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THE REPLACEMENT OF CALCIUM CARBONATE WITH CALCIUM CHLORIDE AND CALCIUM FLUORIDE IN A WHITEWARE BODY

BY

CHARLES RICHARD ROSENBAUM

A
THESIS
submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree Of
BACHELOR OF SCIENCE IN CERAMIC ENGINEERING
Rolla, Mo.
1933.

Approved by C. M. Dodd
Associate Professor of Ceramic Engineering.

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TABLE OF CONTENTS

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INTRODUCTION

A great deal of work concerning the utilization of Fluorite in enamels has been done, but only two of the later experiments will be referred to, as the subject bears only a remote relation to the material discussed in this paper. Stucker[1] says that in enamels for sheet steel the limiting factor in the use of fluorine bearing compounds is the fluorine and limits the quantity used to from .58 to .8 equivalents.

Dr. Karmaus[2] states that calcium fluoride is valuable as a cheap flux in enamels, that 5 % considerably lowers the melting point of the enamel, that the composition of the glass has no effect on gas loss, and finally that fluospar has the largest fluxing action of any of the fluorine bearing minerals.

In the system $CaF_2 - Al_2O_3$ the temperature was found to be 1270° C and the composition of the eutechtic 72.1 % CaF_2 - 27.9 % Al_2O_3.[3]

A. S. Watts[4] in an experiment attempting to determine the best form of calcium to add to a cone 12 porcelain body found that the replacement of whiting with fluorite gave a yellow color and therefore he condemns the use of fluospar for this reason, because under other than ideal firing conditions it tends to give a greater porosity than does whiting, and has a greater tendency to blister.

H. E. Ashley[5] in an experiment involving a cone 4 body somewhat similar to the cone 6 body used in this experiment found that whiting was more effective than fluorite, added in equal amounts, in increasing shrinkage and decreasing porosity. Fluospar was found to be superior in promoting translucency and increasing mechanical strength.

Apparently there has been no work done to replace whiting with $CaCl_2$ in clay bodies; this omission is perhaps due to the reasons mentioned later in conjunction with calcium bromide and calcium iodide.

OBJECT

In the steel industry it is a common metallurgical practice to add fluospar (CaF_2), to a slag to render it more fluid. Ladoo[6] states that the fluospar, thus added, forms eutechtics with the silica, alumina, calcium and barium sulfates, rendering them more fusible. The fluospar does not decompose, but forms solutions or eutechtics with other substances in the slag. He further states that calcium chloride ($CaCl_2$) has been used for this purpose but is apparently not as active, necessitating larger quantities per charge. It is also probably more expensive.

Calcium carbonate ($CaCO_3$) is commonly used as a flux in the ceramic industry. It occurs naturally in some clays and is added to most white ware bodies other than hard paste porcelains to increase the degree of vitrification. It was proposed, therefore, to replace the calcium carbonate in a whiteware body with the halitic salts of calcium. The heavier salts, the bromide ($CaBr_2$) and the iodide (CaI_2), were not used because of their cost, their solubility, and their low decomposition temperatures.

The reasons for attempting to replace the carbonate with the fluoride and chloride are: (1) The desired degree of vitrification may possibly be reached at a lower temperature; (2) The present price of these materials is; calcium carbonate \$ 1.95/100 pounds, calcium fluorite (as acid grade fluospar) \$ 1.75/100 pounds, and calcium chloride \$ 0.95/100 pounds.[7]

MATERIALS

Fluospar -

The fluospar used was obtained from the Rosiclare Lead and Fluospar Mining Company, Rosiclare, Illinois, and was commercial acid grade. Acid grade fluospar is a naturally occurring mineral that contains at least 95 % CaF_2, the rest being in the main calcite ($CaCO_3$). Fluospar has the following physical and mineralogical properties:[6]

Formula - CaF_2
Crystalline form - Isometric
Cleavage - Octahedral
Hardness - 4
Specific gravity - 3.01 - 3.25
Melting point - 1270 - 1387° C.

Calcium chloride -

The material used was the common commercial dessicating agent. This salt is very cheap, being produced in large quantities as a by-product of the Solvay process for making soda-ash. It is very hygroscopic, tending to take up enough water to form the hexahydrate. This water may be removed by heating to 350° C.

[8]Crystalline form - Hexagonal
Melting point - 29° C.
Solubility - 4000 grams/liter.

Feldspars -

The feldspars used were:

Buckingham Potash feldspar
Goudy Soda feldspar

as obtained from the Consolidated Feldspar Corporation, Trenton, New Jersey. They were ground to pass 200 mesh.

Flint -

The flint was the usual potters flint, ground to pass 200 mesh as obtained from the Pennsylvania Pulverizing Company, Lewistown, Pennsylvania.

Clays -

No. 4 Kentucky ball clay
Florida Kaolin
English china clay

These were used as obtained on the open market.

METHOD OF PROCEDURE

Series a and b were straight line variations of the following body taken as a standard, as shown in table I.

Table I

Body composition -

English china clay	38 %
Ball clay	10 %
Buckingham potash feldspar	30 %
Pennsylvania flint	20 %
Whiting	2 %
	100 %

The whiting was replaced with calcium halides as follows -

Member No.	% $CaCO_3$	% CaF_2	% $CaCl_2$
a1	2.0		.0
a2	1.5		.5
a3	1.0		1.0
a4	.5		1.5
a5	.0		2.0
b1	2.0	.0	
b2	1.5	.5	
b3	1.0	1.0	
b4	.5	1.5	
b5	.0	2.0	

Each body was ground through 100 mesh, the calcium salt added, and the body reground for an hour with a few balls to insure thouough mixing. The members were tempered with 10 % water, aged for 24 hours, and then dry pressed into bars 1 in. x 1 in. x 8 in. on the laboratory hand dry press. All of the bars were fired to cone 2 according to the schedule shown in Fig. 1. The following properties were observed: total shrinkage; modulus of rupture; and absorption. The test methods followed were those outlined by the American Society for Testing Materials. The absorption was found by placing the bars in an autoclave under vacuum for two hours.[9] Results are tabulated in table III.

