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Effect of chemicals on color and durability of Iowa Devonian shale products

Maynard Paul Bauleke
Iowa State College

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UMI®
EFFECT OF CHEMICALS ON COLOR AND DURABILITY 
OF IOWA DEVONIAN SHALE PRODUCTS

by

Maynard Paul Bauleke

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

Major Subject: Ceramics

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1956
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INTRODUCTION

When an attempt is made to improve on what nature has provided us with there are always several possible results. The attempt may result in a better product all around, or as so often happens, only one particular property may be improved. Several other physical properties may become inferior to their original state. The benefits obtained from the improvement of one physical property may be completely nullified by the loss of other desirable physical properties. The resulting product may have an over-all poorer quality than before the attempted improvement was made.

The Problem

In many areas of the world there exist deposits of shales and clays that contain large amounts of carbonates, sulfides and soluble salts. Upon firing, the carbonates break down into free oxides which upon exposure to moisture hydrate and cause the ware to disintegrate. The sulfides decompose to release sulfur gases that may react with the carbonates to form sulfates. The sulfates have a slight solubility and will migrate to the surface of moist ware to form a white scum. In the structural clay industry the term scum, as used in this thesis, means a surface coating of salts appearing during drying and firing. The soluble salts present will create numerous scumming problems. New ways are always being sought to eliminate or reduce the above impurity problems.
The Object

Interest has been shown (1) in the use of ammonium chloride as an accelerator to remove black coring from structural clay ware. The present work was undertaken to evaluate the effects of ammonium salts on the fired and unfired physical properties, of an illitic shale rich in carbonates, containing abundant soluble salts and some sulfides. Such a shale is found in the Devonian system of northcentral Iowa.

Problem Approach

Six relatively economical ammonium salts were selected for evaluation: urea, mono-basic ammonium phosphate, di-basic ammonium phosphate, sodium ammonium phosphate, ammonium nitrate and ammonium chloride. Preliminary tests were run on each ammonium salt to determine the effect various percentages had on color and surface condition of the shale fired to various maturities. Color was selected as the determining criterion for the best percentage addition because it was the one thing that the average buyer of material could evaluate for himself.

The absorption values were determined for all percentage additions. Absorption values are commonly used to grade the fired product.

The specific items evaluated after the optimum addition percentage was determined were:

1. Transverse strength, dry and moist
2. Moisture expansion
3. C/B ratio
4. Frost resistance
5. Oxidation behavior
6. Removal of sulfur
7. Reduction in hydration of free lime

The above seven items will give an indication of how the ammonium salt will effect the over-all qualities of the fired product. Two firing maturities were selected. Cone 07 which is the commercial firing maturity and cone 02 which is approximately the limiting maturity without bloating the shale.

The effect of the ammonium chemicals on the viscosity of a shale slip was used to determine the variations they might cause in a plastic shale.

No attempt was made to develop new techniques for determining or evaluating the physical properties. Standard methods were used wherever possible. Numerical data were analyzed by application of statistical methods when readily applicable.
PREVIOUS INVESTIGATIONS

In the past the physical properties of high carbonate content shales have been felt to be governed by the carbonate content. When high carbonate shales are fired above 900° C, the carbonate breaks down into free oxides. Usually the troublesome carbonates are calcium and magnesium carbonates. Unless the newly formed oxides of calcium or magnesium react with other materials present they will be present as uncombined oxides in the cooled ware. The free oxides, especially calcium oxide, will hydrate in the presence of moisture causing a swelling of the oxide particle and ultimate cracking of the ware. Calcium oxide is also known as calcia and free lime, the latter being the common term used in the structural clay industry.

Three general approaches towards the elimination or reduction of the carbonate problem have been taken (2):

2. Fine grinding of the carbonate so it will react more readily.
3. Chemical additions to react with the carbonates.

The first method is usually uneconomical for shales used in the manufacture of low cost structural clay products. However, a partial removal of carbonates may be accomplished by selective mining, screening or the use of lime-pebble removal machines. Fine grinding is usually accomplished by the combination of a hammermill and vibrating screens. The oversized material is either recirculated or thrown away. For best
results the oversize material should always be thrown away.

