

Studies in the Chemistry

of

AL-KALI (القلي)

or

GLASSWORT

(Preliminary investigations of
its industrial possibilities.)

BY

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KALI OR GLASSWORT

I. Introduction:-

Kali or glasswort (1) is a herb that grows in the Syrian desert. The ash of this plant is rich in sodium and potassium carbonates; thus its name Kali (2). It is also called glasswort because of its use in glass-making instead of the alkalies. The ancients knew something about this herb and used it as a cleansing agent. It was mentioned in the bible in more than one place. "If I wash myself with snow water and make my hands never so clean"; Job 9:30. "For though thou wash thee with lye and take thee much soap etc..." Jeremiah 2:22. "...for he is like a refiner's fire and like fullers' soap"; Malachi 3:2. In the preceding statements, "snow water," "lye" and "soap" designate the same arabic name Al-oushnan.

Lane's Arabic-English lexicon says:

"Al-oushnan or Al-ishnan but the former is of higher authority than the latter (Kali or glasswort); a thing or

(1) The Arabic name for it is Al-oushnan

"Glasswort is a name for plants containing much alkali and on that account formerly used in glass-making, (a) a plant of the genus Salicornia, called also pointed glasswort. (b) Salsola Kali, called also prickly glasswort." The Shorter Oxford English Dictionary.

"Glasswort: any of several low saline seaside herbs, formerly used in glassmaking." The Practical Standard Dictionary.

(2) "Kali (Arab.; see Alkali), also applied to berilla (salsola soda) latinized Kalium, whence the symbol K for potassium." The Shorter Oxford English Dictionary.

substance well-known with which clothes and the hands are washed; good or profitable (as a remedy) for the mange, or scab and the itch; clearing to the complexion, cleansing, emmenagogue (1) and abortive".

Lane refers to it as a "thing or substance" but in Syria the plant itself from which this "thing or substance" is extracted is known as Al-Gushnan. In Lebanon, and especially among soap manufacturers, the ash of the plant is known as Kali or Buluss. It is used exclusively nowadays in soap-making due to the shortage of sodium hydroxide caused by the war.

Looking at the herb from the botanical point of view and to put it where it belongs in the plant kingdom, I will hereby quote the Encyclopedia Britannica: "Glasswort, a name given to *Salicornia herbacea* (also known as marsh samphire), a salt marsh herb widely distributed in the northern hemisphere - with succulent, jointed, leafless stems, in reference to its former use in glass-making, when it was burnt for barilla (2). *Salsola Kali*, an allied plant with rigid, fleshy spinous - pointed leaves, which was used for the same purpose, was known as prickly glasswort. Both plants belong to the *Chenopodiaceae* family."

The family therefore contains more than one, and probably more than two, genii which, altho they may differ a little as to the amounts or kinds of solids they contain, serve the

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- (1) Emmenagogue; a medicine or substance that stimulates or renews the menstrual flow.
 - (2) Barilla, an impure soda formerly used for the making of soda soap and glass but now employed very little. It was obtained from the ashes of the fleshy plant (*salsola soda*), called in Spain Barilla, grown specially for this product

same purpose.

The plant grows in the Syrian desert because most of this desert is a salt-marsh plain. As the soluble salts in the sap of the plant (1) depend upon the nature of the soil in which the plant grows, and as the nature of the soil differs in different districts, we expect to find samples of the same plant taken from several places to be different in the amounts and kinds of salts they contain. This may be one reason why the results of the analysis of one sample, and sometimes its general behavior, do not agree with another sample. A more important reason for this disagreement is the fact that people who burn the plant (2) for sale mix the ash with soil or sand to increase its weight. The quantities added of these foreign materials differ with different persons and circumstances. An attempt should be made by someone to study the geological features and the nature of the soil of the several districts in which the plant grows, in order to be able to put certain specifications for the ash produced in each one of them; thus forcing the cheating by the dealers to drop to a minimum if not to put an end to it.

The hydroxide of sodium was introduced to this country towards the end of the Nineteenth century. Before that date

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- (1) It is supposed that not all the soluble salts found in the ash of glasswort come thru the sap as some of them may have deposited on the fleshy stems and leaves as they are washed away by rain water or currents of wind.
 - (2) It is an established fact among people who deal with the ash that if the plant is burnt before it dries the soluble contents of the ash will be more than if it is left to dry and then burnt.

soap-making depended entirely upon the ash of glasswort. The method practiced by soap-makers was simple: a big cylindrical kettle made of iron (about five to six meters high with a diameter of one and a half to two meters at the top, narrowing down gradually to about half a meter at the bottom), was erected on a specially built place so that fire could be applied. A tap for hot water to flow out, into a stone vessel, was located at a point about one third the distance from the bottom. About two and a half tons of olive oil were introduced to the kettle with some Kali solution from a previous batch. When the liquids had boiled for sometime the tap was opened to allow hot water to flow to a vessel filled with ash. After stirring for a short time this water was made to flow to a second and a third and probably to a fourth vessel to give the suspended impurities enough time to settle. The solution in the fourth vessel became clear and was carried back and sprayed on the surface of the kettle (1). The soluble salts were consumed by the oil and the water was drawn again from the tap to repeat its cycle. When the ash in the vessel became exhausted and seemed to have lost all its soluble salts the residue was thrown away and fresh ash was supplied.

The process was continuous and the time required for the batch to get ripe i.e. for the oil to saponify as completely as possible was from three to four days. One and a half tons of ash were necessary to bring the operation to an end. Assuming that one hundred kilograms of oil need fifteen kilograms

(1) Occasionally lime-water was also sprayed on the surface.

of alkalies (a mixture of sodium and potassium hydroxides), the two and a half tons of oil will need about 400 kilograms. As this amount is provided by one thousand five hundred kilograms of ash the percentage of available bases in ash would be about twenty six. It must not be forgotten that a primitive process of this sort, no matter how efficient it would be, would not dissolve all the solids in the ash; moreover some of these solids would remain unused in the water.