The second series was a triaxial study in which the calcium salts vary as shown in fig. 5. The following body was taken as a standard:

No. 4 Kentucky ball clay	10.0 %
Florida kaolin	10.0 %
English china clay	30.0 %
Goudy soda feldspar	15.5 %
Pennsylvania flint	25.0 %
Whiting	1.5 %

The body without the calcium salt was blunged, filter pressed, and ground through 100 mesh in a ball mill. To each member the flux was added and the whole member reground for an hour to insure proper mixing. The members were then tempered with 10 % water, aged for 24 hours, and dry pressed as indicated in the cone 2 study. The bars of this series were fired to cone 6 in an oil fired muffle kiln according to the schedule indicated in fig. 2. Properties were determined as in the previous study except that the absorption test was made according to the American Society for Testing Materials method for electrical porcelain.[10] Test results are recorded in table IV.

The properties obtained in the cone 2 run were plotted as indicated in fig. 3 and 4, and for the cone 6 triaxial study in fig. 6, 7, and 8.

DATA AND OBSERVATIONS

All of the bars broke with a distinctly conchoidal fracture.

The color of the bars was observed as indicated below.

Cone 2 Study.

a - series

The color varied in this study from 2 % $CaCO_3$, giving the best color, to the poorest, given by 2 % CaF_2, which had a slight yellowish tinge.

b - series

The color varied in this study from 2 % $CaCl_2$, giving the best color, to the poorest, given by 2 % $CaCO_3$.

Table II

Cone 6 Study

Member No.	Color
1	8
2	7
3	12
4	4
5	5
6	13
7	1
8	9
9	10
10	14

Table II cont.

Member No.	Color
11	2
12	6
13	3
14	11
15	15

(No. 1 indicates the best color and No. 15 the poorest.)

Physical properties of the bars were observed as shown below.

Table III

Cone 2 Study

Body No.	% Total shrinkage	% Absorption	Modulus of Rupture lb./sq. in.
a1	6.56	11.84	1505
b1	7.36	12.41	1460
c1	3.87	17.82	1065
d1	2.72	19.29	940
e1	2.69	19.83	1440
a2	7.44	7.58	2225
b2	8.52	7.44	2135
c2	5.56	6.87	3000
d2	8.72	6.98	1665
e2	7.32	9.44	2015

Table IV

Cone 6 Study

Body No.	% Total shrinkage	% Absorption	Modulus of Rupture lb./sq. in.
1	9.10	8.84	2840
2	10.70	6.79	3120
3	10.28	6.98	2410
4	10.50	8.43	2630
5	10.30	3.99	2970
6	12.30	5.82	3330
7	9.93	7.58	3330
8	11.30	5.40	3190
9	11.58	4.62	3850
10	11.21	3.51	3550
11	12.28	6.55	3260
12	10.50	5.69	3370
13	10.63	7.51	3595
14	10.50	2.98	3780
15	11.80	2.58	4290