Many instances of the use of chemical additions are referred to in the published literature. Chemical additions can not be expected to produce results without the aid of fine grinding. Lipinski (3) reports that the addition of CaCl₂ under one percent proved a good means of avoiding lime damage. However, fine grinding and correct firing procedure must be observed. Efflorescence was not increased. Small additions, seven tenths to one percent, of NaCl are recommended by Elyumen (4), but his work was done on a clay containing less than one and one-half percent calcium carbonate. This amount usually does not cause any trouble unless it is present in coarse granules. The addition of powdered coal to the brick mix, i.e., grinding powdered coal with the shale, has been reported (5) as counteracting the effects of lime.

Although the following is not strictly a chemical addition it can be considered in this category. Kaufmann (6) and Marschner (7) recommend leaching out the free lime from the bricks immediately upon their removal from the kiln. If water is present in liquid form instead of vapor form the hydrated oxide will be taken into solution as it is formed. This will reduce the volume of the hydrate formed and remove the possibility of the hydrated material exerting pressure on surrounding cavity walls.

Barker and Troug (8) showed that small additions of sodium carbonate to a limey clay caused the clay to develop greater plasticity, lessened the tendency to laminate and crack during forming and drying, and produced a ware with higher fired strength and lowered water absorption.
An early worker in the ceramic field, Seger (9), suggested that the extreme upper limit of calcium carbonate should be twenty-five percent and should be finely ground and uniformly distributed throughout the clay. Occasionally a clay running as high as thirty to thirty-five percent could be used. Any higher calcium carbonate content produced a burned product that had a great tendency to disintegrate and to form a dense white scum. In Iran (10), where the climate is arid, clays containing as much as thirty percent calcium oxide, over fifty percent calcium carbonate, have been used for brick making. Serious firing problems were encountered.

Rieke and Voelker (11) found that at 900° C. a large part of the calcium oxide would react with the clay mineral to form a calcium-alumino silicate. However, it took a much higher temperature to cause the magnesium oxide to react. Krause (12) found that between 500° and 800° C. large quantities of alumina were dissolved by the calcium oxide. A Swiss investigator (13) found that lime-rich clays formed considerable quantities of 2CaO·Al_{2}O_{3}·SiO_{2} (gehlenite) when fired to 1000° C.

Brownell (14) studied the crystalline phases developed in a shale containing more than thirty percent calcium carbonate. No free lime was found. As soon as the carbonate was decomposed the calcium oxide reacted with the clay minerals and silica. Between 840° and 1000° C. gehlenite was formed. Above 1000° C. the gehlenite reacted with the free silica to form CaO·SiO_{2} (wollastonite) and alumina. Jeuthe (15) stated that with high lime bodies the effect of a higher temperature reached by increasing the soaking time was harmful. The long soaking period caused some of the calcium silicates to break down into another
form of calcium silicate and free lime.

If the limey shale contains sulfates and sulfides along with the carbonates an additional problem is created. Such impurities can cause the formation of soluble salts which cause either scum or efflorescence on the surface of the ware. The standard method of treating the soluble sulfate problem is through the addition of barium carbonate to the shale. To be effective the shale must be finely ground and thoroughly mixed with the barium carbonate. A comprehensive review and a complete bibliography of soluble salt problems have been prepared by Brownell (16) and Stahman (17).

There appears to be no satisfactory method of combating the effects of large amounts of free lime through the addition of small quantities of chemicals. Best results have been obtained by fine grinding and firing to a high enough temperature to accelerate the reactions between the clay minerals, free quartz and lime. The problem of soluble salt formation has been treated in the past by the addition of barium carbonate. Judging from the amount of recent work on the problem people are interested in increasing the efficiency of the reaction.
EXPERIMENTAL PROCEDURES AND FINDINGS

Raw Materials and Chemicals

Source of shale

Rice's Dictionary of Geological Terms (18, p. 369) lists the following definitions for a shale.

A laminated sediment, in which the constituent particles are predominately of the clay grade ... A sedimentary rock consisting of more or less consolidated fine muds.