Caustic soda was not welcomed at first by soap-makers in this country because, according to them, it burns the clothes and it is difficult to be handled. It took them about ten years before they could master the technique of its use. Since then Kali ash lost its importance as a vital product in the market. With the outbreak of the war and when the importation of sodium hydroxide from abroad became more and more expensive, the idea of Kali ash to be used in soap-making was revived.

Before closing this introduction I would like to make it clear that it is a long time since this ash was known to contain valuable salts and that this discovery is not to be attributed to this generation or to the one preceding it. But the important problem which is calling upon us for a solution is to devise a practical method for the extraction and separation of these precious salts on an industrial scale.

The problem is fresh and quite promising from the scientific and industrial points of view. The chemist can foresee

what a field of investigation he has before him when he realizes that the extract of Kali ash, not to say anything about the residue, contains not less than ten different salts. It is as complicated as the water of the Dead Sea, if not more so.

This paper is not written in attempt to solve all the riddles of Kali but it does merely open the door of an old castle full of antiquities. The writer hopes that this preliminary study will stimulate the spirit of investigation in other scholars of chemistry who may succeed in drawing the boat to a safe harbour.

II. The Ash.

1. Outside appearance.

The glasswort herb is burned in the open air, before it gets very dry, the ash is collected and sold under the commercial name, Kali or Buluss. It is composed of coarse solid particles having different sizes. The color of the ash varies in different samples from light grayish to dark grayish and sometimes to black. The outside appearance of the material gives a man of experience some indication about the quality of the ash and the percentage of soluble salts it contains. This is not a reliable test for purchasers and a better one will not be used by them unless it is simple and could be performed in a short time. As the value of the ash depends entirely upon the carbonates and hydroxides (formed by hydrolysis in solution) found in it, a quick determination of the total alkalinity of a certain sample would be a sufficient criterion for its evaluation. The writer suggests the following method which gives quite satisfactory results.

2. A suggested method for quick testing.

A weighed sample of about two grams is crushed and boiled with 20⁻⁴⁰ ccs of water for five minutes, filtered and washed twice using 5⁻¹⁰ ccs of water each time (washings being added to the filtrate). The whole solution is titrated with N HCl, methyl orange used as indicator. The volume in ccs of HCl taken multiplied by 0.053 gives the number of grams of Na₂CO₃ found in the two grams of the ash. If the grams of carbonates are to be known those of Na₂CO₃ are multiplied

by 0.566 (56.6% of Na_2CO_3 is CO_3). The error introduced by the presence of some of the carbonates in the form of K_2CO_3 is slight and may be neglected. Suppose that 10 ccs of N HCl are used to neutralize the whole extract of the sample, therefore, $10 \times 0.053 = 0.53$ grams of Na_2CO_3 found in 2 grams of the ash.

$$\frac{0.53}{2} \times 100 = 26.5\% \text{ of the ash is } \text{Na}_2\text{CO}_3$$

or

$10 \times 0.053 \times 0.566 = 0.2999$ grams of carbonate found in 2 grams of the ash.

$$\frac{0.2999}{2} \times 100 = 14.995\% \text{ of the ash is carbonate.}$$

Suppose that all the carbonates in the sample exist as K_2CO_3 , therefore, $10 \times 0.069 \times 0.435 = 0.3$ grams of carbonate found in 2 grams of the ash.

$$\frac{0.3}{2} \times 100 = 15\% \text{ of the ash is carbonate.}$$

If all the carbonates were found in the form of K_2CO_3 and the calculations made on the assumption that they all exist as Na_2CO_3 , the error would have been very slight namely 0.005%. It must be borne in mind that most of the carbonates actually exists as Na_2CO_3 and therefore the actual error is much less than 0.005%. Another source of error may be introduced by the fraction of CO_2 (liberated on the addition of acid) that dissolves in the solution and lowers its pH thus making the volume of the acid less than what it ought to be. This error may be brought down to a minimum by heating

the solution during the titration period to about 60°C thus liberating nearly all the CO₂. The third and most important factor which may lead to inaccurate results is the fact that the ash, before it is crushed and well mixed, is not a homogeneous mixture. The composition of the sample therefore, may not represent the composition of the whole ash under investigation. In such a case it is left to the skill of the analyst in choosing the sample and to his sound judgement in reporting the results. With all the disadvantages it has, the previous method is the most convenient one by which the purchaser can, in less than ten minutes, evaluate the stuff offered to him.

3. Qualitative analyses.

A qualitative analysis of several samples of the ash shows the presence of nearly the same ions. The cations generally found are those of sodium, potassium, aluminum, ferric, ferrous, magnesium and calcium, while the anions are the carbonate, chloride, sulfate, phosphate, silicate and sulfide. Tests were not made for lithium, rubidium, and caesium.

4. Quantitative analyses.

The salts which are of interest to us, and which constitute the majority of the water-soluble contents, are those of sodium and potassium carbonates. The phosphates, especially those left in the residue, are of importance because this by-product would be useful as a fertilizer, since it may also contain some potassium. The results of

the analyses of three samples are given in the following table.

	percent of soluble salts in sample	Percent of Na_2CO_3 if all CO_2 exist as such	percent in the soluble salts				percent in the residue		
			Na	K	CO_2	P_2O_5	P_2O_5	carbo-naceous substance	H_2S
Sample A	58.5	77.5	50.1	1.32	43.9	0.181	1	15.4	liberated with HNO_3
Sample B	50.5	62.2	24	9.1	35.2	1.5	0.024	3.7	traces
Sample C	48	52.3	20	7.6	29.6	1.1	0.5	5	liberated with HNO_3
Percent in the original sample									
Sample A		45.37	17.6	0.77	25.6	0.1	0.415	6.39	
Sample B		31.4	12.1	4.59	17.7	0.66	0.012	1.535	
Sample C		25.1	9.6	3.65	14.2	0.53	0.124	2.075	

From the table it is shown that if all the alkali metals (sodium and potassium) are found in the solution as carbonates, the percentage of the latter should be higher in the three samples. It is obvious that these metals are

also found in the form of other salts. Assuming that all the carbonates are found as sodium and potassium salts the percentage of the alkali metals existing as carbonates would be 88.8 in sample A, 92 in sample B, and 92.7 in sample C. These percentages may be higher than what they ought to be because some of the carbonates may exist in the form of other salts. The solution of sample A was colorless, due (it may be) to high percentage of carbonaceous matter in it.

