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Vol. I.

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ORIGINAL PAPERS.

ON THE CHEMISTRY OF CERTAIN ALGAE OF THE PACIFIC COAST.

By DAVID M. BALCH, S.B. HARV.

Received September 13, 1909.

Like most sea-washed regions throughout the world, our Pacific Coast produces many algae peculiar to itself, and some that are more cosmopolitan in character. Some of these are gigantic in size and pelagic as to locality, covering the ocean at about the 10-12 fathom line with dense fields of their floating foliage. Others, of far lesser growth, are littoral, forming in favored localities a dense fringe at about the limit of extreme low tide, and even beneath tidal fluctuations.

It is my purpose in the following pages—after a brief description of some of the most prominent species and varieties, together with their habitat, range, character and general features—to present numerous analyses of the inorganic constit-

uents of each at different stages of their development, and in some instances of different members of each, with remarks on some unexpected results of these researches. Then will follow a dissertation on the economic value of certain of the huge Laminariaceae, and on measures proposed for the exploitation of our marine forests and the utilization of their products for the needs of commerce. The case of kelp *versus* wood as material for distillation will be argued at some length. Also the relative advantages, and disadvantages, that govern the winning of potassium from its ocean sources—unlimited in abundance and ceaselessly renewed—and the exploitation by mining of its terrestrial deposits, which, in certain localities, seem also almost inexhaustible.

A peculiar and most interesting sea-weed, *Nereocystis*, is found in favorable localities all along the western coast of North America, from warm temperature to subarctic regions. Point Conception, Calif., may be regarded as the boundary roughly separating the southern from the northern species; for, although the species overlap in the Santa Barbara Channel, and the northern species may possibly occur even further south, it does not appear that the southern species has been recognized north of Point Conception.

Whether this plant is an annual or a biennial has been matter for debate, but the question seems merely one of definition; there can be no seasons proper at the bottom of the sea. Commencing life late in the autumn, it perfects itself in the following year, the southern species demanding about 12 months, and the northern about 15 months for its life work. Consequently, it is a plant of very rapid growth, its huge bulk and abundant store of alkaline salts being the product of little more than a single year.

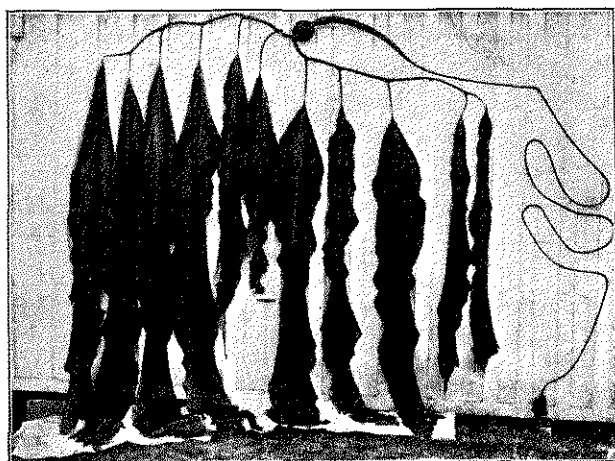
I. Nereocystis gigantea—now better known as *Pelagophycus Porra* Setchell—is the southern species. Taking San Diego Bay as a center, this plant is fairly abundant for a hundred miles both north and south. Its northern limit has been stated above; its southern is uncertain. It is reported on good authority as growing in company with *Macrocystis pyrifera*—they usually occur associated—at Mag-

dalena Bay, some 500 miles south of San Diego; it probably grows in localities favoring its increase at many intermediate points.

This plant is popularly known as the "Elk Kelp," from the fact that as it lies stranded on a beach and robbed of its leaves by the action of the surf, the incurved arms garnished with the stout, spiky bases of the petioles, strongly remind one of spreading antlers.

(The accompanying illustration, from a medium-sized specimen in a nearly perfect condition, fairly represents its peculiar form.)

It grows about the 10-12 fathom line from loose rocks, or sunken reefs. When full grown it may consist of a solid cylindrical stem some 60 feet in length by one-half inch in diameter, which, starting from the small, highly-branched holdfast that attaches the plant to its base, abruptly expands near its terminus into a hollow cylindrical slightly



conical tube—named the apophysis—which may exceed 6 feet in length by 3 inches in diameter—separated by a sharp choke, or constriction, from a nearly spherical bladder, which rarely exceeds 8 inches in diameter. No true proportion exists between bladder and apophysis—either may be overdeveloped; they are connected by a short and very narrow internal canal. From a common point at the apex of the bladder issue at nearly right angles two opposite horizontal arms, several feet in length, solid, distinctly flattened, and bearing along their upper edge the petioles of the leaves. The petioles, about six in number for each arm of a mature plant, and separated irregularly by intervals of several inches, are stout at the base but quickly become rounded and very slender; they

average 6 or 8 inches in length; each petiole carries a single leaf, but as the petioles are frequently cleft, or divided, near the base, any base may carry two leaves—possibly more. Very rarely specimens have been observed in which the petioles issue alternately from the upper and lower edge of the arm. The leaves differ in shape, size, and texture; these variations may be governed by the progress of their development. The plant as stranded rarely bears even remnants of its immense fronds; or, if the petioles be strong enough to stand the strain, only a few inches of their thick leathery bases—all else has been removed by the surf. The perfect leaves may reach 15 feet or more in length by 20 inches in diameter; they are cuneate at the base, ruffled at the edges, sometimes roughened on the surface by slight spiny projections; often smooth, glossy, and nearly transparent; their color is a rich yellowish brown; the texture sometimes very brittle and flimsy, sometimes comparatively tough. The fluorescence (or sori) occurs in broad dark patches on the leaves.

