotation from 1835 Ordnance Survey Reports shows (41):

> Kelp (an impure kind) mixed with much sand and earthy matter was formerly obtained in great quantities from different species of Fucus but the price of the article has declined so much of late as scarcely to defray the cost of preparing it and bringing it to market. Soap boilers in the neighbourhood still use it in preference to barilla. Barilla is not manufactured, as the plant by the burning of which it is obtained (the Salsola kali) grows very sparingly along the coast.

As well as being exported, kelp was also imported into Irish ports from Scotland, the Scillies and the Channel Islands as a source of alkali and there was a vigorous trade in this commodity. L'Amie (42) gives some of the advertisements in the Belfast papers for renting kelp shores and for selling kelp, and Table 1 shows some typical 18th century advertisements. Such advertisements continued to appear well into the 19th century.

Table 1. Some 18th century adverts for kelp (42)

Friday, 5th. August 1763 *Belfast Newsletter*

> Cargo of excellent new kelp made last May on the Western coast near Sligo, remarkable for good strong Wrack is arrived to be sold on the Kay out of the ship by James Hamilton at the corner of Linenhall Street.

Tuesday 12th. July, 1768 *Belfast Newsletter*

> 40 tun of kelp, pure and well made now lying at Gransha shore, in the Barony of Ardes and County of Down, to be disposed of. Apply the Reverend Nicholas Hamilton, Ballyabigin or Mr. James Neill, Greyabbey.

Friday, 28th. January 1780 *Belfast Newsletter*

> About 30 tons Galway kelp and the like quantity of Kelp made in the Lough of Strangford to be sold exceedingly cheap by a person leaving this Kingdom. Apply William Johnston, Co. Down.

Tuesday, 16th. August 1785 *Belfast Newsletter*

> To let from November next Island Mahee with the kelp shores thereof; the particular good qualities of its kelp and Grazing are well known. Apply Robert Hamilton, Ardmillan

Phase 2: Iodine from seaweed 1811 - ~1940

The end of the Napoleonic wars and the manufacture of purer synthetic alkali from the early 1820s meant that kelp production for alkali was no longer profitable, as its price collapsed. It was also hard, back-breaking work and the rewards were small for the effort and time involved. Kelping had resulted in population growth in Scotland in coastal areas, and also in Ireland, and the collapse of the industry led to starvation and emigration. Contemporary commentators also deplored the fact that kelp-making meant that people were not working their land, and the "manurial" value of seaweed was also being lost. It was literally going up in smoke.

Just when all seemed lost for the kelp industry, a fortuitous discovery by Bernard Courtois in 1811, a French saltpeter (potassium nitrate) manufacturer, saved the day. He was extracting potassium salts from kelp liquor as part of the process of making saltpeter. Shortage of saltpeter for gunpowder, due to the British naval blockade curtailing imports from India, had led to kelp being used as a source in France. He noticed that his copper pans were corroding and after some investigation and treating the residue with concentrated sulfuric acid, he observed the production of a violet vapor, which condensed to blue-black crystals (43). The new substance was quickly identified as a new element by Gay-Lussac (who named it) and also by Humphry Davy, who competed with Gay-Lussac for the priority of discovery, naming and characterization of this new element. One of the surprising things about this serendipitous discovery was that it hadn't happened before, as iodine is easily liberated from its compounds.

When saltpeter manufacture from this source became unprofitable, due to renewed imports from India, Courtois started making iodine on a small scale around 1822 by displacing iodine from solution using chlorine. (44, 45). Other French manufacturers started up soon after and France became an important producer of iodine from kelp until the early 20th century, only rivalled by Scotland. Courtois, like Le Blanc before him, didn't make a financial success out of his discovery. In 1817 Andrew Ure discussed the production of iodine from kelp using a modification of Courtois' original method, and suggested that kelp residues from soap boiling might a valuable source of iodine. This quotation also indicates the value placed on kelp by soap boilers (46):

> As many of the Scotch soap manufacturers use scarcely any other alkaline matter for their hard soaps except kelp, it occurred to me that in some of their residuums a substance might be found, rich in iodine. Accordingly, after some investigation, I found a brown liquid of an oily consistence, from which I expected to procure what I wanted. This liquid drains from the salt, which they boil up and evaporate to dryness from their waste leys for the soda manufacturer.

