A FUSION METHOD FOR THE PRODUCTION OF

SODIUM FLUORIDE


Thesis

by

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# A FUSION METHOD FOR THE PRODUCTION OF SODIUM FLUORIDE

The ultimate object of this research is to develop a commercial method of converting calcium fluoride (fluorspar) into sodium fluoride (NaF), which is very valuable as an insecticide and as a preservative for wood, especially railroad ties[1] and telephone and telegraph poles. The chief competitors of sodium fluoride as a wood preservative today are zinc chloride ($ZnCl_2$) and creosote, but as creosote has the advantage over zinc chloride in that it resists being leached out, neither zinc chloride nor sodium fluoride can serve as a substitute for creosote in very moist sections of the country, although they are considerably cheaper[2]. Zinc chloride is, however, being used very extensively to treat ties in the drier sections of the country. For example, $2,500,000 worth of $ZnCl_2$ was produced in the United States in 1920 and over 95% of this was used to treat railroad ties. This shows that if NaF was able to compete with the $ZnCl_2$ there would be a large market for it. The following table from Chem. and Met. Eng. (23, 1124, 1920) is good proof that NaF is as good a wood preservative as $ZnCl_2$, if not better.

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[1] Ry. Maintenance Eng., 16 (142-4), 1920.

[2] Ry. Maintenance Eng., 16 (338-9), 1920.

## COMPARISON OF ZINC CHLORIDE AND SODIUM FLUORIDE
## AS WOOD PRESERVATIVE

|  | $ZnCl_2$ | NaF |
|---|---|---|
| Solubility in water | $\infty$ | 4% |
| Toxicity | Enough to materially increase the life of the wood. | Over twice as toxic as $ZnCl_2$. |
| Corrosive effect on steel | Somewhat corrosive, but is commonly used in steel apparatus. | Much less corrosive than $ZnCl_2$. |
| Effect on paint | Cannot be successfully painted over. | Does not injure or effect paint. |
| Convenience of shipping | Shipped in 50% solution or solid; but solid form is deliquesent and must be sealed in air-tight containers. | Shipped in dry powder in slack cooperage. |
| Cost, 1920 | .08 cts. per lb. | .15 cts. per lb. |
| Cost, Apr. 1925 | .08$\frac{1}{2}$ cts. per lb. | .08$\frac{3}{4}$ cts. per lb. |

As indicated in the above table the price of NaF is almost as cheap as $ZnCl_2$ and if the price of NaF could be reduced by even one cent per lb. it could compete with $ZnCl_2$ at the present prices. This is assuming that NaF is as good as $ZnCl_2$ and the table indicates that NaF is considerably better.

The present method of producing NaF by the action of concentrated $H_2SO_4$ on fluorspar, and the dissolving of the resulting hydrofluoric acid in either a sodium hydroxide or a sodium carbonate solution, involves many difficulties due to the fact that HF is very poisonous and corrosive, which make it difficult and expensive to handle. The method which has been proposed to do away with hydrofluoric acid in the process is the direct fusion of the calcium fluoride with a sodium salt and the leaching out of the NaF produced.

This fusion method was the basis for the research carried out by H. W. House and W. N. Lacey. House started out with a mixture of calcium fluoride, silica and sodium carbonate, which gave a very poor yield on fusion and leaching. His low yield was probably due to too much and uneven heating which (as will be shown in this report) have a great effect on the yield. Later House tried charges of fluorspar and sodium carbonate, without the silica, which gave better yields, but they would have been still better if he had continued with the silica.

Lacey obtained a much better yield using silica with the charge, so it was decided to continue with the same charge as that Lacey used. The silica probably reacts with the calcium to form the insoluble calcium silicate and the fluorine is then in a position to combine with t the sodium from the sodium carbonate, to form NaF. The carbon dioxide from the sodium carbonate that combines with the fluoride is driven off as a gas, while a large portion of the excess sodium carbonate remains unchanged and is recovered in the leaching solution.

The equation that expresses the above reaction is as follows:

$$CaF_2 + Na_2CO_3 + SiO_2 \longrightarrow 2NaF + CaSiO_3 + CO_2.$$

The temperature at which the reaction takes place is between 650°C and 775°F and as this temperature is below the melting of the compounds involved, the reaction must go on at the surface of the particles. This means that the reacting substances must be ground fine and thoroughly mixed to get the best results.

Some of the other methods used for the laboratory production of NaF or have been suggested for its commercial production will be listed below.

(1) "Sodium fluoride is obtained by calcining a mixture of fluorspar, calcium carbonate, glauber's salt, and coal, followed by leaching with water and crystallizing".[3]

(2) "J. J. Berzelius says that fluorspar is not decomposed when fused with alkaline hydroxide or carbonate, but P. Berthier showed that this is wrong, fluorspar is decomposed when fused with a mixture of silica and sodium carbonate".[4]

(3) Experiments of Berthier: $CaF_2 + K_2CO_3$ fused. Equal molecular proportions gave more fusible mass and greater yield of KF than $2K_2CO_3 + CaF_2$.[5]

(4) N. Rose found fluorspar completely decomposed when fused with a mixture of silica and sodium carbonate.[6]

(5) The manufacture of soluble fluoride by treatment of sodium fluosilicate with alkalies.[7]

[3]Jean, Techn. J.B. 1868, 199.
[4]Mellor, p. 694.
[5]Ann. Chim. Phys. 36, 253, 1828.
[6]Mellor, Comprehensive Treatise, p. 694.
[7]Ulman, Chem. Abst., 9, 2578.

(6) Manufacture of sodium fluosilicate.[8]

(7) Sodium fluoride is obtained by dissolving ammonium fluoride in sodium chloride. Ammonium fluoride is produced by heating together calcium fluoride and ammonium sulfate. The sodium fluoride separates on cooling.[9]

(8) Same method as above, except that ammonium fluoride and ammonium sulfate are heated together, and the ammonium fluoride vapor condensed.[10]

(9) A suspension of sodium fluosilicate is treated with sodium carbonate at such a rate that the mixture remains acid or neutral and sodium fluoride plus silicon dioxide are separated by fractional settling.[11]

### Analysis of the Fluorspar for $CaF_2$

As the fluorspar $(CaF_2)$ that was to be used in the research was impure and the analysis of it not known, a representative sample of the fluorspar was analyzed for $CaF_2$, thus furnishing a more accurate basis on which to calculate the percent conversion.

The method of analysis[12] consisted essentially of converting the fluoride present into sulfate by heating the sample of fluorspar in a platinum crucible with an excess of sulfuric acid (conc.), and then driving off the excess acid. From the increase in weight, due to the replacing of the fluoride by the comparatively heavy sulfate radical, the percent of $CaF_2$ can be calculated. The results of the different determinations made will be given in the following table.

[8]Chem. Abst. P. 2, 605.
[9]Chem. Abst. P.11, 1527
[10]Chem. Abst. P. 12, 981
[11]Chem. Abst. P. 13, 2112
[12]Cairns, Quan. Anal. page 45.

The first thing one will notice in the results obtained is that the method used is somewhat uncertain, but because of the simplicity of the method indicated and because a high degree of accuracy was not necessary, a more complicated and exact method was not used.

The reason for the low result in analysis No. 1 is probably due to the small amount of acid used, which in turn accounts for the fact that only 30 minutes was needed to drive off the excess acid and heat the crucible and contents to a red heat. In the third determination the sulfuric acid was heated alone, in order to determine the amount of dissolved solids, if any, in the acid. There was no residue after the acid was driven off, which shows that there could be no error from this source. Determination 6-a is with the same sample as 6, only the crucible is reheated, and a lower percentage is obtained, which shows that it was not heated long enough in 6.

