

CERAMIC APPLICATIONS OF ZEOLITES

by

Harry John Beckemeyer

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Chemical Engineering

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

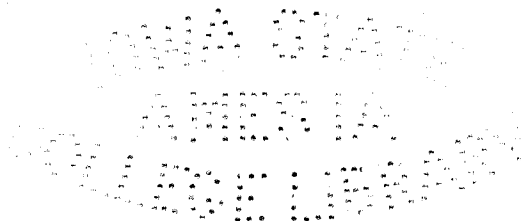
Head of Major Department

Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1949



UMI Number: DP13115

INFORMATION TO USERS

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleed-through, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

UMI[®]

UMI Microform DP13115

Copyright 2005 by ProQuest Information and Learning Company.

All rights reserved. This microform edition is protected against unauthorized copying under Title 17, United States Code.

ProQuest Information and Learning Company
300 North Zeeb Road
P.O. Box 1346
Ann Arbor, MI 48106-1346

79347

1	I. INTRODUCTION
3	II. REVIEW OF LITERATURE
12	III. METHOD OF PROCEDURE
12	A. General
16	B. Zeolite in Ceramic Glazes
16	1. Preliminary Glaze study
18	2. Glaze studies
21	3. Non-milled Glazes
22	4. Effect of water content on Glazes
23	C. Stabilization of Zeolite
24	D. Zeolite in Ceramic Bodies
24	1. Zeolite in casting slips
27	2. Hydrogen zeolite in casting slips
29	E. Raw Materials
32	IV. RESULTS AND DISCUSSION
32	A. Zeolite in Ceramic Glazes
32	1. Preliminary Glaze study
36	2. Glaze studies
46	3. Non-milled Glazes
47	4. Effect of water content on Glazes
49	B. Stabilization of Zeolite

Page

TABLE OF CONTENTS

TP810
B3880

SEP

C.	Zeolite in ceramic bodies	54
1.	Zeolite in casting slips	54
2.	Hydrogen zeolite in casting slips	65
V.	CONCLUSIONS	75
VI.	SELECTED REFERENCES	79
VII.	ACKNOWLEDGMENT	81
VIII.	APPENDIX	82

LIST OF TABLES AND FIGURES

TABLES

	Page
I. Basic glaze bath compositions	33
II. Glaze batch compositions	38
III. Run 1: Effect of zeolite on casting slips . . .	56
IV. Run 2: Effect of sodium carbonate on casting slips	59
V. Run 3: Effect of hydrogen zeolite upon over-deflocculated casting slips	69
VI. Run 4: Effect of hydrogen zeolite upon an over-deflocculated casting slip	71

FIGURES

1. Thermal curves	50
2. Effect of Zeolite on Casting Slips	58
3. Effect of Na_2CO_3 on Casting Slips	60
4. Relationships of Slip Properties	61
5. Effect of Hydrogen Zeolite on Over-Deflocculated Casting Slips	68
6. Effect of Hydrogen Zeolite on Over-Deflocculated Casting Slips	72
7. Relationships of Slip Properties	73
8. Calibration of MacMichael Viscosimeter	85

I. INTRODUCTION

Zeolites have been used primarily as ion exchange agents for quite some time, the first authentic record having been reported in the papers of Bacon published in 1627. The first publication of any consequence appeared in 1852,¹ and since that time much work has been accomplished and many pages written concerning zeolites.

However, very little of this work has dealt with the uses of zeolites, specifically for ceramic purposes, except perhaps as related to the treatment of water utilized in ceramic processes.

The possibility that zeolites might adsorb metallic ions capable of producing color in ceramic ware has been established.² However, no investigation has been made nor data presented comparing the advantages and disadvantages of glazes containing zeolites with those of the same composition without the zeolite. This was one of the primary purposes of this investigation. It was desired that a composition of glazes containing the coloring agents added as adsorbed ions on the zeolite be made with glazes of the same ultimate chemical composition but

¹Way, J. T. Power of Soils to Absorb Manure. Journal Royal Agr. Soc. 13: 123-142. 1852.

²Irish, L. T. and Wells, E. D. The Use of Zeolites for Coloring Clays and Related Products. Unpublished B.S. Thesis. Ames, Iowa, Iowa State College Library. 1938.

with the coloring agents added as oxides.

That zeolites have the ability to exchange sodium ions, which are so necessary in clay casting slips, led to another investigation of other potential uses in the ceramic field. To investigate this aspect, the possibility of the use of zeolite as a replacement for feldspar was considered but not thought to be too logical due to relative costs involved. One use of zeolite that was felt possibly advantageous over present methods was as an electrolyte or deflocculant for casting slips. This was strictly a new use neither considered nor mentioned in any previous work.

In trying to accomplish and achieve the desired or expected results, some of the incidental factors arising in connection with the major problems proved rather interesting if not exasperating, and where possible, they were investigated.

II. REVIEW OF LITERATURE

The term zeolite originally indicated a class of hydrate alumina silicate minerals. When it was found possible to produce synthetically materials of similar composition and properties, the term zeolite was applied to these also. This has resulted in confusion in the use of the term since these synthetic materials do not belong to the class of minerals originally involved.

The introduction of organic materials that are able to function in a manner similar to the original zeolites has further complicated the usage of the term. Practical producers of this material would do well to name their product "ion exchange materials" or something similar, but the term zeolite has become so deeply imbedded that its indiscriminant use will undoubtedly continue.

The use of the term zeolite in this report was not intended to include the organic exchange materials but the sodium-alumina-silicate materials, and more specifically the synthetic gels, as the latter was the type used.

Zeolites have been defined by one author¹ as a group of crystalline solids, hydrated alumino-silicates of mono- and di-

¹Hey, M. H. The Nature and Relations of Zeolites: A Review. Trans. Ceramic Soc. (England) 36: 84. 1937.

valent bases, in which the ratio $(R^{++}R_2^+)O : Al_2O_3$ is unity, which are capable of losing a part or all of the water without a structural change, which are capable of absorbing compounds to replace the water, and which are capable of undergoing base exchange. This definition excludes artificial gels made by precipitation from solutions of sodium aluminate and sodium silicate or made by fusion processes, as these are not crystalline but do fulfill the requisites in all other respects.

Clays are the nearest related natural minerals and can comply with the above definition except for chemical composition. The main differences existing between zeolites and clays are essentially a function of differences in structure, which in turn result in differences in composition, crystal habit and size, and others.

In comparing the properties of clays and zeolites, one finds that in clays only a part of the mono- or divalent cations are exchangeable whereas in zeolites all are exchangeable. It is also found that the rate of base exchange of clays is greater than the rate for zeolites by a factor of 10^5 . This has been attributed to the existence of larger channels in the clay ($10A^\circ$ as compared to 2.9 to $3A^\circ$ for zeolites) and to lower energy of binding water. Cation migration is considered only possible in the wake of water migration, and zeolites bind their water more firmly.

Zeolites ordinarily can not enter into reactions involving

the hydrogen ion since the exchange capacity is so high, and attempts to produce such a reaction result in a hydrogen zeolite which is quite unstable. Hydrogen clays on the other hand are stable and easily prepared by use of acids.

Certain clays, bentonite for one, exhibit lattice expansion and contraction when treated with water, whereas other clays do not. Zeolites usually exhibit a fair amount of lattice change but are limited both in this and the amount of water, whereas the clays may not be.

In the manufacture of zeolite a portion of fine particles¹ is produced during the crushing process. Hydration of the material causes decrepitation resulting in additional fines. The amount of these has been reported to be millions of pounds yearly. These are too small for use in ion exchanges as the rate of flow of liquid will be materially lowered. That these fines might be of profitable use in ceramic industry was the original incentive for this research. In 1938 Irish and Wells² did some research in an attempt to find a method of utilizing these finds. Their idea was to use these fines as a base material for colorants in ceramic products. It was their thought that by replacing the sodium ions of the zeolite with various metallic ions, normally introduced as oxide colorants

¹Callahan, J. R. Synthetic Zeolite. Chemical Engineering 56: 92. 1949.

²Irish, L. T. and Wells, E. D. op. cit.

in ceramic products, a better color distribution and more uniform product would result. They successfully displaced sodium with manganese, copper, iron, cobalt, nickel, chromium, zirconium, and uranium.

Irish and Wells were able to obtain good colors, comparable in their estimation with colors obtained from the use of metallic oxides, but they considered their glazes as a whole rather unsatisfactory due to the extremely high fusion temperatures necessary for the zeolite. They were using a large percentage of zeolite and were desiring rather low melting glazes. To lower the fusion temperatures of the glazes fluxes were added, but this resulted in a decrease of acid resistance.

In 1939 Haldeman and Erdman¹ undertook an investigation continuing and expanding the work of Irish and Wells. While Irish and Wells had worked with commercially prepared zeolites, Haldeman and Erdman chose to develop their own zeolites, some of which would fuse at lower temperatures. They found that by the substitution of boron for the aluminum in synthetic zeolites that the fusion temperatures could be lowered to those obtainable in ordinary industrial kilns.

The fusion tests were made by heating the samples in the flame of a meeker burner by means of a steel spatula. They reported that the material fused very well and in so doing

¹Haldeman, G. W. and Erdman, A. C. The Use of Zeolites as Pigments in Ceramic Colors. Unpublished B.S. Thesis. Ames, Iowa, Iowa State College Library. 1939.

developed an appreciable amount of adherence to the steel. This latter fact indicated to them the possibility of using the zeolite as an enamel. It should be noted, however, that they worked with stainless steel and not the easily oxidized enamelling iron or steel common to the trade.

Haldeman and Erdman used a raw lead base glaze to which they added borosilicate zeolites in amounts up to 50%, the zeolites having been saturated with one of the following metallic ions: iron, copper, nickel, manganese or cobalt. In all cases they reported good color in the glazes.

In 1940 Eddy¹ attempted to produce a red glaze by means of zeolite pigments. His initial work was accomplished using a commercial type gel which he fused over a gas burner. Unable to obtain the desired red color he tried to duplicate and improve the customary chrome tin pink used industrially. Zeolites were prepared using tin instead of aluminum and calcium in place of sodium. These zeolites were treated with varied amounts of chromic acid. When these did not produce the anticipated color, ferric nitrate was also used in an attempt to introduce the iron along with the chromium ion. However, he was still unable to obtain the red color which ceramists would readily welcome and appreciate.

There are numerous publications available which contain

¹Eddy, O. R. Zeolites as Pigments for Ceramic Wares. Unpublished B.S. Thesis. Ames, Iowa, Iowa State College Library. 1940.

information on glazes, the chief sources being the Journals of the American Ceramic Society and the Transactions of the American Ceramic Society.

These publications and one other¹ were consulted in regard to properties, compositions, and characteristics of glazes in general. No specific mention will be made of the review of this literature other than to say that in every non-fritted or raw glaze, the alkali is introduced as a feldspar. The fact that the composition of feldspar (albite) is theoretically $1.0 \text{ Na}_2\text{O} \cdot 1.0 \text{ Al}_2\text{O}_3 \cdot 6 \text{ SiO}_2$, which is rather close to the composition of synthetic zeolite, led to the decision to substitute the zeolite for the feldspar in the glaze rather than to attempt to add the zeolite to a given glaze, as was previously done. This would permit comparison of the same definite compositions obtained using different raw materials.

Glazes are usually colored by means of additions of metallic oxides. These oxides are present in the unfired glaze as finely distributed particles which later dissolve in the glass formed during firing.

Zeolites can adsorb these same metals as ions which, when the whole is incorporated in the glaze, should produce an ionic distribution. That this ionic distribution would produce better colors upon the melting of the glaze than would the

¹Parmelee, C. W. Outlines of Essentials of Glaze Composition. Copyrighted March, 1929.

oxides was the primary consideration in this part of the investigation.

Insofar as published information on the use of zeolite in ceramic bodies is concerned, there seems to be none. There has been a considerable amount of material published concerning clays, clay minerals, and allied topics but in no instance has the use of zeolite on clays, clay bodies or clay systems been reported.

Both clays and zeolite have several properties in common which may be the reason that no attempt has been made wherein the one can be used to control or influence the other. As previously mentioned both are capable of base exchange, and uses of both are generally controlled or directed by means of sodium ions.

The fact that clays do exhibit base exchange is well established. The reason they are able to do this is still considered debatable and will not be discussed here. Grim¹ has presented perhaps one of the best discussions upon the structure of clay and the theoretical aspects of base exchange related thereto. Johnson and Norton² present a very detailed discussion of the mechanism of deflocculation of clay in water systems as produced by sodium ions, the latter being provided

¹Grim, R. E. Relation of Composition to Properties of Clays. Journal Amer. Ceramic Soc. 22: 141. 1939.

²Johnson, A. L. and Norton, F. H. Fundamental Study of Clay. II. Deflocculation in Clay-Water System. Journal Amer. Ceramic Soc. 24: 189. 1941.

by sodium hydroxide. They were working with pure clay, however, and not a composite ceramic body as was used in this investigation. Johnson and Norton were able to substantiate certain theories regarding the role of the sodium ion, concluding that monovalent cations must be on the clay and that the medium must contain a slight excess of hydroxyl ions. In a later article¹ the same authors discuss the practical aspects of casting as can be explained or controlled through base exchange.

In 1947 Phelps² published a series of articles presenting the practical side of casting control as well as the theoretical.

The most general deflocculants used are sodium carbonate and sodium silicate. Others reported as successful are sodium tannate³ and ammoniacal solutions⁴ when used under certain conditions.

The details of the theory of base exchange and its influence on clay which one may conclude from these previously mentioned

¹Johnson, A. L. and Norton, F. H. Fundamental Study of Clay. III. Casting as a Base Exchange Phenomenon. Journal Amer. Ceramic Soc. 25: 12, 336. 1942.

²Phelps, G. W. Clays - Deflocculation and Casting Control. Ceramic Age 49: 162. 1947; Ceramic Age 49: 226. 1947; Ceramic Age 49: 298. 1947; Ceramic Age 50: 119. 1947; Ceramic Age 50: 158. 1947; Ceramic Age 50: 218. 1947; Ceramic Age 50: 277. 1947; Ceramic Age 51: 9. 1948.

³Richardson, H. K. Small Cast Thorium Oxide Crucibles. Journal Amer. Ceramic Soc. 18: 65. 1935.

⁴Hepplewhite, J. W. Use of an Ammoniacal Electrolyte for a Plastic Body. Bull. Amer. Ceramic Soc. 18: 191. 1939.

articles, are rather long and complicated. They may be summarized briefly as involving the counterbalancing of negative charges on the clay by preferentially adsorbed positive ions such as calcium, sodium or hydrogen. The degree of counterbalancing is influenced by the charge, the hydrated size, and the amount or number of counter ions able to be close enough to the clay particle to exert influence. These are involved with and related to the pH of the medium.

The type of ion surrounding the clay particle determines whether clay particles will have an attraction or repulsion for each other and in this way influences the entire clay system. Clay particles with sodium ions adsorbed tend to repel each other and remain deflocculated or separated, provided sufficient water is available to permit this. Clays with calcium or hydrogen ions behave in the opposite manner in that they are attracted to each other, forming aggregates, and settle out of suspensions.