All of the shales used in this study were obtained from the pits of the Rockford Brick and Tile Company and the Mason City Brick and Tile Company. Both shale pits are located in the same geological unit: the Juniper Hill member, Lime Creek formation, Upper Devonian series. This area has been described in detail by Gwynne (19).

The Rockford shale, coded R-4, differs from the Mason City shale, coded M-4, in that all of the overburden has been removed but only a fraction of the siltstone has been removed. In M-4 the siltstone has been removed but the overburden is blended in. Beneath the overburden both shale banks have a uniform blue-gray color.

Both companies supplied the shale in the form of mortar mix. The R-4 mortar mix was ground run of the pit shale. The M-4 mortar mix was manufactured from rejected dried drain tile which contained the normal plant addition of barium carbonate for drain tile of one pound per ton.

Particle size determination

The particle size distribution curves of the two shales, M-4 and
R-4, were determined by the hydrometer method using the equipment described by Norton and Spiel (20).

Sodium pyrophosphate, $\text{Na}_4\text{P}_2\text{O}_7\cdot\text{10H}_2\text{O}$, deflocculant was used in place of the recommended Daxad-23. This modification was made on the basis of the work reported by Vinter and Larson (21) and Davidson (22). They found the sodium phosphates were superior dispersing agents for calcareous clays.

To check the validity of this change for the shales under investigation, two gram samples of shale, additions of one-half, one, one and one-half and two percent of deflocculants and twenty five mls. of water were mixed in test tubes. At the end of twenty four hours the one percent addition of sodium pyrophosphate suspension showed suspended material to the top of the test tube, whereas the one percent addition of Daxad-23 suspension showed about one centimeter of clear water and considerable settling of material. At the end of three days all the Daxad-23 suspensions had settled out completely, but all the sodium pyrophosphate suspensions of one percent or more still showed muddy water to the top of the test tube. The dark suspended material was mainly some form of organic matter. In the settled portion of the sodium pyrophosphate deflocculated shale there appeared distinct layers of particle size differentiation. The top layer had a grayish white color, a striking contrast to the rest of the column. The settling time required for the gray-white material indicated that it should contain the clay minerals found in the shale. A sample was removed for X-ray identification.

Samples were run in duplicate. The amount remaining on a 325 mesh screen was approximately the same for each shale, seven percent.
Casagrande nomographic charts were used to calculate the equivalent diameters of the particle size. The particle size distribution curves are shown in Figure 1.

The results of the particle size determinations support earlier observations that the Rockford shale bank contains more material of silt size, 1.2 to 2 microns, than the Mason City shale bank. If all the material below two microns is considered to be clay mineral particles the M-1 sample has about 43 percent while the R-1 sample has about 37 percent. The six percent difference between the two shales corresponds roughly to the difference in the carbonate content of the two shales.

**Determination of clay minerals and accessory impurities**

**Differential thermal analysis method.** Differential thermal analysis curves were made for the two shales using an apparatus similar to that described by Berkelhammer (23). A specially built Bristol program controller was used to regulate the temperature increase and to record the 500° C. temperature interval lines on the sensitized paper. Tracings, as shown in Figure 2, were made of the galvanometer deflection curve on the sensitized paper.

A comparison of the two curves indicates that the R-1 shale has more of its carbonate in the form of dolomite, however in the M-1 sample limestone appears to be more dominant than dolomite. This is shown by the double endothermic reaction that occurs between 700° and 900° C. The small sharp endothermic reaction peak above 550° C. is attributed to quartz. The exothermic reaction between 400° and 500° C. is due to the combustion of carbonaceous material and the oxidation of pyrite. Under
Figure 1. Particle size distribution curves of Devonian shale.
Figure 2. Differential thermal analysis curves of Devonian shale.
a binocular microscope particles of pyrite were plainly visible. Between 100° and 150° C. there occurs an exo-endothermic reaction that can not be wholly attributed to the dehydration of the material. Dehydration of mechanically held water never occurs exothermically in clays. Grimshaw (24) states that such a reaction is indicative of the tridymite form of quartz.

Both curves lack the reaction of large amounts of clay mineral, but this is typical of illitic shales that contain less than fifty percent of the clay mineral. Both shales were analyzed as received. No attempt was made to remove any of the non-clay minerals.