So much for the mature plant. The infant specimens consist simply of a spherical bladder about $\frac{3}{4}$ inch in diameter, crowned by two opposite, short oval leaves, and having a very slender, thread-like stem a few inches in length, terminated by a very small and delicate holdfast; apophysis and arms do not seem to be present even in a rudimentary form. How this fragile little plant can germinate, anchor itself, and grow in the ocean depths, 70 feet beneath the surface, is an interesting matter for consideration. When the bladder has grown to a diameter of about $1\frac{1}{2}$ inches the development of its arms is in progress and consists at first of one petiole each with a terminal leaf; their development progresses by fissure of the terminal. The bladder may reach 3 inches in diameter before the apophysis—which is merely a modified form of the bladder, and serves the same purpose, *i. e.*, to keep the plant upright—is much in evidence; then it increases rapidly in size as the needs of the plant demand.

Pelagophycus contains very little cellulose as woody fiber; the bulk of the plant is composed of sound fleshy cellular tissue saturated with saline solutions, and protected by a thin, glossy external bark, or varnish. Approximately some 90 per cent. of its weight is water. When exposed to the sun and wind the plant dries rapidly; the beautiful leaves, after a few hours' exposure, resemble greenish gray tissue paper; stem and arms dry more

slowly but are finally converted into a horny substance, very tough and elastic, and not easily broken across or crushed into pieces. The bladder and apophysis contain no liquid in their cavities; owing to the thickness—from $\frac{1}{2}$ to $\frac{3}{4}$ of an inch—of their fleshy walls they dry slowly, unless split longitudinally or quartered. When the drying has reached a certain stage these parts become covered with a very heavy saline efflorescence, and to such an extent that when bladders from small plants are dried entire nearly 50 per cent. of the salts they contain are thus exuded. With the stem and arms this efflorescence is much less.

* * * * *

In the following studies of the inorganic constituents of algae, specimens were collected at different stages of growth, and in different seasons of the year. They were dried by exposure to sun and wind until efflorescence commenced, then under glass, and finished at 125° C. A weighed portion was then charred, the char exhausted, and the lixivate brought to a known bulk in centimeters. From this, measured portions were taken for analysis.

I. Pelagophycus Porra (collected in January, 1905), at a very early stage of growth when the plants lacked apophysis, and in many cases arms.

EXPERIMENT I.

Bladders entire from $1\frac{1}{2}$ to $2\frac{1}{2}$ inches in diameter were sun-dried under glass; efflorescence was very copious, light and flocculent. They were then broken up, the salts separated by sifting, and drying finished at 125° C. A quantity weighing 1500 grams, was then charred with proper precautions; the char, 939 grams, was packed in a percolator and exhausted with hot water, 2000 cc. extracted 593.5 grams of salts; 1000 cc. additional 114.6 grams; 500 cc. additional 5.7 grams; 250 cc. additional 1.2 grams. The lixivates, colorless and odorless, were brought to 3750 cc. and were found to contain 715 grams of anhydrous salts. Measured portions were taken for analysis:

	Per cent.
Analysis 1 { CO ₃ equals.....	1.01
SO ₄ "	1.33
Cl "	51.01
K "	34.91
Na "	11.74
	<hr/>
	100.00

K was det. by platinum—Na by difference.

To the above 1500 grams belong the effloresced salts shaken from it. This was lightly charred to

separate a little organic matter, dissolved in water, filtered from a little mechanically mixed sand, and solution brought to 2250 cc. This contained 601 grams of anhydrous salts.

	Per cent.
Analysis 2 { CO ₃ equals.....	0.030
SO ₄ "	0.097
Cl "	47.880

These effloresced salts are nearly C. P. potassium chloride. This most interesting and unexpected result will be considered at length further on.

To determine, then, the constituents of the alkaline salts of the young bladders of the *Pelagophycus* the above solutions were mixed in proper proportion and 7.92 grams of the resulting salts analyzed as follows:

	Per cent.
Analysis 3 { CO ₃ equals.....	0.57
SO ₄ "	0.67
K "	40.91 (by platinum)
KCl, with a little sulphate, 78 per cent.	
NaCl, with a little carbonate, 22 per cent.	

Consequently, our 2100 grams of dried bladders have given us 1316 grams (62.67 per cent.) of alkaline salts, of which 78 per cent. (1026 grams) is anhydrous potassium chloride. This equals 48.85 per cent. of the raw material. A large trace of iodine—about 0.1 of one per cent.—is also present.

EXPERIMENT II.

The material used for Exp. I, as above stated, came from very young plants. We will now examine the salts yielded by the bladder, 8 inches in diameter, and the apophysis of a large and mature plant, collected Oct. 1, 1907. Cut into slices and dried under glass; efflorescence not flocculent, but crusty—like candied fruit—and somewhat discolored. Salts were removed by light pounding; both salts and residue were dried at 125° C.; they weighed respectively 92 and 315 grams (407 grams of dry material). This was charred and lixiviated as usual and gave 243 grams of anhydrous salts, or 60 per cent. of the material.

The effloresced salts agree closely with Exp. I.