Obviously, for casting purposes a sodium clay is necessary in order to avoid both settling and the extreme water content found necessary for movement of particles with calcium or hydrogen ions. Since the zeolite is able to furnish the sodium ions, this part of the investigation was undertaken.

III. METHOD OF PROCEDURE

A. General

It was anticipated at the outset that certain difficulties might arise if zeolite were to be incorporated in a typical ceramic glaze. It was decided that a general comparison between a feldspar glaze and a zeolite glaze be made in order to determine the course of a more definite investigation.

To do this, cobalt seemed the most logical ion to use since it is a very good coloring agent and produces stable colors. The zeolite¹ was saturated with cobalt nitrate, then milled with the other ingredients to form the glaze. At the same time, feldspar glazes were made of the same chemical composition as the zeolite glazes in order to obtain a comparison between the two. These glazes were applied to ceramic bodies and fired in electric kiln. One of the difficulties involved in the foregoing was knowing accurately the amount of cobalt absorbed by zeolite. Since coloring ions other than cobalt are to be used ultimately, it was felt that an overall method of determining the amount of coloring ions should be used. After study of analytical literature and making inquiry of analytical chemists, the answer seemed to be to treat zeolite with definite volumes of solutions of known normalities.

¹The zeolite was provided by the Culligan Zeolite Company, San Bernardino, California.

The liquid over the zeolite was checked for presence of the ion involved to determine when all had been picked up. To facilitate standardization of these solutions in the future, a brief amount of time was devoted to the use of a colorimeter to see if it might prove accurate enough in determining normalities. This was found to be fairly accurate but was not as precise as had been anticipated. It was therefore discarded.

After making and determining the normality of various solutions of Co^{++} , Fe^{+++} , Ni^{++} , Mn^{+++} , and Cr^{+++} , five batches of zeolite were each treated with one of the above solutions. These treated zeolite samples were incorporated into individual glazes and applied to ceramic bodies. For comparison, glazes were made using feldspar instead of zeolite and using oxides of the coloring ions. In other words, for every glaze containing zeolite and a coloring ion, a glaze of the same composition, but compounded according to common practice, and of the usual materials was made in order to have a good comparison of results.

These latter glazes were applied to ceramic bodies, all of which were of identical composition. Test pieces with each glaze were fired to three different cone equivalents in an effort to ascertain not only any differences in the final glazes but also if any differences existed in the ease of melting or glass formation. Again an electric kiln was used for the firing.

Because of certain results of the above study and because of other tendencies in the behavior of some of the zeolite glaze on drying and firing, mainly excessive shrinkage, an attempt was made to determine the causes and how they could be minimized or obliterated. Samples of the zeolite were heated to various temperatures for various lengths of time and tested for the solubility of the sodium ions. In conjunction with this an attempt was made to find the influence of temperature upon the removal of water from the zeolite. This was done by means of thermal analysis equipment.

Acid leaching was also investigated in an attempt to see if the troubles arising might be caused by the presence of excess sodium ions.

Since the composition of zeolite was so near to that of feldspar the possibility of its use in a ceramic body was deemed important enough to investigate. A study of a series of body compositions in which the zeolite was used to replace feldspar in varying amounts did not indicate that the use of zeolite would be beneficial enough or improve the body to a great enough extent to warrant economically its use instead of feldspar. On the contrary, the excessive amount of sodium available seemed to produce a body with great thixotropic tendencies resulting in forming difficulties. The clay picked up the sodium for the zeolite in exchange for its calcium. For casting purposes, the presence of sodium ions would be beneficial, but for jiggering, or other forming processes

using a plastic mass, it resulted in a body difficult to form and handle.

Therefore, the possibility of the use of zeolite in casting slips was investigated. There were two phases of this investigation and both seemed to have interesting industrial possibilities. The first of these is the use of sodium zeolite as a means of deflocculating clay slips. Varying amounts of the zeolite were added to a casting slip which had previously been proved satisfactory with the use of sodium carbonate as the deflocculant. The influence of the zeolite upon the viscosity and pH of the slips was found.

A second investigation was conducted on the use of a hydrogen zeolite to correct for the presence of excessive sodium ions in casting slips. The hydrogen zeolite was prepared by treating milled zeolite with dilute hydrochloric acid until the presence of aluminum ions in the filtrate was detected. The zeolite was then washed until chloride-free.

The hydrogen zeolite thus obtained was added in varying amounts to over-deflocculated casting slips in order to lower the pH and to remove the excess sodium ions. The viscosities of the slips were determined in each case.

B. Zeolite in Ceramic Glazes

1. Preliminary glaze study

As a preliminary determination of the possibilities of the use of zeolite in glazes, the following base composition was chosen for investigation:

0.6 PbO		
0.2 K ₂ O	0.4 Al ₂ O ₃	2.4 SiO ₂
0.2 CaO		

Two series of glazes were compounded using zeolite as a source of the K₂O and part of the Al₂O₃ and SiO₂ in one instance, and using feldspar as a source of these three oxides in the second instance. Both of these series were to be made with varying amounts of cobalt to provide comparison of the methods of introduction of this element.

The two end members of each series were made (one containing no cobalt and the other the maximum amount to be used) and intermediate glazes were obtained by blending these two extremes.

Glaze number 1 contained no cobalt but otherwise had the same composition as glaze number 10 which contained the maximum amount. Both were compounded using zeolite. Glaze number 21 contained no cobalt whereas glaze number 30 had the maximum amount added as the oxide; both, however, were made using feldspar. By blending glazes number 1 and number 10,

intermediate glazes of varying cobalt content were obtained which could be compared with the intermediate glazes formed by blending glazes number 21 and number 30.

After calculation of the proper amounts of ingredients to be used so that all of the glazes would have the same base composition, the necessary amount of zeolite for glaze number 10 was weighed and treated with 400 milliliters of cobalt nitrate solution. The amount of cobalt in the original solution was determined by precipitation using $\text{NaNH}_4\text{HPO}_4$, heating the precipitate and weighing as the pyrophosphate. Similarly the amount of cobalt in the solution after contact with the zeolite was checked for cobalt content. The difference between the cobalt contents of the two was an indication of the amount of cobalt picked up by the zeolite.

The correct amount of ingredients to produce 1000 grams of each end member (numbers 1, 10, 21, and 30) was weighed and placed in laboratory ball mills. Eight hundred milliliters of water were added to each mill and the glaze was ground for 4 hours. After removal of the glaze from the mill, the water content of each glaze was determined by drying a sample of about 25 cc. of each at 110°C . This information was needed since the blending was done on a wet basis. The proper amount of each end member to be used to produce 100 grams of each intermediate glaze (numbers 2, 3, 4, etc., and numbers 22, 23, 24, etc.) was calculated. These amounts were then blended. All of these glazes were applied to small clay body pieces by

dipping. After the pieces were dried and properly marked with cobalt ink, they were all fired to cone 3 in an electric kiln. After cooling and upon removal they were examined, and a comparison was made between the two series to ascertain if possible the effect of the zeolite upon color formation and glaze properties in general.

2. Glaze studies

From the facts garnered in the foregoing and from a desire for additional information it was decided that several of the other transition elements be studied for comparison of glazes with and without zeolites, and that certain changes be made in the method calculation and preparation of the glazes.

It was decided that solution would be made of various transition elements and the normality determined volumetrically. These solutions were to be used as standards in a Duboseq colorimeter for checking the replacement solutions as the standards were being depleted. This was an attempt to avoid tedious titration. The solutions were purposely made of different concentrations in order to study the effect of both low and high concentration in the glazes.

About 10 pounds of commercial zeolite were ground in a disk pulverizer and placed in a stone ware jar. Repeated washings with distilled water, the latter being decanted after the zeolite settled following each addition, resulted in a product whose slurry had a pH of around 9.0. After drying,

this product was used in the following glaze preparations.

Five hundred gram amounts of zeolite were weighed and each treated with one of the previously prepared solutions of CoCl_2 , $\text{Cr}_2(\text{SO}_4)_3$, NiCl_2 , and FeCl_3 . These were treated by pouring 300 ml. of each solution onto the zeolite, previously wet with water, and allowing this to remain for one week. After checking to make certain none of these ions was in solution, indicating that all had been tied up by the zeolite with which it was in contact, these samples were now washed with distilled water to remove the replaced sodium and the anion associated with the coloring ion. Washing was discontinued when a pH of 9 was reached. After drying, these materials were ready for incorporation into glazes.

The glaze to be used was again the same base glaze as in the initial investigation:

0.6 PbO

0.2 Na_2O

0.4 Al_2O_3

2.4 SiO_2

0.2 CaO

After calculation of the correct amount of individual constituents for 1000 grams of each glaze containing Fe, Co, Ni, etc., and a base glaze containing no colorant, these were weighed and placed in individual ball mills, each mill containing the same number of balls of approximately the same size. Eight hundred grams of water were added to each, and all were milled for 6 hours. The glazes were removed and stored in individual half gallon glass jars, later to be applied to

ceramic test pieces.

Glazes were also calculated using feldspar instead of zeolite as a source of the sodium oxide and part of the alumina and silica.

The coloring elements were added as oxides in these glazes. Again 1000 grams were weighed, milled six hours with 800 ml. of water, and then stored in glass jars. The zeolite glazes containing Fe, Co, Ni, etc., were blended with a zeolite glaze containing no coloring element in order to get variations in the amounts of the elements, so that probably variations in intensities could be compared with the corresponding feldspar blended glazes. After the blends were made, each was applied to three ceramic testpieces by spraying. These applications were of normal thickness, and were as consistent as could be possible, care having been taken to build up the glaze layer to the same thickness on every piece. The feldspar glazes were applied in a like manner to other pieces of this same ceramic body and were applied to as nearly the same thickness as possible, again by spraying.

After each piece was marked for identification, they were fired in an electric kiln. One piece with each zeolite glaze and a piece with each feldspar glaze were fired to cone 4. A second group of one piece each of all blends was fired to a lower temperature, cone 2, while the remainder of the pieces were fired to cone 01. This firing to different cones was done to determine the effect, if any, of the zeolite upon the

rate of fusion.

After removal from the kiln all the pieces were examined and the comparison made between those with zeolite and the corresponding feldspar glazes.

3. Non-milled glazes

It was thought that perhaps zeolite might prove beneficial in production of glazes which need not be ground or mixed in a ball mill. No specific data was found to substantiate or refute the wisdom of such an investigation.

It is known that in the milling of glazes, the mixing resulting is perhaps more important than the grinding effected. Therefore, zeolites, being theoretically able to afford a better ion distribution than an oxide addition, should perhaps make better colored glazes than would feldspar and the oxide.

Cobalt zeolite glazes were prepared using the same composition as before. Prior to cobalt ion treatment the zeolite was prepared in the same manner as that used in the casting slip investigation.

A feldspar glaze was prepared of the same composition as before, and the theoretical amount of cobalt oxide added as existed in the zeolite glaze. Both of these glazes were mixed by the use of a high speed laboratory mixer, for all practical purposes -- a malted milk mixer. The mixing was for half an hour.

All of these glazes were fired to a temperature of 1140° C.

in an electric kiln.

4. Effect of water content on glazes

In making the preliminary examination of the possibility of use of zeolite in glaze, one fact seemed evident. The zeolite glazes tended to shrink more on drying, producing in some cases tearing or crawling upon drying or subsequent firing. To investigate this further, 1500 grams of the following glaze were made by milling for four hours then dividing into portions which were adjusted to various values of specific gravity by use of the correct water content.

Zeolite	276
Whiting	51
Litharge	341
Clay (Florida)	42
Flint	190
	<hr/>
	1000

After application by dipping of both a thin layer and a thick layer of all glazes to clay test pieces and careful drying, the glazes were fired to cone 4 and examined. This was all done in an attempt to find if the water content affected tearing to any extent, and if so, what the optimum content should be for satisfactory glazes.

C. Stabilization of Zeolite

The tendency of some glazes made from zeolite to exhibit tearing or crawling was undesirable. Two things were believed to be involved here: the normally high amount of shrinkage involved in almost all such gels, and secondly, the presence of an excessive amount of sodium ions which could easily affect the clay in the glaze. An attempt was made to render the zeolite into an inert state so that the sodium would be no longer replaceable, and so that no expansion or shrinkage would occur upon hydration or dehydration. This was done by heating the zeolite to various temperatures for various lengths of time and then determining if the sodium still tended to leave the zeolite, both from the particles as such and then from the crushed material. The examination of the crushed zeolite seemed to be of more importance since use of any stabilized zeolite industrially would probably include a crushing operation after stabilization. If the zeolite were crushed prior to any attempt at stabilization, the washing which would be necessary prior to its use would be extremely difficult and tedious, due to the fine size of material.

In order to ascertain at approximately what temperature the water would be lost, thermal analyses of several of the zeolites were made. It was found that the temperatures at which the water was lost could readily be ascertained, but this did not indicate a permanent or stabilizing change.

Therefore, it was necessary to determine the latter by trial and error with regard to temperature and time. However, the results of the thermal analysis did prove rather interesting and will be discussed later.

These attempts at this method of stabilization were carried out at fifty degree intervals for various lengths of time, all having been accomplished in an electric furnace.

Another attempt toward stabilization was by means of a leaching process using dilute hydrochloric acid to remove the sodium. By this means the excess sodium could be removed more rapidly than by continual washing by water. The resulting product of this procedure was thought to have other uses as will be mentioned later.

In conjunction with the leaching, a sample of zeolite was dialyzed in an attempt to find if it could be in any way stabilized by this method in any reasonable length of time.

D. Zeolite in Ceramic Bodies

1. Zeolite in casting slips

In order to investigate the effect of zeolite on casting slips, the following composition known to be castable, was chosen:

English China (Exeter)	38
Ball Clay (Bedminster)	10
Feldspar	30
Whiting	2
Flint	20

The zeolite to be used as a deflocculating agent for the above composition was prepared as follows. Commercial zeolite, unwashed, was milled for 8 hours then washed with distilled water. At first decantation was used later followed by vacuum filtering. This washing with water did not seem to lower the pH appreciably, so dilute HCl was added until the pH dropped to 8. After washing, the pH rose to 9.5. Additional HCl lowered the pH to 5.5 but after standing overnight went to 6.05. Washing with distilled H₂O until chloride free raised the value to 7.8. After drying the pH was now found to be 9.85, indicating a possible breakdown of the material upon dehydration and further rehydration, resulting in a liberation of additional sodium ions which in turn resulted in an increased pH.

Six thousand grams of the body composition were weighed, and by means of an electric stirrer mixed with 3000 grams of water in the stoneware jar. After thorough mixing, the slip was screened through a 150 mesh-per-inch brass sieve and poured onto a plaster slab to decrease the water content. The sieving was done to remove carbonaceous and any other foreign matter in the clay. When the material had been dewatered to a plastic state it was kneaded by hand to insure adequate distribution of all materials throughout the mass. This was done to avoid the possibility of separation or segregation of any of the materials due to differences in particle size or density while the dewatering was being accomplished. The mass

was placed in a stoneware jar and dried completely at 110° C.

