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MINERAL ANALYSIS OF STEFFEN'S WASTE FROM THE MANUFACTURE OF BEET SUGAR

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The beet molasses or mother liquor from the crystallization of sugar in the beet sugar industry contains considerable sucrose due to the presence of non-sugars which affect the solubility. It has been shown that the presence of these non-sugars tends to hold more sucrose in solution than if the solution were sugar only. The separation of this residual dissolved sucrose is accomplished by the addition of lime. The insoluble precipitate, tricalcium saccharate $3CaO.C_{12}H_{22}O_{11}.4H_2O$ is removed by filtration and converted into sugar by treatment with water and carbon dioxide and subsequent concentration. The filtrate is heated to precipitate more of the saccharate. The precipitate is removed by filtration and this final filtrate is known as Steffen's Waste. It contains not more than .3 percent sucrose.(1)

The disposal of the waste is complicated by its high organic content. Efforts have been made to determine any valuable constituents present and the best mode for their separation. The development of a profitable means of separation of these materials from the waste would help to solve the disposal problem as well as to materially reduce the cost of production.

The present investigation was carried out with the idea of determining the variation in mineral content of the waste from different localities. Thirteen samples of one barrel each of the dilute waste were obtained from factories scattered from Michigan to Utah, as follows: Colorado — Swink, Fort Collins, Delta, Loveland; Michigan — St. Louis, Blissfield; Nebraska — Grand Island; Utah — Spanish Fork, Lewiston; Wyoming — Torrington, Worland; Iowa —Mason City (pond), Mason City (campaign).

The samples were treated with carbon dioxide to remove the calcium and concentrated. Concentration was carried out in a vacuum evaporator in the Chemical Engineering Laboratory at the State University of Iowa.

CONCENTRATION OF THE WASTE

Determinations were made of the specific gravities and weights

of the dilute wastes, the specific gravities after treatment with carbon dioxide gas to a faint color with phenolphthalin as indicator and the weights and specific gravities after concentration. (See Table I.) Specific gravities were determined at 25°C. by the West-

Table I — Specific Gravities and Weights of Waste Before and After Concentration

PLACE	SP. G. BEFORE	SP. G. AFTER	SP. G. CONCENT.	WT. DILUTE	WT. CONC.
Swink, Colo.	1.016	1.014	1.420	433	8.5
Delta, Colo.	1.014	1.013	1.410	422	4.0
Loveland, Colo.	1.020	1.014	1.396	420	7.5
Ft. Collins, Colo.	1.013	1.010	1.406	421	8.5
St. Louis, Mich.	1.022	1.015	1.408	427	22.0
Blissfield, Mich.	1.011	1.008	1.440	413.5	6.5
Grand Island, Nebr.	1.015	1.009	1.392	420	9.0
Lewiston, Utah	1.012	1.009	1.404	420	8.5
Spanish Fork, Utah	1.014	1.010	1.414	444	13.0
Torrington, Wyo.	1.016	1.012	1.460	426	7.0
Worland, Wyo.	1.012	1.007	1.454	400	5.0
Mason City, Ia. (P)	1.017	1.016	1.392	417	16.0
Mason City, Ia. (C)	1.018	1.014	1.415	423	12.5

phal balance. The variation in gravity of the waste was found to be about $\pm$ .001 for 10° change of temperature.

In each case the specific gravity is reduced by carbonation due to the removal of calcium as carbonate.

The weight of the concentrates obtained from barrels of waste weighing from 400 lbs. to 444 lbs. varies from 4 to 22 lbs. There is no correlation with the amount obtained. The highest yield is 22 lbs. from St. Louis, Michigan. The Mason City samples were next with yields of 12 to 16 lbs. The lowest yield was 4 lbs. from 422 lbs. from Delta, Colo. There was no correlation between volatile matter or residue on ignition and the yield. (See Table II.)