Heating Curve - Cone 2 Study

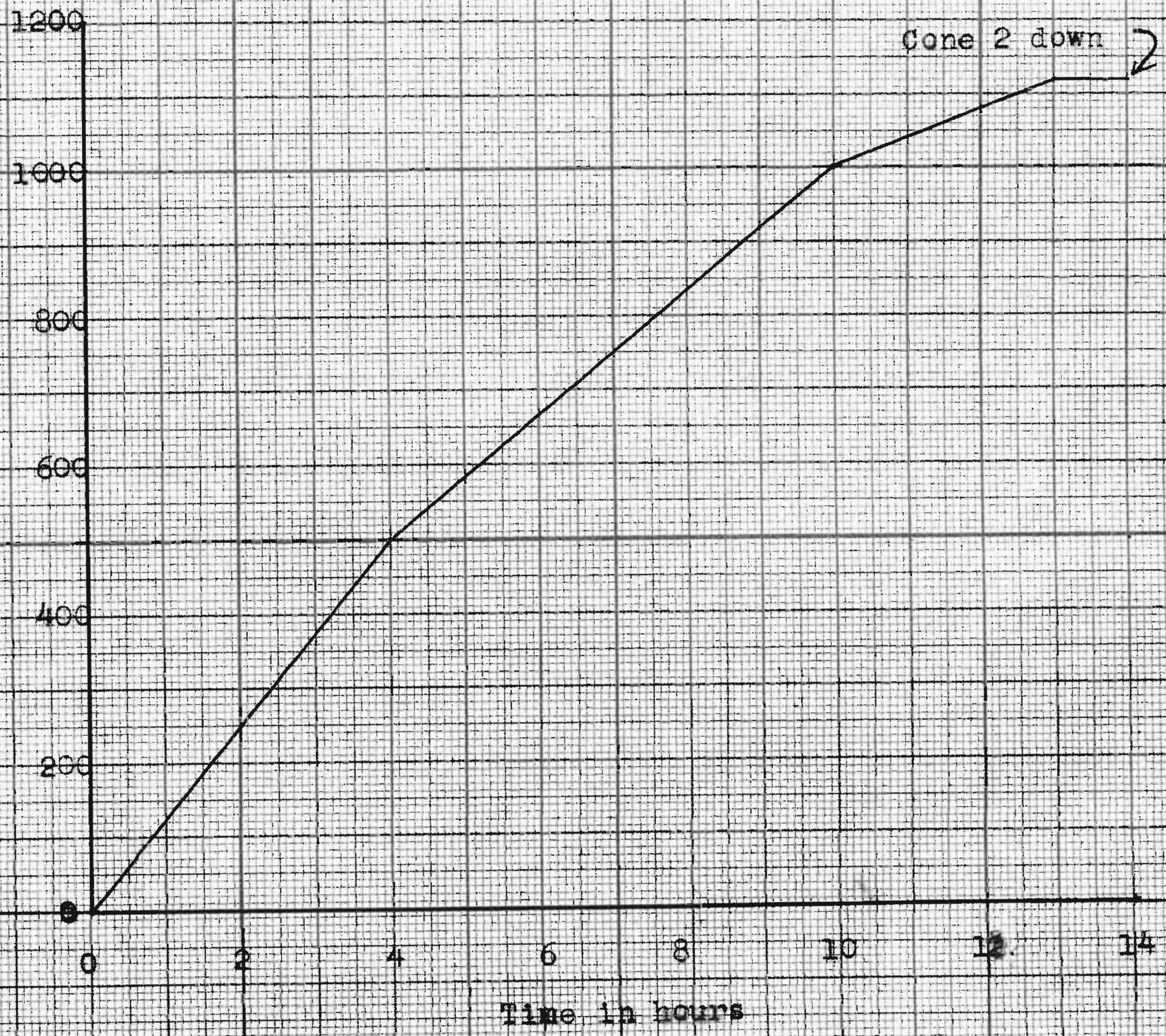


Figure 1