Ure goes on to describe how he discovered that acidifying the liquid with concentrated sulfuric acid (diluted to 50%), cooling and filtering, removed crystallized salts and precipitated sulfur. He then added solid manganese dioxide as an oxidizing agent (suggested by William Wollaston) and heated the mixture, whereupon iodine sublimed over. He reports how he optimized the procedure with regard to the amount and concentration of acid, the amount of manganese dioxide used and the temperature. This method was to become the most common method for extracting iodine from kelp liquors in Scotland and Ireland. The French continued with the chlorine-displacement method. It is not clear when iodine was first made commercially in Scotland, but there are hints that Ure bought up the kelp residues from soap-boilers to make iodine. By mid-century Glasgow had become a major center of iodine production with up to 20 manufacturers in 1845. One of these was a J. Ward who presumably was the same John Ward who started a factory in Rathmelton (now known as Ramelton), County Donegal in 1845.

There was no initial demand for iodine, except as a chemical curiosity and a subject for chemical research, but it quickly found uses in medicine, as a cure for goiter and as an antiseptic. It was used in the early photographic processes and in the production of dyestuffs, and demand grew steadily from the 1840s onwards.

The Extraction Process for Iodine

In 1853 Sheridan Muspratt, son of James Muspratt, started publishing his successful encyclopedia on industrial chemistry, *Chemistry: Theoretical, Practical & Analytical* in monthly parts and in it he describes the current methods used for extracting iodine from kelp and mentions the Donegal factory (19, 47):

> The course pursued in its manufacture is simple. The several fuci and algae which contain it, are collected by inhabitants of places adjacent to the sea-shore, and dried in the air, after which shallow rectangular pits are dug wherein the dried material is burned. The semi-vitrified ash that remains is broken up by sprinkling a little water upon it while it is hot. This is the kelp of the Scotch and Irish, and is the same as the varec of the Continental producers; it is purchased by the several manufacturers, in order to extract from it the iodine and other salts. For this purpose it is reduced to a coarse powder, which is placed in rectangular filters, having an inner perforated bottom of sheet-iron. ….

> Several manufacturers … may be found, among whom may be mentioned Mr. Whitelaw of Glasgow, and Mr. John Ward of the country Donegal, Ireland.

William Paterson had become the dominant Scottish manufacturer of iodine from kelp by 1862, processing 80% of the kelp, and he bought kelp from Ireland for his Glasgow factory into the 1880s.

The process can be summarized as follows (see Muspratt (48) for more details). Seaweed was collected, dried and then burnt on the seashore in primitive open kilns to form a glassy mass, known as kelp (Figure 2). This was then shipped by sea to the end-users, and when iodine became the major product, these manufacturers (also known as lixiviators) were mainly located in Scotland and Ireland. The crushed kelp was lixiviated (leached) in cast-iron baskets in order to extract the soluble salts. This was done is a series of interconnected tanks. Concentrated liquor was taken off at the bottom and water added at the top, in what was known as a Shanks' battery.

In a series of evaporations of the resulting concentrated kelp liquor, potassium chloride, potassium sulfate, sodium chloride and sodium sulfate were removed by crystallization. These were filtered off separately and sold as by-products. The potassium salts were especially valuable up to the 1870s for use as fertilizer and in gunpowder, after which cheaper supplies became available from Germany. The residual liquor contained iodides, bromides and sulfur compounds. Concentrated sulfuric acid was added (1 part in 7) and allowed to stand for 36-48 hours. The sulfur compounds (sulfides and sulfites) decomposed, H_2S and SO_2 gases were given off and sulfur was deposited, together with more salts. Sulfur was another saleable by-product. After filtering, the acidified liquor was placed in an iron retort (with a lead still-head) and heated to 60 °C (140 °F). Manganese dioxide (MnO_2) powder was added as the oxidant and the solution boiled to expel the iodine as vapor (~100 °C). This was condensed in a series of connected glass or pottery receivers called udells. The iodine was purified by sublimation as required. The solid iodine was packed in small barrels known as kegs, each containing 1 cwt (112 lb.).

Muspratt describes other processes that had been developed as alternative methods of treating kelp to extract iodine, as do Muspratt and Molinari (47) and Mellor (45). The variety of methods that had been developed indicates the importance of this industry by the middle to late 1800s, when kelp was still the main source of iodine. (The detail of the various processes will be discussed in a future article.) From 1874 iodine started being imported into Europe as a by-product of the Chilean nitrate industry, and eventually this came to dominate the iodine industry. Iodine was available from this source in vast quantities—Chile could produce 5,100 tons a year when total world consumption was only 500 tons. However, a cartel was set up between the iodine producers to "fix" iodine prices, which lasted 61 years and served the interests of Chile as well as European producers, by regulating prices (49). This allowed the uneconomic production of iodine from seaweed to stagger on until around the 1930s in Glasgow, although it only finally ceased in France around the mid-1950s. It is interesting to note that China still has factories today extracting iodine and other chemicals from seaweed, as a by-product of algin production.