	Per cent.
Analysis 4 { CO ₃ equals.....	a trace
SO ₄ "	0.79
Cl "	47.21
K "	51.62
KCl, 98.72 per cent. by platinum.	

Here again we have nearly pure potassium chloride.

A sample of salts obtained by evaporating the mixed lixivates gave:

	Per cent.
Analysis 5 { CO ₂	1.07
SO ₄	1.68
Cl.....	47.06

The ratio of KCl to NaCl was found to be as 80 is to 20. Consequently, the 407 grams of material, which gave 243 grams of crude salts, will yield 47.76 per cent. of potassium chloride. Agrees closely with results obtained in Exp. I.

EXPERIMENT III.

Branches.—From a large plant, solid flattened stems having petioles, and small portions of the tough bases of the leaves still attached. Material dried at 125° C. equals 210 grams. Charred and lixiviated as usual gave 104.7 grams salts.

	Per cent.
Analysis 6 { CO ₂ , equals.....	0.92
SO ₄ ".....	3.60

As we approach the leaves the percentage of sulphates augments, and we find iodine also increasing. In the salts from bladder and apophysis iodine rarely exceeds 0.1 of one per cent. In the salts from the arms we find 0.328 per cent. Alkaline chlorides are closely as in the preceding analyses. We have then from the arms of the plant 50 per cent. of their weight in crude salts, the value of which is increased by the iodine present.

EXPERIMENT IV.

Leaves.—We now reach the leaves—the laboratory wherein the mysterious, possibly inexplicable, operations of this most interesting plant are carried on, its other members being merely store-houses for their products. Nov. 16, 1906, collected the leaves, nearly intact, from two medium-sized plants, largest 8 feet long, 18 inches wide; a rich golden brown in color, leathery and rather thin; fine print could be read easily through the fresh leaf, which closely resembles corrugated glass. Leaves from one plant darker in color, thicker and apparently more mature. Contained 85 per cent. of water.

617 grams dried at 125° C. gave 174.68 grams of salts (28.31 per cent.) of the following composition:

	Per cent.
Analysis 7 { CO ₂	0.83
SO ₄	6.77
Cl.....	45.72
K.....	31.41
I.....	0.85
KCl.....	49.24
K ₂ SO ₄	12.27 equals 61.51 per cent. potassium salts.

Although the product of crude salts from the leaves is only about one-half that of other mem-

bers of the plant, their value is much greater on account of their large percentage of iodine.

Thin flimsy leaves, of quite different character, from another plant were then examined with closely approximate results. 115 grams gave 32.65 grams of salts, or 28.40 per cent., composed as follows:

	Per cent.
Analysis 8 { CO ₂	0.86
SO ₄	7.31
Cl.....	44.47
I.....	0.875

EXPERIMENT V.

Stem.—All parts of the plant have been examined except the long cylindrical stem, which I have taken up last, because in bulk and weight it is the least important member, and, moreover, can rarely be collected entire. Though apparently solid the stem has a central pith, or core, much softer than the surrounding tissues.

Stems from 10 to 12 feet in length from several young plants were coiled, sun-dried and finished at 125° C. They were then about 1/8 inch in diameter, and very tough and elastic. 90 grams gave 33.76 grams of salts (37.20 per cent.), composed as follows:

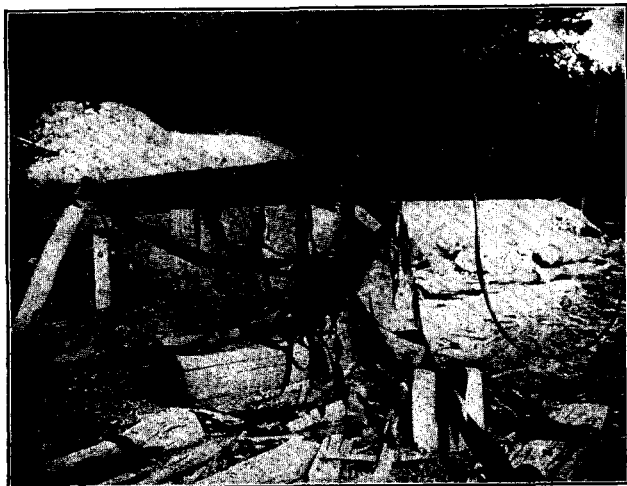
	Per cent.
Analysis 9 { CO ₂	1.81
SO ₄	7.66
Cl.....	42.71
I.....	0.55

To the above observations on *Pelagophycus porra* will be appended some remarks on the distribution of iodine; and also on the inorganic constituents insoluble in water—the true ash. We now pass to the northern representative of these giant *Laminariaceae*.

II. Nereocystis Leutkeana.—Commencing a little south of Point Conception, California, and extending into the Arctic and even to the shores of Kamtschatka, we have in this plant one of the most common and interesting algae of our north Pacific coasts. It is present everywhere, whether obstructing with its growth bays and island passes, or torn loose and wave-tossed, or stranded on their shores. Firmly anchored at a depth of from 8 to 10 fathoms by its branching holdfasts to submerged reefs, or scattered rocks, it covers with its streaming strap-like fronds patches acres in extent so densely as to impede navigation. That this plant differs greatly in form from the southern species is evident from the illustration.

(Photograph of specimen from San Juan Island, Puget Sound, opposite page.)