It was decided that the most reliable result for the percent of $CaF_2$ in the fluorspar could be obtained by averaging the results obtained in the following determinations: 2, 4, 5, 6-a, 7, 8, and 9. This average gives 95.3% $CaF_2$ which is probably correct to within 1.0%, and 95% will be used in calculating the amount of $CaF_2$ converted to NaF.

## Method of Calculation

$$\frac{\text{Wt. of Residue}}{\text{Wt. of Sample}} \frac{(CaSO_4 = 136.1)}{(CaF_2 = 87.07)} \times 100 = \% \ CaF_2 \text{ in sample.}$$

RESULTS OF THE ANALYSIS OF FLUORSPAR FOR $CaF_2$

| No. of sample | Weight of sample gms. | Cc. $H_2SO_4$ added | Approximate time heated. Min. | Weight of residue $CaSO_4$, etc. gms. | % $CaF_2$ in sample. |
|---|---|---|---|---|---|
| 1 | 1.0085 | 1.1 | 30 | 1.6152 | 91.5 |
| 2 | 1.0695 | 2.3 | 45 | 1.7797 | 95.0 |
| 3 | | 2.0 | 40 | None | |
| 4 | 1.0634 | 2.0 | 50 | 1.7394 | 93.7 |
| 5 | .9417 | 2.0 | 45 | 1.5899 | 96.7 |
| 6 | 1.0404 | 2.0 | 35 | 1.7705 | 97.6 |
| 6-a | 1.0404 | 2.0 | 45 | 1.7611 | 97.2 |
| 7 | 1.0072 | 2.0 | 40 | 1.6521 | 94.1 |
| 8 | 1.0174 | 2.0 | 40 | 1.7194 | 96.8 |
| 9 | 1.0296 | 2.0 | 45 | 1.6802 | 93.7 |

## Analysis of "Trona"

As a successful operation of the fusion method depends upon a cheap source of sodium carbonate, and as a pure carbonate is not necessary, the mixture of sodium carbonate ($Na_2CO_3$) and bicarbonate ($NaHCO_3$) known and sold under the name of "Trona" was selected as the most logical source of supply. In the first place "Trona" was the nearest supply, coming from Owens Lake (Inyo Co. Calif.), and also it costs only about one-third as much as $Na_2CO_3$ per pound. The difference in purity offsets part of this difference in price, but taking the purity into consideration, the $Na_2CO_3$ from "Trona" costs considerably less per unit $Na_2CO_3$ than other commercial $Na_2CO_3$. In order to be able to calculate the amount of $Na_2CO_3$ or its equivalent in $NaHCO_3$ used, the "Trona" was analyzed for $Na_2CO_3$ and $NaHCO_3$.

The method of analysis used was the ordinary two-end point titration, except that the new mixed indicators proposed by Stephen G. Simpson[13] were used. That is: a one-gram sample is dissolved in 50 cc. distilled water and it is then titrated with 0.500 N. $H_2SO_4$ using Indicator No. IV (see below) which gives the end-point for the conversion of the carbonate to the bicarbonate. Indicator No. V is then added to the same solution and the solution again titrated with the same acid solution until the second end-point is reached.

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[13]Ind. and Eng. Chem. Vol. 16, No. 17, pp. 709, 1924.

## Indicators

I.    Thymol blue    -0.03 gms. + 1.42 ml. 0.05 N. NaOH, dil. to 25 ml.

II.   Cresol red    -0.01 " + 0.58 ml. 0.05 N. NaOH, dil. to 25 ml.

III. Bromphenol blue -0.02 " + 0.66 ml. 0.05 N. NaOH, dil. to 25 ml.

## Indicator 1st End Point

IV.   1 vol. Cresol red to 2 vol. thymol blue (use three drops)

## 2nd End Point

V.   Use four drops of bromphenol blue.

The sulfuric acid solution was standardized by using a sample of $Na_2CO_3$ (special analytical quality), which was kept in the oven for three hours at 115°C, and titrating the $Na_2CO_3$ with the acid using the above indicators.

After several trial analyses to get familiar with the color changes, the two following were taken to calculate the normality of the $H_2SO_4$.

(1) Wt. of $Na_2CO_3$ - - - - - 1.0000 gms.

37.99 cc. $H_2SO_4$ sol. to neutralize

$$\frac{2 \times 1000}{37.99 \times 106} = .497 \text{ N. of } H_2SO_4 \text{ sol.}$$

(2) Wt. of $Na_2CO_3$ - - - - - 1.0000 gms.

38.00 cc. $H_2SO_4$ to neutralize

$$\frac{2 \times 1000}{38.00 \times 106} = .496 \text{ N. of } H_2SO_4$$

Average = .4965 N. of $H_2SO_4$ sol.

### Analysis of Trona

(1) Wt. of sample (not dried) = 1.0000 gms.

1st End-point 8.84 cc. $H_2SO_4$ sol.

2nd " " 25.83 cc. " "

$$\frac{8.84 \times .4965 \times 106}{1000} \times 100 = 46.5\% \ Na_2CO_3$$

$$100 \times \frac{(25.83 - 2 \times 8.84) \ .4965 \times 84}{1000} = 29.8\% \ NaHCO_3$$

in Trona Sample No. I

(2) Wt. of sample 1.0000 gms.

1st End-point 8.77 cc. $H_2SO_4$

2nd " " 25.86 cc. "

$$100 \ \frac{8.77 \times .4965 \times 106}{1000} = 46.2\% \ Na_2CO_3$$

$$\frac{100 \times (25.86 - 2 \times 8.77) \times .4965 \times 84}{1000} = 30.6\% \ NaHCO_3$$

No. II

$$\frac{(29.8 + 30.6)106}{2 \times 2 \times 84} = 19.07 \ "Na_2CO_3" \ \text{in the form of } NaHCO_3$$

$$\frac{46.5 + 46.2}{2} = 46.35 \ "Na_2CO_3" \ " \quad " \quad " \quad " \ Na_2CO_3$$

65.42% "$Na_2CO_3$" in the Trona.

Note: The above indicators are probably all right to use where the operator has a chance to become used to the color changes at the end-points, but for a limited number of determinations even with a "comparison color" it is very hard to get the results to check. This is mainly due to the great number of color changes and the fact that the end-points are not very sharp.

### Analysis of Charge after Fusion

The method used by House and Lacey, which consisted of precipitating calcium oxalate[14] with the calcium fluoride, was given up after a number of trials, because of the difficulties encountered in filtering and weighing the precipitate.

The method finally worked out and used was a direct filtration of the precipitate using "filtercel". The procedure for this method will be given in some detail.

A portion or all of the charge recovered after fusion is ground so that about 90% will go through an 80 mesh screen. It is then weighed and poured into about 700 cc. of boiling distilled water which is allowed to cool with frequent stirring. (This process has been found to leach out practically all of the soluble material from the sample). After it has cooled the solution and residue is poured into a liter volumetric flask and diluted to one liter. This is then allowed to stand over night to let the fine particles settle (or a portion of the solution can be filtered). As two samples of the solution were taken in each case, care was taken in getting the first portion of the solution without disturbing the fine residue. The volume of the solution taken to analyse for NaF was chosen so that the weight of $CaF_2$ precipitate would not exceed 1 gm. as it was much more difficult to filter a large amount of $CaF_2$ than a small amount. If a high degree of accuracy is not desired a sample that will produce between 0.25 and 0.50 gms. of $CaF_2$ is much more convenient to filter. The samples

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[14] Zeit. f. Anal. Chem., 51, 1912, p. 14.

of solution are then acidified with acetic acid and brought to boiling to decompose the carbonate present. An excess of $CaCl_2$ solution (100 gms. per liter) is then added to each sample and the solution allowed to cool and the precipitate of $CaF_2$ to settle.

