Thesis.

An Article on Salt.

by

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Few persons know how salt is made, or on what its excellence or inferiority depends. Those who use it for preserving meats and fish, or for flavoring dairy produce notice that it is of different degrees of purity, but even their preferences are often founded on mere prejudice

It is a strange fact that in England the people for a long time insisted on using a salt made in France from sea water, called "Bay Salt", which contained about twice the impurities of their own salt made at Liverpool. On our own coast the fishermen persisted in importing a salt, for preserving their fish, that was manufactured on the Mediterranean coast of France, while the fishermen there would not use it, but much preferred an article made on the Atlantic coast. The French

government appointed a commission of chemists, who reported, after investigation, that the Mediterranean salt was exactly as good for fish preservation as that made on the Atlantic coast, the only difference being that the latter was not so clean as the former.

At Dieuze is manufactured a "gray salt" to accommodate the prejudices of customers. "It is made by adding common clay to the brine in the pans until the required hue is obtained. Much of the prejudice that has existed in England, France and this country with regard to this article, has been excited by men who did not know how to use it properly and who have attributed their consequent failures to the quality of the salt.

On the other hand there is no doubt that failures do occur from the use of a poor quality of salt, especially in the manufacture of dairy products.

The various purposes for which salt is used require that the manufacture should be conducted with reference to the object in view and

thus we have difference in grain and purity. The same salt that is used for pork packing would not do for butter making, as the object in the former is preservation, while in the latter it is flavor. Certain impurities that do not at all effect the preserving qualities of salt, would give to butter a bitter, rank taste, that would entirely unfit it for the table. No one who has not looked into this matter has any idea of the chemical differences that exist in salt made at different manufactories, and of the different grades of salt made at the same manufactory.

As these chemical differences effect in a marked degree its value as an article of commerce, I propose in this paper to consider briefly

1st What constitutes a good salt.

2nd Short description of salt manufacture from natural brines and how to secure it purity.

3rd The efficiency of these purifying processes as shown by analyses.

4th Analyses of foreign and domestic salts showing their comparative merits.

Common salt, muriate of soda, or according to the modern system of Chemical nomenclature, Sodic chloride, is a Chemical combination of the gas Chlorine and the metal Sodium 60.68 per cent former, 39.32 latter. In great salt manufacturing districts such as are found in Central New-York, Michigan and Canada, where millions of bushels of salt are made yearly by the Evaporation of natural brines, great care is taken to produce an article containing as little impurity as possible; in fact Competition is, to a certain extent, based upon this characteristic of the manufactured product.

A good salt depends to a controlling degree, 1st Upon the quality of the saline liquid from which it is obtained. 2d Upon the time and attention paid to its drainage. The compounds which form generally the impurities in salt, and almost universally occur in brines, are sulphate of calcium and

the Chlorides of Calcium and magnesium. These Chlorides are very deleterious, not only on account of their deliquescent properties, but also because they render salt bitter to the taste. Inferior brines contain less sulphate of calcium and more of the injurious Chlorides. It is a well established fact and deserving of attention that the more sulphate of lime found in the brine the less there will be of the Chlorides.

The salt of commerce is principally of three kinds, Coarse or Solar salt; fine, or boiled salt, and ground or dairy salt, which is also used as table salt.

It has been known through historic time that a solution of Chloride of sodium when placed in a position favorable for evaporation, will deposit salt in the form of Crystals. Large quantities of salt are made in this country and Europe from sea water by Solar heat; evaporating it in shallow pans.

Of late years, in Central New-York, Michigan and Nebraska, the natural brines have been evaporated in this way to a great extent. In these districts, by experience and pains taking, they have arrived at the production of a very superior solar salt. A description of the "modus operandi" at Syracuse N.Y., where very extensive works of this kind are situated will explain the process.

The brine as it is pumped from the wells at this place contains usually, slight traces of the carbonate of the protoxides of iron, together with one half per cent sulphate of lime, a very small percentage of the chlorides of magnesium and calcium, and sixteen or seventeen per cent chloride sodium.