Its slender whip-like stem, the upper one-third of which becomes hollow and gradually expands in diameter from less than $\frac{1}{2}$ to 3 or 4 inches, terminates in a small oval bladder separated from the stem by a slight constriction. In an average plant the solid portion of the stem may be 40 feet, the hollow part—the apophysis—about 20 feet in length, the bladder 4 or 5 inches long and about 3 inches in diameter. The huge branching arms, that



carry leaf petioles, so conspicuous in *Pelagophycus*, are entirely lacking. Its small oval bladder is crowned by a dense mass of narrow fronds which vary in length from 10 to 30 feet. It forms asexual spores in great numbers on the surface of its fronds from August to December in localities about Puget Sound. Its period of growth comprises about 15 months; germinating in the autumn, it perfects itself about the close of the following year.

EXPERIMENT I.

Effloresced salts, from specimens collected at San Juan Island, Puget Sound, about June 1, 1907, were first examined. These had fallen from air-dried material and were mixed with a little organic matter; they were lightly charred, dissolved in water, the solution filtered, and evaporated to dryness. The specimen thus obtained was purely white, weighed 197.8 grams, and had the following composition:

	Per cent.
Analysis 10 { CO ₃	0.082
SO ₄	0.090
Cl.....	47.740

Consequently, we have here potassium chloride—a crude and unpurified product—that very nearly reaches the requirements of a C. P. article. Not a trace of iodine was present, but sodium and magnesium could be recognized.

EXPERIMENT II.

Bladder and Apophysis.—The specimen examined was collected about October 1, 1906, and sent me, undried, from Seattle, Washington, by express. It was evidently stranded, for the leaves were fragmentary and much decayed; the hollow portion of the stem—which carried a very small oval bladder—measured 15 feet in length; the solid part 25 feet.

The hollow portion effloresced very strongly during the drying, and when finished at 125° C. weighed 262 grams, which yielded 153 grams of salts, or 58.51 per cent. of its weight. Composition as follows:

	Per cent.
Analysis 11 { CO ₃	0.026
SO ₄	1.180
Cl.....	48.580
K plus Na.....	50.220

The ratio of K to Na was found to be nearly as 80 is to 20. Iodine was present slightly exceeding 0.1 of one per cent.

EXPERIMENT III.

Stem.—The solid portion, 25 feet in length, of the stem of the above plant furnished 171 grams of dried material, from which 57.3 grams (33.51 per cent.) of salts were extracted.

	Per cent.
Analysis 12 { CO ₃	4.41
SO ₄	3.92
Cl.....	42.15
Iodine, two determinations,	0.39–0.41 per cent.

In the condensation of iodine in the solid portion of its stem, this plant agrees with its congener, *Pelagophycus*, and, as will be shown further on, this feature is common to most of the hard-stemmed algae.

EXPERIMENT IV.

Leaves.—The leaves from Experiments 2 and 3 being badly decayed and not fit for use, others (fragmentary) collected from young plants about June 1, 1907, at San Juan Island, were utilized. Dried at 125° C., they weighed 607 grams. Charred and lixiviated, they gave 270.3 grams of salts, or 44.53 per cent. composition, as follows:

	Per cent.
Analysis 13 { CO ₃	0.52
SO ₄	5.26
Cl.....	46.52
I.....	0.117
K.....	36.55 det. by platinum
Total potassium salts equal	71 per cent.

On comparison with Analysis 7, it will be seen that the amount of crude salts from leaves of N.

Leut. is more than 50 per cent. higher than from those of *Pelagophycus*, or as 44.53 is to 28.31. Also that their percentage of potassium is higher as 71 is to 61.5, while iodine is present only as 0.117 is to 0.85. But the leaves of *Pelagophycus* came from a fine mature specimen collected in November, while those from N. Leut. were from young undeveloped plants collected late in May. Consequently, comparison is faulty, and this matter will be settled by further investigation as soon as mature leaves can be obtained. The increase in sulphates and the storing of iodine in the solid stem both warrant the expectation of a higher percentage in mature leaves.

III. Macrocystis pyrifera.—Unlike the preceding, this huge and vigorous plant enjoys a very wide range, and seems indifferent as to temperature. Along our coast it extends from Magdalena Bay, Mexico, to Sitka, Alaska; on the South American coast it abounds throughout Fuegia and around Cape Horn and extends north well up toward the equator. It is abundant on the coasts of New Zealand, the southern coasts of Australia, and of scattered islands throughout the Antarctic Ocean. Different species may be noted, but as yet the northern and southern species are considered to be identical.

This plant differs greatly, both in habit and appearance, from the *Nereocystes*. In localities favoring its growth it forms a dense belt, or grove, covering the surface of the ocean about the ten-fathom line with broad meadows of its graceful foliage. Anchored by its immense holdfast, which may exceed 3 feet in diameter, it quickly branches into a large number of round solid stems, usually less than one-half inch in diameter, and often far exceeding 50 feet in length. From these stems alternately, and at distances usually approximating six inches, grow pear-shaped bladders measuring—according to the development of the plant—from $\frac{1}{2}$ to 1 inch in diameter, and from 2 to 4 inches in length; the upper, or bulbous, part of the bladder is crowned with a single lanceolate leaf, from 1 to 2 feet in length, beautifully proportioned, and of a rich yellowish brown. According to general statement, the spores—sori—occur on submerged, bladderless leaves near the holdfast.