III. Extraction.

1. Factors which introduce difficulties.

The extraction of water-soluble salts from the ash of glasswort is a problem by itself. When done on an industrial scale the difficulty lies in the fact that the ash which contains - among other things - sand and soil, cakes and prevents the water from penetrating thru the material. This caking is due to the formation of crystals, by the concentrated solution, which will tend to bind together the particles of sand and other foreign matter. Another and more important reason for it is the presence of the silicates of sodium, aluminium and probably calcium - the latter two are the chief constituents of cement. The effect of the former decreases as the solution becomes more dilute. That of the latter also decreases, but to a less extent, as the soluble part of the ash is removed by the solvent.

A certain sample of the ash was extracted in a kettle several times with boiling water (brought to the boiling point

by applying direct fire to the kettle). Altho the material was occasionally stirred by the hand (using an iron rod) a lining was formed on the inner walls of the kettle with an average thickness of about one inch and nearly as strong as a piece of concrete having the same dimensions. This is probably due to the fusion together of salts, including the silicate, caused by high temperature. The same phenomenon is met with when the plant is burnt for its ash. High temperature fuses the salts which shrink together and form lumps of different sizes having the strength of ordinary rock. These lumps constitute the purest form of the ash and contain the highest percentage of sodium salts.

The presence of these lumps in the ash introduces a new factor to the problem namely crushing or powdering the material before the solvent is added. This increases the surface exposed to the action of the solvent, thus rendering the operation of extraction quicker and more complete.

2. Methods used in chemical engineering.

As the methods used in extraction depend, in the first place, upon the nature of the material to be extracted, the apparatus differs in different operations. From the point of view of chemical engineering the devices used for coarse solids fall in three classes: open tanks, diffusion batteries, and drag classifiers. The third one, drag classifier, is used when the granular material in the charge is to be leached out; thus it does not serve our purpose and must

be excluded from the present discussion. The simplest form of the first device consists of an open tank with a false bottom or a filter of some sort. If a series of such tanks is used, we have what is called an extraction battery. The solvent is allowed to percolate down thru the charge, and is drawn off below the false bottom. The material in any tank is stationary until it is completely extracted. By suitable arrangements water can be introduced to, and solution drawn off from any tank at any time. Such a process is known as the Shanks process. This does not work in the case of the Kali ash because the charge cakes and prevents the solvent from percolating freely thru it.

The diffusion battery system is similar to Shanks' but applied to materials thru which water does not pass freely. The solvent is introduced to closed vessels (instead of open tanks) under pressure. Such a device is used in beet-sugar industry and for the leaching of black ash in the soda and sulphate process for paper pulp, but cannot be applied successfully to the Kali ash. The reason is that no matter how high the pressure is, under which the solvent introduced to the vessel, (1) the material will not be completely bathed in it due to caking. Moreover the solution must be rather concentrated to be of any use for further operations. The mechanical energy used to produce pressure may be employed for stirring and pumping thus giving much better results.

(1) It can't be very high because the amount of solvent entering the vessel per unit time must be fixed by the concentration desired.

5. Method suggested by the writer (with a diagram).

It seems that the best device to be recommended for the extraction of Kali ash is a modified form of the open tanks - battery system. The crushed material is charged into a tank or vessel (tank A) (1) of iron or concrete, having a flat bottom with an outlet in it, to be opened for discharging the residue after complete exhaustion. The tank must be provided with an agitator. When the solution reaches the desired concentration (usually saturation) the agitator is stopped for one or two hours so that most of the suspended impurities will settle in the bottom. It is then siphoned or allowed to flow to another tank or vessel (tank B) where it is left for an overnight. At this stage nearly all the suspended impurities settle down leaving a clear, but usually not colorless, liquid ready for carbonation. Water is again added to tank A and stirring is resumed until the material fails to give a saturated solution. It is then washed and the washings drawn to a third tank C, similar to A, having a fresh charge of the material. The saturated solution from C is also led to B. When the residue in A is completely exhausted it is removed from the outlet in the bottom and a fresh charge is introduced. The washings of other tanks are now pumped to it. More than one tank of type A, B, C, ...etc. may be used depending upon the demand. All have the same construction except in the B type no agitators are needed. By this method an extraction battery is constructed and by

(1) Refer to the diagram page 15.