In 1862 the young English chemist Edward Stanford published an important paper describing improved methods of obtaining iodine from seaweed (13), the first of many papers he produced on the utilization of seaweed (50). In this paper he reviewed the history and uses of seaweed, and then went on to describe his improved process, known as the char process, using destructive distillation of dry seaweed in a kiln, to extract increased amounts of iodine and other useful by-products from seaweed, which he hoped would make the industry economically more viable. He comments on the state of the iodine from kelp industry in 1862 (13):

> Kelp, however, is the only commercial source for its production, and the immense value of iodine, in photography and medicine particularly, has given an impulse to the manufacture of kelp, which renders it by far the most important of all the applications of seaweed.
>
> As at present carried on, it has many disadvantages; these are well-known to chemists, but probably from the fact that it is conducted on desolate shores, at a considerable distance from centers of civilization, it has not yet received that attention its importance demands…

He goes on to say that

> The manufacture is at present limited to a few parts of Great Britain, the western and northern islands of Scotland, the north-west coast of Ireland, and Guernsey.

At that time Mr. William Paterson of Glasgow processed nearly 80% of the kelp produced in Ireland and Scotland, a total of 10,000 tons in 1860-61, worth on average £4 a ton. 60% of the kelp came from Ireland. Stanford notes that only a small portion of British kelp is lixiviated (that is extracted) outside Scotland, in Ireland

and Guernsey. He also gives statistics on French production of chemicals from seaweed in seven factories.

Irish Iodine Works

Figure 1 shows where kelp was lixiviated and iodine extracted in Ireland. Muspratt had mentioned John Ward of Donegal, and in the Great Exhibition of 1851 in London there was a display of Irish chemicals obtained from seaweed (51):

> I observed in the great exhibition a case of chemical stuffs produced from Irish sea-weeds—viz., iodine, chloride of potassium, sulphate of potash, and alkaline, or kelp-salt—manufactured in the Ramelton Chemical Works, by the exhibitor, Mr. John Ward. These works, the first of their kind started in Ireland, were established by Mr. Ward, in March 1845, in Ramelton, a small town on an arm of Lough Swilly, county Donegal. Previous to their establishment the people of the north-west coast of Ireland had comparatively no home market for the produce of their industry, in so far as regarded the manufacture of kelp from sea-weed, consequently but little was produced; but since the opening of the works in Ramelton by the enterprising exhibitor, who was generally considered at the time to be making a rather bold experiment, a large annual consumption of kelp at the works has caused it to be made in much greater abundance, and the prices raised to such an extent, causing thereby not only a large circulation of money in that part of Ireland, but has conferred great benefits on the neighbouring coast, by the extensive employment it affords to the poorer classes round the districts, who, but for this field of commerce having been opened up almost at their own doors, would, in many cases, be unemployed, and in desperate circumstances.
>
> In the town of Ramelton the chemical works have been of the greatest benefit, by the number of workmen and labourers employed in and around it, and the very considerable shipping trade, in vessels ranging from 50 to 120 tons, which the importation of manufactured stuffs has been the means of bringing to Lough Swilly.
>
> Before concluding these brief remarks, I cannot refrain from expressing my high opinion of the talent and energy displayed by Mr. Ward in founding and carrying on such an extensive undertaking, where few would have hazarded such an enterprise.
>
> The cultivation of national industry must, at all times, be regarded as of the utmost importance in every country, but more especially in Ireland; and it cannot fail to be looked upon as reflecting the highest credit on all who have contributed so largely as Mr. Ward has done to this important end, and the well-known and widely-spread liberality of that gentleman has brought its own reward in the increasing and flourishing state of the works, and also, the high name that his manufactured stuffs, viz., chloride of potassium, sulphate of potash, &c., has gained in the London and continental markets.