This plant is doubtless perennial, though its life may not extend over many years. It attains great bulk and weight. Detached leaves and branches are constantly brought to shore by the surf; during rough weather it is often stranded in vast

quantities, and entire plants many hundred pounds in weight strew the beaches; these usually include plants of *Pelagophycus* in their tangled masses, but they are never entire. Its texture throughout is much tougher than in the *Nereocystes*, and there is a lower percentage of water in its tissues. Its leaves develop in drying an odor as peculiar, and almost as agreeable, as that of new-mown hay—a characteristic odor that is permanent.

Macrocystes, then, consists of three principal parts—the stem, the bladder and the leaf. These were taken from a large, mature, plant—collected October, 1907—dried as usual and examined separately. From the material, about 1600 grams in all, a small deposit of effloresced salts fell during the drying.

EXPERIMENT I.

Effloresced salts, charred, dissolved, filtered and evaporated; weighed 43.25 grams; analysis as follows:

	Per cent.
Analysis 14 { CO ₃	0.087
{ SO ₄	0.590
{ Cl.....	47.710

No iodine: faint trace of Mg.

Here again we have nearly pure potassium chloride.

EXPERIMENT II.

Leaves.—These were fragmentary, and mostly from the basal portion of the leaf next the bladder. 297 grams, treated as usual, gave 64.7 grams of anhydrous salts, equal 21.80 per cent.

	Per cent.
Analysis 15 { CO ₃	1.80
{ SO ₄	11.20
{ Cl.....	40.44
{ I.....	0.70

EXPERIMENT III.

Bladders.—These varied in length from 3 to 4 inches, and were nearly 1 inch in diameter. 565 grams gave 232.5 grams salts, or about 41.15 per cent.

	Per cent.
Analysis 16 { CO ₃	1.08
{ SO ₄	3.15
{ I.....	46.96
{ C.....	0.54

EXPERIMENT IV.

Stems.—About $\frac{1}{2}$ inch in diameter. 688 grams, treated as usual, gave 201.75 grams salts, or 29.32 per cent.

	Per cent.
Analysis 17 { CO ₃	3.96
{ SO ₄	5.08
{ Cl.....	42.12
{ I.....	0.64

Iodine is very evenly distributed throughout the tissues of this plant.

The solutions were mixed in proper proportions and analyzed:

	Per cent.
CO ₃	2.38
SO ₄	4.91

Carbonate and sulphate were then changed to chloride and potassium determined by platinum:

	Per cent.
Analysis 18 { Cl.....	50.81
{ K.....	39.41

The potassium salts present in the crude salt from *Macrocystis* are as follows:

	Per cent.
KSO ₄	8.79
KCl.....	67.76
	76.55

The leaves were fragmentary; had they been intact the amount of sulphate would have been somewhat larger and the chloride less.

The following analysis is from perfect leaves of a smaller and less mature plant:

	Per cent.
Analysis 19 { CO ₃	3.43
{ SO ₄	12.50
{ Cl.....	38.05
{ I.....	0.507

Three branches with perfect leaves from a young plant were dried. Stems and bladders equaled 730 grams; leaves 2100 grams. The proportion varies, but the leaves may be regarded as forming from two-thirds to three-fourths of the entire weight of the plant.

A careful study of the results of the foregoing analyses leaves us face to face with certain problems of much interest to science, but not easy of comprehension and difficult to explain. It will be noted that these algae, particularly *Pelagophycus* and *Nereocystis*, are very rich in potassium chloride—their tissues are gorged with this salt; and this is true not only of the mature plant—when it has attained great bulk and weight, produced its spores, and accomplished its life work—but of the infant plant, just entering life, consisting of little more than two small leaves and a bladder weighing a few grams, which is even richer in potassium.

The comprehensive analysis of sea-water by Dittmar, from specimens collected by the Challenger expedition, assigns to it the following composition. Sp. Gr. 1.026. In 100 parts of water 3.5 parts of salts, as follows:

NaCl.....	77.758	Also traces of Br, I, Fl, P, Si, Au, Ag, Pb, Cu, Zn, Co, Ni, Fe, Mn, Al, Ba, Sr, Li, and other elements.
MgCl.....	10.878	
MgSO ₄	4.737	
CaSO ₄	3.600	
K ₂ SO ₄	2.465	
MgBr.....	0.217	
CaCO ₃	0.345	
	100.000	

It will be observed that potassium sulphate is present in sea-water in the proportion of about

2.5 per cent. of 3.5 per cent., or 0.087 per cent., which very nearly equals 0.04 or $\frac{1}{25}$ of one per cent. of potassium.

Although growing in a medium in which sodium abounds, the algae assimilate the far less abundant potassium, preferably as chloride; and, as seems probable without modification, for the organic acids of the plant are chiefly contained with Ca and Mg.

A phenomenon of much interest is the extrusion of potassium chloride, in a state of almost chemical purity, through the skin, or outer tissue, of the drying plant. The salt does not appear until drying is far advanced and the skin of the bladder has become soft and pliable, when it passes rapidly as a light, flaky efflorescence; which, if the material is protected under glass, may reach half an inch in thickness. The composition of the effloresced salts is given in Analyses 2 and 4, and of the crude salts from which they come in Analyses 3 and 5. But Analyses 3 and 5 do not give correctly the composition of the saline solution from which the salts effloresced; they give its composition after carbonization and lixiviation of the charred tissues that contained it. Before these processes its composition was far more complex, inasmuch as organic compounds of calcium, magnesium, sodium, phosphates, and other matters were present.