In this branch of the manufacture at Syracuse, as well as in all others, great pains is taken to free the brine as far as possible from the above impurities. To accom-

flish this, the brine, which when fresh is clear and colorless and more or less charged with Carbonic acid, is drawn into shallow vats, where it remains until it has parted with its Carbonic acid; and the iron, which becomes speedily oxidized, has separated and fallen to the bottom in the form of the red-hydrated sesquioxide. The brine is then drawn off into a lower set of vats where, after a certain degree of evaporation is reached, the sulphate of lime is almost entirely precipitated and crystals of salt begin to form. It is now what is termed saturated brine or "Pickle". To keep the coming salt free from the Gypsum already deposited, the pickle is drawn off into still another and lower set of vats, where the crystals of salt collect. These crystals of almost pure salt are washed with a fresh pickle and then shoveled into perforated tubs where they drain a few hours before being carted to the store-house.

The chlorides of magnesium and calcium being very deliquescent do not separate as crystals but remain in the mother liquor so that with care, sufficient draining, and from time to time renewing the pickle with which the salt is washed, a much purer article is obtained than would be supposed from the previous analysis of the brine. In fact salt made in this way, on account of the slowness of the process is almost entirely free from deleterious substances.

In stormy weather the brine is protected by covers which are built on rollers so as to run over and completely shelter each vat.

In 1872 there were in use at Syracuse forty-four thousand covers. From these vats two crops of salt are taken each season; each crop averaging from forty five to sixty bushels of salt to a cover, so that this branch of the industry is very large and

at the same time a cheap process of obtaining a purer article than can possibly be obtained by fine evaporation alone. Most of our "fine" or boiled salt is obtained by the fire evaporation of brine, either in shallow pans or hemispherical cast-iron Kettles. The former are used to a great extent in Europe, the latter in this country. Manufacturers in Europe graduate the size of the salt crystals during the process of evaporation. For this purpose they keep the brine at a low heat in one pan (called the "forheater") until near saturation, when it is drawn into a second where, according to the size of crystal desired the brine is kept at a higher or lower temperature - the slower the evaporation the larger the crystals; while the livelier the ebullition the finer will be the grain, in case of one and the same brine. At Syracuse, where the iron Kettles are used, no graduation of the size of crys-

tals is attempted, but the salt is of uni=
form fineness, much finer than that made
by solar heat. The method there pursued
is as follows;
The brine from the springs, which are from three
hundred and fifty to four hundred and sev=
enty feet deep, is pumped (in some
cases by steam, in others by water power) into
very large reservoirs, built at sufficient
height to distribute the water through mod=
ern aqueducts to all the works in the neigh=
borhood. From the aqueducts the brine is
drawn into tanks two of which, containing
each from five to eight thousand gallons,
belong to each "block" or manufactory. It
remains in these tanks twenty four hours, af=
ter having been mixed with milk of lime.
The milk of lime performs a double of=
fice. It absorbs a portion of the carbonic
acid of the carbonate of the protoxide of iron,
thus hastening the precipitation of whatever
iron there may be, in the form of the

sesquioxide, and also it decomposes the chloride of magnesium, forming the oxy-chloride of magnesium and chloride of calcium, the former of which is precipitated. The brine after having been through this process of decomposition and precipitation in the first tank, is drawn into a second and similar one from which it is conveyed through a six inch discharge pipe to the Kettles in the Block. This discharge pipe is connected with each Kettle by a spout so that fresh brine may be drawn into it at any time.

The Kettles rest over a flue, on trunnions; they are hemispherical in form, twenty six inches deep and fifty-two inches in diameter, with a capacity of one hundred and fifty gallons. The first seven Kettles are protected from the extreme heat of the fire, (which is situated in the front part of the flue) by a perforated arch. When evaporation has commenced,

a small, round, shallow pan, with an upright handle, is placed in the bottom of each kettle, for the purpose of receiving the sulphate of lime which separates from the salt begins to form. As soon as the salt begins to form these pans are removed and emptied. Often more than half of the brine in the kettle has evaporated the salt is dipped out with a long handled ladle into a basket which rests above the kettle on short pieces of scantling, where it remains until all the brine has drained out, when it is deposited in bins constructed for the purpose at the side of the flues. It is required, by law to remain in these bins fourteen days before it can be packed for market. The salt from each kettle is kept by itself until examined by the Inspector, who is a State officer - and whose duty it is to see that no salt is offered for sale that is not up to the required standard

The fuel used is bituminous coal. Twelve tons of this fuel manufacture about six hundred bushels of salt; this amount is often used in twenty four hours.

Salt manufactured as in the foregoing processes is often pure enough, without any further manipulation for most of its uses in commerce, but for the manufacture of cheese and butter and for table use a higher grade is required.