In the catalogue for the Great Exhibition of 1851 seven British and two French companies displayed their products from seaweed, and as well as John Ward, an E. Bullock & Co., Galway is also listed. J. Ward of Glasgow was bought by the British Seaweed Co. Ltd. in 1867 (Stanford's company) (52). In 1887 the company was still in existence, but it was now owned by James O'Mahony. The site of this factory in Green Lane, Ramelton is still known and the remains were only demolished 30 years ago, though some traces still remain (7). I have not yet managed to find out anything about the firm of E. Bullock in Galway, although it was obviously well known in 1851-2 and also displayed at the Cork Exhibition in 1852 (53):

> Iodine is manufactured almost exclusively from kelp, which is the ash resulting from the burning of sea weeds. The iodine in a ton of sea weeds might be put into a small bottle; and the other products of value, sulphate and muriate of potash are very small compared to the bulk of the material from which they are obtained.
>
> The ingredients for extracting the iodine, are comparatively few; therefore the importance of the manufacture of these products, as well as iodine of potassium, by Messrs. Bullock of Galway, and in the County Donegal by Mr. John Ward, at Ramelton, within a few miles of where the kelp is burned, is an interesting feature of the advancement of Irish chemical manufactures. Formerly iodine was almost altogether prepared in England, Scotland, and on the continent.

At least two other enterprises existed in Ireland for the chemical utilization of seaweed in the 19th century: in Galway and in County Clare. Robinson (1986) describes the kelp industry on Aran and the role of the Irish Iodine & Marine Salts Mfg. Co. Ltd. (54) based in Galway, later relaunched as the Marine Salts Company. A site on the bank of the Corrib in Galway is still referred to locally as "The Iodine," though this refers to part of the factory set up in 1863 by the Irish Iodine and Marine Salts Manufacturing Company (55) and used for converting the waste from iodine extraction into fertilizer (56).

This company was founded in 1863 by Thomas H. Thompson, Sir James Drombraine and Richard Young. They may have been operating Stanford's char process according to Booth (50), though initially they were using

Figure 4*: The iodine works on Long Walk in Galway, ca. 1865, courtesy National Library of Ireland.*

McArdle's patent wet process. Certainly, Stanford was well aware of their activities, as the cuttings in his notebook shows, and he complained that they were infringing his patent (57). By 1865 they had a factory operating in Galway on Long Walk (Figure 4), and were building one at Port Chorrúch on the Aran Islands, across the water from Galway. The 1860s was a boom time for the iodine industry, just before Chilean iodine arrived on the scene, which would sweep the board of kelp-derived iodine. The new enterprise was reported in the local paper (58):

> Iodine Manufactory. The Marine Salts Co. of Ireland (Ltd.) want to increase their operation. They have a factory at Long Walk, Galway, and buildings in Arran for drying and burning kelp to be taken as ash to Galway. The Company has originated a process of converting seaweed to ash which is patented. There are twenty-six men employed under Mr. Glassford in Galway. The following substances are produced in abundance: Muriate of potash (used in the manufacture of powder, for which there is a brisk demand in Liverpool), Sulphate of potash (used in the manufacture of fine glass), Glauber salts, Soda salts (for the manufacture of coarse glass). The grand result produced from the factory is Iodine, with a standing order from London for as much as possible. The refuse makes manure.

The works manager Mr. Glassford was the same person who described the kelp industry in 1848 (12). By 1867 the Marine Salts Co. claimed to be the third largest iodine manufacturer in the United Kingdom. The Aran Islands produced around 700 tons of kelp a year and this had previously been sold to agents of Scottish manufacturers like William Paterson. The competition for the kelp production was solved by the land-agent on Aran, Mr. Thompson, declaring that kelp could only be sold to him, effectively setting up a monopoly, where he decided what price should be paid and defining his own 22.5 cwt. ton (rather than 20 cwt.). This sounds bad but the "long" ton of 21 cwt was normal practice in the kelp industry in Scotland and Ireland, due to the accidental, and sometimes deliberate, adulteration of the kelp by sand and stones. Robinson (1986) has a good discussion of this unsavory episode, which ended when the factory on Aran closed in 1870 after the fall in iodine prices, and in 1872 Thompson was forced to relinquish his monopoly. Robinson writes (59):

> At the time of the iodine boom… there must have been lines of shore-workers trudging up the shingle with weed to feed the machinery of the factory.

The workers were paid a penny a basket for seaweed. The ruins of a kelp factory can still be found at Port Chorruch on Aran's best kelp shore, a decayed "outpost of Victorian industrialism," as Robinson expresses it. The Irish Iodine and Marine Salts Mfg. Co. finally closed in 1876, having gone into liquidation.

Booth (1978) (50) refers to the setting up of an iodine factory in Freagh, County Clare in 1878 by the North British Chemical Co. Ltd. (Stanford's company), and quotes a letter in Stanford's papers dated 1884 which refers to

> Mr. Ross … who thoroughly understands their patent process by retort, is to superintend the Freagh chemical works which are now to commence.