The filtering layer in the Gooch crucible is the most important part of this method of analysis as a precipitate of $CaF_2$ is always very finely divided and will go through any ordinary filter. The filtering layer consists of about 1/3 of an inch of asbestos packed down very firmly and on this is added a layer of filtercel about 1/16 to 1/8 inches thick. The filter is then washed thoroughly and dried at 210°C (see diagram) for 2 hours. Complete new filters were not made every time as the $CaF_2$ precipitate could be scraped off the top and a small amount of new filtercel added.

The sample is then filtered by suction through a small weighed Gooch crucible (1 inch in diam.). As much of the liquid is decanted off as possible, to hasten the filtration. The precipitate is then washed with about 25 cc. of distilled water. The filter and precipitate are then dried at 210°C in the air bath and then allowed to cool in a desiccator, after which it is weighed.

From the weight of the $CaF_2$ precipitate, and the ratio of the total weight of the charge after fusion and the amount used in the analysis, the percent of conversion can be calculated. The above ratio is found for each charge by experiment as follows: the crucible plus the charge is weighed before fusion and again after fusion, and from this can be found the loss in weight of crucible and charge during

fusion. Then by subtracting from this loss the loss in weight of the crucible, the loss in weight of the charge alone is found. Then the weight of the charge after fusion can be found by subtracting the loss in weight on fusion from the original weight of the charge. The amount of charge actually recovered after grinding in each case is found by weighing. The loss in weight of the crucible alone was found by heating a similar crucible under the same conditions and finding the loss. This loss is approximately 1.5 gms. for the average crucible and average heating.

Some of the advantages of this method of analysis over the similar one using the oxalate are:

(1) The procedure is simplified due to the elimination of the sodium oxalate solution and the running of the blank on the oxalate solution.

(2) The filtration is easier because of the much smaller amount of precipitate to handle.

(3) The method used is more accurate, because the error in the blank determination is eliminated, and also the oxalate precipitate absorbs moisture rapidly which makes it very hard to weigh accurately.

(4) The calculations are also simplified somewhat by eliminating the oxalate.

The data for a sample run will be given with the method of calculation:

Mix no. 45

Wt. of Trona ($Na_2CO_3$) . . . . . . . . . . . 50 gms.

" " Sand ($SiO_2$) . . . . . . . . . . . 30 "

" " Fluorspar ($CaF_2$) . . . . . . . . . . 20 "

Total weight of charge . . . . . . . . 100 "


Wt. of charge plus crucible before fusion . . . . . . . 528.5 gms.

" " " " " after " . . . . . . . 497.3 "

Loss in weight of charge and crucible . . . . . . . . 31.2 "

Average loss in weight of crucible . . . . . . . . . 1.5 "

Loss in weight of charge alone . . . . . . . . . . 29.7 "


Wt. of charge after fusion = (100 - 29.7) = 70.3 gms.


Wt. of charge recovered from crucible = 53.5. (This takes into
account the loss on grinding and handling, therefore it equals the
amount of sample leached.)

Leaching solution diluted to 1000 cc.

Two 50 cc. portions taken for analysis.

Analysis (1)

Wt. of Gooch crucible (no. 1) . . . . . . . . . .16.8632 gms.

" " " " " " plus $CaF_2$ ppt. . . .17.3818 "

" " $CaF_2$ ppt. . . . . . . . . . . . . . .5186 "

Analysis (2)

Wt. of Gooch crucible (no. 4) . . . . . . . . . . 16.0310 gms.

"   "   "   "     "   " plus $CaF_2$ ppt. . . . _16.5470_ "

"   " $CaF_2$ ppt. . . . . . .   . . . . . . . . .5160 "

Average of analysis (1) and (2) = $\dfrac{.5186 + .5160}{2}$ = .5173 gms.

(100%) $\dfrac{(.5173)(20)(70.3)}{(20)(.95)(53.5)}$ = 71.7% $CaF_2$ converted to NaF and recovered.

(Note: .95 is the fraction of $CaF_2$ in the fluorspar; see analysis of fluorspar.)

(100%) $\dfrac{29.7}{100}$ = 29.7% loss in weight of charge on fusion.

### Fusion

Most of the fusions were carried on in a 5" by 5".(inside dimensions, approx.) cylindrical fire clay furnace, having a 1" hole at the bottom into which fitted the end of a gas burner. This was covered with a fire clay top with a $1\frac{1}{2}$" hole in it to let out the gases. The charges fused in this furnace were placed in a $2\frac{1}{2}$" by 4" fire clay crucible, a new one being used each time. The fusions which are marked as "stirred" (see table of results which follows) were stirred nearly all the time of fusion with a wrought iron wire.

Runs nos. 49, 50, 53 and on were not fused in the fire clay crucibles as indicated above, but were spread on a flat tray and this heated in a small muffle furnace. Charges 49 and 50 (see table) were fused in an iron tray with an area of 9 sq. inches, while charges 53 and on were fused in nickel trays with an area of 30 sq. inches.

The following table gives a record of each individual mix
and the results obtained with some of the conclusions to be drawn.
The more general conclusions will be given later.

| No. of mix | "Trona" equiv. To 64.4% ($Na_2CO_3$) | Charge Sand ($SiO_2$) | Fluorspar (95% $CaF_2$) | Total weight of charge | Loss in weight on fusion | % loss of weight | % $CaF_2$ converted and recovered | Charge stirred | Total time of heating (min.) | Time in 2nd "Solid" Stage (min.) | Condition of product after fusion. | Purpose of Run and Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 25 | 8 | 10 | 43 | 13.6 | 31.6 | 43.1 | no | 22 | - | Glassy; light grayish green. | To check results of Lacey. Low yield, due to carrying it too far and too high temperature. |
| 2 | 50 | 16 | 20 | 86 | 28.6 | 33.5 | 9.8 | no | 23 | - | Glassy; green | Another trial to check. Impossible to leach if present in glassy form. |
| 3 | 50 | 16 | 20 | 86 | 25.5 | 29.7 | 53.0 | " | 12 | - | Part glassy;part granular; part not fused. | An attempt to eliminate glassy form. Impossible to heat evenly in furnace and conditions used. |
| 4 | 50 | 16 | 20 | 86 | 24.3 | 28.3 | 50.4 | " | 15 | - | Part glassy; part granular;not mixed. | Same as 3. Not homogeneous; shows need of stirring. |
| 5 | 50 | 16 | 20 | 86 | 19.2 | 22.2 | 45.1 | " | 6 | - | Part granular; large part not fused. | Better furnace used with better heat control. The part not fused was not taken as part of sample leached. |
| 6 | 50 | 16 | 20 | 86 | 26.6 | 31.0 | 44.5 | " | 9 | - | Glassy;light gray | Too glassy to get good yield. |
| 7 | 50 | 16 | 20 | 86 | 20.6 | 24.0 | 23.6 | 1 m. | 17 | - | Semi-glassy;gray | Tried stirring. Poor yield due to lack of experience. |
| 8 | 50 | 16 | 20 | 86 | 25.5 | 29.7 | 27.1 | yes | 11 | - | More granular than7 | |
| 9 | 50 | 16[1] | 20 | 86 | 27.3 | 31.8 | 65.9 | " | 14 | ½ | Homogeneous; light gray; granular | No. 9 and 10 to find effect of fine sand; 80 mesh. Stopped heating just after 2nd Solid stage. |
| 10 | 50 | 16 | 20 | 86 | 26.7 | 31.1 | 65.0 | " | 12 | ½ | Same as 9; easy to grind. | Coarse sand used again. Heating conditions same as no. 9. |
| 11 | 50 | 16 | 20 | 86 | 30.7 | 35.7 | 50.3 | " | 18 | 6[2] | Glassy; hard to grind;light green | To study the physical change in charge on fusion. This was carried too far to get good yield. |
| 12 | 50 | 25 | 20 | 95 | 26.9 | 27.3 | 74.1 | " | 15 | ½ | Same as 9. | Nos. 12, 13 and 14 to find effect of large excess $SiO_2$ (14 gms. theor. amt. $SiO_2$). |
| 13 | 50 | 14 | 20 | 84 | 24.8 | 29.6 | 61.6 | " | 13 | ½ | Same as 9. | No excess $SiO_2$. |
| 14 | 50 | 10 | 20 | 80 | 23.2 | 29.0 | 51.6 | " | 14 | ½ | Same as 9. | Less than required $SiO_2$. |
| 15 | 46 | 16 | 20 | 82 | 23.2 | 28.3 | 64.9 | " | 13 | ½ | Same as 9. | To check value obtained in nos. 9 and 10 and to show what effect decreasing the carbonate has (116.5% theor. used.) |
| 15-a | 46 | 16 | 20 | 82 | 23.2 | 28.3 | 0.131 | " | 13 | ½ | No. 15 reground and releached. | To check the leaching used. Seems to be nearly complete. |