Heating Curve - Cone 6 Study

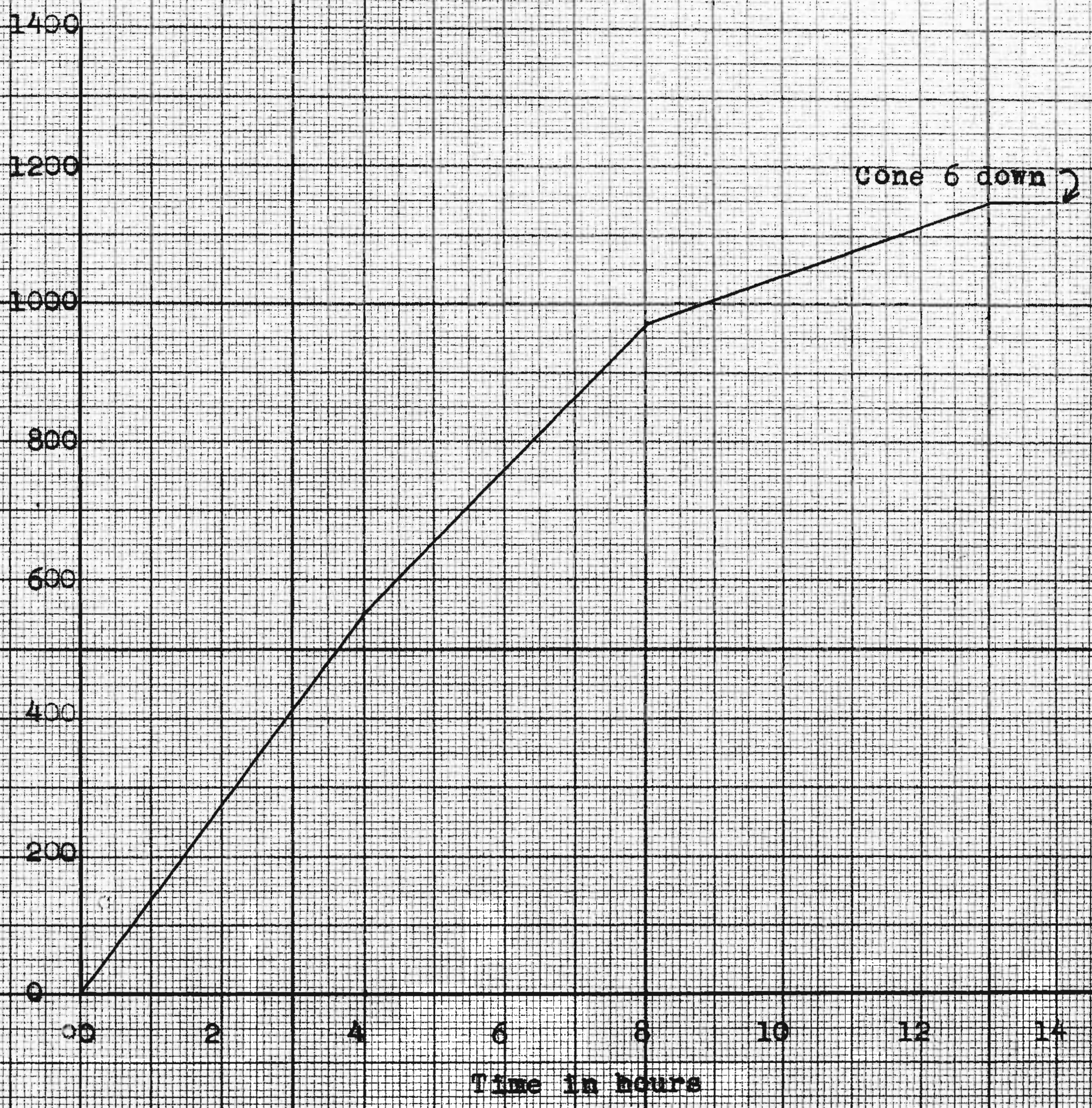