However, letters in the local papers in 1878 indicate that the factory was built and about to start production in early 1878 (60). In 1878 Robert Galloway said in a paper that no iodine was then being made in Ireland. The Galway works had closed, the Freagh plant had still to produce and he seems to think that the Ramelton plant had also ceased production by this date (61). The remains of this factory at Freagh were only demolished in 1999 (62). It is not certain when it closed, but the local story is that it was closed after a worker, the worse for drink, fell into the hot ash and was killed (63). Certainly by the end of the 19th century it seems that none of the Irish iodine factories was still in production, the one in Ramelton being the first to start and the last to close.

Kelp production still continued on a small scale into the 20th century, but the kelp was now all exported. Kirby (1953) records that the burning of kelp for iodine manufacture in Ireland only stopped in 1953 (64):

> Up until 1953, kelp also continued to be burnt for iodine in Eire, the amount of ash produced ranging

> from 330 tons to 1,335 tons annually with a value of £3 15s. 3d. to £8 11s. 4d. per ton.

The kelp was usually exported to Scotland, and when that industry closed in the 1930s, it was then sent to France for extraction of the iodine. Chapman (1970) writes, "In the 19th. century much of the Irish kelp was shipped to Glasgow for the extraction of iodine" (65).

It would seem that the Scottish iodine industry, which had started sometime before 1840, closed in the 1930s (at the collapse of the iodine cartel) and the last Scottish kelp was made around that date. The last shipment left N. Uist in 1934. The industry survived in France until mid-1950s. Kelp continued to be burnt in Ireland until the 1940s.

As was the case with other industries in the 19th century, the stronger Scottish or English companies bought out and closed smaller Irish companies to consolidate their own markets. As we have seen there was fierce competition for the kelp from Aran in the late 1860s between the local Irish company and agents for Scottish companies (66).

Payment for kelp was always a problem as the buyers appear to have used chemical sleight of hand rather than proper analysis to determine payment, as this passage from Robinson's book indicates (67):

> Before he would buy, the agent would test the kelp for iodine content. He would crumble together two or three little pieces taken from different parts of the lot, put a pinch of the powder into a test-tube and do something mysterious with a drop of sulphuric acid; the islanders would take it as a hopeful sign if when the treated sample was thrown on the ground they saw a smoke of iodine vapour arising from it. Then after a calculation the agent would announce his verdict, acceptance or rejection, good price or bad.

Seamus Mac an Iomaire gives a similar, contemporary account (3):

> The sampling man goes around with a hammer and bucket, taking a small bit off each slab. The kelp makers know him as well as a bad halfpenny. When the sample is taken he brings it into the assayer's office, and the name of the person who owns the pile is on the ticket on the bucket. The man inside has a glass as a means of assaying, and according to what the glass shows he will pay its value to the kelp maker.

However, if chemical analysis was not properly carried out by the agents, they had only themselves to blame as they were as likely to pay over the odds as under the odds for kelp. The problem of accidental or deliberate adulteration of the kelp was always a problem and adding sand, stones, even varnished rocks, was sometimes considered fair game by the kelpers, if they could get away with it.

Phase 3: Alginates from Seaweed ~1880-Today

The last, and still continuing phase, of production of chemicals from seaweed is the extraction of alginates and related compounds. This originated from the researches of E.C.C. Stanford (68), who was the first to extract impure algin from seaweed in 1881. He patented the process and published articles describing it and its potential uses. Krefting (1896) (69) later made a pure sample. Chapman has a useful chapter on "Algin and Alginates" (70). Alginic acid and its salts (the sodium salt is known as algin) are polysaccharides found in brown seaweeds, and comprise between 15-40% of the dry weight. As with almost all chemicals in seaweeds, the percentage varies from species to species, from sample to sample, and with the season! Norway has become an important center for alginate research.

Although Stanford suggested many uses for alginates and continued to work on seaweed until the end of his life in 1899, their potential was not realized for nearly half a century. In Canada and the USA the Kelco Company started extracting alginates from seaweed in 1929 and was still a major producer until 1999 when it was taken over by Monsanto, and later by ISP Alginates. The first company to produce alginates from seaweed in Europe was started in Scotland in 1937 and it took some time for the alginate industry to grow.