Twelve samples of 200 grams each were weighed and placed in glass packing jars. To each were added 66 $\frac{2}{3}$ grams of water (33 $\frac{1}{3}\%$ of dry weight). No zeolite was added to one of these slips, but to the remainder were added 0.5, 1.0, 1.5, 2.0, 3.0, 5.0, 10.0, 15.0, 20.0, 25.0, and 30.0 grams respectively. After thorough stirring and 48 hours of aging, these slips were tested for viscosity and pH. Erratic results were attributed to differences in densities arising from the fact that the zeolite absorbed water from the slips changing the properties; checking of individual densities proved that variations in these did exist. It was found that by the addition of about one gram of water per gram of zeolite the density for all could, with slight additional adjusting, be fixed at 1.80 grams per cubic centimeter. Determinations of viscosity and pH now gave more logical results.

For a comparison with this same basic slip, with sodium carbonate used as the deflocculating electrolyte, 10 fractions of 200 grams each were weighed and placed into glass packing jars. Quantities of c.p. sodium carbonate were added each to a slip as follows: 0.25, 0.50, 0.75, 1.00, 1.125, 1.25, 1.50, 1.75, 2.00, and 2.25 grams.

After sufficient mixing, the densities were adjusted to 1.80 and the slip aged for 48 hours prior to testing. The viscosities and pH values were found for these slips and compared with the slips to which zeolite had been added.

The MacMichael viscosimeter used for the viscosity determinations was calibrated by means of glycerine solutions of known viscosity.

2. Hydrogen zeolite in casting slips

Approximately 1000 grams of zeolite were ground (wet) in a ball mill for about 12 hours. After the ball mill contents were emptied into a stone ware jar, hydrochloric acid was added until the pH of the slurry reached 5.0. Rinsing with distilled water until no chloride ions were present resulted in an increase in pH to 9.5. After the material was dried, when a sample was wet with an excess of water, the pH was found to be about 10.5, this increase being attributed to the sodium released by decrepitation of the zeolite during the dehydrating and hydrating periods.

In order to accelerate this acid treatment, a quantity of solution of HCl having a pH of 1.5 was prepared and used. The zeolite was again wet with an excess of water, and the acid added to this slurry. After a short while the pH of the supernatant liquid arose to 5.0, as the sodium was slowly going into solution. After the liquid was decanted and fresh acid and water added, the pH dropped below this. Ultimately the value of the supernatant liquid reached 4.5, 4.2, and finally at 4.1, at which point evidence was found of the solution of the aluminum. A test for the presence of aluminum had been made

at each leaching and as soon as the test indicated its presence, acid treatment was stopped. This product, to be referred to as hydrogen zeolite in this work, was washed with distilled water until chloride free, at which time the pH of the decanted liquid was 6.7, the same as the distilled water.

As a method of quickly checking the presence of adsorbed hydrogen ions on the zeolite, a small sample of zeolite was placed in a beaker with excess water. To this was added a salt (sodium chloride) solution. The pH dropped with each addition until a minimum of 4.26 was reached, indicating that the supernatant liquid now contained hydrochloric acid as result of the ion exchange.

To determine the effect of this hydrogen zeolite on over-deflocculated slips, 200 gram samples (dry weight) of casting slip were prepared as previously described, and to each were added 1.75 grams of sodium carbonate. These samples obviously over-deflocculated, as indicated by both its own behavior and from previous work on this slip. To these were added 1, 2, 3, 5, $7\frac{1}{2}$ and 10 grams of hydrogen zeolite and the density adjusted to 1.80 grams per cubic centimeter. After adequate mixing by use of a mechanical shaker for 12 hours, the viscosity and the pH of each were determined and the results examined.

Since zeolites do exhibit lower base exchange rates than do clays it was thought that perhaps a variation from the above results might be obtained if not as much reaction time were allowed as had been permitted in the first investigation.

Therefore, a casting slip of the same body but of a lower electrolyte content (1.50 grams of Na_2CO_3 per 200 grams of dry slip) was prepared again with the density at 1.80 grams per cubic centimeter. To this slip were added two grams of hydrogen zeolite and after a mixing for a few minutes by manual shaking in a closed container the values of pH and viscosity were determined. Four grams of zeolite were added and the process repeated. Additions of the hydrogen zeolite in increments of one gram were made and the procedure repeated for each addition. At intervals the density was checked, any slight adjustments necessary were made, and data for the specific run just completed were redetermined.

E. Raw Materials

1. Zeolite

Empirical formula: $\text{Na}_2\text{O} \cdot 1.1 \text{Al}_2\text{O}_3 \cdot 5.5 \text{SiO}_2 \cdot x\text{H}_2\text{O}$

When dried at 110°C . it weighs about 25 pounds per cubic foot. Of this, 25 pounds, 10% or 2.5 pounds represents water.

Exchange capacity is reported by the supplier as 12,000 grains of CaCO_3 per cubic foot of drained material, which weighs about 50 pounds per cubic foot.

Disregarding the water in the formula, the zeolite has a formula weight of 504.7.

2. Exeter china clay

Chemical composition:

SiO_2	- 48.01%
Al_2O_3	- 38.90
MgO	- 0.84
FeO	- 0.28
$(\text{NaK})\text{O}$	- 1.06
L.O.I.	- 11.49

Empirical formula: $1.00 \text{ Al}_2\text{O}_3 \cdot 2.09 \text{ SiO}_2 \cdot 1.67 \text{ H}_2\text{O}$

Formula weight 260.0 (which includes the trace of alkalies).

3. Minpro feldspar

Chemical composition:

SiO_2	- 70.30
Al_2O_3	- 18.30
Fe_2O_3	- 0.10
CaO	- 0.60
K_2O	- 5.40
Na_2O	- 5.19
Loss	- 0.24

Empirical formula: $0.0705 \text{ CaO} \quad 1.183 \text{ Al}_2\text{O}_3 \quad 7.716 \text{ SiO}_2$
 $0.5517 \text{ H}_2\text{O}$
 $0.3778 \text{ K}_2\text{O} \quad 0.004 \text{ Fe}_2\text{O}_3$

Formula weight = 660.05.

Litharge - PbO , assumed pure, no data available.

Whiting - CaCO_3 , assumed pure, no data available.

Flint - SiO_2 , assumed pure, no data available.

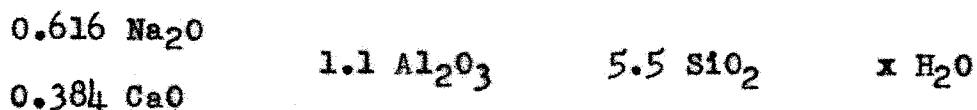
The oxides of cobalt, nickel, chromium, iron, and copper were all assumed pure, no data being available.

IV. RESULTS AND DISCUSSION

A. Zeolite in Ceramic Glazes

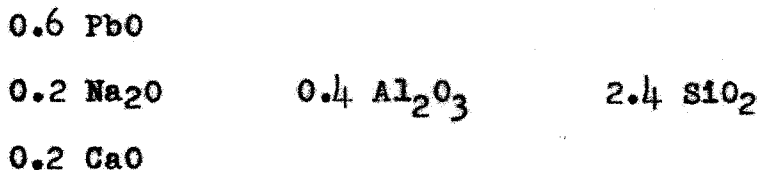
1. Preliminary glaze study

Assuming that zeolite had the capacity previously stated, it was calculated that theoretically cobalt ions would be picked up to such an extent that the formula would be changed to:



This has a formula weight (neglecting water) of 509.7, 5.65% of which may be considered as cobalt oxide.

The following basic glaze composition was used throughout this work.



To determine the correct amount of each ingredient necessary for a 1000 gram batch of glaze #10, the usual method of glaze calculations was used. Similarly glazes #1, #21, and #30 were calculated.

The amounts of raw materials used are shown in Table 1.

Table I

Basic glaze batch compositions

Material	Glaze #1	Glaze #10	Glaze #21	Glaze #30
Cobalt zeolite		483.5		
Sodium zeolite	304.2			
Feldspar			382.0	382.0
Whiting	54.3	52.7	49.1	49.1
Litharge	363.0	352.0	373.0	373.0
Clay	126.9	28.6	107.3	107.3
Flint	151.0	82.9	88.0	88.0
Cobalt oxide	_____	_____	_____	<u>25.5</u>
	999.7	999.4	999.4	1024.9

In order to make glaze #1, zeolite was dried at 110° C. for 24 hours, and 304.2 grams were weighed out for use. This amount was calculated considering the theoretical water content of the zeolite. Similarly, 478 grams of this dried zeolite were weighed and treated with a saturated solution of cobalt nitrate, the solution having been in contact with the zeolite for thirty hours. The excess solution was decanted, and the zeolite was washed.

The cobalt determination on aliquots of the solution prior to zeolite treatment and after were made by means of the phosphate precipitation and ignition. This was a difficult and involved procedure which was discarded from future work as

being inaccurate. The average of several determinations did indicate the cobalt picked up by the zeolite and calculated as the oxide was 2.685% of the original zeolite. This value is only about one half of the amount that the zeolite is reported capable of absorbing. That the zeolite did not pick up more cobalt is probably due to the fact that the sodium ions were not removed as the exchange process occurred, but they were left in the supernatant liquid to be removed with the unadsorbed cobalt.

Also, the exchange capacity of this zeolite is calculated on basis of calcium ions. Certainly, the same number of calcium ions picked up would not be the same as cobalt ions due to different sizes of ions or different ionic radii. It was not anticipated or believed that this extreme difference in amounts, 5.65% (theoretical) and 2.69% (actual) is due only to the difference in ionic sizes.

It was necessary to proceed now on the knowledge of actual cobalt picked up rather than on the amount theoretically possible, as the original calculations had been based. After correcting for this, the glazes #10 and #1 were blended to produce glazes containing CoO as 0.25%, 0.50%, 0.75%, and 1.0% of the melted weight.

Similarly, glazes #21 and #30 were blended to provide glazes with these same amounts. After applying to clay test pieces and firing, the glazes were examined and compared, and several conclusions were drawn.

The theoretical calculation regarding water content of zeolites was misleading, and in the next investigation the amount of water to be lost must actually be determined through fusion.

The method used for determining the amount of ions exchanged was not satisfactory. Another method using, say, standardized solutions should be developed.

The colors produced by the zeolite were beautiful, varying from a pale blue for those glazes with the smaller amounts of cobalt to a deep royal blue for the glazes with the largest amounts.

Actual comparison of intensities of color produced by the two types of glazes was difficult as the thickness of the applied glaze was not the same on all pieces. Therefore, a method of controlling the glaze thickness was deemed necessary in the further investigation.

It was noted that some of the zeolite glazes exhibited tendencies toward tearing. It was felt that this was resulting from drying cracks occurring in the glaze surface. These cracks opened further upon firing, and the surface tension of the molten glaze prevented healing or smoothing over. To correct this defect, it was decided that an investigation be made upon the influence of the water content upon the zeolite. It was also felt that spraying of the glaze would prove advantageous in minimizing or eliminating this defect.

2. Glaze studies

As a result of study No. 1 and from the observation made thereof, it was decided that solutions of known normality be used for treatment of the zeolite. Therefore, the following solutions were prepared.

<u>Solution</u>	<u>Normality</u>	<u>Method of Standardization</u>
$\text{Cu}(\text{NO}_3)_2$	1.9613	Ammoniacal solution titrated with standard KCN
NiCl_2	0.6739	Titrated with standard KCN
CoCl_2	0.3182	Titrated with standard KCN
FeCl_3	0.4060	Reduced with SnCl_2 and titrated with $\text{K}_2\text{Cr}_2\text{O}_7$
Cr_2SO_4	0.7012	Oxidized with ammonium persulfate, KI and acid added; liberated iodine titrated with $\text{Na}_2\text{S}_2\text{O}_3$

The loss of weight by the zeolite was determined by heating it to a good red heat in a Meeker burner. This was found to be 17.23% of the original weight.

Therefore, 500 grams of zeolite, which was the amount treated with each solution of coloring ions, actually contained 413.9 grams of dehydrated zeolite.

$$\frac{(413.9)(1.0)}{504.7} = 0.821 \text{ eq. of } \text{Na}_2\text{O}$$

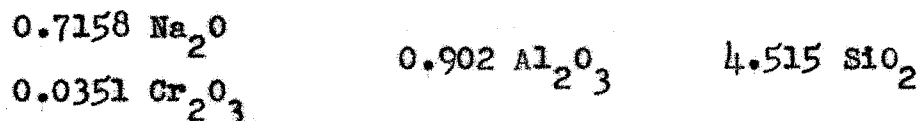
$$\frac{(413.9)(1.1)}{504.7} = 0.902 \text{ eq. of } \text{Al}_2\text{O}_3$$

$$\frac{(413.9)(5.5)}{504.7} = 4.515 \text{ eq. of } \text{SiO}_2$$

Since 300 cc. of 0.7012 normal chromic sulfate were used,

$$\frac{(0.7012)(31)(0.3)}{62.0} = 0.1052 \text{ eq. of } \text{Na}_2\text{O} \text{ replaced as } \text{Cr}_2\text{O}_3$$

Therefore, the chrome zeolite now has the formula



The formula weight (dehydrated) is 412.92 and when hydrated, 499.12.

In a similar manner the empirical formulae of 500 gram amounts of the other treated zeolites were calculated and found to be as follows:



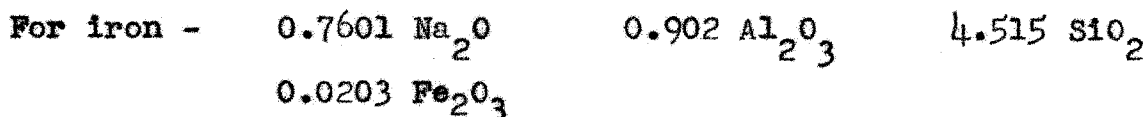
Formula weight - 419.32

Formula weight, hydrated - 505.47



Formula weight - 415.44

Formula weight, hydrated - 501.59



Formula weight - 413.63

Formula weight, hydrated - 499.78



Formula weight - 414.18

Formula weight, hydrated - 500.93

These zeolites were incorporated into glazes in amounts shown in Table II.

Table II
Glaze batch compositions

Raw material	Amounts in Glazes					Base Glaze
	Chromium	Copper	Nickel	Iron	Cobalt	
Treated zeolite	365.3	486.6	364.6	312.7	341.2	
Sodium zeolite						322.2
Litharge	350.5	339.1	350.2	370.2	352.2	354.4
Whiting	52.4	50.7	52.4	55.3	52.6	52.9
Clay	100.6	37.5	101.3	117.2	114.2	123.8
Flint	<u>131.2</u>	<u>86.1</u>	<u>131.4</u>	<u>144.6</u>	<u>139.8</u>	<u>146.8</u>
Raw weight	1000.1	1000.0	999.9	1000.0	1000.0	1000.0
Melted weight	902.5	889.6	902.4	908.3	905.1	907.1
Adsorbed ion as oxide - % of melted weight	0.4325	2.535	0.6075	0.2477	0.2695	

Glazes containing the following amounts of colorants calculated as oxides were obtained by blending the metallic ion bearing glazes shown in Table II with the base zeolite glaze. These glazes were applied to clay pieces and fired.