[1] fine   [2] semi-solid

| No. of mix | "Trona" equiv. To 64.4% (Na$_2$CO$_3$) | Sand (SiO$_2$) | Fluorspar (95% CaF$_2$) | Total weight of charge | Loss in weight on fusion | % loss of weight | % CaF$_2$ converted and recovered | Charge stirred | Total time of Heating (min.) | Time in 2nd "Solid" Stage (min.) | Condition of product after fusion. | Purpose of Run and Remarks. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 16 | 37 | 16 | 20 | 73 | 19.1 | 26.2 | 61.7 | yes | 13 | ½ | Same as 9. | 94% theor. am't. Na$_2$CO$_3$ used in form of Trona as in above cases. |
| 17 | 46 | 16 | 20 | 82 | 22.2 | 27.0 | 63.6 | " | 11 | ½ | Same as 9. | To check no. 15 |
| 18 | 46 | 16 | 20 | 66 | 8.9 | 13.5 | 61.6 | " | 9 | ½ | Same as 9. | An equiv. am't. of Na$_2$CO$_3$. To prove value of Trona as source of Na$_2$O. |
| 19 | 30[1] | 16 | 20 | 83.6 | 17.6 | 21.0 | 62.4 | " | 9 | ½ | Same as 9. | An equiv. am't. of NaHCO$_3$ instead of Trona. |
| 20 | 47.6[2] | 16 | 20 | 82 | 24.4 | 29.8 | 72.6 | " | 23 | 19.5 | Same as 9 | To find the effect of holding the charge in 2nd solid form. |
| 21 | 46 | 16 | 20 | 82 | 24.9 | 30.4 | 64.9 | " | 21 | 11[3] | Same as 9 | Held charge in semi-solid form; hatter than no. 20. |
| 22 | 46 | 16 | 20 | 82 | 24.4 | 29.8 | 70.7 | " | 15 | 4[4] | Same as 9. | Held at same temp. as no. 21 but only 4 min. |
| 23 | 46 | 16 | 20 | 82 | 24.6 | 30.0 | 45.1 | " | 13 | 5 | Same as 9 | No. 23 and 24 to study effect of rapid cooling by pouring red hot charge into water. |
| 24 | 46 | 16 | 20 | 82 | 24.6 | 30.0 | 51.1 | " | 27 | 12 | Same as 9 | Same as 23, but was held in solid form longer than 23 and at higher temp. |
| 23-a | 46 | 16 | 20 | 82 | 24.6 | 30.0 | 64.2 | " | 13 | 5 | No. 23 reground and releached. | Nos. 23-a and 24-a are nos. 23 and 24 ground and releached. |
| 24-a | 46 | 16 | 20 | 82 | 24.6 | 30.0 | 71.0 | " | 27 | 12 | No. 24 reground and releached. | Same as no. 24-a. |
| 25 | 50 | 25 | 20 | 95 | 27.5 | 29.0 | 68.3 | " | 11 | .5 | Dark gray granular | To check no. 12 in which large excess SiO$_2$ used. Somewhat lower yield than 12 (74.1%) |
| 26 | 50 | 25 | 20 | 95 | 28.6 | 30.1 | 73.6 | " | 16 | 7 | Light gray granular | To check no. 12; good check. |
| 27 | 50 | 30 | 20 | 100 | 30.0 | 30.0 | 76.6 | " | 15 | 5 | Granular | To find the effect of still larger am't. SiO$_2$. Increased the yield. |
| 28 | 50 | 40 | 20 | 110 | 28.5 | 25.9 | 43.6 | " | 22 | 12 | Light gray; tendency to be glassy. | A further increase of SiO$_2$. Low yield due to too high temp. Pasty when stopped heating. |
| 29 | 50 | 35 | 20 | 105 | 28.6 | 27.3 | 52.1 | " | 19 | 8 | Very light gray; somewhat glassy. | " " " " " " " |
| 30 | 50 | 30 | 20 | 100 | 28.0 | 28.0 | 49.9 | " | 17 | 8 | Somewhat glassy. | To check no. 27. Poor yield because of too high temp. Poor heat regulator. |
| 31 | 50 | 40 | 20 | 110 | 27.1 | 24.6 | 72.2 | " | 17 | 5 | Light gray; very granular; easily crumbled. | Repeating mix. no. 28. Higher yield due to lower temp. and better temp. regulation. |

[1] Na$_2$CO$_3$   [2] NaHCO$_3$
[3] Pasty and solid.
[4] Pasty.

| No. of mix | "Trona" equiv. To 54.4% ($Na_2CO_3$) | Weight in grams. Charge | | Total weight of charge | Loss in weight on fusion | % loss of weight | % $CaF_2$ converted and recovered | Charge stirred | Total time of heating (min.) | Time in 2nd "Solid" State (min.) | Condition of product after fusion | Purpose of Run and Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Sand ($SiO_2$) | Fluorspar (95% $CaF_2$) | | | | | | | | | |
| 32 | 50 | 35 | 20 | 105 | 28.4 | 27.0 | 78.3 | yes | 18 | 5 | Same as 31. | High yield due to lower temp. and better temp. regulation. |
| 33 | 50 | 30 | 20 | 100 | 28.3 | 28.3 | 79.1 | " | 14 | 5 | " | Probably very close to the best conditions of temp. control. |
| 34 | 36[1] | 30 | 20 | 86 | 21.3 | 24.8 | 54.7 | " | 16 | 6 | " | To determine the effect of decreased Trona with increased $SiO_2$, Decreased yield due mainly to low Trona - as temp. regulation good. |
| 35 | 41[2] | 30 | 20 | 91 | 24.4 | 26.8 | 69.8 | " | 14 | 5 | " | (Nos. 34, 35, 36) effect of decreased Trona. |
| 36 | 46[3] | 30 | 20 | 96 | 23.9 | 24.9 | 63.0 | " | 16 | 5 | Dark gray | Low yield due to too low temp, as indicated by low % loss in wt. of charge on fusion. |
| 37 | 45 | 30 | 20 | 95 | 26.7 | 28.1 | 67.2 | " | 19 | 5 | Gray fine granular | To check better yield. |
| 38 | 46 | 30 | 20 | 96 | 27.3 | 28.4 | 69.2 | " | 16 | 5 | Gray; granular | To check no. 37; good check. |
| 39 | 60 | 30 | 20 | 110 | 34.3 | 31.2 | 68.3 | " | 18 | 6 | Light gray; fine granular | Effect of large excess Trona; heating conditions good. Seems to get hotter without changing to 2nd solid stage. |
| 40 | 50 | 30 | 20 | 100 | 30.2 | 30.2 | 70.5 | " | 15 | 5 | Very light gray granular | To check no. 33 which was highest yield so far. No apparent reason for lower yield than no. 33 except loss in wt. higher. |
| 41 | 50 | 30 | 20 | 100 | 31.3 | 31.3 | 59.2 | " | 15 | 5 | Tendency to be glossy | To check no. 33. Low yield due to too high temp. on fusion. |
| 42 | 50 | 30 | 20 | 100 | 29.3 | 29.3 | 67.8 | " | 12 | 3 | Light gray; fine granular | To check no. 33; low yield. Might be due to too low temp. or too short time of holding charge in 2nd solid stage. |
| 43 | 50 | 30 | 20 | 100 | 28.0 | 28.0 | 77.7 | " | 10 | 1 | Gray, granular | To check no. 33. Heated quickly by hot fire; somewhat pasty but this was offset by short time of holding. Short, high temp. seems desirable. |
| 44-a | 50 | 30[4] | 20 | 100 | 30.6 | 30.6 | 64.0 | " | 16 | 5 | Coarse, slightly glassy, part of 44. | To check no. 33. (Not stirred enough to be homogeneous, so was divided into two parts to analyse no. 44-a.) To check effect of fine $SiO_2$. |
| 44-b | " | " | 10 | " | " | " | 74.1 | " | " | " | Fine gray granular part of 44. | no. 44-b (see above) |
| 45 | 50 | 30 | 20 | 100 | 29.7 | 29.7 | 71.7 | " | 11 | 4 | Gray granular | To check no. 33; very slightly pasty when taken out of crucible. Coarse $SiO_2$ used to compare with fine $SiO_2$ in no. 44. |
| 46 | 50 | 30[5] | 20 | 100 | 28.1 | 28.1 | 73.1 | " | 13 | 4 | Gray granular size of peas | To check no. 33 and use coarse $SiO_2$. |
| 47 | 50 | 30[4] | 20 | 100 | 30.8 | 30.8 | 67.0 | " | 21 | 8 | Gray granular | Another trial with fine $SiO_2$; not carried far enough so was reheated before it cooled materially. |