Table II — Residues and Volatile Matter

PLACE	P.P.M. RES. ON EVAP.	P.P.M. RES. ON IGN.	P.P.M. VOLATILE
Swink, Colo.	18,922	10,167	8,754
Delta, Colo.	17,680	7,165	10,514
Loveland, Colo.	21,406	11,179	10,227
Ft. Collins, Colo.	15,441	7,395	8,046
St. Louis, Mich.	29,818	8,738	21,080
Blissfield, Mich.	14,977	4,864	10,113
Grand Island, Nebr.	22,194	8,075	14,119
Lewiston, Utah	18,059	6,548	11,511
Spanish Fork, Utah	18,370	8,594	9,766
Torrington, Wyo.	21,218	10,302	10,915
Worland, Wyo.	20,773	9,910	10,863
Mason City, Ia. (P)	29,699	9,466	20,233
Mason City, Ia. (C)	27,054	8,991	18,063
Average	21,200	8,561	12,639

The weight of the concentrated material obtained depends on the dissolved substance in the waste, which is affected by seasonal variation in the composition of the beet, and in the water used in the process. (2)

In this work the dilute wastes after carbonation were analyzed for comparison. The waste before carbonation has varying amounts of excess lime added in the precipitation of the sugar.

DETERMINATION OF RESIDUE, VOLATILE MATTER AND ASH

Fifty cubic centimeter samples of the waste were evaporated in platinum dishes, dried at 100°C. and weighed. Any higher temperature caused decomposition with a freeing of amines. The residue was ignited by charring over an open flame and then placing in an electric muffle at a dull red heat. The ash was weighed and saved for analysis. It was very difficult to get checks on ignited samples due to the high potassium content of the waste. Potassium carbonate was formed which melted and enclosed particles of unburned carbon. The residues on evaporation and ignition and the volatile matter in the different samples are shown in Table II.

There is a wide variation from 4,864 at Blissfield, Mich., to 11,179 at Loveland, Colo., in the residues and from 8,046 at Fort Collins, Colo., to 21,080 at St. Louis, Mich., in the volatile matter. The remaining samples do not vary much from the average, 8,561 for the residues on ignition and 12,639 for volatile matter. Here as in concentration the amounts depend on the character and quantity of material in solution. Low ash and high volatile matter as in the case of St. Louis, Mich., indicate high organic content of the waste. High ash indicates concentration of inorganic salts in the waste. High inorganic material may come from the concentration of the water used in the process or from high inorganic matter in the beets. Plans are being made to analyze the water used in the different factories. There is no apparent correlation between geographical distribution and the residue and volatile matter. The samples from Mason City, Iowa, and from St. Louis, Mich., which gave the largest residue on evaporation gave highest volatile matter, indicating the largest amounts of organic material in solution.

ANALYSIS OF THE ASH

Analysis of the waste was carried out in general according to Standard Methods of Water Analysis. Sodium and potassium were determined by the perchloric acid method using normal-butyl alcohol for the final separation, in place of ethyl alcohol. This modified method has the advantage of being a precipitation method

rather than one in which the sodium perchlorate is dissolved away from the potassium salt. The sodium and potassium found are shown in Table III.

Table III — Sodium and Potassium Content of Ash

PLACE	K	Na	TOTAL
Swink, Colo.	27.76	16.40	44.16
Delta, Colo.	33.38	13.70	47.08
Loveland, Colo.	35.25	12.65	47.90
Ft. Collins, Colo.	32.50	16.40	48.90
St. Louis, Mich.	33.70	15.01	48.71
Blissfield, Mich.	36.17	10.40	46.57
Grand Island, Nebr.	36.46	10.87	45.33
Lewiston, Utah	35.18	8.79	43.97
Spanish Fork, Utah	28.84	22.29	51.13
Torrington, Wyo.	36.41	10.58	46.99
Worland, Wyo.	36.01	11.50	47.51
Mason City, Ia. (P)	40.72	7.52	48.24
Mason City, Ia. (C)	40.06	8.21	48.27
Average	34.64	12.64	47.28

The potassium found does not vary with geographical location. Swink, 27.76 percent, and Spanish Fork, 28.84 pecent, have low and Mason City, 40.06 percent, has high potassium. All of the other samples are fairly close to the average, 34.64 percent. About one-third of the ash from Steffens Waste is potassium. The waste is a possible source of potassium, if it can be obtained economically. There is a greater variation in the sodium values found, from Spanish Fork, 22.29 percent to Mason City, 8.21 percent. Again there is no correlation with geographical location.