Chromium glaze: 0.10%, 0.20%, 0.30%, 0.40%, 0.4325% as Cr_2O_3

Copper glaze: 0.50%, 1.0%, 1.5%, 2.0%, 2.535% as CuO

Nickel glaze: 0.15%, 0.30%, 0.45%, 0.6075% as NiO

Iron glaze: 0.05%, 0.10%, 0.15%, 0.20%, 0.2477% as Fe_2O_3

Cobalt glaze: 0.05%, 0.10%, 0.15%, 0.20%, 0.2695% as CaO

The feldspar glazes were all of the following base composition, to which were added coloring oxides equivalent to 5% of the melted weight for the chrome, iron, and copper glazes, and 2% for nickel and cobalt.

Feldspar	396.2
Litharge	373.6
Whiting	51.6
Clay	105.2
Flint	73.4
	<hr/>
	1000.0

The melted weight of this amount of glaze is 965.1. Therefore, 48.255 grams of color oxide were used to obtain 5% additions and 19.302 grams to obtain 2% additions.

These color oxides were added in the original amounts in greater quantity than the corresponding zeolite glaze contained in order that sufficient amounts of oxide would be available to enable comparison with any glaze improved in coloration due to the zeolite.

As mentioned in the procedure, these feldspar glazes containing metallic oxides were blended with the base glaze containing no coloring ions in such amounts that the same percentages of oxide were in the blended glazes as were in the corresponding blended zeolite glazes.

The results of examination and comparison of these glazes are as follows.

The chromium glazes of low color ion content were very pale yellow-green, and as the chromium content increased, the intensity and depth of color did likewise, reaching a deep lemon color.

The copper glazes produced a pale pastel color of apple green which increased to a deep green for the maximum copper content.

The nickel glazes had an extremely pale brown color for the lower nickel contents and progressed to a rather deep tan, bordering upon a chocolate-brown as the nickel reached its maximum.

The iron-bearing glazes were colorless in the lower content glazes and were only faintly yellow at maximum iron content.

The cobalt glazes varied from a rather light blue for those glazes of minimum cobalt content to a full blue at maximum content.

It was rather difficult to determine by the naked eye any differences between the zeolite glazes and feldspar glazes in amounts or intensity of color. In order to make certain that variations in thickness between the glazes were not interfering with a true comparison of the results, a micrometer caliper was used to measure the thickness of the test piece alone and the thickness of the test piece and glaze combined. The difference between these represented the glaze thickness. In anticipation of the desirability of this comparison the glaze had been removed from one corner of each test piece after glaze application and prior to firing.

Were it possible to remove a very thin section of each glaze and measure either the absorption of light or, conversely the transmission of the light, it might be possible to ascertain any difference in the color.

One thing was apparent that indicated a general difference in the two types of glazes. The small bubbles that were present in most of the glazes were compared for size and amount. These bubbles arose from the fact that the kiln was allowed to climb steadily to the desired temperature. No slowing or changing of the rate of heating was attempted. Had the kiln been held for a few hours at or near the maximum temperatures, perhaps many or all of these would have escaped.

Observations with the naked eye ascertained the presence of many large bubbles in the feldspar glazes. While the zeolite glazes had some large bubbles, the amount seemed to be less per unit area than in the feldspar glazes. There did seem to be quite a few small bubbles, however. Use of a microscope for examining the glazes substantiated these observations. Many smaller bubbles were found below the surface in the feldspar glaze. In many instances these were obscured from the naked eye by the larger bubbles.

In this connection it was seen that the surfaces of the feldspar glazes, although impervious, had quite a few shallow pinholes resulting from the breaking of these bubbles as they escaped. The zeolite glazes, while showing slightly pinholed surfaces in some instances, did not, as a group, have as many surface irregularities.

Not as recognizable but also evident under the microscope was the fact that the glazes fired to Cone 01 tended to have more bubbles than those fired to Cone 2. Similarly, the glazes fired to Cone 4 had lost some of their bubbles and consequently did not seem as pinholed.

The differences in the sizes and amounts of bubbles found in the feldspar glazes and those in the zeolite glazes can be attributed to differences in ease of melting.

The zeolite glazes evidently formed glasses which at given temperature were less viscous than were the glasses in the feldspar glazes. Since, in firing, each piece with a zeolite glaze had been placed in the kiln next to the feldspar glaze of the same composition, the possible effect of any temperature differences can be neglected. Therefore, any difference in viscosity of the fused glaze must be attributed to differences in ease of melting.

It should be noted here that no crystals or particles of undissolved material were evident even when examined with a microscope. That sub-microscopic crystals could and did exist is entirely probable. This is especially true in the feldspar glazes fired to the lower temperature. Although it was impossible to see any individual crystals in these, some of the feldspar glazes had a matte appearance. The glaze fired to higher temperatures had a glassy appearance indicating the absence of the crystals which produced the matte effect at the lower temperature.

Of all the constituents in the glazes, the lead oxide should melt at the lowest temperature and, therefore, should be

the first to aid in glass formation. The other constituents would be dissolved in this glass, either by chemical reaction, direct solution, or a combination of both. Since the zeolite or the feldspar is present in larger amounts than the remaining constituents, these would be an influencing factor in glaze formation.

Theoretically, the zeolite with a lower silica content should be able to form a glass at a lower temperature than would the feldspar. This is evident from inspection of the phase diagrams. This and one other factor are involved in explaining the greater ease of melting of the zeolite glazes.

The zeolite is a softer material and is more readily reduced in size by ball mill action than feldspar. The latter has a hardness of 6 (Moh's Scale), whereas the zeolite is less than 2. The latter determination was difficult due to the small size of particles available, but it was sufficient indication.

Since the glazes were milled under the same conditions, the zeolite particles were ground to a much finer state. This finer state of subdivision provided more surface area and enabled the glaze particle to fuse more readily. Their fusion resulted in a more rapid solution of the remainder of the constituents of the glaze. The feldspar particles were larger and required more time for fusion.

It is believed that the feldspar was all dissolved in heating to Cone 01, but that all of the other constituents, especially the flint and clay, had not been taken completely into solution. The zeolite is believed to have been all

dissolved and to have aided in taking the remainder of the constituents into solution.

Another comparison between the two types of glazes was not readily apparent but became so as time passed. The feldspar glazes began to show evidences of crazing about a month after removal from the kiln. This defect was found in more of these glazes as time passed, until after three months time most of the feldspar glazes which had been fired to cone 01 were crazed. The zeolite glazes did not craze except in one or two instances. These few instances were the result of extreme glaze thickness following the tearing and crawling previously mentioned.

The crazing is a result of an extreme difference in the coefficients of expansion of the clay body and the glaze. The glaze, having a higher coefficient, contracts more upon cooling, resulting in stresses developing throughout. Over a period of time these stresses, aided by expansion and contraction due to normal temperature changes, became great enough to overcome the inherent strength of the glaze producing a rupture.

The thickness of the glaze is a factor involved with crazing. Thicker glazes always tend to craze more than a thin glaze of the same composition placed upon the same body. However, the thickness of most of these glazes was about the same so the crazing should be considered independent of this factor. Zeolite glazes of the same thicknesses as the feldspar glazes did not craze. Several exceptionally thick zeolite glazes did craze, but not to any appreciable extent.

The possibility of metastability being the cause of crazing has been proposed. No information is available on this, but if it were assumed to be the cause, the same reasoning would be applicable as is used concerning differences in expansions.

The crazing can again be related to the fact that the zeolite aids in faster melting and solution formation than does the feldspar. The composition of the glass phase of the feldspar glaze is higher in sodium or alkali content than the glass in the zeolite glaze fired to the same temperature, since the more refractory materials are not completely in solution. That glasses or glazes high in alkali exhibit large coefficients of expansion as compared to low alkali glasses is a well known fact.

Again considering the melting of the two types of glazes, one concludes that the zeolite aided in melting and the formation of a greater amount of glassy phase at a given temperature than the feldspar. The zeolite glaze was completely a glass at Cone 01. The feldspar glaze was not completely in solution. Undoubtedly all of the lead oxide and the feldspar plus part of the other constituents were melted. However, this glass did not contain enough silica and perhaps alumina (if the clay were not completely dissolved) to have the same glass composition and consequently the same coefficient of expansion as the zeolite glaze.

Upon firing to the higher cone equivalents, the feldspar glaze ingredients were completely dissolved, forming glazes of the same composition as the zeolite glazes. These glazes

exhibited only a little crazing when fired to Cone 2 and no crazing when fired to Cone 4, except in the extremely thick glazes.

Some of the zeolite glazes still exhibited tendencies toward tearing and crawling. The use of spraying instead of dipping had in general improved the quality of all the glazes - feldspar and zeolite.

3. Non-milled glazes

The results of the non-milled glazes were very interesting. The feldspar glazes had been well fused but were speckled throughout due to the presence of undissolved cobalt oxide. That these specks were well distributed in the glaze is indicative of fair mixing, but complete dispersion, such as results from ball mill action, was not found.

The zeolite glaze had excellent color distribution and exhibited no specks. The advantage of an ionic distribution of the element adsorbed by the zeolite over the oxide distribution is quite evident.

Since an excessive amount of water is needed for excellent mixing, it was found the glaze tended to tear. However, this defect was avoided by lowering the water content to a minimum and by applying the glaze by spraying rather than dipping. In all events the zeolite glazes had vastly much better color distribution than did the feldspar glazes. In the latter glazes the color quite often varied in intensity on the same pieces. In addition the presence of the dark specks was unsightly.

The use of zeolite as a color carrier is well demonstrated. Such a method of compounding a glaze should be of great value to the home artist or anyone else interested in making his own glazes, but who does not have a ball mill available for use with the oxide type glaze. If ground zeolite were not available, some could easily be produced by means of a mortar and pestle. This would permit the hobbyist to make his own colors in various shades.

4. Effect of water content on glazes

The glaze was divided into six portions, the water contents of which were to be so adjusted that the glazes would have densities of 1.65, 1.60, 1.55, 1.50, 1.45, and 1.40 grams per cubic centimeter respectively. However, difficulties in adjusting the water content resulted in glazes of the following final densities: 1.67, 1.63, 1.58, 1.50, 1.46, and 1.42.

The results of the firing operation indicate that the higher water content glazes (or lower densities) had less tendency toward cracking on drying and showed less tearing after firing. The results also showed that thickness of application was of little or no significance as the thinly applied glazes showed tearing similar to the thicker glazes. Both of these facts were contrary to what had been expected.

It is explainable, however, when one realizes that the clay pieces to which the glaze was applied are porous and tend to absorb readily some water from the glaze. In the case of the

low water content (high density) glazes, most of the water was absorbed at once setting up stress, resulting in cracks which later produced tearing. With the higher water content glazes the porous piece again absorbed water, but there remained sufficient water to be removed more slowly by further absorption and by surface evaporation. In the case of slow removal, the glaze was able to partially relieve stress set up, thus avoiding most of the cracks. These cracks did tend to open up on subsequent firing, but not nearly to the extent that the cracks on the higher density glazes did.

All of the glazes did exhibit some tendency toward tearing. This same glaze with feldspar instead of zeolite gave very little trouble on drying or firing except in extreme thick applications and these healed over on firing. From this it was concluded that the finely ground zeolite was tying up an appreciable amount of water, and underwent a considerable amount of shrinkage upon the removal of the water. This led to an attempt to find approximately what volume change was involved during dehydration.

A second conclusion from this investigation was that in working with zeolite glazes, applications should be made by spraying rather than dipping, as this tends to eliminate or minimize drying troubles.

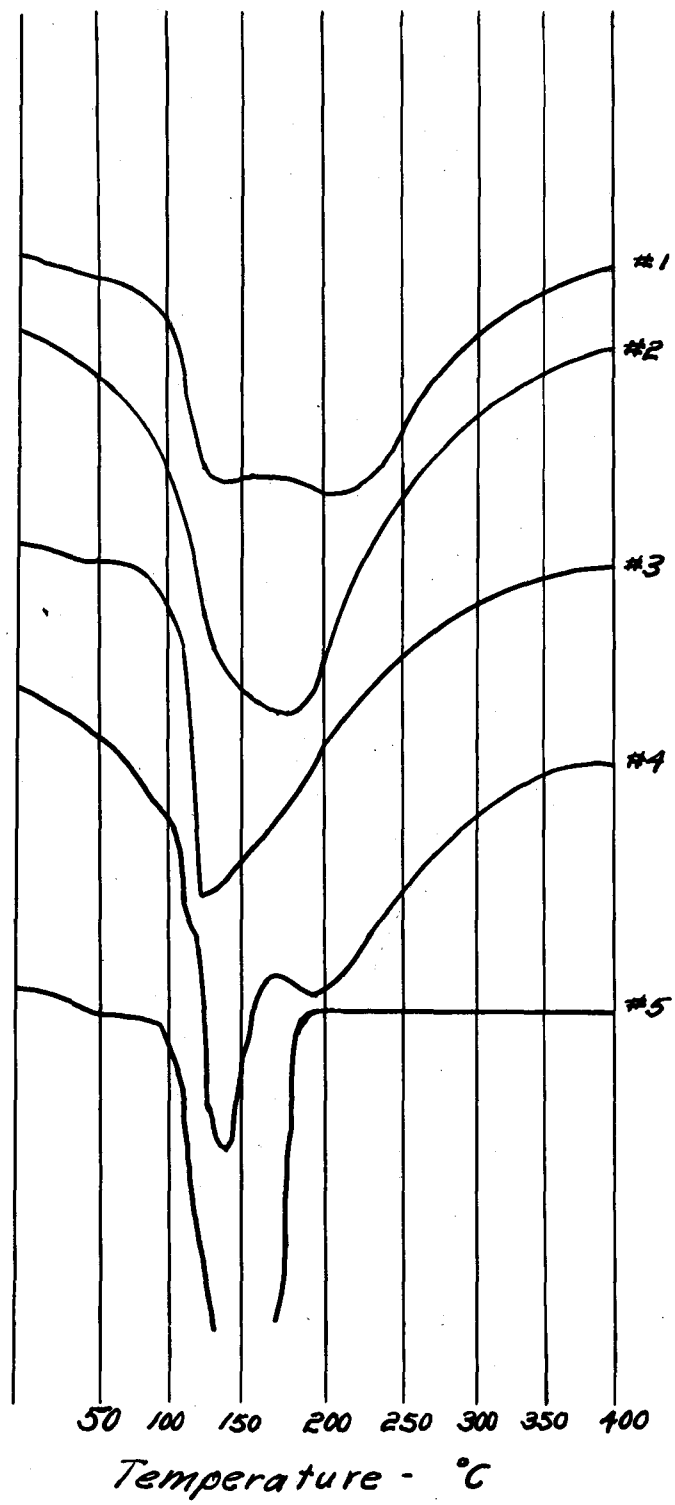
B. Stabilization of Zeolite

A thermal analysis of the commercial zeolite, crushed but unwashed, was made. The result is shown as Curve #1 of Figure 1. This curve indicates that the water begins coming off slightly before 100°C . and is finally removed by 400°C . Why the curve should have the two dips was difficult to understand at first. It was thought that perhaps two different waters of hydration were involved.