[1] 91% th.
[2] 103% th.
[3] 116% th.
[4] 80 mesh
[5] coarse

Purpose of Run and Remarks.

| No. of mix | "Trona" equiv. To 64.4% (Na2CO3) | Sand (SiO2) | Fluorspar (95% CaF2) | Total weight of charge | Loss in weight on fusion | % loss of weight | % CaF2 converted and recovered | Charge stirred | Total time of heating (min.) | Time in 2nd "Solid" State (min.) | Condition of product after fusion. | Purpose of Run and Remarks. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 48 | 50 | 30 | 20 | 100 | 28.5 | 28.5 | 65.6 | yes | 16 | 5 | Gray, coarse gran. | Fine $SiO_2$. Slightly pasty on last end; acts the same way as an excess $SiO_2$ in that solid form is over a more limited range. |
| 49 | 5 | 3 | 2 | 10 | $3.0^1$ | 30.0 | 50.6 | no | 6 | - | Dark gray due to iron. | To find the effect of thin layers on metal surface without stirring. Iron vessel used. |
| 50 | 2.5 | 1.5 | 1 | 5 | $1.5^1$ | 30.0 | 19.4 | " | 4 | - | Nearly black due iron | Same as no. 49; low yield due to poor temp. regulation. |
| 51 | $50^2$ [3] | 30 | 20 | 100 | $3.0^1$ | 30.0 | 70.0 | yes | 15 | 4 | Light gray, gran. | To study effect of fine ($SiO_2$) dehydrated silicic acid. |
| 52 | 50 | 30 | 20 | 100 | $27.0^1$ | 27.0 | 70.9 | " | 13 | 4 | Fine, granular | To compare with no. 51. |
| 53 | 30 | 18 | 12 | 60 | 10.4 | 17.4 | 24.4 | no | 7 | - | Dark gray | Layer of charge spread on Ni tray and put in hot muffle furnace. Low yield due to too low temp. |
| 54 | 30 | 18 | 12 | 60 | 10.4 | 17.4 | 17.5 | " | 8 | - | Dark gray | Same as no. 53; still not enough heat. |
| 55 | 30 | 18 | 12 | 60 | 15.4 | 25.7 | 79.5 | " | 3 | - | Light gray | Much hotter furnace than used in no. 53 and 54. |
| 56 | 30 | 18 | 12 | 60 | 17.4 | 29.0 | 75.8 | " | 4 | 1.5 | Very light gray | Higher temp. than used in no. 55. |
| 57 | 30 | 18 | 12 | 60 | 14.3 | 23.8 | 74.9 | " | 4 | 0.5 | Light gray | To check no. 55; not quite as hot as no. 55. |
| 58 | 50 | 30 | 20 | 100 | 23.2 | 23.2 | 79.3 | " | 5 | 1.0 | Light gray | To check no. 55 with thicker layer on tray; hotter than no. 57. |
| 59 | $33^4$ | 30 | 20 | 83 | 16.6 | 20.0 | 61.9 | " | 6 | 1.0 | Light gray | To compare value of $Na_2CO_3$ with Trona. Too hot at end of fusion. |
| 60 | $33^4$ | 30 | 20 | 83 | 12.2 | 14.7 | 62.1 | " | 5 | 1.0 | Light gray | Same as no. 59. Temp. control seemed all right. |
| 61-a | 50 | 10* | 20* | 80 | 19.0 | 23.8 | 85.2 | " | 12 | 7.5 | Gray | To study the effect of using some of leached out residue in charge with a decrease of $SiO_2$. Calculated on basis of 20 gms. $CaF_2$. |
| 61-b | 50 | 40* | 20* | 110 | 19.0 | 17.3 | 74.1 | " | 12 | 7.5 | Gray | Same as no. 61-a, only calculated on basis of total $CaF_2$ present, which includes that from residue. |
| 62-a | 50 | 20** | 20** | 90 | 19.3 | 21.5 | 82.5 | " | 6.5 | 1.5 | Gray | Leached out residue from no. 58; calculated on 20 gms. $CaF_2$. |
| 62-b | 50 | 40** | 20** | 110 | 19.3 | 17.6 | 76.2 | " | 6.5 | 1.5 | Gray | Same as no. 62-a. Calculated on basis of total $CaF_2$. 20 gms. and am't in residue added. |

[1] Assumed
[2] Salicic acid
[3] 80 mesh
[4] $Na_2CO_3$

*Also 30 gms. leached out residue from no. 57 (which contains 2.86 gms. $CaF_2$ also) and 10 gms. $SiO_2$.