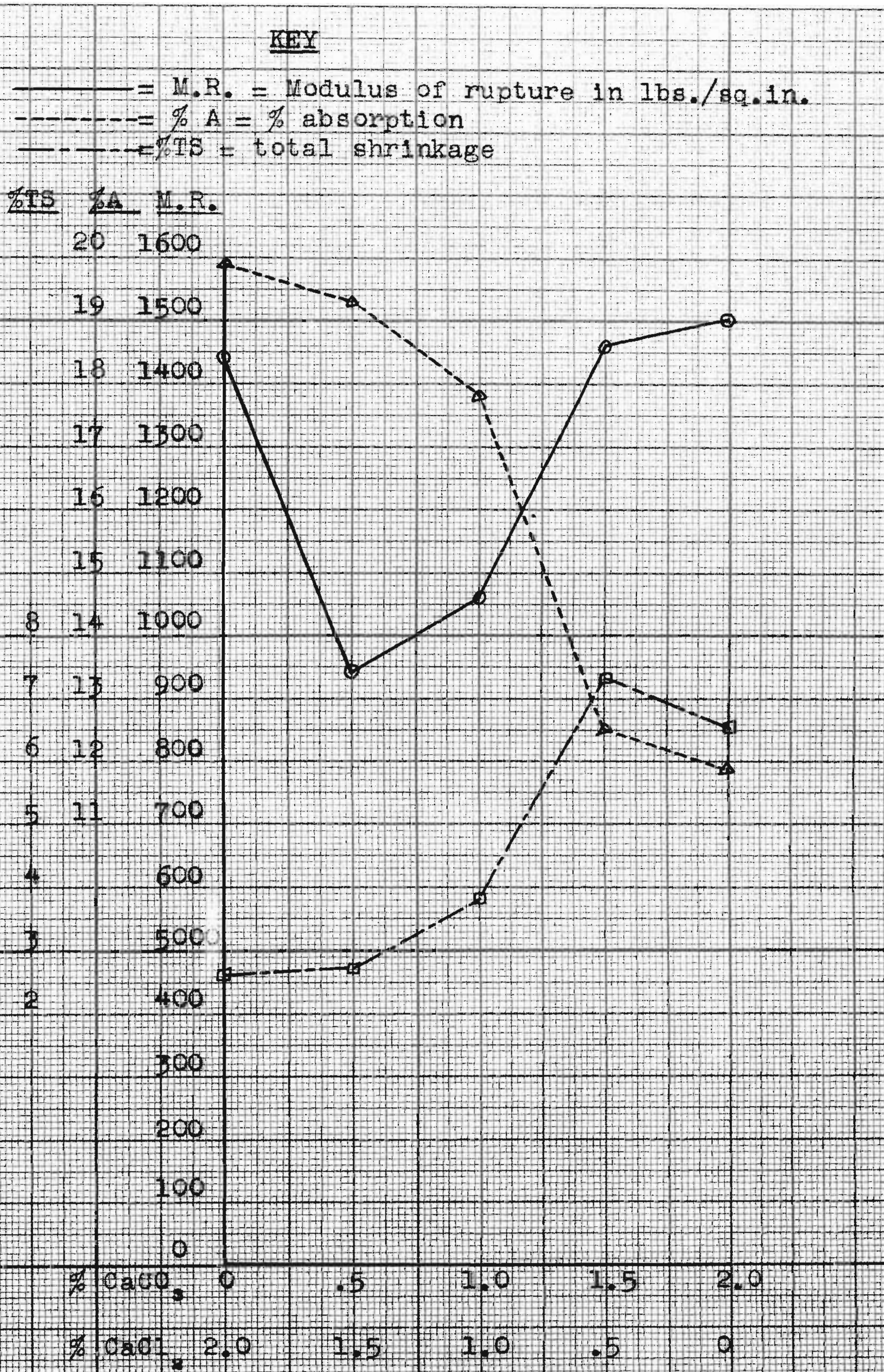
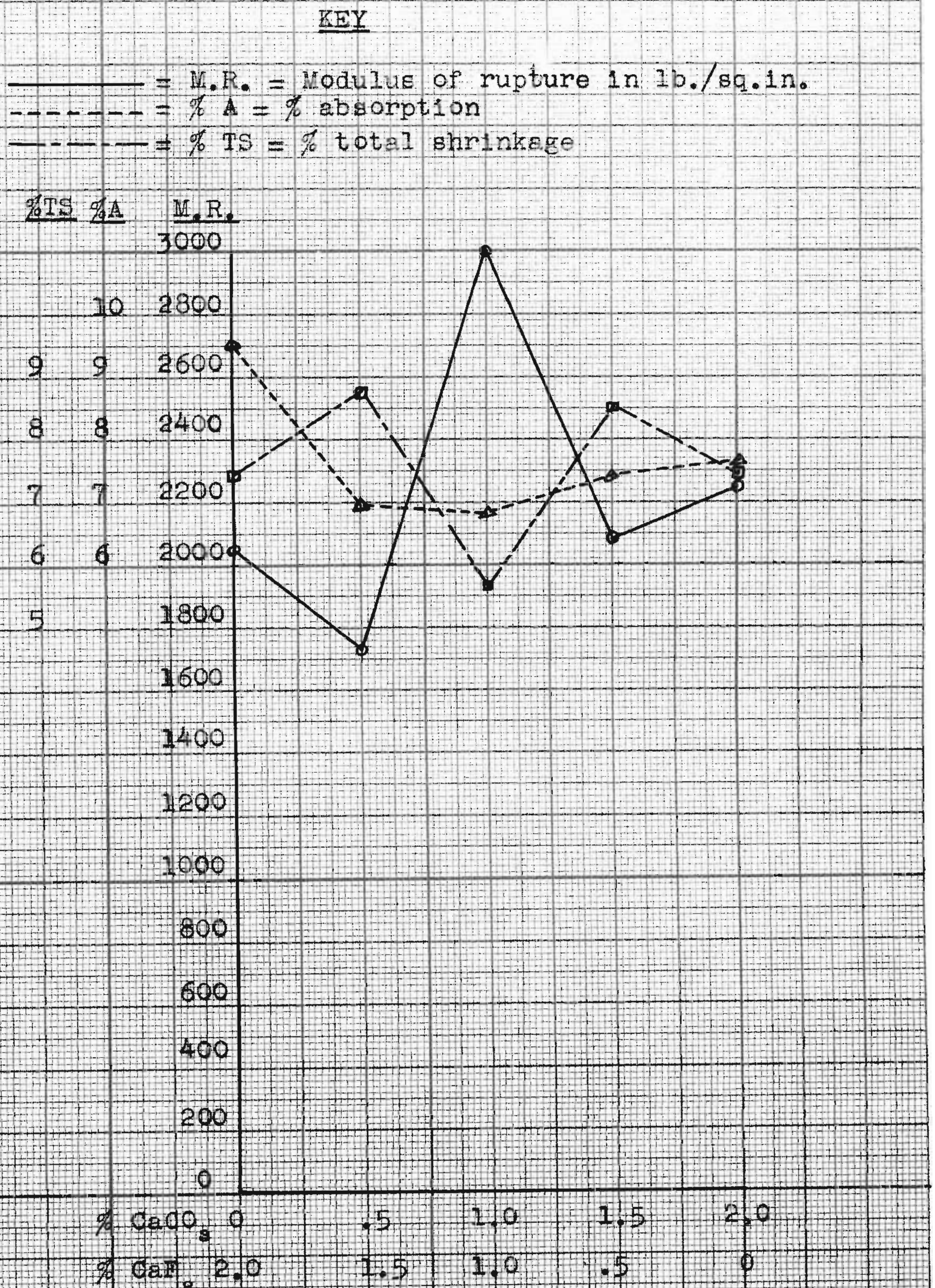