In the case of *Nereocystis*, the stems from several large plants, not sufficiently dry to have become brittle, were headed up in a barrel where they remained for nearly two years. On removing the material a few pounds of effloresced salts remained, shaken off during the operation. Their composition is given in Analysis 10, the composition, after carbonization, of the crude salts whence they came in Analyses 11 and 12.

And, again, from *Macrocystis*. The extruded salts come from the bladders and stems, the leaves do not effloresce; their composition is shown in Analysis 14; that of the saline mixture, after carbonization, from which they come in Analyses 16 and 17. It will be noticed that these show a far larger proportion of alkaline carbonate and sulphate than the preceding, nevertheless their effloresced salts are equally pure.

These natural processes, and their results, are not easy to comprehend or explain. They remind one of the operations of osmosis or dialysis, but results thus obtained by no means correspond as is shown by the following experiment:

A quantity of dried material was ground to a coarse powder, mixed to a thin paste with water, and dialyzed through parchment paper. The

liquor from the outer vessel, evaporated to dryness, yielded a yellowish granular salt; 9.56 grams were taken for analysis. Heated to incipient redness, they blackened and considerable organic matter burned off; they were then dissolved in water and solutions and washings brought to 250 cc. Carbonaceous residue on filter was incinerated and gave 0.092 g. of gray ash consisting chiefly of phosphate of lime and magnesia. The solution had the following composition:

	Per cent.
Analysis 20 { CO ₂	0.13
{ SO ₄	0.35
{ Cl.....	50.51

The organic matter burned off weighed 0.83 gram. The proportion of chlorine denotes the presence of about 25 per cent. of sodium chloride. On the whole, salts obtained by dialysis differ essentially from those extruded by the drying plant.

The percentage of sulphuric acid has a wider range than any other constituent of the soluble salts of the algae; less than one per cent. is often present, but I have recognized as high as 47.50 per cent. in the crude salts of a certain rockweed. Its proportion varies greatly in different members of the same plant, a fact everywhere apparent in the preceding analyses. It usually predominates in the leaves. Many algae rich in sulphates are correspondingly rich in iodine, but there are many exceptions.

I have given in the foregoing pages a concise description of the range, relative abundance, life habits, and chemical composition of our three most prominent giant kelps. It now remains to consider their economic value, and the most practical methods for the utilization of their products. It will have been noted that they all abound in potassium salts; that their brief life seems devoted to the task of extracting these salts from the medium in which they grow and storing them in their tissues; that they provide potassium compounds in a state of purity directly suited to our needs.

If we trace potassium to its source we shall find it in the feldspars present in all primitive, or igneous, rocks. Common granite contains about 40 per cent. of feldspar—about 7.5 per cent. of alkalis: gneiss, mica, slate, syenite, etc., are analogous in their composition. Potassium, in addition to its many uses in the arts, is indispensable as a food producer; any source from whence it can be easily and abundantly obtained is of vast importance to humanity. Its natural sources are obvious—feldspathic rocks, deposits of mineral salts, growing plants. Since feldspar is everywhere, and con-

tains some 15 per cent. of potassa, why not seek it directly at its source? Because the extraction of potassium from orthoclase, common feldspar, is too difficult and expensive to be practicable. The second source is deposits, beds of natural salts in some localities of vast extent. Our third source is growing plants; and as, obviously, for many reasons land plants are not available as material, we turn to the ocean forests, to marine plants, for our supply. The ocean is a vast reservoir for potassium salts dissolved by the action of the elements from the rocks and carried by the rivers to the sea. They have accumulated there for ages; and, although potassium oxide constitutes but one-twenty-fifth of one per cent. of the weight of sea water—about eleven ounces in a cubic yard—if we take the trouble to calculate the number of cubic yards in a single cubic mile of ocean water, we regard with amazement the mass of potassium oxide contained therein; it is as limitless and inexhaustible as the nitrogen of the atmosphere. If by any means at our command we attempt to extract the dozen ounces of potassium contained in each ton of sea water, we shall find ourselves engaged in a difficult and unremunerative endeavor which we cannot successfully accomplish.

But our marine forests are quietly and ceaselessly accomplishing this task for our advantage. Each plant of the giant kelps stores up yearly, in addition to other valuable products, potassium chloride most liberal in quantity, and of remarkable purity, as the result of a natural process. We have but to gather the plant and utilize its products. If we are not wise enough to do so, the plant having reached maturity decays, its products return to the ocean, are taken up by its successors in the ensuing year, and the opportunity is ours once again.

In the matter of the utilization of the kelps on a large scale for the demands of commerce, two subjects for discussion come next in order:

I. How the raw material can be gathered and handled most conveniently. II. How its several products can be most advantageously extracted. The first is the more important, for on it largely depends the financial success of the enterprise.

I. Gathering the Kelp.—Certain seaweeds—notably *Laminaria saccharina*—have for ages found their uses whether as applied directly to the soil for fertilizing material, or in supplying crude raw material on a small scale for certain branches of

manufacture. This industry was confined to countries where labor was cheap, and to seasons of the year when there was little else to do. The plant was cut by hand from outlying reefs and brought to land by boats, or collected where it lay stranded in masses after heavy gales. In either case the material was spread in a convenient place, dried as thoroughly as the weather permitted, drawn into heaps, and burned, the very impure ash resulting was used as a basis for manufacture. The whole process was unscientific, crude, wasteful, and costly in the highest degree; and nothing but the high prices obtained for the several products could have justified such methods. At the present day steam power must be substituted for hand labor, and the sources of waste closed.