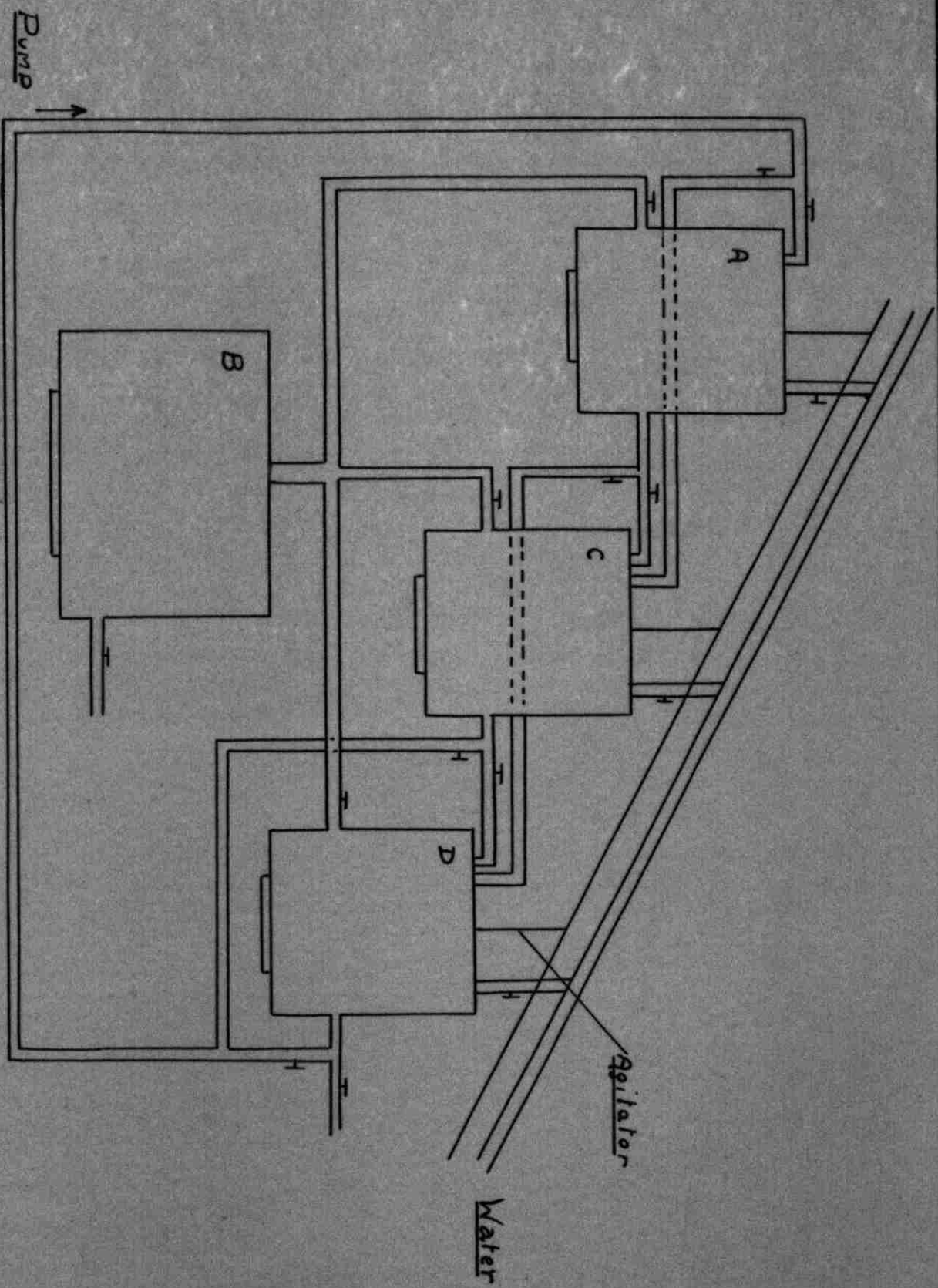


DIAGRAM of EXTRACTION APPARATUS

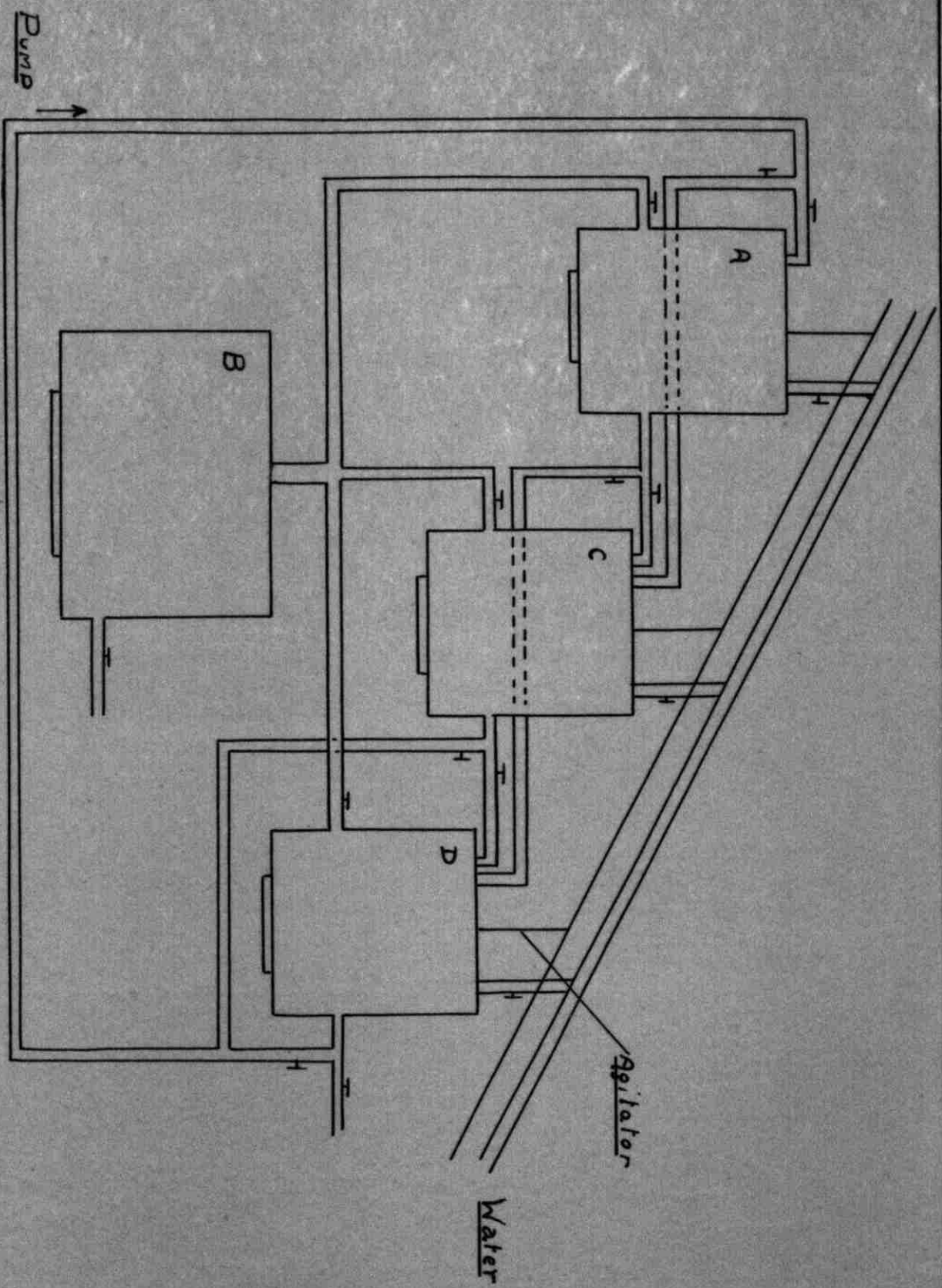


DIAGRAM of EXTRACTION APPARATUS

means of a suitable piping system the solvent may enter any tank and the solution may be drawn off of any tank (if saturated, to the B series) at will. The charging and discharging of any tank at a time is also possible. The operation is rather continuous and all dilute solutions are used again; only concentrated ones are drawn to the B series where, in an overnight, they deposit an appreciable quantity of sodium carbonate crystals in the decahydrate form. The clear saturated solution for carbonation (crystals of sodium bicarbonate are better formed in a concentrated solution) is removed. Crystals of the carbonate, mixed with suspended impurities, are dissolved in a small quantity of hot water (water of crystallization is about 63%) filtered, and recrystallized to a purer $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. The solution can be filtered before it enters the B tanks but the operation is more expensive due to the big volume of the solution; meanwhile it leads to the same results namely a clear solution for carbonation and a rather pure form of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$.

4. Effect of stirring and Temperature.

Stirring is very essential in the A,C,D ... etc. series of tanks to increase the dissolving efficiency of the solvent and to reduce the tendency of caking to a minimum. Several trials showed that the amount of salts extracted by a certain volume of cold water from a given quantity of material without stirring, would have been extracted in a much shorter time if agitation was applied. If hot water is used the time required would be still shorter due to the

greater solubility of the carbonates in it. As hot water demands heat energy which may or may not be cheap, the question is, therefore, which is more economical to use cold or hot water. This of course depends upon the cost of fuel. A plant built for such an industry has to be provided with a boiler, which is indispensable, if the dilute solutions of potassium and sodium hydroxides, produced later by causticization, are to be concentrated by evaporation. The presence of a boiler, or any other source of heat will reduce the cost of heat energy and make it possible for manufacturers to use hot water.

IV. The Solution.

The soluble solids extracted from the Kali ash were a mixture of organic and inorganic compounds. The yellowish brown color of the solution was an organic pigment which could be removed by bone-black. The organic matter will not be discussed in this paper and our attention will be directed towards the inorganic salts.

1. Inorganic salts.