Figure 2



Graph showing effect of replacement of CaCO$_3$ with CaCl$_2$ in a whiteware body at cone 2.

Figure 3



Graph showing effect of replacement of $CaCO_3$ with CaF_2 in a whiteware body at cone 2.

Figure 4

% of Calcium salts at each
triaxial point.

Point	$CaCO_3$	$CaCl_2$	CaF_2
1	1.500	-	-
2	1.125	.375	-
3	1.125	-	.375
4	.750	.750	-
5	.750	.375	.375
6	.750	-	.750
7	.375	1.125	-
8	.375	.750	.375
9	.375	.375	.750
10	.375	-	1.125
11	-	1.500	-
12	-	1.125	.375
13	-	..750	.750
14	-	.375	1.125
15	-	-	1.500

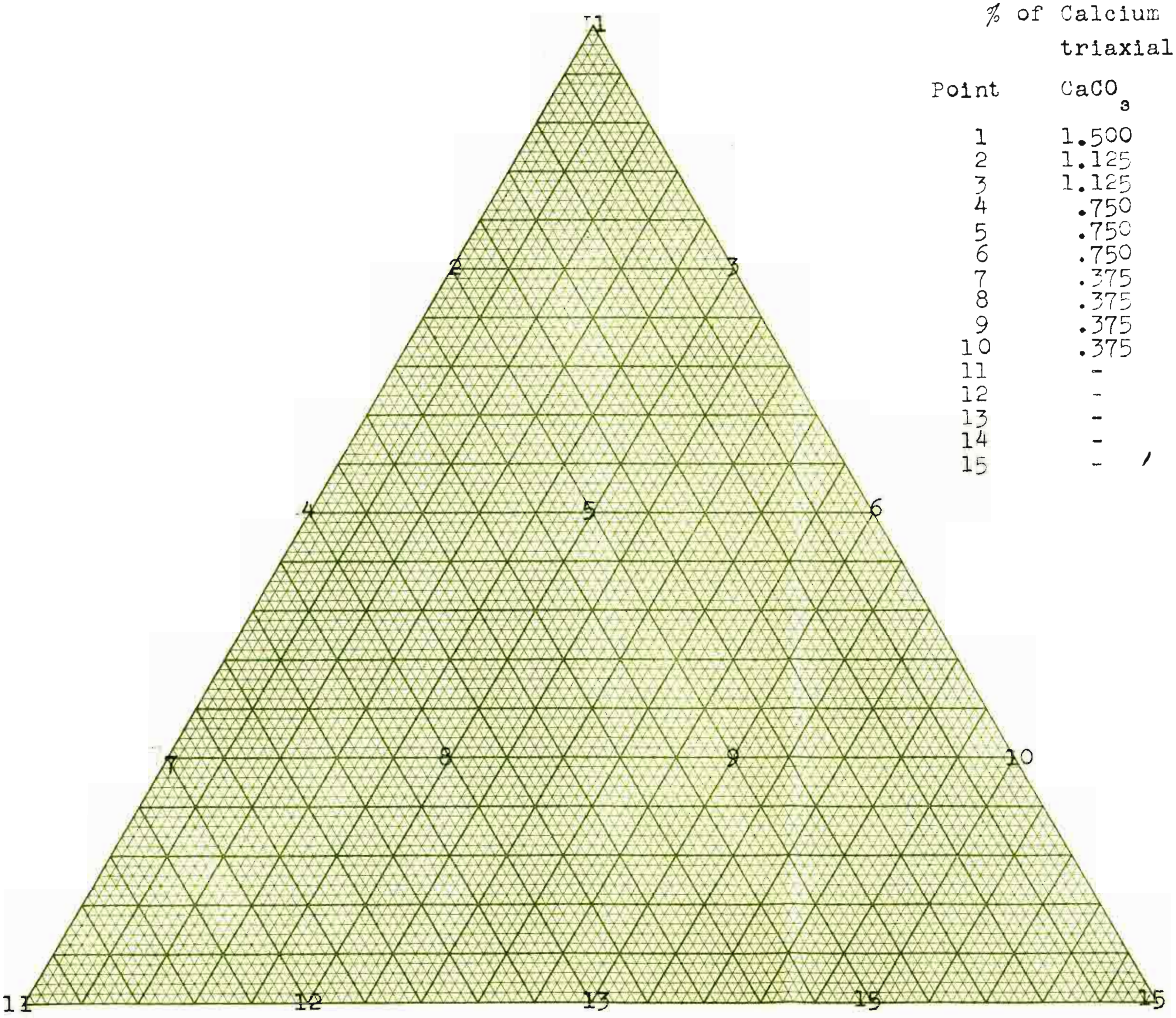


Figure 5

% shrinkage cone 6 study

Vertical Interval - 0.5%

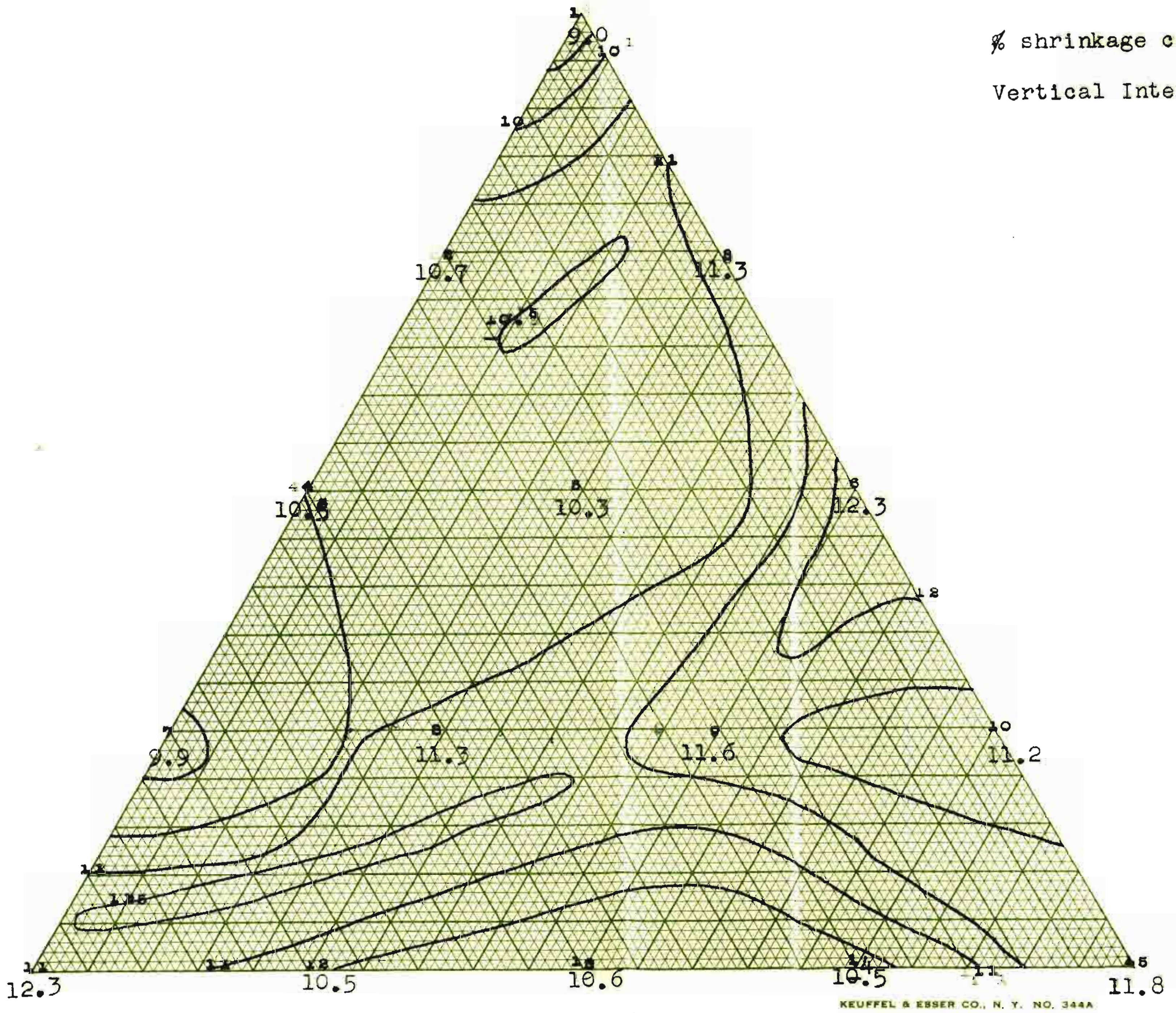


Figure 6

% Absorption cone 6 study
Vertical Interval = .5%

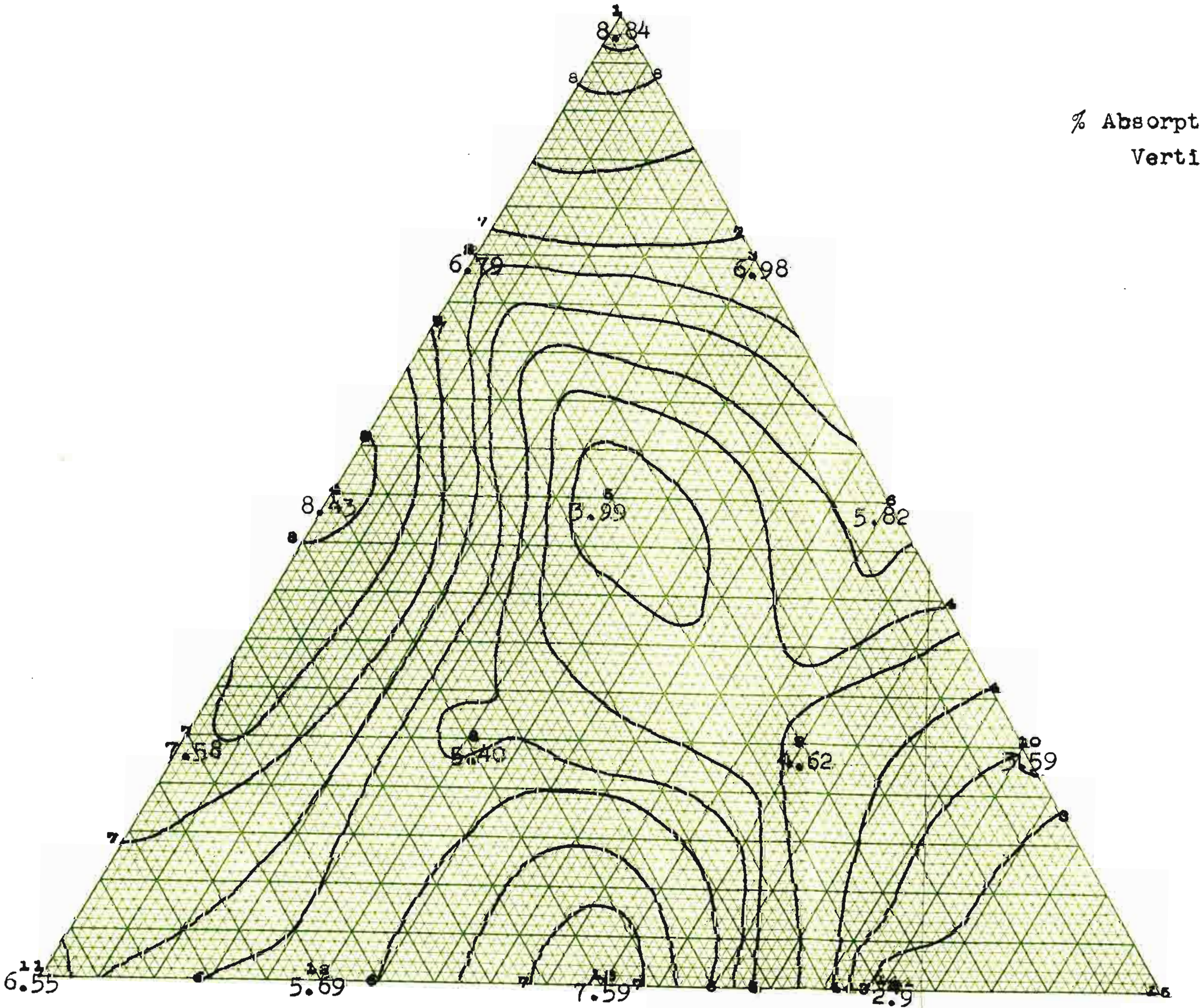


Figure 7

Modulus of Rupture cone 6 study

Vertical Interval = 100 lb/sq.in.