For dairy purposes salt must not necessarily come from any particular source, but its fitness depends entirely on its chemical and mechanical composition. It should be of a neutral reaction and have a purely saline taste; free from any offensive odor, and without stain of color; it should be of uniform grain; small enough to dissolve readily, and what is not less essential, should contain no colored specks.

Salt is not used at the dairy for preserving the produce, but for flavoring purposes. If it contains even small quantities of the chlorides of calcium and magnesium they soon impart to the butter or cheese a bitter taste; this has been noticed espec-

ially in warm climates.
How to get rid of these noxious chlorides and thus produce a salt eminently fitted for dairy purposes, was a vexed question for a long time, but of late years it has been solved and successfully accomplished at Syracuse if not elsewhere The machinery for the process is patented and owns its simplicity and scientific accuracy to Prof. Charles A. Goessman who devoted years to its construction.
The principal underlying the process, is that carbonic acid has a greater affinity for magnesium and calcium than it has for sodium, consequently if by any means carbonate of soda can be supplied to the salt containing these chlorides, they will, under suitable conditions, give up their chlorine, and we will have instead of the chlorides of calcium and magnesium, the carbonates of those elements, and the chloride of sodium,

so that we have not only gotten rid of our impurities but put in their place pure salt. The reactions that took place are the following;

$$CaCl + NaClO_3 = CaClO_3 + NaCl.$$

$$MgCl + NaClO_3 = MgClO_3 + NaCl.$$

It will be seen also that as a preliminary step to adding the Carbonate of soda, a great deal may be accomplished by simply washing the salt, which is to be purified with a superior "salt pickle", for the following reason. The chlorides of calcium and magnesium are very deliquescent and consequently remain to a great extent with the mother-liquor when the brine is evaporated, but what little does get with the salt must be in the mother-liquor adhering to the crystals. Now if the salt be washed by a superior pickle, the old mother-liquor that was left adhering to the crystals, will be carried off in the washings, so that but little of the rank chlorides

mill remain. But let me describe the process as it is carried on by the American Dairy Salt Co. of Syracuse, at their mills.

The first step is the preperation of a supersaturated salt pickle. For this purpose, a certain amount of salt is added to a brine that has been analyzed, and the amounts of the chlorides of calcium and magnesium determined. To remove these objectionable chlorides, a corresponding quantity of carbonate of soda, previously dissolved in brine, is added. As has been explained above, a mutual decomposition takes place, forming the carbonates of calcium and magnesium and chloride of sodium. The carbonates are of a different character and are removed by settling and filtering. The pickle is now ready for use.

Both boiled and solar salt are washed with this pickle, the former in the same form it comes from the blocks, while the latter is crushed

fuses so that it may present more surface to the purifying liquor.

Having a salt, to be treated, of a well known composition, the process becomes simple and exact. From eighty to one hundred bushels of salt (amts of MgCl and CaCl known) are put into a tank and covered to the depth of four or five inches with the above described pure brine or pickle, and the calculated amount of carbonate of soda, to decompose the chlorides in the salt, added. The mixture is kept in lively agitation for the space of from twenty to thirty minutes, which is long enough for thorough decomposition to take place. The salt is now removed from the pickle and put into a store-room to drain for a week before being dried. The pickle is drawn off into vats where the carbonates are allowed to settle. When its composition becomes sufficiently altered to render it unfit for purifying purposes, it is run off into vats and made into salt. Its place is supplied by

a fresh pickle.

The salt thus treated requires to be ground, and before grinding, must be thoroughly dried. The drying is done by large revolving iron cylinders, heated, by a furnace underneath, and having a current of hot air forced through them, to carry off any vapors that may form. The axes of these drying cylinders make an angle with the horizontal of about twenty degrees, so that the salt as they revolve, gradually descends from the top of the cylinder, where it comes in, to the bottom, falling at last into salt elevators which carry it to the top of the building to be ground.

The process of grinding is similar to that of grinding wheat, though it requires skill and experience to grind it so as to preserve a granular form to the salt. The salt mills have a peculiar kind of millstone set in a way to grind as desired.

The question naturally arrises in this connection; is it not likely that at times an excess of Carbonate of Soda is added, thus contaminating the salt by leaving this compound with it in the free state?

In the first place, on account of the cost of Carbonate of Soda, the amount of it required to Just affect the object in view, is carefully calculated.