Altho the composition of the solution varied with different samples, a cold-water extract generally contained most of the salts found in the ash. Calcium, magnesium, sulfide, and sometimes iron, were found in traces. In a hot-water extract these ions were found in greater amounts due to the increase in the solubility of their salts with

temperature. H_2S gas was also liberated during the extraction and very distinctly detected by its odor. As the solution was strongly alkaline alumina and silica were most probably in the form of $Na_2Al_2O_4$, $K_2Al_2O_4$, Na_2SiO_3 and K_2SiO_3 . The rest of the ions may have been in any form of simple, double or complex salts that would exist in an alkaline solution. Most of the salts were sodium and potassium carbonates.

When an acid was added to the residue (of some samples) left after extraction H_2S was liberated. This showed the presence of a sulfide insoluble in water; it was, most likely, iron sulfide. How do we account, therefore, for the liberation of H_2S when boiling water was added to the ash? Some of the sulfide may have been in the form of the readily soluble sulfides of sodium and potassium. Hot water increased the hydrolysis of these salts with the formation of H_2S . This was liberated on boiling but the black sulfide of Fe was slightly affected and thus it was left in the residue.

2. Hydrolysis.

When a saturated cold water extract was heated till boiling a white turbidity first appeared and then turned to a gelatinous white precipitate (1). It was filtered and the filtrate diluted to double its volume and heated; the turbidity appeared again and the gelatinous precipitate settled. The same phenomenon was repeated when the solution

(1) A certain saturated solution did not show this turbidity. On dilution the precipitate appeared.

was diluted to about twenty times its volume.

In a hot-water extract the same precipitate was shown but it turned pale brown on standing due to the presence of $\text{Fe}(\text{OH})_3$. It was examined and proved to be a mixture of alumina and silica gels with some $\text{Fe}(\text{OH})_3$. The extensive hydrolysis, which was favoured by dilution and high temperature, was due to the presence of the aluminates (silicates also hydrolyse) which are soluble in alkaline solutions. $\text{Al}(\text{OH})_3$ and nearly all the forms of alumina would precipitate by diluting and heating such solutions. The precipitate would settle on standing in the form of white powder, leaving behind it a clear liquid. This is a typical behavior of the hydroxide of aluminum which changes on standing to one or more of the several forms of alumina. When this precipitate was calcined at high temperature Al_2O_3 became insoluble in acids.