The analysis of the ash of beet roots shows both sodium and potassium present in fairly large amounts, (3). The amounts have been shown to vary with the species of the beet and the kind of fertilizer used, (4). If this is true, then there is every reason to expect that the composition would vary with the soil and surface water in which the beets were grown. If the composition of the beet root varies, then there will be a corresponding variation in the waste water. It is evident that local conditions are the determining factors in so far as sodium and potassium are concerned. The sums of the sodium and potassium are comparatively constant. The difference between the highest and the lowest being 7 percent.

The treatment with lime tends to precipitate any magnesium present in the water as the hydroxide and in only two cases was there a trace of it found. Calcium was removed before concentration by carbonating the water. The amounts of silica and iron and aluminum oxides are practically negligible. The sample from St. Louis, Mich., gave about 2 percent aluminum oxide. Since the

amounts of these positive ions were negligible no further mention need be made of them.

Chlorides were determined by titration with standard silver nitrate using potassium chromate as indicator. Analyses were first made to determine the chloride in the original waste. The amounts in parts per million of the original waste and in percent calculated to ash are shown in Table IV.

Table IV — Chloride Determinations on Original

PLACE	P.P.M.	PERCENTAGE
Swink, Colo.	1,426	14.03
Delta, Colo.	1,185	16.54
Loveland, Colo.	1,775	15.88
Ft. Collins, Colo.	1,065	14.40
St. Louis, Mich.	373	4.27
Blissfield, Mich.	288	5.92
Grand Island, Nebr.	1,014	12.56
Lewiston, Utah	957	14.61
Spanish Fork, Utah	1,233	14.25
Torrington, Wyo.	872	8.46
Worland, Wyo.	845	8.53
Mason City, Ia. (P)	78	.82
Mason City, Ia. (C)	772	4.40

The amounts of chloride follow very closely the geographical distribution. Four samples from Colorado have high chloride about 15 percent. Two Michigan samples low chloride averaging about 5 percent. Two samples from Utah are comparable with those from Colorado averaging about $14\frac{1}{2}$ percent. The samples from Nebraska and Wyoming are intermediate.

Chlorides determined in the ash were lower in every case but one, the pond at Mason City. The amounts of chloride in the ash do not show the same correlation with location as do the amounts in the original. (Table V).)

Table V — Variation in Chlorides Before and After Ignition

PLACE	ORIGINAL	ASH	DECREASE
Swink, Colo.	14.02	7.27	6.75
Delta, Colo.	16.53	10.56	5.97
Loveland, Colo.	15.878	10.57	5.30
Ft. Collins, Colo.	14.401	6.37	8.03
St. Louis, Mich.	4.26	1.57	2.69
Blissfield, Mich.	5.92	2.86	3.16
Grand Island, Nebr.	12.55	7.97	4.58
Lewiston, Utah	14.61	6.70	7.90
Spanish Fork, Utah	14.34	9.23	5.11
Torrington, Wyo.	8.46	5.88	2.58
Worland, Wyo.	8.52	5.69	2.83
Mason City, Ia. (P)	.82	1.88	1.06
Mason City, Ia. (C)	4.404	2.21	2.19

The loss of chloride in the ash may be due to one of two reasons. (1) the presence of some organic compound which precipitated a silver salt, (2) part of the chloride may have been volatilized in ashing. If the later is true it is possible that ammonium chloride or a chloramine formed from the decomposition of organic compounds and volatilized on ignition.

Sulphates were determined by precipitation with barium chloride from acid solution of the ash. Carbonates were determined by titration of the ash with standard acid using methyl orange as an indicator. The results for carbonates and sulfates are shown in the following table. (Table VI.)