X-ray identification of the clay minerals. The shales of the Devonian region have been spoken of as having the illite clay mineral present but no proof of identification other than that of differential thermal analysis could be found in the literature (25). A sample of the clay mineral in shale R-4 was fractionated out and sent to the Illinois Geological Survey for mineral identification. Bradley's method (26) of preferred orientation was used in mounting the sample for X-ray diffraction. The X-ray pattern showed the clay minerals present to be illite and chlorite. A tracing of the X-ray pattern with the d-spacings marked is shown in Figure 3. Table 1 has the d-spacings tabulated.

According to Grim (27, p. 65, 69) these clay mineral structures are:

The illite basic structural unit is a layer composed of two silica tetrahedral sheets with a central octahedral sheet. The tips of the tetrahedrons in each silica sheet point towards the center of the unit and are combined with the octahedral sheet in a single layer, with a suitable replacement of OH by O. The unit is the same as that for montmorillonite except that some of the silicones are always replaced by aluminums and the resultant charge deficiency is balanced by potassium ions.

A chlorite structure consists of alternate mica-like and brucite layers.
Figure 3. X-ray diffraction pattern of clay minerals found in Devonian shale.
An X-ray pattern of the unpurified shale showed the same minerals as found by the differential thermal analysis including the positive identification line for tridymite.

Determination of carbonate content of shales

During recent years new methods of titrating calcium and magnesium have been developed based on their reaction with a chemical known as versenate (disodium-dihydrogen-ethylene-diamine-tetra acetic acid). The method used is essentially that developed by Cheng (28) for the analysis of limestone.

Since the method is simple and rapid it could be easily adapted to plant quality control work or to shale pit exploration. An outline of the procedure and the necessary solutions are given in Appendix A.

The average results of the chemical analyses are given in Table 2. Shale R-4 contains 6.65 percent more carbonate than shale M-4. The
Table 2

Chemical Analysis

<table>
<thead>
<tr>
<th>Shale</th>
<th>Percent CaCO₃</th>
<th>Percent CaO</th>
<th>Percent MgCO₃</th>
<th>Percent MgO</th>
<th>Total carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>R-4</td>
<td>13.58</td>
<td>7.62</td>
<td>8.67</td>
<td>4.18</td>
<td>22.25</td>
</tr>
<tr>
<td>M-4</td>
<td>9.20</td>
<td>5.03</td>
<td>6.40</td>
<td>3.14</td>
<td>15.60</td>
</tr>
</tbody>
</table>

differential thermal analysis curves indicated that the R-4 shale should have more of its carbonate present in the form of dolomite. Assuming that all the magnesium carbonate present would be in the form of dolomite and calculating the amount of dolomite that could be present, on a mol basis, shale R-4 would have 74 percent of its carbonate present as dolomite, while shale M-4 would have 82 percent. This illustrates that caution should be used in applying quantitative statements to the differential analysis curves. The proper statement for the differential curves should be that R-4 shale has more carbonate present.

In 1945 Hammer (29) reported the following analysis for the shale from the Rockford pit:
Rockford Shale Analysis

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ignition Loss</td>
<td>13.82%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>49.91%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>11.44%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4.35%</td>
</tr>
<tr>
<td>FeO</td>
<td>0.47%</td>
</tr>
<tr>
<td>MgO</td>
<td>4.53%</td>
</tr>
<tr>
<td>CaO</td>
<td>7.01%</td>
</tr>
<tr>
<td>K₂O</td>
<td>4.58%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.67%</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.03%</td>
</tr>
<tr>
<td>Sulfide S</td>
<td>0.12%</td>
</tr>
</tbody>
</table>

The values obtained by the versenate method for CaO and MgO are in good agreement considering the variability of the shale bank and the period of time between samplings. No recent analysis was found for the M-4 shale.