3. Concentration.

We refer to the concentration of such solutions in terms of specific gravity or degree Be'. The point of saturation varies greatly with temperature so that it is rather vague, from the quantitative point of view, to refer to saturated solutions as such. A saturated solution prepared in November at room temperature ($20 - 25^\circ\text{C}$) was $37^\circ \text{Be}'$ while another one prepared in January at room temperature ($10 - 15^\circ\text{C}$) was $27^\circ \text{Be}'$. Thus it had a wide range of

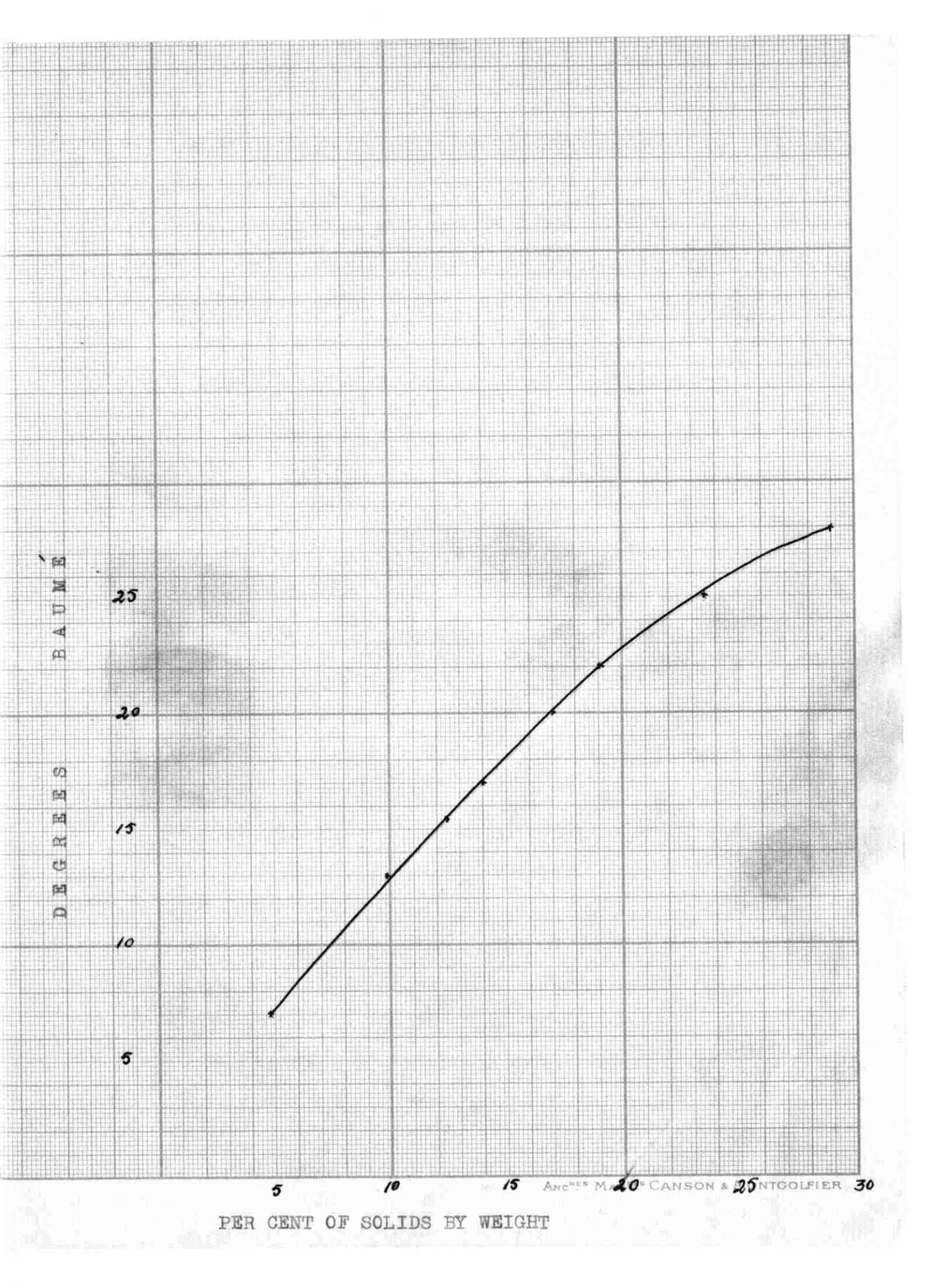
BAUME
DEGREES

5
10
15
20
25

5 10 15 20 25 30

PER CENT OF SOLIDS BY WEIGHT

ANCOR'S M. 20th CANSON & 25th NTGOLFER



concentration and contained different quantities of soluble salts.

A curve showing the relation between the soluble contents of a Kali solution and its degree Be' , is shown on the opposite page. This is of some help if the quantity of soluble salts found in a solution of a certain Be' is to be approximately and quickly determined.

4. Separation of the carbonates of sodium.

The solution to be carbonated was, and must always be saturated and clear. When this was decanted from its container (where it was left for about 24 hours) the crystals of $Na_2CO_3 \cdot 10H_2O$, mixed with suspended impurities, were removed from the bottom and dissolved in hot water. From this solution, after filtration, three forms of the carbonates were prepared. The solution was boiled and when it became saturated crystals of the monohydrate $Na_2CO_3 \cdot H_2O$ appeared floating on the surface of the liquid. They were filtered while the solution was still above $60^\circ C$. If left to cool below $50^\circ C$ they would begin to disappear and around $40^\circ C$ would completely dissolve to reappear in another phase. At $37^\circ C$ a new phase, the heptahydrate, $Na_2CO_3 \cdot 7H_2O$, began to form and was filtered when the temperature was a little bit above $30^\circ C$. The filtrate was left to cool to room temperature and the crystals formed were of the decahydrate form $Na_2CO_3 \cdot 10H_2O$.

V. Carbonation and Causticization.

(A). Carbonation.

A sample of the ash (sample B, P.10) was extracted in a kettle with hot and then with cold water; the two solutions were mixed together and brought to saturation by evaporation.

1. Solution A.

Two liters of this saturated solution (sp. gr. 1.245 and 33°Be) were carbonated. Crystals of bicarbonates were removed by filtration at different intervals. The operation continued until no more crystals were formed by passing carbon dioxide gas thru the solution for four hours. The solution remained after the removal of all the bicarbonates had a concentration of 22°Be. Five samples of crystals were removed for analyses, the fifth being the last.