A steam scow, or launch, properly fitted with labor-saving appliances, would seem to be the best vehicle for gathering and transporting kelp. It could move quickly from place to place, select the best fields for its operations, cut the plant, draw it on board, carry to shore and unload its cargo—all by steam power and at minimum cost—for, inasmuch as a dredge can raise a cubic yard of silt or sand from a considerable depth and transport it where needed at very moderate cost, there is no reason why a properly equipped craft cannot handle a ton of seaweed to equal advantage.

Handling the Material.—Let us suppose that a cargo of kelp has been landed at the wharf of a drying shed; the next step is to get it into condition for transportation. Freshly lifted from the sea the plant contains from 85 to 90 per cent. of water, is heavy, bulky, and unmanageable, and must first of all be deprived of its superfluous moisture. Though drying progresses very rapidly under the influence of sunshine and wind, in many points this method is objectionable. Drying by artificial heat is to be preferred, and there are methods in common use, perfectly applicable to seaweed, by which large masses of coarse material are easily and cheaply desiccated. If the material is to be transported—for instance, from several drying sheds at long intervals to a central manufacturing plant—drying should not be pushed too far, but stopped when an efflorescence of salts begins to appear the material is then soft and pliable, and can be pressed, like hay or cotton, into small space; a ton of wet kelp can thus be reduced to a small bale weighing not more than 250 pounds, in which form it is easily transportable and its contents will keep indefinitely, unchanged and without loss. If drying be

carried too far, efflorescence is profuse, the material becomes too tough and elastic to be easily managed, and there is considerable loss in the handling.

II. Treatment of the Dried Material for the Extraction of the Several Products.—Kelp, dried and handled as mentioned above, still contains some 15 per cent. of water. The alkaline salts—chlorides, sulphates, iodides—which constitute from 40 to 50 per cent. of its weight are contained in much vegetable tissue. When inorganic matters unaffected by moderate heat are to be separated from organic, our most obvious course of procedure is to decompose the latter by burning. This process is best carried on by dry distillation, for in this way we can collect, or utilize, products of value both condensable and non-condensable arising from the decomposition of the organic matter.

The distillation of wood—as now largely practised in many countries—may be cited as an example of the progress and results of this operation. Well seasoned, air-dried wood, of any hard variety, is heated in suitable containers; decomposition begins at about 150° C. and is practically complete at 430° C. The chief products are formed continuously throughout the entire process, which proceeds in three characteristic periods: from 150° to 280° acetic acid, methyl alcohol, and wood creosote are the chief products; from 280° to 350° large volumes of gases are given off; from 350° to 430° solid hydrocarbons are distilled. Additional volatilization can be obtained by increased and protracted heating, but only to the extent of about 1.5 per cent. It will be noted that a very moderate heat—not much above the melting point of lead, 325° C.—is sufficient for the greater part of this operation.

The behavior of kelp under similar treatment is analogous but by no means parallel, nor are its products the same. In the distillation of wood the main products are the condensable volatile substances; the charcoal is of little consequence. With kelp it is just the opposite; the char saturated with mineral salts is by far the most important product of the operation. From wood, the watery parts of the distillate are acid; from kelp they are neutral, or slightly alkaline, proving the presence of ammoniacal compounds. In other respects the condensed products are approximately the same.

In the case of wood, complete volatilization is of little consequence; charring need not be perfect; with kelp it must be absolutely so, for, if the

char holds unexpelled any portion of the organic products of decomposition, the lixiviates from such char will not be odorless or colorless, and consequently of little use for the production of pure salts. Fortunately, this perfection of the char can be ensured by certain modifications of the process; lixiviates from such a char will yield colorless salts of any degree of purity desired. All iodine present can be easily recovered from the waste liquors of the several operations.

Kelp versus Wood.—Let us now consider the case from the practical and commercial point of view, and compare the results to be expected from the similar handling of a weighed quantity of each of the above natural products.

Hardwood—preferably beech—selected where it most abounds, is cut, split, stacked—all by manual labor—seasoned for at least a year, and then transported to the plant for distillation. Kelp is cut, loaded, landed, dried and baled—all by the best mechanical labor-saving appliances; and then in a compact and easily handled form transported to the plant for distillation. Both, save for a necessary, but inexpensive, modification in the case of kelp, are treated alike and at the same cost of manufacture.

One ton of thoroughly dried beechwood gives an average yield of 120 pounds of dry calcium acetate, 8 gallons of tar, 6 gallons of alcohol and acetone.

These, which may have a commercial value of some six dollars, represent all the products usually marketed from a ton of dry wood; the charcoal—some 30 bushels—and gases resulting from the operation are utilized as fuel in the establishment.

The condensed products from the distillation of kelp are analogous to those from wood, and may be regarded as approximating them in value. But here all comparison ceases; the non-volatile portion, the charcoal saturated with alkaline salts, is by far the most important product of the process.

One ton of thoroughly air-dried kelp, in addition to valuable by-products volatile and non-volatile, may be depended on for a minimum yield of 500 pounds of pure potassium salts, 3 pounds of iodine.

These are worth above twenty dollars in the markets, and the presumptive value of the several by-products should warrant the statement that the average yield of a ton of air-dried kelp may be stated at twenty-five dollars (\$25.00)—an average which is far more likely to be exceeded, espe-

cially as regards iodine, than reduced in quantity or value.