To see if used zeolite had the same characteristics, a sample was taken from a water softener tank after regeneration. After drying, this was analyzed, and the result is shown as Curve #2. This curve shows only one large dip, indicating a continuous removal of water. This seemed to indicate that the unused zeolite contained some material not evident in the used material.

A sample of zeolite was treated with hydrochloric acid and converted to a hydrogen zeolite. This was dried, crushed, and analysis made giving the results shown as Curve #3. The water loss again begins at about 100°C . and reaches a maximum rate at about 125°C ., then decreases, becoming complete at about 400°C .

Since zeolite contains quite a bit of sodium which is released upon crushing, it was suspected that perhaps sodium carbonate might be present and might have its own water of hydration. To a sample of hydrogen zeolite was added 10%

Thermal Curves*Figure 1*

stock sodium carbonate. After mixing well, an analysis was made, giving the results shown by Curve #4.

This curve gives a slight resemblance to Curve #1 in that two dips are present. Since it was impossible to decide for certain which of the dips is caused by the water in the zeolite and which is caused by moisture in the sodium carbonate, it was necessary to make a determination using only sodium carbonate.

Curve #5 is a determination using a sample of stock sodium carbonate. This indicates that the water in the sodium carbonate begins leaving at about 100°C ., reaches a maximum rate at about 150°C ., and is completely removed at a temperature of about 180°C .

Therefore, it was concluded that the two dips in Curve #1 result from the removal of water from the zeolite itself and from the sodium carbonate present in the zeolite. This water is removed from normal zeolite at the greatest rate when a temperature of about 175°C . is reached. The water from the sodium carbonate is removed at the greatest rate at about 150°C . Therefore, these two removals overlap in temperature and result in twin dips. The superimposing of Curves #5 and #2 on Curve #1 bears this out.

The main result of this investigation was to prove the presence of sodium carbonate in the unwashed zeolite. In order to remove this expeditiously, it was decided that acid leaching would be the best and quickest method. Therefore, the zeolites

to be used in subsequent investigation in this work were washed with hydrochloric acid followed with distilled water rinses.

It should be noted that in all instances these analyses were actually made to a final temperature of 900°C . in case any further reactions would be apparent. However, none was found, and to facilitate plotting, the straight horizontal line extending to 900°C . has been cut off at 400°C ., and only the data from room temperature to 400°C . has been plotted.

The results of the thermal analysis indicated two facts. One of these is that a fair amount of sodium carbonate is present in new, unwashed zeolite. This led to a decision that the easiest way to remove it is by acid leaching. This method was used (after this experiment) for the preparation of zeolite which was free of excessive sodium ions and will not be discussed here. The second of these facts is that all of the water is not removed until 400°C . The temperature rendering it unable to exchange ions must be above this, since exchange occurs when the zeolite is hydrated.

To determine this temperature, five-gram samples of dried, ground zeolite were put into crucibles, and the crucibles were placed in a laboratory furnace. The furnace was heated at the rate of about 400°C . per hour, and, beginning at 450°C ., a crucible was removed at 50° intervals. These samples were tested for exchange ability by means of cobalt nitrate. It

was found that any sample heated above 850° C. was incapable of ion exchange. This is a rather higher temperature than had been anticipated. Even though incapable of base exchange at this temperature, the zeolite is still capable, after being ground subsequent to heating, of releasing sodium ions.

Five-gram samples of zeolite were heated to temperatures of 800° C. and above at intervals of 50° C. Various lengths of time were chosen at intervals of one hour each. Crushing of the sample and measuring of the pH of 25 ml. of distilled water placed with the zeolite, indicated the presence of any excess sodium ions.

The results of this experiment indicated that 3 hours at 1000° C. or 5 hours at 950° C. were necessary to prevent the release of any appreciable amount of sodium. The temperature of 950° C. was the minimum.

Zeolite which was treated with cobalt and heated to this 1000° C. for 3 hours was incorporated into a glaze of the same base composition previously used. This glaze, when fired to Cone 4, had a very good color as before, but no tendencies of tearing or crawling resulted. This practical test indicated that the stabilization of the zeolite resulted in a good glaze free of any drying defects.

In an attempt to determine the feasibility of removing the excess sodium ions by electrical energy, 100 grams of ground zeolite, unwashed, were placed in a laboratory cell using parchment paper. Using 215 volts, the cell initially

drew 0.18 amperes. As time passed, the current dropped, but the pH of the liquid in the cathode chamber remained high, above 10.0. After 20 hours the current had dropped to about 0.07 amperes and tended to remain at this value, indicating that perhaps the excess sodium was removed and that the replaceable sodium was now coming off.

When the pH of the liquid left in contact with this zeolite for a short while after crushing was determined, it was still found to be about 9.0, indicating that all of the sodium had not been completely removed.

It was, therefore, concluded, in view of the time and power involved that this would not be a logical manner of stabilizing the zeolite even if it could be done with more time.

C. Zeolite in Ceramic Bodies

1. Zeolite in casting slips

The results of this part of the investigation are rather interesting and unique. Sodium carbonate, with or without sodium silicate, has long been the customary electrolyte added to most commercial casting slips. Either of these two compounds can furnish sodium ions as well as provide anions which tend to precipitate the undesirable calcium, magnesium and other similar cations. The silicates of these cations are by far more insoluble than the carbonates. From the data obtained

it is evident that the zeolite is capable of accomplishing this same effect.

Since these casting slips under discussion are concentrated suspensions of various shaped and sized particles, one need not assume that they would behave as a simple liquid insofar as viscosity is concerned. It has been thought that very low concentration suspensions of very small spherical particles may perhaps behave as a liquid, but no experimental proof is available. In other words, there is no reason to assume that the rate of shear is proportional to the shearing stress, when it is known that with practically all such suspensions as these that the opposite has always been true. The rate of shear is not proportional to the shearing stress. To avoid any misrepresentations or erroneous assumptions, the values of the viscosimeter readings are left in degrees of rotation, as found experimentally. However, the viscosimeter was calibrated by means of solutions of glycerol in order that, if at a future date, the information should be needed or desirable, it would be available. This information is included in the appendix.

Another reason that these data are left in degrees of rotation is that the accuracy of the viscosimeter, when read to the nearest degree, does not warrant expansion to the large values which would result in changing to centipoise. In other words, since one degree of rotation corresponds to approximately 175 centipoise, the accuracy of the readings in the latter units would certainly be questionable and might be in

error of 75 to 100 centipoise. Therefore, this alone might well be reason for not converting.

TABLE III

Run #1: Effect of zeolite on casting slips

Slip No.	Grams Zeolite Added	% Zeolite Added	Viscosimeter Reading, Degrees	pH of Slip
1	0.0	0.00	Too viscous to measure	7.42
2	0.5	0.25	"	--
3	1.0	0.50	"	--
4	1.5	0.75	60	7.78
5	2.0	1.00	9	7.85
6	3.0	1.50	5	7.96
7	5.0	2.50	6	7.96
8	10.0	5.00	6	8.16
9	15.0	7.50	5	8.32
10	20.0	10.00	10	8.30
11	25.0	12.50	16	8.32
12	30.0	15.00	22	8.34

A number 22 wire was used to obtain all the readings. All slips had a density of 1.80 grams per cubic centimeter.

Slips numbers 4 and 5 exhibited slight tendencies toward thixotropy. The rest were seemingly free of this characteristic.

Zeolite used was commercial material, ground in a ball mill and washed with HCL to remove excess alkali, then rinsed with distilled water until chloride-free. The pH was 7.8, but later went to 9.85 upon drying and rehydration.

The foregoing discussion has been made as an explanation of the use of degrees of rotation as the units, but it should not be construed as indicating any fallacy in the method involved or the conclusions drawn from the results. These data are used on a relative or comparative basis rather than on an absolute.

From the data shown in Tables III and IV and Figures 2 and 3, it is evident that both zeolite and sodium carbonate are capable of reducing the viscosities of slip to the same minimum value. Both of these also when added in excess are capable of increasing the viscosity of slips. The fact that the zeolite deflocculated slips decreased to 5° then increased to 6° , later to decrease to 5° prior to rising can perhaps be attributed to slight errors or limitations of the methods involved. That the minimum values did not remain at either 5° or 6° , as one would normally expect, but varied between the two can be attributed perhaps to slight temperature variations, slight water content variations due to evaporation, thixotropic or other properties of the slip not easily discernable, or combinations of any or all of these and others. In any event, the general trend is evident, although the individual values might be in slight error.

It is noted that slips numbered 9, 10, and 11 had the same pH values while that of 12 is only slightly higher. This can

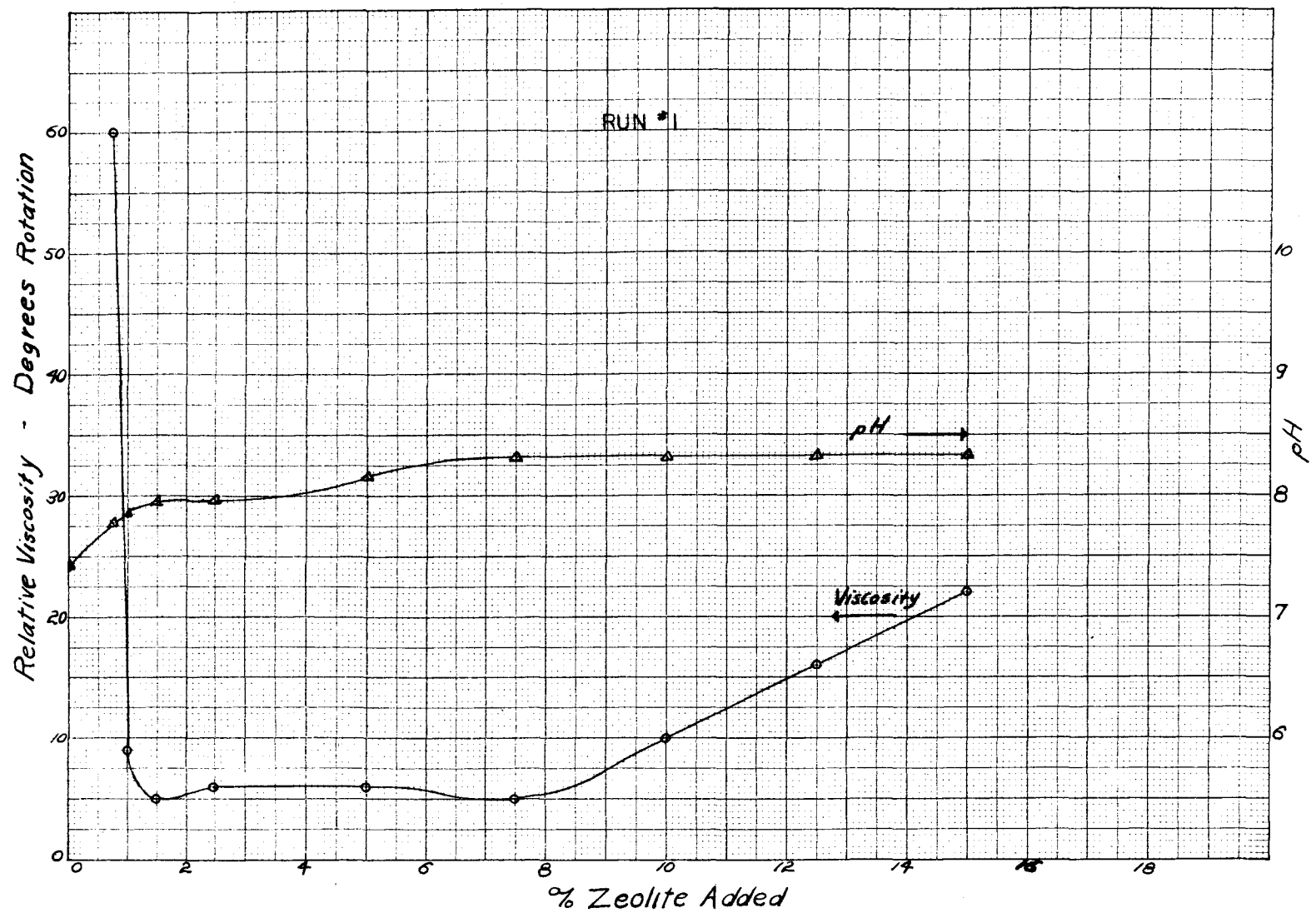


Figure 2. Effect of Zeolite on Casting Slips.

TABLE IV

Run #2: Effect of sodium carbonate on casting slips

Slip No.	Grams Na_2CO_3 Added	% Na_2CO_3 Added	Viscosity Reading, Degrees	pH of Slip
20	0	0	Too viscous to measure	7.42
21	0.250	0.1250	11	8.20
22	0.500	0.2500	6	8.54
23	0.750	0.3750	5	8.98
24	1.000	0.5000	8	9.34
25	1.125	0.5625	11	9.56
26	1.250	0.6250	19	9.72
27	1.500	0.7500	29	9.80
28	1.750	0.8750	38	9.88

A number 22 wire was used to obtain all the readings. All slips had a density of 1.80 grams per cubic centimeter. All slips showed a slight tendency toward being thixotropic but not enough to cause trouble.

The sodium carbonate used was commercial grade, as would be used around and in most industrial ceramic plants.