Table VI — Comparison of Chloride, Sulfate and Carbonate in the Ash

PLACE	CL ASH	CL ORIGINAL	SO_4 ASH	CO_3 ASH
Swink, Colo.	7.27	14.02	14.15	26.72
Delta, Colo.	10.56	16.53	14.22	27.68
Loveland, Colo.	10.57	15.88	10.54	27.71
Ft. Collins, Colo.	6.37	14.40	12.42	28.82
St. Louis, Mich.	1.57	4.26	4.33	39.88
Blissfield, Mich.	2.86	5.92	6.74	35.65
Grand Island, Nebr.	7.97	12.55	7.44	32.36
Lewiston, Utah	6.70	14.61	8.30	31.07
Spanish Fork, Utah	9.23	14.34	9.76	30.70
Torrington, Wyo.	5.88	8.46	10.26	33.70
Worland, Wyo.	5.69	8.52	11.26	31.63
Mason City, Ia. (P)	1.88	.82	7.81	36.63
Mason City, Ia. (C)	2.21	4.04	8.54	35.72

The sulphates like the chlorides in the original samples vary with geographical location. Those in Colorado and Wyoming are high, Utah, Iowa and Nebraska intermediate, and Michigan low. It is questionable if any sulfate would be extracted from the beet. It probably comes from the water used.

The carbonates are formed by the burning of organic compounds. Any calcium would be present as the oxide after ignition. Previous investigators have reported bicarbonate in the ash. (5) This does not seem reasonable at the temperature at which ignition was carried out.

Titration using phenolphthalin and methyl orange indicated only the normal carbonate. Since carbonate is formed by burning the organic salts we would expect to find a correlation between the amounts of carbonate and sodium and potassium present. Comparisons are shown in Table VII.

The relation between the amounts of alkalis present and the amount of carbonate is nearly constant. Where the chlorides and sulphates are high the carbonate is low. A part of the sodium and

Table VII — Comparison of Sodium, Potassium and Carbonate in the Ash

PLACE	K	Na	K-Na	CO₃
Swink, Colo.	27.76	16.40	44.16	26.72
Delta, Colo.	33.38	13.70	47.08	27.68
Loveland, Colo.	35.25	12.65	47.90	27.71
Ft. Collins, Colo.	32.50	16.40	48.90	28.82
St. Louis, Mich.	33.70	15.01	48.71	39.88
Blissfield, Mich.	36.17	10.40	46.57	35.65
Grand Island, Nebr.	34.46	10.87	45.33	32.36
Lewiston, Utah	35.18	7.06	42.24	31.07
Spanish Fork, Utah	28.84	22.29	51.13	30.70
Torrington, Wyo.	36.41	9.47	45.88	33.70
Worland, Wyo.	36.01	11.50	47.51	31.63
Mason City, Ia. (P)	40.72	7.52	48.24	36.63
Mason City, Ia. (C)	40.06	8.21	48.27	35.72

potassium is united with chloride or sulphate. Hypothetical combinations made later in the paper show this relation more clearly.

The complete analyses for all samples are shown in Tables VIII and VIIIa.

Table VIII — Complete Analyses

	1	2	3	4	5	6	7
K	27.76	33.38	35.25	32.50	33.70	36.17	34.46
Na	16.40	13.70	12.65	16.40	15.01	10.40	10.87
Mg	00.69	00.00	00.00	00.00	00.94	00.00	00.00
Ca	00.88	00.99	00.75	00.73	01.87	6.14	00.36
Cl	7.27	10.56	10.57	12.42	1.57	2.86	7.97
SO₄	14.15	14.22	10.54	12.54	4.33	6.74	7.44
CO₃	26.72	27.68	27.71	28.82	39.88	25.65	32.36
SiO₂	00.00	00.00	00.00	00.00	00.00	00.00	00.23
R₂O₃	00.53	00.29	00.29	00.30	01.91	00.70	00.23
Undet	16.59	−.82	2.22	.80	6.69	1.34	6.08
	100.00	100.00	100.00	100.00	100.00	100.00	100.00

1. Swink, Colo.   5. St. Louis, Mich.
2. Delta, Colo.   6. Blissfield, Mich.
3. Loveland, Colo.   7. Grand Island, Nebr.
4. Ft. Collins, Colo.