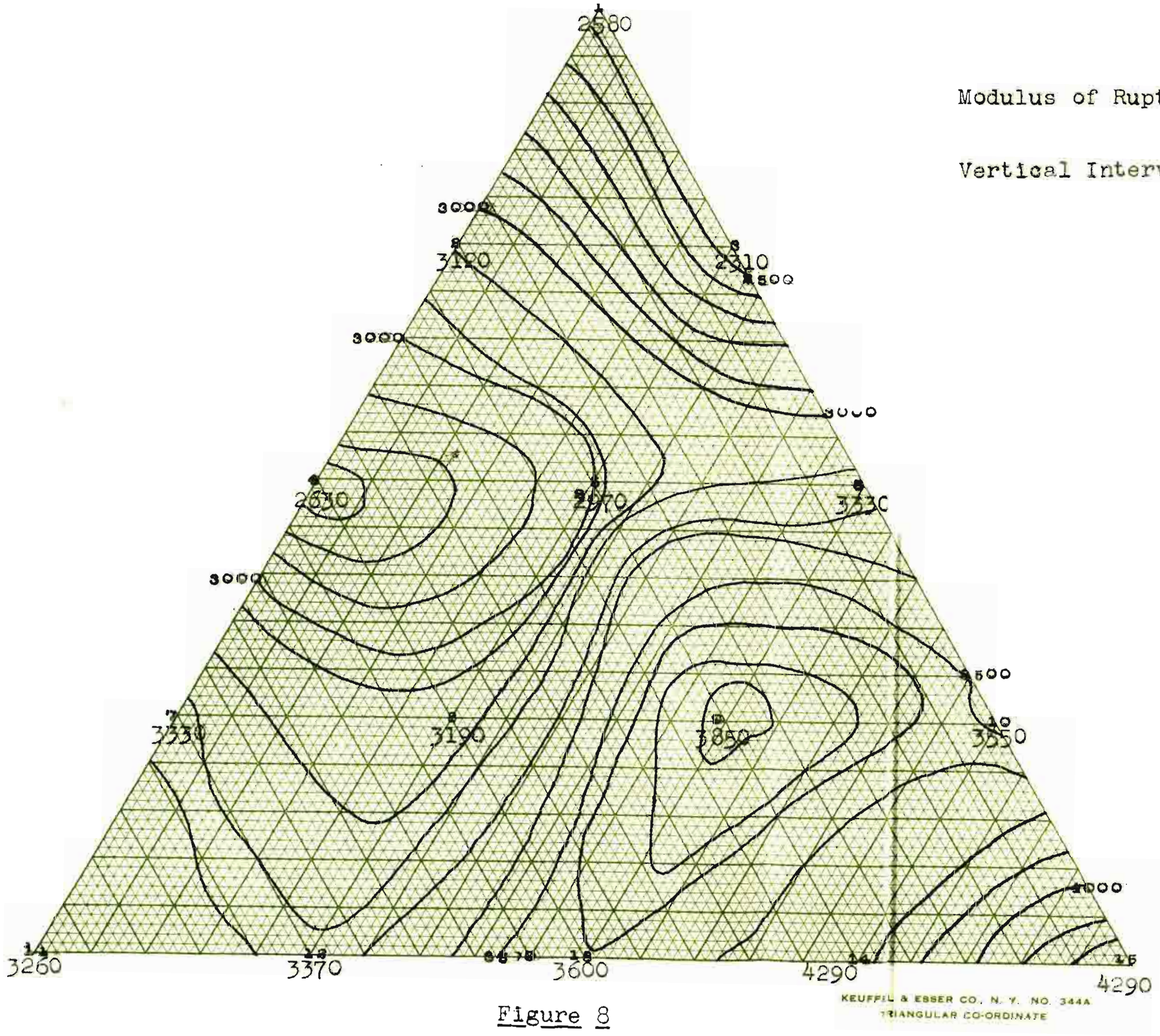


Figure 8

INTERPRETATION OF RESULTS

Cone 2 Study

From the curves, fig. 3 and table III it will be seen that the replacement of $CaCO_3$ with $CaCl_2$ gives a body which has generally poorer characteristics than has the body containing $CaCO_3$. These characteristics may be classified as follows:

1. a markedly definite increase in absorption.
2. a markedly definite decrease in total shrinkage.
3. a slight loss in strength.

Thus it may be inferred that there is less glass formation where the $CaCO_3$ is entirely replaced with $CaCl_2$. The only redeeming feature of this replacement is the better body color obtained.

A very definite decrease in strength may be noted at the intermediate points on the modulus of rupture curve. This is probably due to lack of vitrification at these stages. This may be due to either of several causes, interaction between the calcium salts to form a maximum point on a two phase area, or this may be the result of the loss of the Cl_2 from the $CaCl_2$, which may occlude on the surface of the CaO formed according to the equation, $CaCl_2 + \text{heat} = CaO + Cl_2$, masking it. This gas evolution prevents reaction with the other ingredients and also prevents shrinkage.

From fig. 4 it will be seen that when $CaCO_3$ was totally replaced with CaF_2 very little change in results was obtained except that the color was poorer. It will also be noted that when $CaCO_3$ and CaF_2 are added in equal proportions a definite decrease in absorption and a marked increase in strength took place. The writer believes that this increase in strength is the result of an eutechtic being formed between the $CaCO_3$ or CaO and the CaF_2. The increase in vitrification may also be due to the dissociation of these materials. This dissociation frees F_2, which reacts with the feldspars, silica, etc., to lower the temperature of glass forming.

From the above discussion it may be seen that the substitution of $CaCl_2$ or CaF_2 for whiting has no marked advantages and quite difinite disadvantages in the body at this temperature.

Cone 6 Study

An examination of table IV and fig. 6 shows that the addition of either of the halitic salts definitely increases the total shrinkage. This shrinkage is not regular but follows generally the shrinkage curves obtained in the cone 2 study in the following ways:

1. There is the greatest amount of shrinkage at the point (member 6) where the amounts of CaF_2 and $CaCO_3$ are equal. This is probably due to the evolu-

tion of the active gas F_2 or the formation of an eutechtic between the $CaCO_3$ and CaF_2.

The shrinkage between the $CaCO_3$ and CaF_2 decreases markedly at member 7; this shrinkage is perhaps due to the formation of a maximum point. The theory of the masking of CaO is not tenable here as member 11 shows very high shrinkage.

The drop in shrinkage between the $CaCl_2$ and CaF_2 members may be due to the relativly large amount of gas formed or to the formation of a maximum point.

Fig. 7 and 8 and table IV should be examined together since they show the same thing, i.e. the amount of glass formation. These figures show substantially the same things: a drop in amount of glass formed at the midpoint of the $CaCO_3$ - $CaCl_2$ mixtures. The reasons for this drop have been discussed above.

It will be seen that strength decreases definitely and absorption decreases in the same manner as the point of maximum CaF_2 is reached. Thus member 15 from the standpoint of properties is the best in the series, but from a viewpoint of color is decidedly the poorest.

All things considered it can be said that the replacement of $CaCO_3$ totally or in a major portion with either $CaCl_2$, CaF_2 or a mixture of these will improve the body materially.

APPLICATIONS TO THE CERAMIC INDUSTRY

The writer does not suggest any present applications to the ceramic industry, because (1) no work has been done at temperatures higher than cone 6; (2) no attempts have been made to correct the detrimental color of the fluorite bearing bars; (3) no definite conclusions have been reached as to the reactions taking place between the fluxes; and (4) because the work done at these temperatures was only partial, a larger number of members being necessary for complete results.

SUGGESTIONS FOR FURTHER RESEARCH

Suggestions for further research may be divided into those related directly to the bodies studied and those relating to the fluxes alone.

Suggestions relating to bodies studied.

1. That a triaxial be prepared for the cone 2 study and the amount of calcium salt increased to 3 %.

2. That members be prepared for the cone 6 study varying only one half as much as did those in the present study.

3. That a study similar to the cone 6 body be prepared and fired to cones 8 and 10.

4. The calcium salts should be proportioned by equivalents of CaO in place of by weight percent.

Suggestion relating to the fluxes.

1. The writer suggests that the phase relationships, if any, between the fluxes be worked out.

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