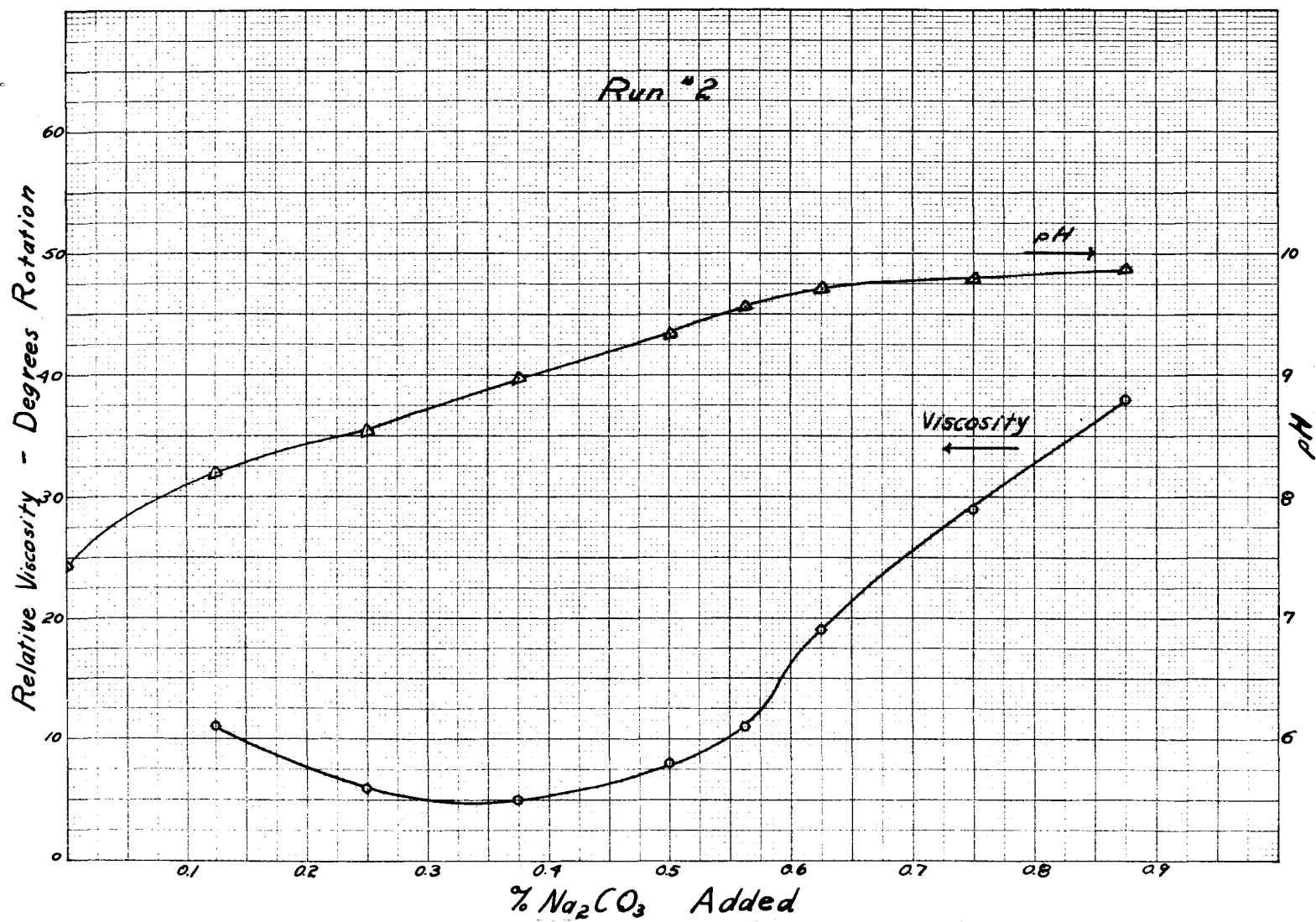


Figure 3. Effect of Na_2CO_3 on Casting Slips.

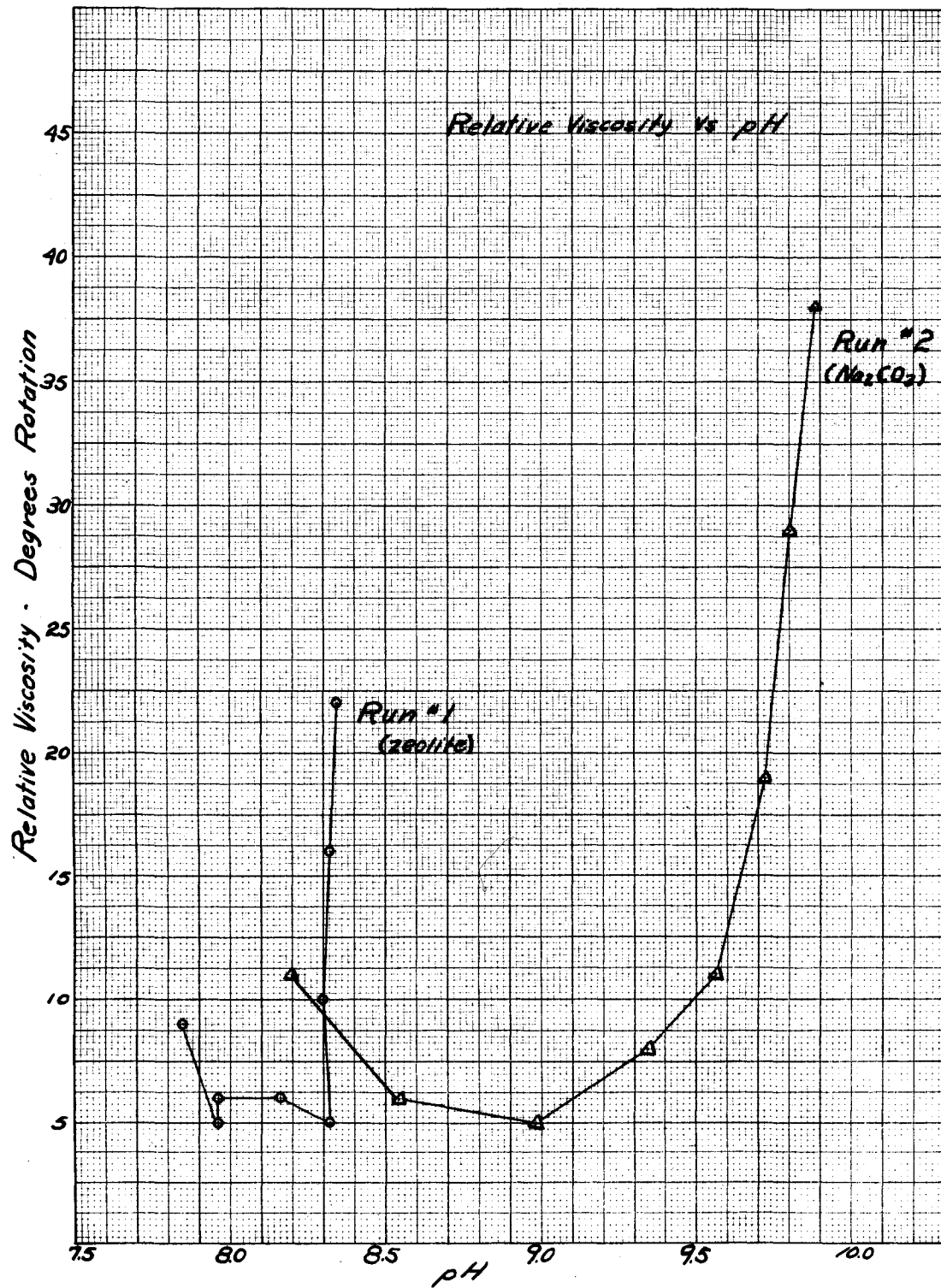


Fig. 4. Relationships of Slip Properties.

be expected when it is realized that the zeolite added is no longer exchanging ions, as the ions are no longer available, all having been picked up. The zeolite alone with water exhibited a pH of 9.85 due to liberation of sodium ions on rehydration. These ions were the first absorbed by the clay. Therefore, the pH of the clay slips would not be expected to reach the value of 9.85.

The minimum viscosities for the slips with zeolite seemingly had a wider range of amounts added. Amounts of zeolite five times as great as that for minimum deflocculation did not increase the viscosity. Addition of one-third more sodium carbonate than that required for the minimum viscosity resulted in an increase of viscosity. This fact alone would permit, by use of zeolites, easier control of commercial casting slips, as any errors or discrepancies due to the human element, careless workmanship, or a combination of both would not be as critical for slips with zeolite as the deflocculant as they would for slips using other electrolytes.

Since many plants use pH meters for slip control, such a device might prove useless with zeolite deflocculated slips. When excessive amounts are used, the pH does not seem to increase appreciably with viscosity. This would necessitate a change in slip control methods, but with zeolite the control should be easier.

Another advantage of the use of zeolite would be found when adding scrap and trimmings to the casting slip for mixing and subsequent reuse. Normally, difficulties are experienced because of variations in electrolyte contents between the scrap and new additions. The electrolyte content of the scrap is variable, depending in general upon the amount of water removed from it while the cast piece is forming in the plaster mold. The variations in electrolyte content would make for difficulty in determining the correct amount of electrolyte needed for any slip which is a mixture of new and old body composition. If zeolite were used as the electrolyte, the variations in amounts present perhaps would not be so dominant as to cause trouble, unless the amount of zeolite were considerably in excess.

Another interesting fact that the data obtained show is that the zeolite slips have their minimum viscosities at lower pH values than do the sodium carbonate slips. This is shown in Figure 4. This is perhaps explainable when one considers that calcium carbonate is slightly soluble and that in the reaction



an excess of sodium carbonate would be necessary to drive this to the right. When the zeolite is used, the calcium ions from the clay are picked up by the zeolite and are no longer in a position to interfere with the adsorption of sodium ions by the clay.

In some instances protective colloids have been used to resist over-deflocculation due to additions of excessive electrolytes.¹ These additions afford greater stability of the slip.

Since a range of amounts of zeolite additions is possible with the same slip conditions resulting, the zeolite can be assumed to be performing to a certain degree the same functions of the protective colloids, that of preventing over-deflocculation.

The use of zeolite in conjunction with enamel slips would be another application for its deflocculating ability. Most enamel slips contain only about 7% clay or less. Very slight changes in electrolyte amounts, therefore, have an appreciable effect upon the system because of this small amount of clay. Zeolite, having a wide range, would permit easier control than other electrolytes.

A question which might be raised in regard to the addition of zeolite to a body would concern the effect of the former upon the fired properties of a body. That is, a sodium aluminosilicate is being added which might alter the properties. However, since the amount to be added is so small, 1.5% being adequate to deflocculate the slip used, it should not noticeably affect the fired properties. Were it found to do so, which is highly improbable for most bodies, a slight reduction in the amount of feldspar used should easily compensate for the zeolite. In any event, it should present little or no problem.

¹Phelps, G. W. Clays -- Deflocculation and Casting Control. Ceramic Age. 51:9. 1948.

This work has shown qualitatively and quantitatively the influence of zeolite upon a casting slip and has demonstrated advantages of this material over sodium carbonate, the common electrolyte. The advisability of the use of zeolite for a clay of an extremely high base exchange capacity, such as bentonite, is rather doubtful, however. The amount of zeolite needed would be exorbitant and would undoubtedly influence the properties of the system. For the more common clays the zeolite would be very effective and advantageous.

2. Hydrogen zeolite in casting slips

The hydrogen zeolite treated by acid leaching was sufficiently fine grained to pass through a 200 mesh-per-inch sieve. In contact with distilled water it had no effect upon the pH. A sodium chloride solution of 6.98 was lowered to a value of 4.26 by the zeolite, indicating a fair exchange ability. Even after being six months in an uncovered jar on a laboratory shelf, the zeolite was still capable of lowering a solution to the same pH. This latter observation seems to establish the fact that the hydrogen zeolite so made does remain stable, at least in so far as its ability to exchange ions is concerned.

One of the problems that was presented in the preparation of this zeolite was its tendency to cake or form coarse particles upon drying. These particles were broken down fairly easily by means of a mortar and pestle, yet they did not tend to slake readily or divide into their original individual fine particles

as existed prior to the acid treatment. The process of leaching and rinsing was accelerated by use of a vacuum filter to aid in liquid flow. This could conceivably result in closer packing of particles, which would not prevent the slaking but would materially retard it. Evidently the grinding action in the ball mill reduced some of the material to such a colloidal state (as evidenced by excessive shrinkage) that some of the material was becoming gelatinous when wetted and behaving as a binder for the larger particles. Regardless of the reasons involved, it was found necessary to use a mortar and pestle to reduce the zeolite again to a powder prior to its introduction into clay slips.

From the data of Run #3 as presented in Table V, it is evident that hydrogen zeolite is capable of removing the sodium ions from a clay body slip sufficiently to bring the slip back through its limits of minimum viscosity. From inspection of Fig. 5, it can be seen that the data obtained indicate a reverse of the results obtained when sodium zeolite is added in increasing amounts to a casting slip. The viscosity is lowered to a minimum, and further additions of zeolite result in an increase.

The values of viscosity and pH obtained in this run are comparable with the respective values found in the study of clay slips deflocculated by sodium carbonate but not with the values for sodium zeolite deflocculated slips. This is to be

expected, as the hydrogen zeolite is merely picking up sodium ions in solution and replacing them with hydrogen.

This decrease in sodium ion content changes the equilibrium existing between the ions on the clay particles and the ions in solution, resulting in a change in behavior of the suspension as a whole.

If the previously expressed idea for difference of the pH value for the same viscosities of sodium zeolite deflocculated slips and sodium carbonate deflocculated slips is to be considered true, then it would explain the pH values obtained. Conversely, the values obtained lend support to the idea. It can be seen from Table IV that the minimum viscosity of sodium carbonate deflocculated slips is obtained at a pH of 8.98. From Table V it is seen that with the addition of hydrogen zeolite, the minimum viscosity is obtained at a pH of 8.55. This lower pH can be attributed to the exchange reaction occurring.



The presence of the carbonic acid would result in a lowering of the pH.

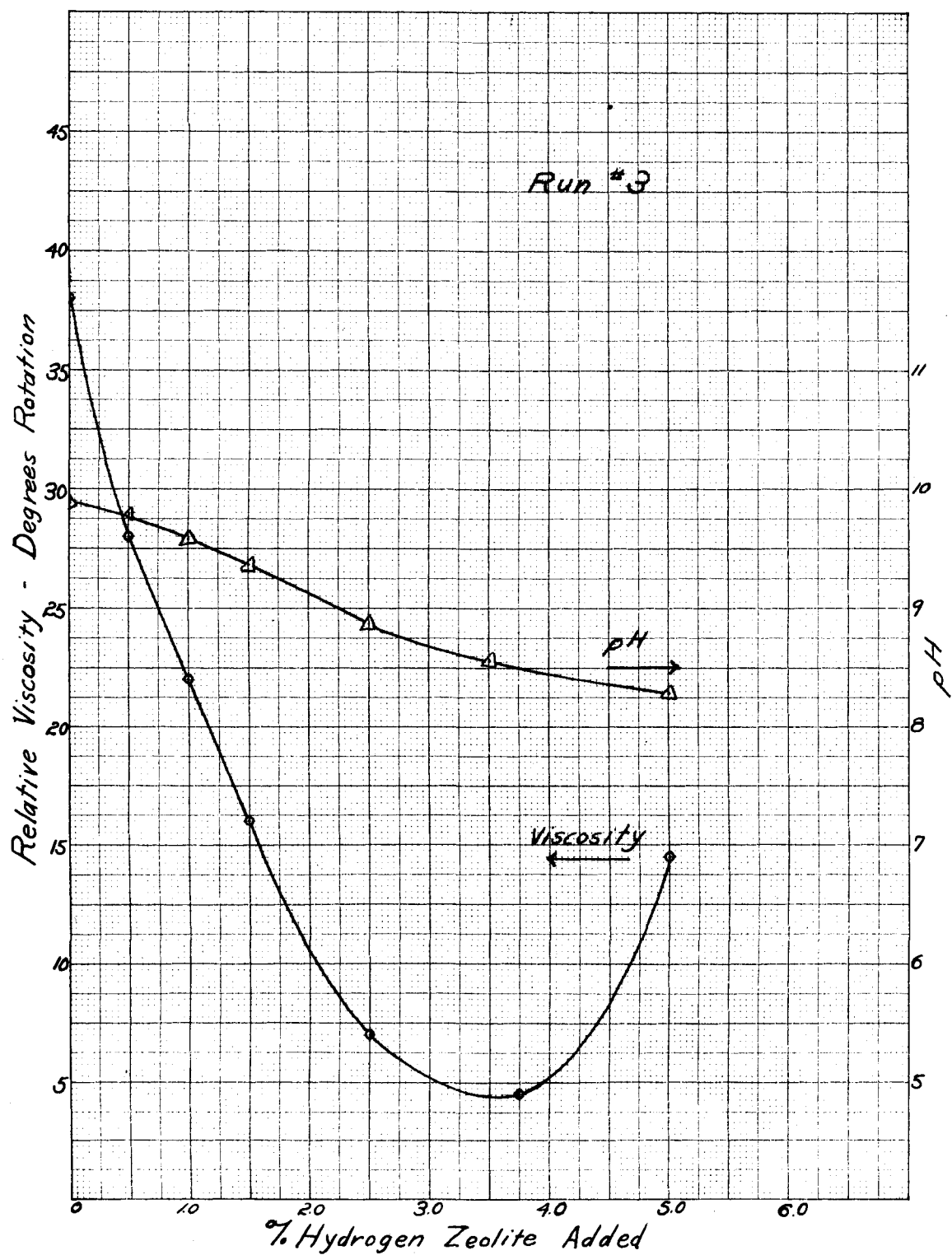


Fig. 5. Effect of Hydrogen Zeolite on Over-deflocculated Casting Slips.