**Also 20 gms. leached out residue from no. 58 (which contains 1.57 gms. $CaF_2$ also) and 20 gms. $SiO_2$.
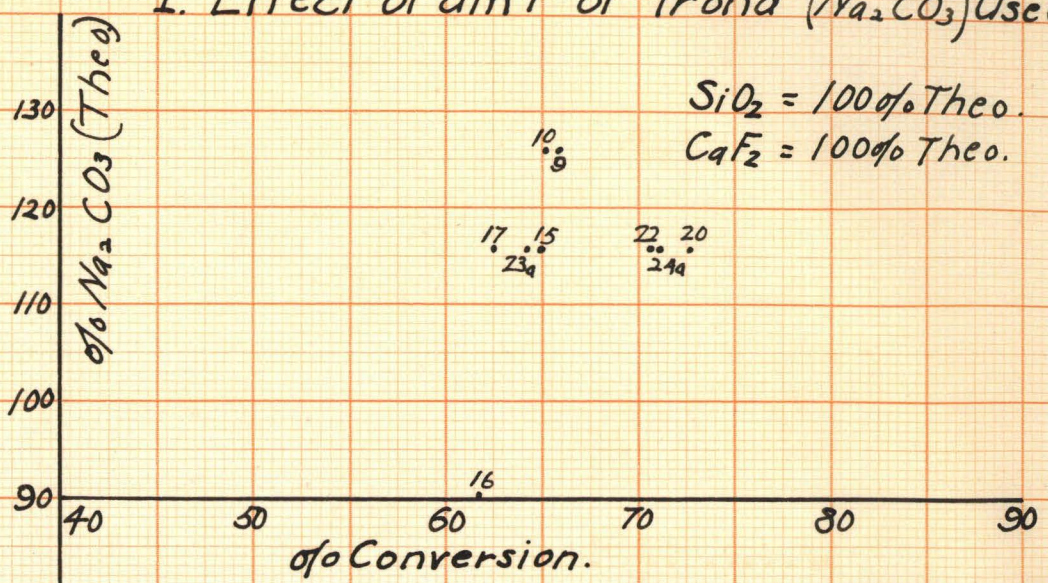
The physical changes in the charge during the fusion are quite marked and the effects of stopping the fusion at a given time were studied in the different mixes. The changes that take place and the approximate temperature of the fusing charge will be given. The temperatures are very rough and were obtained by comparing the color with a color temperature chart. The temperatures given are probably within 100°C and the relative temperatures somewhat closer than 50°C.

(1)  20°C - 500°C.     Drying action only.

(2)  500°C - 600°C.    Some fusion and bubbling ($CO_2$ given off).

(3)  600°C - 675°C.    Completion of fusion.

(4)  675°C - 750°C.    A solid formation again.

(5)  750°C - 800°C.    A second fusion begins (pasty).

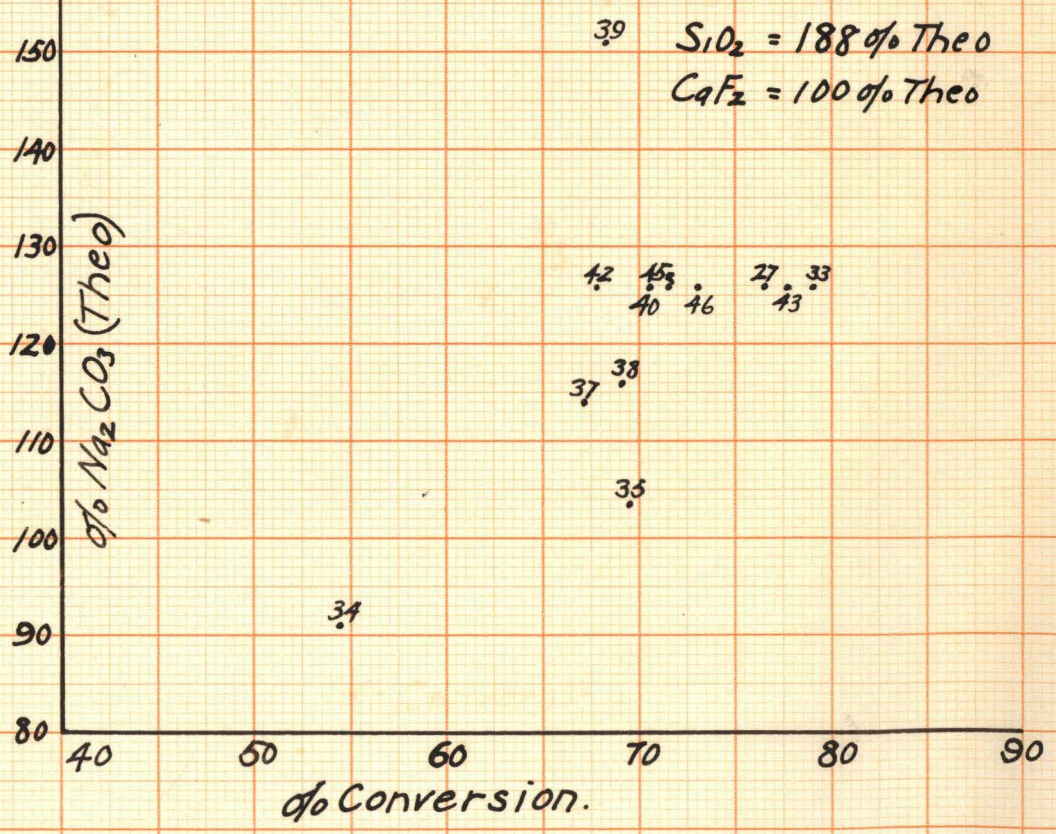(6)  800°C and up.     A viscous liquid (glassy on cooling).

(See conclusions for best condition of temperature control.)

The temperatures as given vary for different amounts of $Na_2CO_3$ and $SiO_2$.
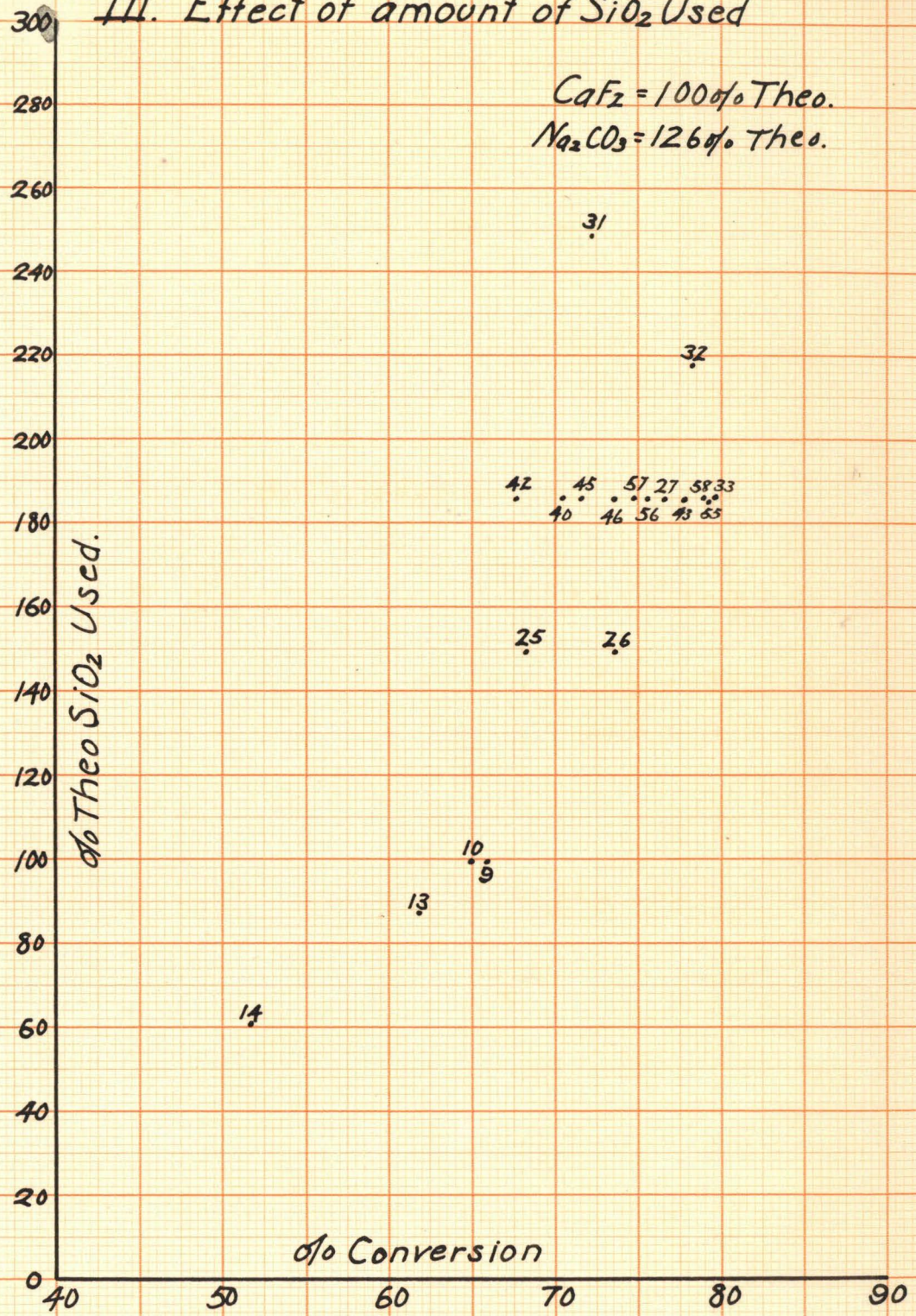
# I. Effect of am't of "Trona" ($Na_2CO_3$) Used

$SiO_2 = 100\% \, Theo.$
$CaF_2 = 100\% \, Theo.$

% $Na_2CO_3$ (Theo)

130

120

110

100

90

% Conversion.