Selection of chemical additions

It has recently been reported (30) that small additions of ammonium chloride had beneficial effects towards the decomposition of pyrite during firing. The presence of ammonium chloride caused the pyrite to decompose at a lower temperature — at least the black core was removed at a lower temperature. This freed the shale of sulfur gases and other combustion gases at a lower temperature and in a shorter period of time, allowing the remaining firing cycle to be carried on at a faster rate.
without the danger of bloating from entrapped gases. The work was carried out on low carbonate content shales.

A study of the relevant equilibrium diagrams (31) shows that phosphorous pentoxide, \( P_2O_5 \), reacts with calcium oxide to form numerous calcium phosphates. The calcium phosphate formed depends upon the molecular ratio of each oxide present. The \( CaO-P_2O_5 \) equilibrium diagram shows that high concentration of \( CaO \) and low concentration of \( P_2O_5 \) favors the formation of \( 4CaO\cdot P_2O_5 \).

Since it was already reported that ammonium chloride could produce a favorable reaction in a shale it was contemplated that perhaps an ammonium phosphate salt would combine the beneficial effects of both ammonia and phosphorous in counteracting the effects of pyrite and calcium oxide.

Three ammonium phosphates were selected. Two of them are fairly economical and abundant in supply as they are used in the manufacture of commercial fertilizers. The third one contains sodium which imparts the effect of a deflocculation agent. For evaluating the effects of the phosphate group three other ammonium salts were also selected. The chemicals with their chemical formulas are listed below. All chemicals used were c.p. standard.
Chemical Additions

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>(NH₂)₂CO</td>
</tr>
<tr>
<td>Mono-basic ammonium phosphate</td>
<td>NH₄H₂PO₄</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>(NH₄)₂HPO₄</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>NaNH₄HPO₄·4H₂O</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>NH₄NO₃</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>NH₄Cl</td>
</tr>
</tbody>
</table>

Properties of ammonium phosphates (32)

In ammonium phosphates a volatile base is combined with a relatively stable and non-volatile acid. Heating converts ammonium phosphates into tacky masses. This property, coupled with their solubility, has lead to their extensive use in fire-retardant compositions for impregnation of combustible materials. Pure mono-ammonium phosphate contains 15.8 percent ammonium and 61.7 percent phosphorus pentoxide. Di-basic ammonium phosphate contains 27.3 percent ammonia and 53.8 percent phosphorous pentoxide.

Mono-basic ammonium phosphate is more stable than di-basic ammonium phosphate. Di-basic ammonium phosphate upon heating decomposes into ammonia and mono-basic ammonium phosphate. This breakdown is noticeable at 125°C. When heated high enough the ammonium phosphates break down as follows:

\[
\begin{align*}
\text{NH₄H₂PO₄} & \rightarrow \text{HPO}_₃ + \text{NH}_₃ + \text{H}_2\text{O} \\
(\text{NH₄})₂\text{HPO₄} & \rightarrow \text{HPO}_₃ + 2\text{NH}_₃ + \text{H}_2\text{O} \\
\text{NaNH₄HPO₄·4H}_2\text{O} & \rightarrow \text{NaPO}_₃ + \text{NH}_₃ + 5\text{H}_2\text{O}
\end{align*}
\]
Monobasic ammonium phosphate reacts with dolomite as follows:

$$3\text{NH}_4\text{H}_2\text{PO}_4 + \text{CaCO}_3 \cdot \text{MgCO}_3 \rightarrow \text{CaHPO}_4 + \text{MgNH}_4\text{PO}_4 + (\text{NH}_4)_2\text{HPO}_4 + 2\text{CO}_2 + 2\text{H}_2\text{O}.$$ 

If calcium sulfate is present in addition to dolomite the following reaction occurs with monobasic ammonium phosphate:

$$\text{NH}_4\text{H}_2\text{PO}_4 + 2\text{CaCO}_3 \cdot \text{MgCO}_3 + \text{CaSO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4 + 2\text{MgNH}_4\text{PO}_4 + \text{Ca}_3(\text{PO}_4)_2 + \text{H}_2\text{O} + 4\text{CO}_2.$$ 

Di-basic ammonium phosphate reacts rapidly with calcium sulfate to form calcium phosphate and ammonium sulfate.

$$(\text{NH}_4)_2\text{HPO}_4 + \text{CaSO}_4 \rightarrow \text{CaHPO}_4 + (\text{NH}_4)_2\text{SO}_4.$$ 

The foregoing reactions illustrate that the ammonium phosphate additions will react with any calcium sulfate present in addition to their reaction with limestone and dolomite. The reaction ties up the free lime and magnesia in the form of insoluble phosphates.