(a) Analyses of bicarbonates.

The results of analyses are shown in the following table. The percentage of NaHCO₃, Na₂CO₃ and potassium in the first two samples was not determined.

Table 2

<u>Sample</u>	<u>% NaHCO₃</u>	<u>% Na₂CO₃</u>	<u>% Potassium</u>	<u>Remarks</u>
1	----	----	----	Not completely soluble in water; the residue is white and partly soluble in acid. Phosphates, chlorides, and sulfates are present.
2	----	----	----	Similar to sample 1.
3	80	13.5	0.93	(Washed) Completely soluble in water. Chloride, sulfate and traces of phosphates.
4	78.1	12.4	1.32	(Unwashed) completely soluble. Chloride is present.

Table 2 Cont'd.

<u>Sample</u>	<u>% NaHCO₃</u>	<u>% Na₂CO₃</u>	<u>% Potassium</u>	<u>Remarks</u>
5	91.5	6.6	0.3	(Washed) Completely soluble in water. Traces of chloride.
A sample of the washings	14.5	44.7	14.2	Chloride, sulfate, phosphate.

As NaHCO₃ was the least soluble among the sodium and potassium salts mixed with it, it could be purified to a certain extent, by washing. The white residue in the first two samples was silica (and alumina) gel. It was thrown down by CO₂ before the bicarbonates, due to the change in the pH of the solution.

2. Solution B.

The material in the kettle was extracted once more with cold water. One liter of this solution (sp. gr. 1.235 and 30°Be) was carbonated and two samples of NaHCO₃ crystals were removed. The solution left after carbonation was about one liter with a sp. gr. of 1.15 and 17°Be.

(a) Analyses of bicarbonates.

Table 3.

<u>Sample</u>	<u>% NaHCO₃</u>	<u>% Na₂CO₃</u>	<u>% Potassium</u>	<u>Remarks</u>
1	76.6	12.8	1.54	Completely soluble in water. Chloride and sulfate are present.
2	92.4	5	0.776	Completely soluble in water. Chloride less than 1. Traces of sulfate.

The white residue which appeared in the first two samples of solution A did not exist in those of solution B. Its absence indicated that the silicates (and aluminates) did not exist, in solution B, in sufficient quantities required for the formation of the precipitate at the existing pH. These salts, being quite soluble in water, were mostly removed in the first extract.

3. Solution C.

A new batch of the same material was extracted with cold water. From the first extract (ten liters of sp. gr. 1.233 and 30°Be) 1.2 Kg. of sodium carbonate (crystallized in the bottom of the container after few days) were removed. The concentration of the solution dropped down to 25°Be.

(a) Removal of the gels.

Six liters of this solution (solution C, 25°Be) were carbonated. It was necessary to find the time required for the removal of the gels by CO₂ so that not to appear in the bicarbonates later on. Meanwhile a minimum of the NaHCO₃ had to be allowed to come out with the gels. The time required depends upon many factors, such as the concentration of the solution, the rate of bubbling of CO₂ gas, temperature, etc... For the solution at hand three and a half hours seemed to be enough. The gelatinous precipitate settled in the bottom of the containers carrying with it all the suspended impurities which had escaped filtration or decantation. Its bluish-white color indicated that it was silica

hydrogel, or probably the hydrosol, as this is most likely to coagulate from a solution of sodium carbonate. After filtering, CO₂ gas was passed again thru the solution (filtrate) for seven hours and crystals of bicarbonates formed were removed (Sample 1). Bubbling of CO₂ was resumed for nine hours and the crystals were also removed (Sample 2). Then the gas was passed thru the solution until no more crystals of bicarbonates were formed. The solution was filtered (17 Be) and the bicarbonates removed (Sample 3).

(b) Analyses of bicarbonates.

These three samples were washed and dried by the centrifuge. The results of their analyses are shown in the following table.

Table 4.

<u>Sample</u>	<u>% NaHCO₃</u>	<u>% Na₂CO₃</u>	<u>% Potassium</u>	<u>Wt.</u>	<u>Remarks</u>
1	---	---	---	175 gr.	Not completely soluble in water. Chloride and phosphate present.
2	94	5.3	traces	400 gr.	Completely soluble. Traces of chloride and phosphate.
3	93.76	4.6	traces	375 gr.	Completely soluble. Traces of chloride.

The insoluble residue in Sample 1 was some of the gel which was not completely removed from solution. No traces of it were found in the other two. It is possible, therefore, to remove the troublesome precipitate by passing CO₂ gas into the solution for a period ranging from three to five hours.

(c) The solution after carbonation.

We have started with six liters (sp. gr. 1.22 and 25°Be) or with 7320 grams of solution and ended with the same volume (sp. gr. 1.13 and 17°Be) or with 6780 grams of solution. The loss in weight (7320 - 6780 = 540 grams) would be the weight of sodium carbonate converted to bicarbonate and removed from the solution. The 540 grams Na_2CO_3 must yield 856 grams NaHCO_3 . Table 4 shows that the weight of the second and third samples, considered 93% pure, was about 721 grams. The rest must have been removed in the first sample which was not more than 80% pure.

The weight of the original ten liters (sp. gr. 1.233 and 30° Be) was 12330 grams ($1.233 \times 10,000$).

$12330 \times 0.36 = 4438.8$ grams of solids in ten liters (36% solids by weight).

$4438.8 \times 0.622 = 2760.93$ grams of Na_2CO_3 in ten liters (Table 1, page 10).

$2760.93 - 1200$ (1.2 kilograms removed from ten liters) = 1560.93 grams remained in ten liters.

$1560.93 \times \frac{6}{10} = 936.6$ grams of Na_2CO_3 in six liters.

$936.6 - 540 = 396.6$ grams of Na_2CO_3 (nearly all in the form of NaHCO_3) remained after carbonation in six liters of the solution.