40    50    60    70    80    90

# II. Effect of am't of "Trona" Used.

$SiO_2 = 188\% \, Theo$
$CaF_2 = 100\% \, Theo$

% $Na_2CO_3$ (Theo)

150

140

130

120

110

100

90

80

% Conversion.

40    50    60    70    80    90

# III. Effect of amount of $SiO_2$ Used

$CaF_2 = 100\%$ Theo.

$Na_2CO_3 = 126\%$ Theo.

The preceding plots are an attempt to indicate graphically the main effect on the yield due to variations in the mix used. Due to the fact that there are many other factors that affect the yield besides the ratio of $Na_2CO_3$, $SiO_2$, and $CaF_2$ in the mix, such as rate of heating, time of heating, stirring, time of holding in second solid stage, etc., it is very difficult to make curves that show one effect only. The points taken were from the charges in which the outside effects were nearly equal or did not enter. That is they represent charges in which there were no obvious reasons for low yields, and not necessarily the charges that gave high yields.

In plot I and II the points represent values in which the $SiO_2$ and $CaF_2$ used were held constant while the $Na_2CO_3$ was changed. The percent theoretical $Na_2CO_3$ is plotted against the percent conversion. The difference between plot I and II is that in I the basis is 100% theoretical $SiO_2$ and 100% $CaF_2$, while in II the basis is 188% $SiO_2$ and 100% $CaF_2$.

In plot III the percent theoretical $SiO_2$ is plotted against the percent $CaF_2$ converted to NaF, while the amount of $CaF_2$ and $Na_2CO_3$ are held constant at 100% and 126% theoretical respectively.

#### The Recovery of NaF from the Fusion Product

Analysis of solution from mix no. 46 for solids in solution (NaF, $Na_2CO_3$ and other solids) is given in detail, as it was considered a fairly representative run. The method of analysis used was as follows.

Four 50-cc. samples of solution were taken. One was acidified with acetic acid and analyzed for NaF (see procedure for analysis of mix for NaF). Another 50-cc. sample was not acidified to destroy the $Na_2CO_3$ but the $CaCl_2$ was added directly and the $CaF_2$ and $CaCO_3$ were precipitated together and the amount of precipitate found by filtering and weighing as in the analysis for NaF. The third 50-cc. sample was evaporated to dryness and the total amount of solid in the solution found by weighing the residue.

A fourth sample was analyzed to find out if there was any $Na_2SiO_3$ in the leaching solution which would be precipitated with the $CaF_2$ and $CaCO_3$, and would tend to make the amount of $Na_2CO_3$ reported, high. The 50-cc. sample was evaporated nearly to dryness in a beaker and then it was transferred to a platinum crucible. Eight cc. of concentrated $H_2SO_4$ was added and the solution evaporated to about 3 cc. The solution was then diluted with distilled water and poured into a beaker. No precipitate ($SiO_2$) formed on dilution which indicated that there was no soluble silicate in the solution.

The calculations and results of the analysis:

Wt. of crucible (Gooch) . . . . . . . 18.9572 gms.

"   "   "   plus $CaF_2$ ppt. . . . 17.4251 "

                .5321 " $CaF_2$

from 50 cc. leaching solution.

$(2)(.5321)84/78 = 1.148$ gms. NaF per 100 cc. leaching solution.

Wt. of beaker plus solid from 50 cc. solution . 57.9156 gms.

"   "   "         57.0950 "

"   "   solid from 50 cc. solution     .8206 "

$(.8208)(2) = 1.6412$ gms. total solids from 100 cc. of leaching solution.

Wt. of crucible (Gooch) . . . . . . . . . 17.4908 gms.

"     "     "     plus $CaF_2$ and $CaCO_3$ ppt.   18.2334   "

"    " $CaF_2$ and $CaCO_3$ ppt. . . . . . . .   .7426   "

$(2)(.7426 - .5321)106/100 = .446$ gms. $Na_2CO_3$ per 100 cc. leaching solution.

Solids in leaching solution (gms. per 100 cc.)

     NaF      1.148 gms.

     $Na_2CO_3$   0.446   "

     $Na_2SiO_3$   0.000   "

   Other solids .047   "

     Total   1.641   "

The boiling point rise of the leaching solution and the purity of the crystals produced by evaporation were next studied. About 6.5 liters of the dilute leaching solution taken from some of the runs with good yields was evaporated to dryness. The volume of solution left and the temperature of the liquid was noted at intervals during the evaporation. Also the crystals that had formed were filtered out of the solution while hot (to keep the $Na_2CO_3$ from crystallizing) several times during the evaporation. The different crystals were washed with a small amount of water, dried, and then analyzed for NaF.

The boiling points, amount of solution left, weight of crystals formed during the period between filtrations, and the percent of NaF in these crystals are given in the following table. The reason the boiling points do not have a steady rise is probably mainly due to the tendency of the solution to become superheated, but since only the approximate boiling point rise was wanted, the temperatures taken are close enough.

It is seen from the table that the last crystals contain very little NaF and that they are nearly pure $Na_2CO_3$ which can be used again. By calculation from the amount of $Na_2CO_3$ recovered in the leaching solution it is found that 14% of the $Na_2CO_3$ in the form of Trona is recovered or that 58% of the excess $Na_2CO_3$ is recovered.

The table also shows that the first two crops of crystals contain more than 99% NaF and that they contain most of the NaF in the solution. By calculation it can be shown that 90% of the NaF is recovered in these first two crops of crystals. If the third and fourth crops are included they contain 97% of the NaF in the form of crystals that are over 98% NaF.

## Table

| Cc. of solution left. | Boiling point of the solution °C. | Gms. crystals formed since last filtration. | % NaF in crystals. |
|---|---|---|---|
| 6500 | - | - | - |
| 1400 | 99°C | - | - |
| 600 | 100.5 | 36.0 gms. | 99.2% |
| 400 | 100.5 | - | - |
| 250 | 100.0 | 16.0 | 99.0 |
| 140 | 101.3 | 3.0 | 92.8 |
| 120 | 102.5 | - | - |
| 95 | 102.0 | 1.5 | 85.8 |
| 50 | 104.2 | 7.5 | 15.5 |
| 0.0 | - | 26.5 | 2.98 |

## The Corrosive Action of NaF Solution

Since a large quantity of the NaF leaching solution would have to be handled in pipes, vats, evaporators, etc. if the described process was to be put on a commercial scale, it was thought advisable to set some corrosive samples. The corrosion tests made were as follows.

I. Wrought iron wire in dilute leaching solution from mix 46. This sample was kept at room temperature all the time.

II. Wrought iron wire in dilute leaching solution from mix 46. This sample was kept hot on a hot plate part of the time, that is when it was convenient.

III.* Strips of copper and steel were placed in tap water which was kept at room temperature.