In the second place, as long as there is any Sulphate of lime in the salt there can be no carbonate of lime in the free state, because the affinity of Carbonic acid for Calcium would give us Carbonate of calcium and Sulphate of Soda. It will be seen by reference to my analysis of Syracuse boiled salt that to add enough Carbonate of Soda to change all the Sulphate of lime to Carbonate would be ruinous, financially.

Having now briefly described this process of purification and, as I think demonstrated its theoretical efficiency I propose to show

how far practically it is a success.
In the first place to give an idea of the constituency of a brine pumped at the Onondaga reservation, I give the following analysis made by myself of water from a well over four hundred feet in depth that has lately been sunken.

50 c.c. of Brine.

Compounds	Weights grammes	Per-Cents	Weights. grammes.	Per-Cents.
$NaCl$.	10.333	20.66	10.3228	20.64
$CaCl_2$	.1942	.3885	.2029	.4058
$MgCl_2$	.1368	.2736	.1431	.2862
$CaSO_4$	.2884	.5772	.2674	.5348
H_2O.	39.046	78.100	39.063	78.133
Totals.	50.0000	100.0000	50.0000	100.0000
Residue from 50 c.c. evap. to dryness.			11.142	22.28

It will be seen by the above that the deleterious chlorides in this particular brine amount to something over six tenths of a per-cent.
Now let me give my analysis of a

Sample of boiled salt from the same locality, and made from a similar brine.

Table of Analysis Syracuse Boiled Salt		
Compounds	Per-Cents.	Per-Cents.
$NaCl$	96.45	96.33.
$CaCl_2$	.318	.414
$MgCl_2$	.124	.116
$CaSO_4$	1.972	1.972
H_2O & Insoluble matter	1.136	1.168
Total	100.000	100.000

The comparing of the analysis of the brine and boiled salt shows little or nothing, because brines vary much, but an analysis of the washed salt would show, approximately, in connection with above analysis of unwashed salt, the efficiency of the process. I give below my results on an analysis of a sample of the Syracuse Factory Filled Salt made for dairy and table use.

Table of Analysis of Syracuse Factory Filled Salt.		
Compounds	Per-Cents	Per-Cents.
$NaCl$	97.96	———
$CaCl_2$	.095	0.2
$MgCl_2$	.034	———
$CaSO_4$	.899	———
H_2O and Insoluble Matter	1.012	———
Totals	100.000	

It will be seen by a careful comparison of these analyses, that the washed salt has one, and fifty-one one hundredths per-cents more Chloride of Sodium than the Unwashed. Now let us suppose that this increment came from the foregoing reactions of Carbonate of Soda on the Chlorides in the boiled salt; and see by further comparison of the analyses, if just chlorine enough has been taken from these chlorides to make, with the Sodium, one & four-tenths per cent of salt.

(In order to have the calculation as clear as possible I have put it in tabular form.)

Comparison Table, washed & unwashed Salt.

Compounds	Per-Cent in Unwashed	Per-Cent in Washed	Difference	Cl. Difference	Per-Cent NaCl
$MgCl_2$	0.116	0.034	0.082	0.07	2.4
$CaCl_2$	0.248	0.2	0.048	0.078	

The amount of chlorine taken from the chlorides of magnesium and calcium in this particular case, is sufficient to combine with enough sodium to form two and four-tenths per-cent of salt.

The disagreement is probably, partly due to the fact that the two samples of salt analyzed were originally made from different brines, and partly to unavoidable errors in the association of acids and bases.

As foreign salt is used in this country to a considerable extent, especially throughout the east, I have added a table, from my own analyses, showing the merits of some of the best brands of imported salt, as compared with Syracuse salt.

(over)

Compounds.	Syracuse Table Salt.	Syracuse Dairy Salt.	Liverpool Fine Salt.	St. Martins Fine Salt.	Turks Island Coarse Salt.	Remarks.
	o/o	o/o	o/o	o/o	o/o	
$NaCl$	96.45	97.96	97.63	97.92	94.04	From a careful study of this table it appears that there is little choice between the Liverpool fine & the Syracuse Factory Filled.
$MgCl_2$	.124	.034	.05	.07	.83	
$CaCl_2$	.318	.095	none	.08	none	
$CaSO_4$	1.972	.899	1.35	.15	1.56	
$NaSO_4$	none	none	.17	none	none	
$MgSO_4$	none	none	none	none	.39	
H_2O and Insol.	1.136	1.012	0.800	1.78	3.10	
Total	100.000	100.000	100.00	100.00	100.00	

All of which is respectfully submitted;

Merrill Bennet.

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