(B). Causticization.

Three liters of the above solution left after carbonation (sp. gr. 1.13 and 17° Be, containing 13.5 % solids by weight or 457.65 grams) were causticized.

1. Solution after causticization.

The volume of the solution after causticization was about four liters (diluted by the milk of lime) with a sp. gr. of 1.07 and 9.5° Be. It contained 8.3% solids by weight (2.22 grams in 25 ccs) or 88.8 grams per liter. Titrated with HCl (phenolphthalein used as indicator) its normality was found to be 0.447. No phosphate was detected; it had been removed by the calcium ion. The following table shows the percentage of some of the contents of this solution.

Table 5 (a)

	<u>Grams per liter</u>
Hydroxide	7.599
Sulfate	7.8
Chloride	18.4
Potassium	9.8

(b)

Potassium hydroxide	13.72
Sodium hydroxide	8.7
Sodium sulfate	11.54
Sodium chloride	30.32

(c)

	<u>Per cent</u>
Potassium hydroxide (of total solids)	15.5
Sodium hydroxide (of total solids)	9.8

(c) Cont'd.

	<u>Per cent</u>
Potassium hydroxide (of total bases)	61.2
Sodium hydroxide (of total bases)	38.8
Hydroxide as NaOH (of total hydroxide)	48.4
Hydroxide as KOH (of total hydroxide)	51.6

In table 5 (b) it was assumed that all the potassium existed as hydroxide and all the chlorides and sulfates as sodium salts.

Before causticization the three liters contained 457.65 grams solids; after causticization the whole solution was found to contain 355.2 grams (88.8 x 4).

$$457.65 - 355.2 = 102.45 \text{ grams lost.}$$

$$\frac{102.45 \times 60}{60 - 34} = 236.4 \text{ grams of carbonate lost.}$$

If all the potassium in this solution (39.8 grams) existed originally as K_2CO_3 , then about 30 grams of CO_2 would have come from it. The rest are assumed to have come from sodium bicarbonate.

$$236.4 - 30 = 206.4 \text{ grams of } CO_2 \text{ came from } NaHCO_3.$$

$$\frac{206.4 \times 23}{4 \times 60} = 19.8 \text{ grams of sodium per liter freed by the removal of } CO_2.$$

In one liter of the solution 5 grams of sodium existed as sodium hydroxide, 3.74 grams as sodium sulfate, and 11.7 grams as sodium chloride, a total of 20.44 grams of

sodium.

After carbonation 398.6 grams of sodium carbonate were found in six liters. Three liters of this solution containing 198.3 grams of sodium carbonate, were causticized. This volume increased to four liters, therefore,

$$\frac{198.3 \times 46}{106 \times 4} = 21.5 \text{ grams of sodium per liter.}$$

The quantity of sodium per liter (21.5 grams) calculated from the results shown in table 1 p. 10 (sodium carbonate is 62.2% of the soluble salts), and that calculated by the loss of CO₂ during causticization (19.8 grams), nearly agreed with that determined by analysis (20.44 grams), in spite of the assumptions made which are partly responsible for these slight differences. In the second case (19.8 grams per liter), for example, it was assumed that all the potassium existed as carbonate and all the sodium as bicarbonate; the two assumptions tend to decrease the quantity of sodium per liter. In a complicated solution like this, such results are not far from being satisfactory.

VI. Conclusion.

The writer would be expected, by now, to give a final decision about the industrial possibilities of Kali ash. What per cent of the carbonates would be secured? Is it possible to make any use of the by-products, especially the residue? Would it pay, in other words, to erect a plant for the extraction and separation of the salts found in the ash? These questions, and lots of others, may be asked by

any person interested in the commercial side of the problem.

It has already been shown that different samples contain variable quantities of salts, but an average one (represented by sample B, table 1) would contain about 50% soluble salts, 62% of which would be sodium carbonate (32% of the original sample). If the extraction apparatus were quite efficient between 85 and 90% of the salts could be removed (with a loss of about 10%). About 43.5% of the sodium carbonate would crystallize out (if no attempt is made to increase this yield). Then by carbonation 57.66% of the remainder would be converted to NaHCO_3 . About 44% of the alkali metals found in the solution would change to hydroxides by causticization. The rest (56%) would be left as chlorides, sulfates, carbonates etc. Such a solution may be used for making soap because the presence of these impurities would not be objectionable. The hydroxides may be separated by fractional crystallization.

In the following table (table 6, a) the weight in kilograms, and (6, b) the percentage, of the products obtained, by crystallization, carbonation and causticization, from the quantity of sodium carbonate (31 Kg.) found in 100 Kg. of ash (sample B) are shown.

Table 6. a (Kgs)

<u>Crystals removed</u>	<u>NaHCO_3</u>	<u>Hydroxides</u>	<u>Loss by extraction</u>	<u>Loss by causticization</u>	<u>Total loss</u>
18.1	9.1	2.95	3.1	3.75	6.85

Table 6. b (per cent)

39.03	29.36	9.52	10	12.1	22.1
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Some of the by-products may be made use of in industry especially the residue, which may contain some phosphorus and potassium. Having these results tabulated, and because other factors should be taken into consideration mainly the prices of the raw material and products, it is left for the reader himself to decide whether it pays or not to extract the salts from the ash on an industrial scale.

The writer hopes that scholars of chemistry who may become interested in the Kali ash, will carry on the investigation on one or more of the following subjects.

1. The various species or genii of the Chenopodiaceae family found in Syria and the geological nature of the districts in which they grow.
2. The specifications of samples obtained from various districts.
3. The industrial possibilities of the residue as a fertilizer.
4. The industrial value of the aluminum found in the ash.
5. The change in quantity of any salt or ion in the solution with concentration.
6. Separation of the salts by fractional crystallization.
7. The organic substances found in the Kali ash.

The end.