TABLE V

Run #3: Effect of hydrogen zeolite upon over-deflocculated casting slips.

Slip No.	Hydrogen Zeolite Added Grams. % of Dry Material	Viscosity Degrees	pH
40	0.0 0.0	38	9.88
41	1.0 0.5	28	9.78
42	2.0 1.0	22	9.58
43	3.0 1.5	16	9.37
44	5.0 2.5	7	8.87
45	7.5 3.75	4.5	8.55
46	10.0 5.0	14.5	8.28

Density of each slip - 1.80 grams per cubic centimeter.
Deflocculant - 0.875% Sodium Carbonate.

The results of Run #4, Table VI and Figures 6 and 7, are fairly similar in general to those of Run #3 but indicate the necessity of both adequate mixing or dispersion of the zeolite throughout the slip and sufficient time for ion adsorption. The agitation of slips for this part of the investigation was accomplished by manually shaking the container with the slip for a period of five or ten minutes. Since, after determining and making any necessary adjustment of the density, the latter followed by additional shaking, the values of viscosity and pH were determined, the discrepancies arising can be attributed to the physical characteristics of the zeolite. As is well

known the rate and ultimate capacity of ion adsorption by zeolites is dependent upon particle size. In Run #4 the zeolite particles had neither the time nor agitation to produce slaking as completely as in Run #3, or to pick up all the ions they were capable of adsorbing. Undoubtedly the slaking is the more important of the two factors. For Run #3 it can be assumed that sufficient slaking time was afforded the particles as is indicated by the smooth continuous curves both of pH and viscosity values.

From the preceding discussion it may be concluded that control of particle size and a minimum of time are essential for accurate results in the control of properties of casting slips by this method.

In passing it might be noted that a slip with 0.75% sodium carbonate was chosen merely to corroborate in a general way the results of Run #3. Had a slip of 0.875% been used and had time and agitation been of no influence, the data from Run #4 would have been the same as from Run #3. The data obtained in Run #4 do indicate in a general way the same trends as in Run #3 and show lower pH values throughout the run. This latter is to be expected, as the pH value was initially lower for a slip with only 0.75% sodium carbonate.

From Table IV it is seen that 200 grams of slip with 0.875% sodium carbonate have 1.25 grams of sodium carbonate in excess for a pH of about 8.55. From Table V it can be seen that 7.5 grams of hydrogen zeolite are necessary to lower the pH of

TABLE VI

Run #4: Effect of hydrogen zeolite upon an over-deflocculated casting slip.

Slip No.	Hydrogen Zeolite Added		Viscosity Degrees	pH
	Grams	% of Dry Material		
50	0	0	29	9.80
51	2	1.0	19	9.46
52	4	2.0	15	8.80
53	5	2.5	11	8.52
54	7	3.5	11.5	8.50
55	8	4.0	12	8.38
56	9	4.5	11	8.30
57	10	5.0	8.5	8.18

No aging of slips between additions. Manual shaking only.
Density of each slip - 1.80 grams per cubic centimeter.
Deflocculant - 0.75% Sodium Carbonate.

the over-deflocculated slip to 8.55; this is equivalent to 0.1667 grams of sodium carbonate per gram of zeolite.

From the original data given concerning the capacity of the original material (12,000 grains of calcium carbonate per cubic foot), it can be found that 0.01714 equivalents of sodium are exchangeable. For material dried at 110° C. this is equivalent to about 0.0725 grams of sodium carbonate per gram of zeolite. The fact that the value of 0.1667 was found experimentally can be attributed to the extremely fine size of the hydrogen zeolites.

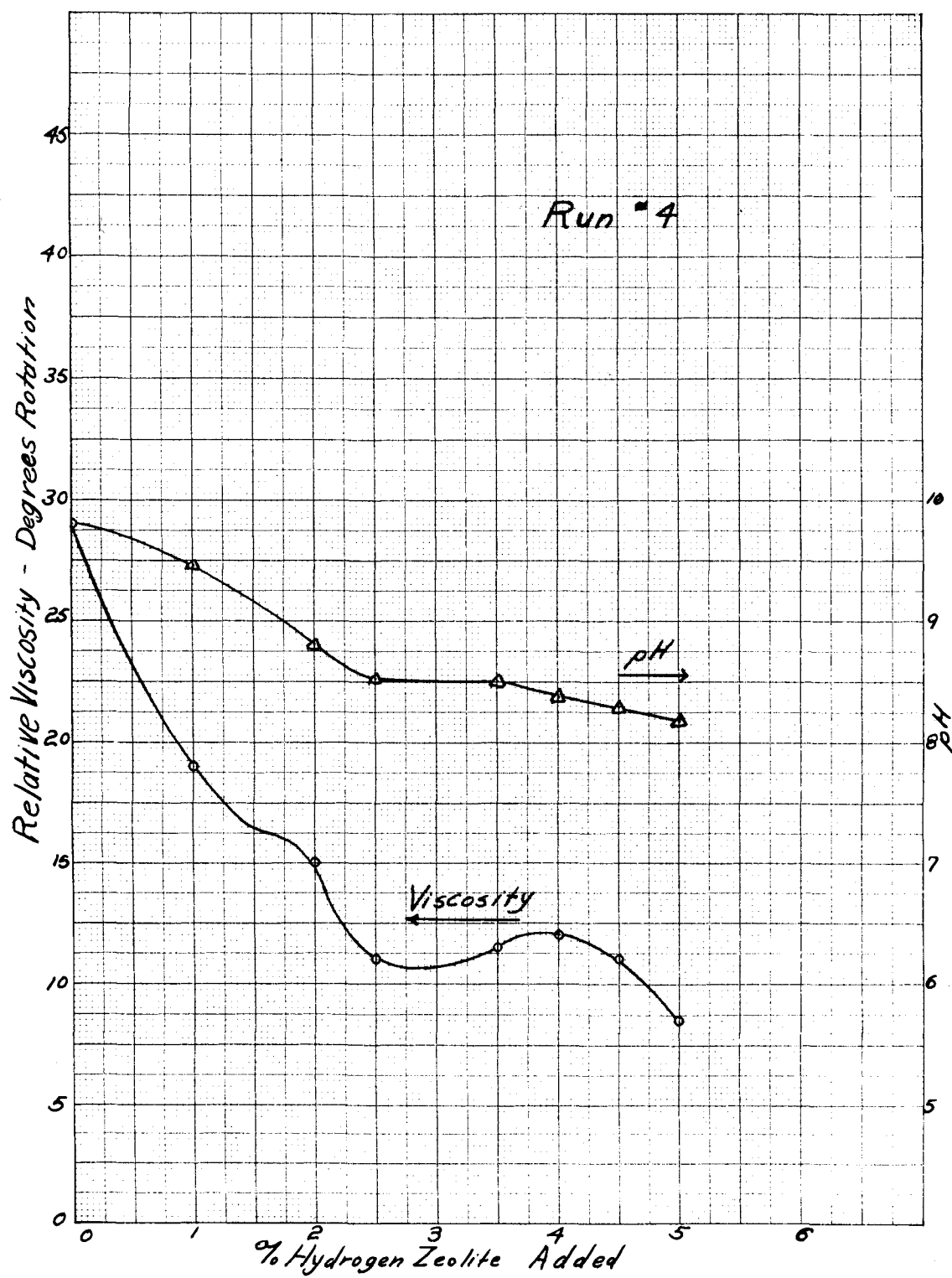


Fig. 6. Effect of Hydrogen Zeolite on Over-deflocculated Casting Slips.

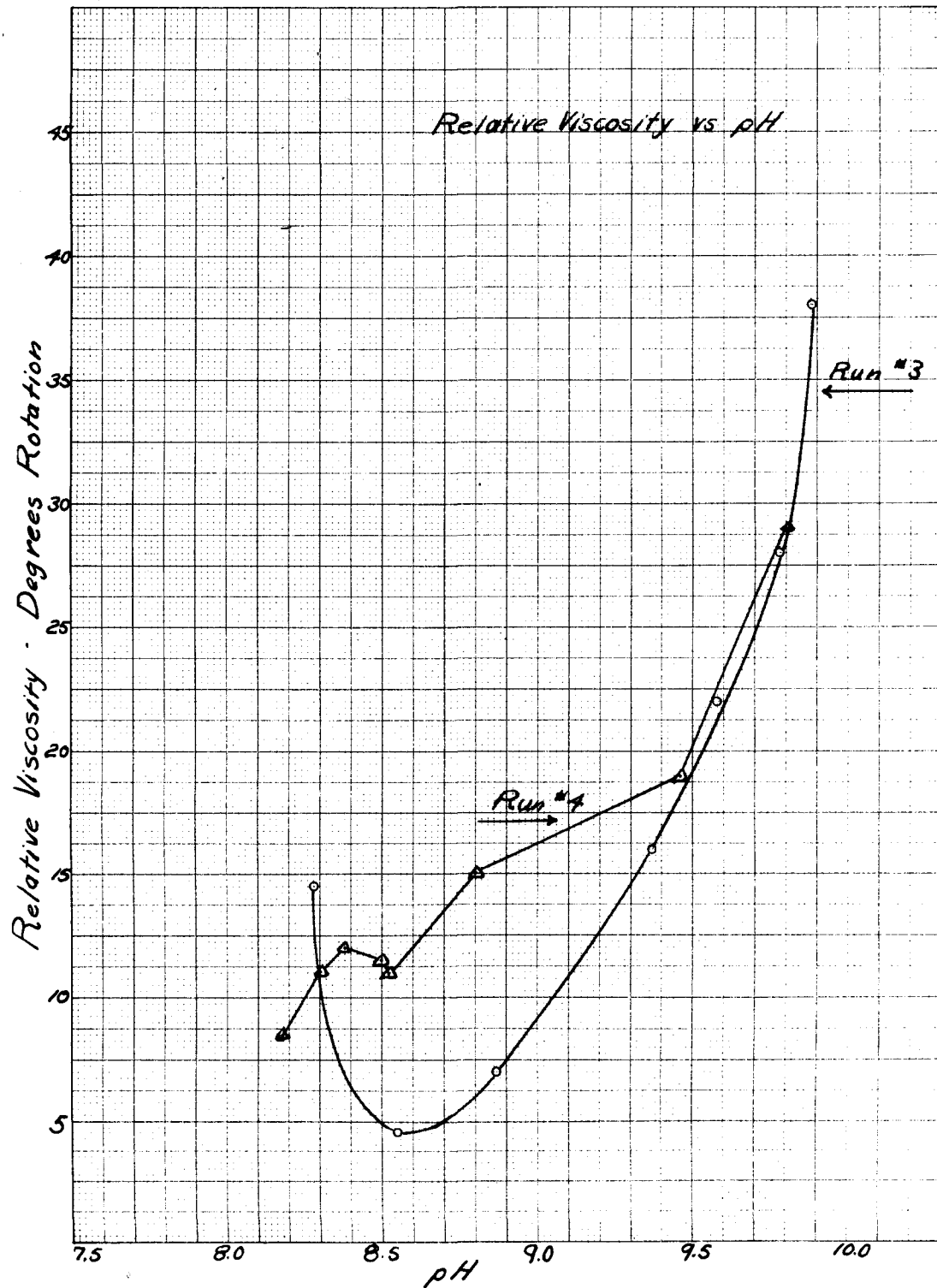


Fig. 7. Relationships of Slip Properties.

The fact that sodium ions were adsorbed by the hydrogen zeolites might suggest other uses for such a zeolite. Ordinarily the alkali ions are only difficultly precipitated or otherwise removed from solutions.

This part of the investigation was prompted by the fact that washing or precipitation by zinc uranyl acetate was the only means available for removal of sodium ions from clay suspensions, and the use of this compound has never been of any importance to the writer's knowledge. Ordinarily the excess sodium ions are removed by filter pressing, which is an operation requiring both time and equipment in addition to material handling. Since the hydrogen zeolite has proved successful, it is possible that there are other commercial practices or operations wherein the removal of sodium or other extremely soluble alkali ions is desirable. With the correct procedure it would be possible to remove these ions rather than just precipitate them as in the case of the zinc uranyl acetate. The stability of the zeolite to repeated acid leaching would be the next factor for study.

For ceramic uses this zeolite would become merely part of the composition and should have only slight effect upon the chemical or physical properties in subsequent operations. An organic zeolite might be used for certain processes, but in ceramic bodies, unless it could be removed, it would cause defects during firing.

V. CONCLUSIONS

A. Experiments were conducted in the preparation and use of zeolites as a carrier of a metallic coloring ion in ceramic glazes. The glazes containing zeolites were compared with glazes made using feldspar and metallic oxides. In each instance the glazes compared had the same ultimate melted

Gold Star	Display	Ref. Room Reserve	Missing
In Use	Physical Sciences	Charged for Home Use	Engr. Reading Room
Period. Reading Room	General Collection	Storage	Bindery
Ref. Room	Ref. Room	Reserve Room	Reserve Room
Address			
Signature			
Title			
Author			
Date of Publication			
Volume			
Call Number			

Doc. ent. de Finance
10/4/48
1038
97.461
50137a
Ostravsky

laze was used as a basic composition.

the following facts have been

g glazes were of excellent color, ker shades. It was difficult, however, means available that these glazes nsity or color distribution to the onal method.

terially aid in the melting of the res the zeolite glazes were less azes. At higher temperatures, identical, the melted glasses for both types of glazes.

exhibited less pinholing and the an did the feldspar glazes fired

to the same temperatures. This is a result of the higher rate of fusion afforded by the use of zeolite instead of feldspar.

4. Some of the feldspar glazes fired to lower temperatures had matte appearances indicating undissolved material, whereas the corresponding zeolite glazes fired to same temperatures had no or only slight matte appearances. This is also related to the ease of fusions.

5. The zeolite glazes had a greater range of firing temperatures than the feldspar glazes. This was exhibited by the fact that the feldspar glazes fired to lower temperatures were not completely in solution. This resulted in their becoming crazed after short periods of time. The zeolite glazes indicated no tendencies toward crazing.