Table VIIIa — Complete Analyses

	8	9	10	11	12	13
K	35.18	28.84	36.41	36.01	40.72	40.06
Na	8.79	22.29	10.58	11.50	7.52	8.21
Mg	00.00	00.00	00.00	00.00	00.00	00.00
Ca	1.16	.86	.58	.33	3.08	.68
Cl	6.70	9.23	5.90	5.88	1.88	2.21
SO₄	8.30	9.76	10.26	11.26	7.81	8.54
CO₃	31.07	30.70	33.70	33.21	36.63	35.72
SiO₂	00.00	00.00	00.09	00.00	00.45	00.24
R₂O₃	.18	.41	.42	.42	.47	.53
Undet	7.62	−2.09	2.06	1.51	1.45	3.81
	100.00	100.00	100.00	100.00	100.00	100.00

8. Lewiston, Utah.   11. Worland, Wyo.
9. Spanish Fork, Utah.   12. Mason City, Ia. (P)
10. Torrington, Wyo.   13. Mason City, Ia. (C)

In several of the analyses there is a high percentage of "undetermined." As it was necessary to use small samples so that complete ashing could be accomplished, any error would be multiplied in most cases one hundred times. By calculating the combining values in accordance with regular water analysis the error is less than one percent. The error is determined by dividing the difference of the total combining values for the positive and negative ions by the sum of the combining values and multiplying by 100.

It was mentioned earlier in the paper that it was very difficult to carry out complete ignition due to the melting of potassium salts which subsequently covered particles of unburned carbon. If such were the case in any sample the residue would be high and all the percentages low. However, calculation of the error as above mentioned would not include this unburned carbon. It therefore seems reasonable that this should explain the failure to obtain 100 percent in some cases. The method of calculating the error is shown in Table IX.

Table IX — Calculation of Combining Values and Error of Analysis for Grand Island, Nebraska

Ion	P.P.M.		Reacting Val.		Combining Value
K	2,730	×	.02557	=	69.80
Na	1,050	×	.04348	=	45.65
Ca	28	×	.04994	=	1.39
					116.84
Cl	654	×	.0282	=	18.44
SO₄	605	×	.0208	=	12.48
CO₃	2,518	×	.0333	=	83.92
					114.84

$$116.84 - 114.84 = 2$$

$$\frac{2}{231.68} \times 100 = .864 \text{ percent error}$$

Errors calculated in the same way for other samples having the largest amounts of undetermined gave the following results:

Place	Undetermined	Error
Lewiston	8.62 percent	.3 percent
Torrington	8.06 percent	.8 percent
Mason City (C)	6.59 percent	.7 percent

An interesting fact was shown by making hypothetical combinations. The sample for Grand Island, Nebr., will be the only one considered here since it would be impossible to consider all of them. The negative ions were used in the order CO_3, Cl, SO_4. The positive ions were used in the order K, Na.Ca. This was done because

it is known that the potassium present and a possible part of the sodium will be in the form of carbonate due to oxidation of the organic compounds containing them. Calculations for the sample from Grand Island are shown in Table X.

Table X — Hypothetical Combinations for Grand Island Waste..

SALT	COMBINING VALUE		EQUV. WT.		P.P.M.	PERCENTAGE
K_2CO_3	69.80	×	69	=	4,816.2	60.81
Na_2CO_3	14.12	×	53	=	748.4	9.44
NaCl	18.44	×	58	=	1,069.5	13.50
Na_2SO_4	12.48	×	71	=	886.1	11.18
$Ca(OH)_2$	1.39	×	17	=	23.5	.29
				Total	7,543.2	95.22
Excess Na – .61			SiO_2 and Al_2O_3		36.0	
				Total	7,579.2	
				Residue	7,920.	
				Difference	340.8	

CONCLUSIONS

1. The amount of concentrate which can be obtained from a given amount of the dilute waste varies with the source of the waste.

2. There is a wide variation in the ash and volatile matter in different samples of the waste.

3. Of the thirteen samples investigated the average potassium content of the waste is about thirty-four percent.

4. The sodium and potassium content of the waste do not have any apparent relation to the geographical location of the plant.

5. The sulphate and chloride values do have a variation with geographical location. Samples from the same districts having relatively the same value.

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