IV.* Strips of copper and steel were placed in a concentrated leaching solution (approx. 4.2% NaF) which was kept at room temperature.

V.* Strips of copper and steel were placed in concentrated leaching solution which was kept hot part of the time (see II).

Each piece of metal was polished bright and weighed before it was put in the solution and after it had set the time indicated in the table. The metal was then cleaned and polished carefully again taking care not to wear away any of the uncorroded metal in the polishing. The metal was weighed again and the loss in weight found. The area of the pieces of metal was found by measurement. The main data obtained and the results are given in the following table.

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*Strips were in same bottle and in contact with each other, which would tend to increase the rate of corrosion of the steel and decrease that of the copper.

Table

| Kind of metal. | Solution | Time set (days) | Area of metal (sq. in.) | Loss in weight (gms.) | Loss mg. per sq. in. |
|---|---|---|---|---|---|
| Wrought iron | I (cold-dilute) | 77 | 1.86 | .0074 | 4.0 |
| Wrought iron | II (hot-dilute) | 77 | 1.89 | .0172 | 9.1 |
| Steel | III (tap water) | 71 | 1.70 | .0648 | 38.1 |
| Steel | IV (cold-conc.) | 71 | 1.71 | .0008 | 0.5 |
| Steel | V (hot-conc.) | 71 | 2.41 | .0040 | 1.7 |
| Copper | III (tap water) | 71 | 2.10 | .0064 | 3.0 |
| Copper | IV (cold-conc.) | 71 | 2.20 | .0002 | 0.1 |
| Copper | V (hot-conc.) | 71 | 2.18 | .0019 | 0.9 |

## Conclusions

The following conclusions are based partly on direct observation and partly on experimental data which has already been given. In some cases the conclusions are only rough approximations and in other cases they should be fairly accurate.

### The Mix

From a study of the runs made it is believed that the best mix to use is 20 parts $CaF_2$, 50 parts "Trona", and 30 parts $SiO_2$. Taking $CaF_2$ as a basis, 50 parts "Trona" (source of $Na_2CO_3$) corresponds to 126% theoretical and 30 parts $SiO_2$ corresponds to about 188% theoretical. This is assuming that the following reaction takes place:

$$CaF_2 + Na_2CO_3 + SiO_2 \longrightarrow 2NaF + CaSiO_3 + CO_2.$$

As already indicated under the work on the leaching solution 58% of excess $Na_2CO_3$ is recovered and can be used again. Also, if some of the leached out residue is used with the mix (see runs 61 and 62) the amount of $SiO_2$ used can be greatly decreased and the yield, considering only the new $CaF_2$ used, is materially increased.

### Conditions of Fusion

The fusion should take place in such a place that the temperature of the fusion mixture never exceeds 750°C (approx.), but the heat should be so governed that it reaches this temperature within a short time (2 to 10 minutes). The charge should be either taken out of the furnace or the temperature not allowed to exceed 750°C soon after it stops bubbling and reaches the second solid stage. A short time of holding at this higher temperature, for instance one minute, will tend to increase the yield, but it seems to reach an equilibrium

soon after one minute and the yield will not increase further and there is a tendency of getting the charge too hot if held too long, which decreases the yield very rapidly.

The rate of cooling does not seem to have any appreciable effect on the yield. (See mixes 23, 23-a, 24, and 24-a.)

The charge must be handled during the fusion so that it is nearly homogeneous all the time, or when it is taken out of the furnace some of the charge will have gone too far, while some of the rest may not have been heated enough.  The best way found to do this was on a flat surface with the charge not more than one cm. thick, if it is heated from both top and bottom.

### Grinding and Leaching

Although very little experimental data was obtained on the a-mount of grinding and the time and conditions of leaching, some observations should not be out of place here.  It was found that the fusion product must be ground in order to get a thorough leaching. (See runs 23, 23-a, 24, 24-a.)  By grinding the fusion product so that 90% goes through an 80-mesh screen over 99% of the NaF is leached out.  (See runs 15, 15-a.)  The time of leaching was not studied but the leaching is complete after the solution (not more than 1% NaF) has been in contact with the ground fusion product for two hours with frequent stirring.  How much this time can be cut down or the concentration increased is not known.  By the use of a counter current system of leaching a concentrated solution (4.2% NaF) can be obtained.

## Crystallization

Since the solubility of NaF does not materially increase with the temperature*, and the solubility is only about 4.2%, a large quantity of water will have to be evaporated. Probably the best way to do this is in multiple-effect evaporators. There will be crystals forming in each effect so that crystal traps will have to be provided for each effect. As the boiling point rise of the solution during evaporation was small (about 5°C) this will not materially decrease the possible number of effects. If the quantity of solution was large enough five or even six effects would not be impracticable and would mean very cheap evaporation. The ordinary steel plate and tubes can be used in building the evaporators as the solution was found to have a much less corrosive action on steel than ordinary tap water.

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*The only data that could be found on the solubility of NaF:

| Temp. °C | Solubility % | Reference |
|----------|-------------|-----------|
| -5.6 | Ice and NaF eutectic | Landolt-Börnstein |
| +15. | 3.85 | " |
| +18 | 4.22 | " |
| +21 | 4.00 | " |
| +25 | 4.03 | " |
| +100 | 4.29 | Z. Ph. Chem. 1912, 82,632. |
| +100 | 4.56 | Mellor, Vol. II, p. 515. |

## Possibility of Economic Production

Although the process has not been carried out on any but a purely laboratory scale, the economic side of the process should be considered, because the first consideration in contemplating semi-commercial production would depend upon a rough estimate of the cost of production. Assuming 80-85% yield, the cost of raw materials would be approximately as follows for one lb. NaF produced.

$CaF_2$ - 1.4 cts.     - Basis \$25.00* per ton for fluorspar.

$Na_2CO_3$ 1.6 cts.     -   "     1.30* per 100 lb. $Na_2CO_3$ and assuming Trona cost 70% as much for the same amount of $Na_2CO_3$.

$SiO_2$   0.6 ct.     - Basis \$18.00* per ton.

Total   3.6 cts. cost of raw material to produce 1 lb. NaF.

The value of the NaF was 8-3/4 cts.* which leaves a margin of 5.15 cts. within which the cost of production must come. This margin is quite large, and if the scale of production was sufficiently large, it probably would not be difficult to keep within these limits.

## Suggestions for Future Work

(1) A development of a continuous method of fusion without stirring and the kind of material that would best stand the fused substance and the high temperature. Nickel which was used for some of the later runs soon becomes brittle. Monel metal was suggested but not tried.

(2) A continuation of the study of the temperature, time of holding, etc. on the charge.

*Prices, April 1925.

(3) Further investigation of the best proportion of the different substances to use. In this connection a very important point to check and work on is the use of the leached out residue. Runs 61 and 62 were a start along this line, and they show interesting possibilities.

(4) After the above points are cleared up, and if they are favorable, the process should be ready to be put on a semi-commercial scale.

The writer at this time wishes to express his thanks to W. N. Lacey for his guiding suggestions in the performance of the experimental work and for the helpful advice and criticisms in the preparation of this report.

Also credit is due W. N. Lacey and Harvey W. House for the use of the results of their work on this fusion process which preceded this work.

## Summary

Sodium fluoride is produced by the fusion of a mixture of $CaF_2$, $Na_2CO_3$ and $SiO_2$ at about 750°C according to the following equation

$$CaF_2 + Na_2CO_3 + SiO_2 \longrightarrow 2NaF + CaSiO_3 + CO_2.$$
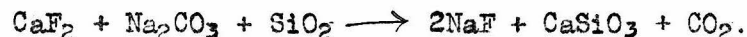
The NaF is recovered by leaching, evaporation, and crystallization in nearly pure form. Yields of 80 - 85% are possible.