6. The ease of crushing and grinding of the zeolite when the glaze was milled was beneficial in aiding the melting process. The extremely fine particle size of the zeolite did result in a tendency of some of the glazes to tear on drying and crawl on subsequent firing. This was minimized by correct application procedure and eliminated by sufficient heating of the zeolite prior to incorporation in the glazes.

7. Glazes of excellent color distribution and intensity can be produced, by use of zeolites, in glazes which have never been milled. Glazes made of feldspar and coloring oxides had speckled appearances, indicating poor color distribution. The advantage of the zeolite in this type of glaze is very apparent and could well lead to a new method of glaze formations.

B. Studies were made on the stabilization of zeolites from which the following conclusions were drawn.

1. Unwashed stock zeolite contains sodium carbonate which can interfere with the expected behavior of the zeolite. It is best removed by means of acid leaching with dilute acid.
2. All of the water of hydration of zeolite is completely removed by heating to a temperature of about 400° C., most of it being lost prior to this temperature.
3. It is necessary that zeolite be heated to 950° C. for at least 5 hours or to 1000° C. for at least 3 hours to prevent the release of sodium upon subsequent grinding.
4. The use of dialysis as a means of removing the excess sodium ions present in freshly crushed zeolite is impractical.

C. Experiments were conducted on the use of zeolites in casting bodies. The following results are known.

1. Zeolite can be used satisfactorily and to an advantage as a deflocculant of clay casting slips. The zeolite is able to furnish the needed sodium ions and at the same time adsorb the undesirable calcium, magnesium, or other ions.
2. Casting slips deflocculated by zeolite have lower pH values for the same water content and viscosity than do the slips deflocculated by sodium carbonate.
3. The zeolite had a greater range of additions than did the sodium carbonate used for comparison. Five times as much more zeolite than the theoretical minimum for deflocculation

could be added. Increasing the minimum amount of sodium carbonate by one-third resulted in an over-deflocculated slip.

4. The treatment of zeolite with hydrochloric acid resulted in a zeolite capable of adsorbing sodium ions and lowering the viscosities of over-deflocculated slip.

5. The use of such a zeolite as mentioned (4) is governed by the particle size, the time allowed for reaction, and the amount of agitation or intimate mixing to insure complete ion exchange.

6. The use of a zeolite which can adsorb sodium ions should prove valuable in other fields as very few methods are available for the removal of sodium ions from solutions.

VI. SELECTED REFERENCES

- Andrews, A. I. Ceramic Tests and Calculations. New York. John Wiley and Sons. 1928.
- Callahan, J. R. Synthetic Zeolite. Chem. Eng. 56:2, 92-3. 1949.
- Eddy, O. R. Zeolites as Pigments for Ceramic Wares. Unpublished B.S. Thesis. Ames, Iowa, Iowa State College Library. 1940.
- Grim, R. E. Relation of Composition to Properties of Clays. Journal Amer. Ceramic Soc. 22:141-51. 1939.
- Haldeman, G. W. and Erdman, A. C. The Use of Zeolites as Pigments in Ceramic Colors. Unpublished B.S. Thesis. Ames, Iowa, Iowa State College Library. 1939.
- Hepplewhite, J. W. Use of an Ammoniacal Electrolyte for a Plastic Body. Bull. Amer. Ceramic Soc. 18:191-192. 1939.
- Hey, M. H. The Nature and Relations of Zeolite: A Review. Trans. Ceramic Soc. (England) 36:84-97. 1937.
- Hodgman, C. D. and Holmes, H. N. Handbook of Chemistry and Physics. 25th ed. Cleveland. Chemical Rubber Publishing Co. 1941.
- Ingleson, H. and Harrison, A. Effect of Temperature on Exchange Capacities of Base Exchange Materials Used in Water Softening. Journal Soc. Chem. Ind. 60:87-92. 1941.
- Irish, L. T. and Wells, E. D. The Use of Zeolites for Coloring Clays and Related Products. Unpublished B.S. Thesis. Ames, Iowa, Iowa State College Library. 1938.
- Johnson, A. L. and Norton, F. H. Fundamental Study of Clay. II. Deflocculation in Clay-Water System. Journal Amer. Ceramic Soc. 24:189-203. 1941.
-
- Johnson, A. L. and Norton, F. H. Fundamental Study of Clay. III. Casting as a Base Exchange Phenomenon. Journal Amer. Ceramic Soc. 25:336-344. 1942.

- Milligan, W. O. and Weiser, H. B. Mechanism of the Dehydration of Zeolites. *Journal Phys. Chem.* 41:1029-1040. 1937.
- Morey, G. W. *The Properties of Glass*. New York. Reinhold Publishing Corp. 1938.
- Newcomb, Rexford, Jr. *Ceramic Whitewares*. New York. Pitman Publishing Corp. 1947.
- Norton, F. H. Color Formation in Glasses and Glazes. *Glass Ind.* 16:45-48. 1935.
- _____. Critical Study of the Differential Thermal Method for Identification of the Clay Minerals. *Journal Amer. Ceramic Soc.* 22:54-63. 1939.
- Parmelee, C. W. *Outlines of Essentials of Glaze Composition*. Copyrighted. March, 1929.
- _____. *Ceramic Glazes*. Chicago. Industrial Publications, Inc. 1948.
- Phelps, G. W. Clays -- Deflocculation and Casting Control. *Ceramic Age* 49:162-169; 226-229; 298-299. 1947. 50:119-120; 158-161; 218-219; 277-278; 1947. 51:9-11. 1948.
- Richardson, H. K. Small Cast Thorium Oxide Crucibles. *Journal Amer. Ceramic Soc.* 18:65. 1935.
- U. S. Bureau of Mines. *Artificial Zeolite, Index of Literature*. U. S. Bureau of Mines Bulletin 328. 1930.
- U. S. Bureau of Mines. *Report of Investigations -- Softening Water with Non-Metallic Minerals*. U. S. Bureau of Mines R. I. 3578. 1941.
- Way, J. T. Power of Soils to Absorb Manure. *Journal Royal Agr. Soc.* 13:123-142. 1852.
- Weyl, Woldemar. *The Chemistry of Colored Glass*. *Glass Ind.* 18:73-78; 93; 117-120; 167-171. 1937.
- Winchell, A. N. Further Studies of the Zeolites. *Amer. Min.* 22:85-96. 1937.

VII. ACKNOWLEDGMENT

The author wishes to express his thanks and deepest appreciation for the interest and valuable aid of Dr. O. R. Sweeney under whose supervision this work was done.

Appreciation is also expressed for the helpful observations made by Prof. C. M. Dodd as the work progressed, and for his encouragement and aid, as well as that extended by Drs. G. L. Bridger, E. F. Ruth, and H. A. Wilhelm.

VIII. APPENDIX

A. Pyrometric Cone Equivalents of Zeolites

Since the commercial zeolite used for this investigation has a lower ratio of alumina and silica to sodium oxide than does feldspar, it was known that the zeolite should be more easily fused. The removal of some of the sodium by leaching should tend to increase this ratio, decreasing ease of fusion. In order to establish a relationship between the ease of fusion of the zeolites and feldspar, a series of cone fusion tests¹ were performed.

Standard size cones were made of feldspar, ground and washed sodium zeolite, and hydrogen zeolite, using an organic binder² to provide formability and aid in the development of dry strength. These cones were mounted in a fire clay plaque with various standard cones, and the plaque was placed in a laboratory gas-fired furnace which is used for such determinations. The first tests of the zeolites indicated that the excessive shrinkage of these materials caused the cones to shrink away from the plaque and become unsupported. They fell or leaned prior to fusion, rendering determinations impossible.

Calcining of the zeolites by means of a laboratory gas burner for about one-half hour resulted in materials which

¹Standard Method of Testing for Pyrometric Cone Equivalent. *Journal Amer. Ceramic Soc.* 11:452-453. 1928.

²Methocel, a methyl cellulose obtained from the Dow Chemical Company, Midland, Michigan.

did not rehydrate or shrink appreciably, at least not enough to interfere with the testing. By observing the deformations of the sodium zeolite cones and the standard cones, it was found that the zeolite had a pyrometric cone equivalent of almost 6. The zeolite cones deformed well after standard Cone 5 and just before Cone 6.

Similarly, it was observed that the feldspar had a pyrometric cone equivalent of almost 7.

The differences between the zeolite and the feldspar cone equivalents substantiates the earlier fusion of the zeolite glazes as compared to feldspar glazes.

The hydrogen zeolite had a pyrometric cone equivalent of almost 11. The action of the hydrochloric acid in removing the sodium is very apparent from this high value.

B. Calibration of MacMichael Viscosimeter

The viscosimeter used in the casting slip studies was calibrated by means of solutions of glycerol. The instrument was operated at speed of 48 revolutions per minute for all measurements, both in calibrating and in measuring. Wire number 22 was chosen from those accompanying the instrument and was used through the work.

Values of viscosity¹ of glycerol at various temperatures were plotted versus these temperatures. From this plot it was

¹Hodgman, C. D. and Holmes, H. N. Handbook of Chemistry and Physics. 25th ed. Cleveland. Chemical Rubber Publishing Co. 1941. p. 1636.

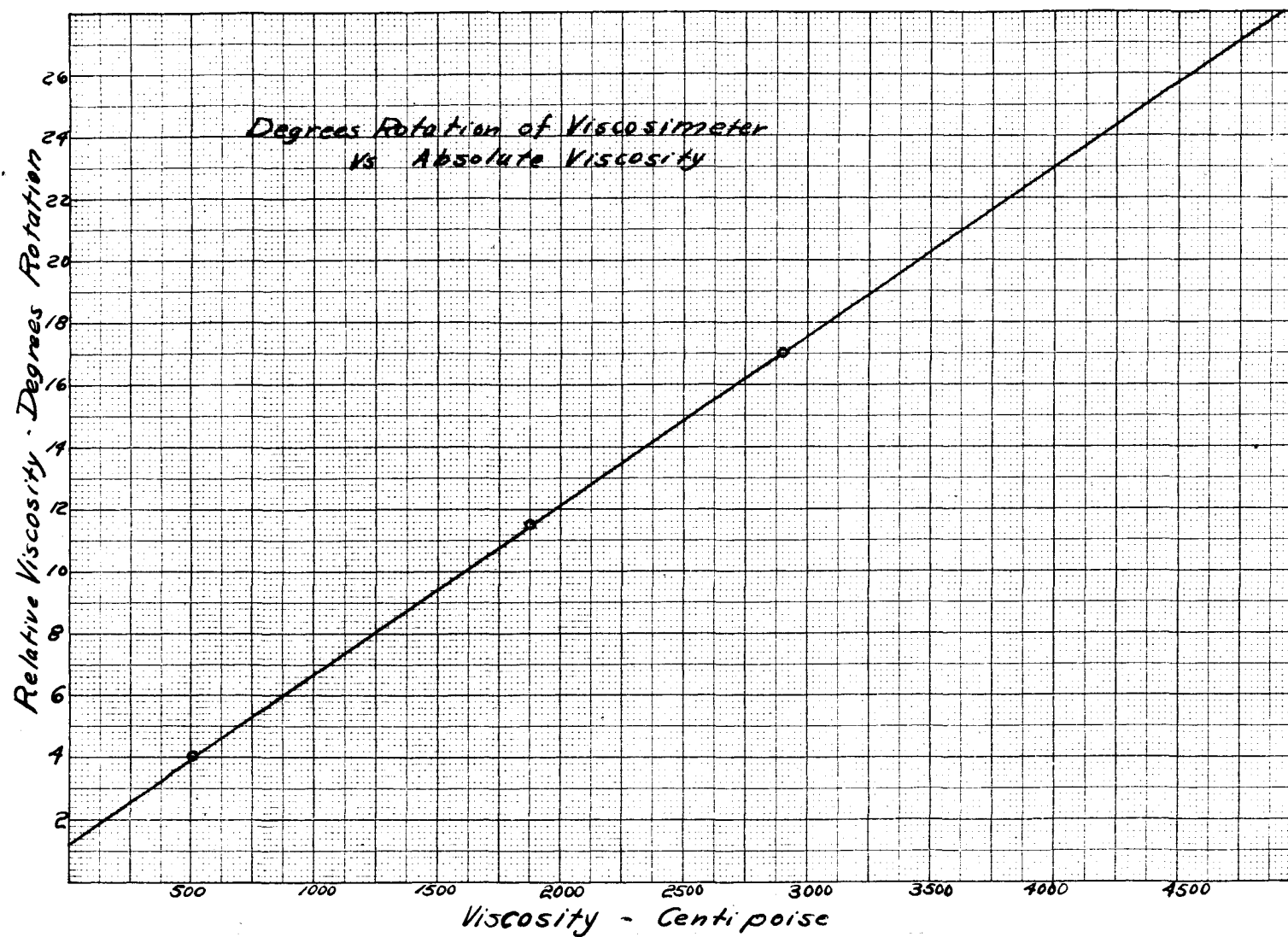


Fig. 8. Calibration of MacMichael Viscosimeter.

possible to find the viscosities of glycerol at temperatures at which the instrument was calibrated. The degrees of rotation of the viscosimeter wire were determined using glycerol solution at three different temperatures - 26.3°C. , 11.3°C. , and 6.6°C. Use was made of the water jacket surrounding the liquid to insure accurate temperature. These temperatures were not purposely chosen but were the ones at which equilibria were reached.

It was found that at 26.3°C. the amount of rotation was 4° , at 11.3°C. the rotation was 11.5° , and at 6.6°C. the rotation was 17° . These values of rotation were plotted versus the viscosity of the glycerol as shown in Figure 8. By use of this plot any of the values reported in the results of the casting body studies can be converted from degrees of rotation to units of centipoise.

C. Volume Changes in Zeolite upon Heating

The amount of volume change of zeolite upon being heated was influencing certain results of this work. An attempt was made to determine the nature and amount of this change.

No simple method being considered applicable or accurate enough, and no elaborate method being available, it was thought that determinations of the densities of zeolite before and after heating would afford the easiest means of volume changes.

Using an analytical balance and stoppered pycnometer, the densities of zeolite were determined prior to heating, after heating to $1000^{\circ}\text{C}.$, and after fusing at Cone 6.

The values of these were found to be 2.0708, 2.3477, and 2.4478 grams per cubic centimeter, respectively. The determination of the unheated zeolite was made using xylene to avoid any tendency of expansion due to hydration. The other determinations were made using distilled water. Temperatures were considered in all calculations. The loss in weight by 3.729 grams of original material heated to $1000^{\circ}\text{C}.$ was found to be 0.689 grams, all considered as water. Using this information and the densities previously mentioned, it was found that, based upon a gram of the dehydrated gel itself, the following volumes existed:

Initial	-	0.590 cc
$1000^{\circ}\text{C}.$	-	0.421 cc
Cone 6, fused	-	0.408 cc

From these it is possible to calculate, based upon the original volume, that the zeolite volume shrinkage was 28.65% when heated to $1000^{\circ}\text{C}.$ and 30.85% when heated to fusion.