How much more promising then in its returns is the distillation of kelp than that of wood. Nevertheless, wood is largely and profitably distilled for its volatile products alone.

One other source of potassium remains to be considered. There exist in certain localities vast beds, or deposits, of mineral salts that carry a large percentage of potassium. These mines are at the present time actively operated and yield a large proportion of the potassium compounds in commerce; their output of low-grade manurial salts for agricultural purposes is immense, and, both as regards quantity and cheapness, beyond competition. But with the purer salts which the numberless claims of manufacture and the arts demand, this is by no means the case. The preparation from their ores of a pure potassium chloride or sulphate is a laborious and expensive operation, and there are no by-products of consequence to reduce the cost of manufacture. But their preparation from kelp presents no difficulties; it yields no rough, complex material so difficult of refinement, for its crudest salts are well on the way toward purity, and can furnish abundantly and cheaply any perfected product that commerce may demand. And again, the by-products from kelp are of prime importance both as regards quantity and value; there is little doubt that they can be made to pay the entire expense involved from the gathering of the raw material to the marketing of its products. Consequently, potassium salts manufactured from kelp should be able to compete in price with any similar products wherever or however produced.

Another most important product of the algae is iodine. This element, of wide use in therapeutics and the arts, was formerly extracted from marine plants; since its discovery in the mother liquors of the purification of Chili-nitre commerce has been supplied chiefly from that source. But the vast deposits of Chili are being rapidly exhausted; their complete extinction is plainly in sight; a few years hence we must look again to the ocean for the world's supply of iodine.

This element, like gold, is present in sea water in infinitesimal proportion. Certain marine plants extract it eagerly, no one can explain how nor why. Two plants are growing side by side on the same stone; in habit, growth and external appearance they are very much the same, but in one of them we find iodine astonishingly abundant, while the

other contains not a trace. The ocean is an inexhaustible treasury of varied wealth, but its riches are stored in so attenuated a form that we are powerless to gather them without the aid of natural processes that go on continually. Marine plants include annually certain portions of this wealth, and offer it for our acceptance like dividends due; should we refuse, it is returned to the treasury, and as time advances offered us again and again.

Nevertheless, the old proverb "*vilior alga*" still holds good; our marine crop is despised and rarely harvested; in speaking of the vegetable growths of the sea the term "weed" is universal. A weed, according to the best definition ever given, is a plant whose virtues yet remain undiscovered. It is fitting, then, that the more prominent members of the numerous genera and species of these plants be studied, and their hidden virtues brought to light.

Assuming it to be not impossible—though by no means probable—that a marine plant may be found sufficiently complacent to have included and stored up gold in its tissues; that such a plant would be widely sought and cultivated there is little doubt. But products of more substantial value to us than gold, by processes that we cannot imitate, are being prepared and stored for us yearly by plants that we at present despise. They draw these products from a source unquestionably inexhaustible. This term is often loosely applied to sources that by no means deserve it; we observe the vast gold reefs of the Rand, and say here is an inexhaustible field for exploitation; we consider the extensive saline deposits of Germany, and repeat the remark; a generation ago we were saying the same of the nitre beds of Chile; that no terrestrial deposit of value can escape depletion the fate of the latter proves.

But with the saline contents of the ocean it is different. They are not only as now existent inexhaustible, but are being constantly augmented, for as long as rain falls on disintegrated rock and its surplus flows into the sea the mineral contents of the ocean will increase.

Every economist views with disfavor the extravagant—in fact criminal—wastefulness of cities great and small, through whose sewers the fertility of a million acres is poured yearly into the sea. The phosphoric and nitrogenous constituents of this waste seem hopelessly lost; but potassium, one of the most important, we can easily recover, for along our coasts are growing with the rapidity

and vigor of the bamboo countless millions of marine plants, each one of which may store up during its short life from one to two pounds of chloride and sulphate of potassium.

We are dependent for our food supply on the fertility of our soils; in order that they may remain productive the constituents that make them so—removed with each annual crop to distant localities—must be supplied from other sources. The chief of these are phosphates, combined nitrogen, and potassa. The first is supplied by animal waste, and by mineral deposits fairly abundant; the atmosphere is a vast reservoir of nitrogen and oxygen uncombined, which we are rapidly learning how to economically combine to produce the products we need; that we can economically win from a similarly inexhaustible source the third element we require, I have endeavored to make plain in the preceding pages.

This paper will be followed by a second on the chemistry of the more important littoral algae, many of which are of interest, and on some other results of the study of marine growths.

I take this opportunity to express my obligation to the courtesy of Prof. Setchell, of the University of California, and to Prof. Frye, of Washington, for valuable information on the nomenclature and habits of these plants.

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NITRATES IN BOILER-WATERS.

By GEORGE S. JAMIESON.

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The determination of nitrates in the analysis of waters to be used for boiler purposes does not appear to be customary, and, indeed, such determinations may be considered unnecessary in cases where potable waters containing only traces of nitrates are under consideration. However, it sometimes happens that manufacturers, in order to save the cost of city water, employ for this purpose ground waters from densely inhabited districts, and in such cases, where nitrates may be comparatively abundant, their determination is believed to be important.

For the last five years the writer has made it a practice to determine nitrates in boiler waters by means of the well-known colorimetric method used in sanitary examinations. Several ground waters have been analyzed which caused severe corrosion as well as a heavy scale in the boilers, and the conclusion was reached that the nitrates were largely