The simplest method of extracting alginates is based on Stanford's original process, which involved adding dilute acid to macerated seaweed, extracting the soluble salts, and leaving the organic residue, composed of algin and cellulose, behind. The alginic acid is then dissolved out in sodium carbonate to give sodium alginate, which when acidified yields pure alginic acid. The original kelp products—iodine and potassium salts—are obtained as a by-product in maximum yield because no heating is involved. This is known as the wet process.

Thomas Dillon and Vincent Barry of University College, Galway did important work on methods of extracting alginates from seaweed in the 1930s. Dillon had earlier written an article (71) encouraging a revival of the Irish iodine and potash industry:

> For about two hundred years seaweed has been a raw material for chemical industry along our west coast.

> For not less than that period, the enormous quantity of seaweed thrown up on our shores has been collected, dried and burned, to obtain the ash known as kelp.

He points out that in 1930 Ireland was the only kelp-producing country that didn't have its own iodine industry, and he compares the neglect of seaweed in Ireland to the relative importance of the industry in Brittany. He goes on to recommend that the industry be revived not solely for iodine production, where competition was strong, but to produce potash for agricultural use in Ireland. It would seem that his words fell on deaf ears in Ireland, but from 1910-1930 potash was extracted from seaweed on the Pacific coast of the USA (72).

In fact the revival of seaweed collection in Ireland after World War II was due to the demand for alginates for food, cosmetics, textiles and other uses. Alginates have become an important ingredient of many foods, including ice-cream. It also has important medical and pharmaceutical uses, for example, as wound and burn dressings. The government set up Arramara Teoranta in 1947 to collect and process seaweed into meal, which was exported to Scotland for processing. The company is currently owned by a Canadian company, Acadian Seaplants. World production of alginic acid is around 25,000 tonnes a year, with China, Norway and Scotland being the main producers. Thus Stanford's vision has come to pass at last.

Conclusion

This brief survey of the Irish "chemicals from seaweed" industry has covered more than three centuries. Happily seaweed is still being collected on Irish shores in the 21st century and processed into saleable products, creating jobs. Seaweed is collected by part-time workers in Connemara and shipped to the Arramara Teoranta factory for converting into seaweed meal. Some small companies produce liquid fertilizers and other high-value products from seaweed. Seaweed is still collected for use an as a green manure, its original use, going back centuries. There is an active Irish Seaweed Industry Organisation (73) based at National University Ireland, Galway.

Seaweed is still a largely unutilized natural resource and massive quantities are produced each year in the oceans of the world and swept ashore on to stormy shores. History has shown what materials can be obtained from seaweed, and it has also been demonstrated that it can be cultivated in seaweed farms, particularly in Japan. Even in Ireland one can see the remains of these seaweed (fucus) farms at several places around Irish coasts, where seaweed was cultivated on stones in shallow waters along the northern coast.

Ireland has suffered in the past by having the local seaweed industry dominated and directed by outside companies, where Ireland exported low-value bulk products (like kelp) and foreign companies produced the value-added products (such as iodine and its salts.) The demands for a sustainable economy and for greener industries, and for job creation, suggest that we should look again at this abundant but underutilized natural resource and develop new industries with 21st century technologies.

In subsequent articles I hope to look specifically at the iodine industry in Glasgow, the fascinating career of Edward C. C. Stanford, and the chemistry of the various processes used for extraction iodine from seaweed.

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Dr. Peter Childs taught Chemistry at university level from 1970 until retiring in 2009, at Makerere University, Kampala, Uganda (1970-76) and later at the University of Limerick, Limerick, Ireland (1978-2009). He became interested in the early Irish chemical industry and has been researching this for the past 20 years. He has worked extensively with Irish chemistry teachers—producing *Chemistry in Action!* magazine since 1980, starting the annual ChemEd-Ireland conferences, and running in-service courses and workshops. He is a past President of the Irish Science Teachers' Association and also of

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The Division of History of Chemistry (HIST) of the American Chemical Society (ACS) solicits nominations for the 2022 HIST Award for Outstanding Achievement in the History of Chemistry. This award, formerly known as the Dexter Award and then the Edelstein Award, continues a tradition started in 1956. The award is international in scope, and nominations are welcome from anywhere in the world. Previous winners of the Dexter and Edelstein Awards include chemists and historians from the United States, Canada, Germany, France, the Netherlands, Hungary, and the United Kingdom.

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The SHAC Morris Award for 2021 has been given to Ernst Homburg for his outstanding work on the history of the chemical industry. His contributions include major studies on the history of the madder industry, his seminal paper on the early history of industrial R&D laboratories and his comprehensive history of twentieth-century chemistry and chemical industry.

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