Fired Color and Scum Formation

Procedure for making preliminary test bars

All shales were ground with a hammermill, screened through a 20 mesh screen and thoroughly mixed. Five hundred grams of shale was weighed out for each bar formed. All chemicals were dry ground in a mortar and pestle before being dissolved in distilled water. Additions made for each chemical on a dry weight basis were 0.25, 0.50, 1.00, 2.00 and 3.00 percent. Twenty five percent water (distilled) of plasticity was used at all times.
The water containing the dissolved chemical addition, and the shale, were placed in a mixing bowl and mixed for five minutes with a Hobart Kitchen Aid mixer using a wire whip beater. The mixing time was controlled by an electric timer installed in the power circuit. Immediately after mixing, the shale was hand pressed into a brass mold forming a bar 1-1/8 x 1-1/8 x 12 inches. The bar was removed, checked for compactness, turned over and repressed into the mold. This method of pressing produced a satisfactory bar. After repressing, the bar was removed from the mold and cut into six two inch bars using a wire cutting rack. The bars were coded, numbered and placed on a pallet to dry. At no time during the drying period were the bars turned, forcing the evaporation to occur from the upper surface and concentrate the soluble salts on it. Bars were air dried for 1/8 hours, then oven dried for 24 hours gradually raising the temperature from 120° to 220°F.

The dried bars were fired to the desired temperature in an electric kiln. A Leeds and Northrup program controller regulated the rate of firing. Unless otherwise noted all firings were made according to the following schedule: 80°F. per hour up to 1600°F. and 33°F. per hour after 1600°F. Test bars were fired to cone 07 (1787°F.), cone 05 (1886°F.) and cone 01 (2030°F.). No draw trials were made as each firing constituted a full kiln.

Visual observations of the effect of additions on raw and fired shale

Untreated shale — unfired state. Both shales had good plastic properties, however, the M-4 shale showed slightly better working properties. This may be attributed to two factors. First, M-4 contains
more particles of clay mineral size than does R-4. Second, M-4 contains a small amount of barium carbonate which Hughes and Johnson (24) report as improving the plasticity of a shale by precipitating the sulfate ion as insoluble barium sulfate.

Unfired shale — fired state. At all firing temperatures a light coating of white scum appeared on the surface of sample R-4. The color of R-4 lightened as the temperature increased. A slight amount of white scum was present along the edges of all M-4 bars at all temperatures. The color slightly darkened at cone 01.

Urea addition — unfired state. For both shales, the addition of urea had very little effect on their plastic behavior. See Figure 10. Additions of one percent or more caused heavy formation of urea crystals on the dried surface of the bars.

Urea addition — fired state. The R-4 bars showed more scum on their surfaces than those containing no addition. The M-4 bars showed no real improvement over the untreated shale. Addition levels that produced heavy surface concentrations of urea salts had thin loosely-held layers of refractory material on them after firing. The layers were easily brushed off.

Color and surface conditions produced by the urea addition are shown in Figure 4.

Mono-basic ammonium phosphate addition — unfired state. As the percent of addition increased the shale became increasingly difficult to form into bars. The shale became granular in nature, exceedingly stiff as if it did not have enough water of plasticity, and it did not easily knit during the hand forming operation. See Figure 10. Additions in
Figure 4. Effect of urea on color and surface condition.

Figure 5. Effect of mono-basic ammonium phosphate on color and surface condition.
excess of one percent showed a deposit of soluble salts on the surface after drying.

**Mono-basic ammonium phosphate addition -- fired state.** The one percent addition produced an R-4 bar that was free of white surface scum. The additions of one half and one quarter percent showed normal scum formation, but the two and three percent additions showed excessive formation of scum. At cone 01 the heavy scum coatings on the R-4 bars started to fuse into a glaze. Additions of one half and one percent produced scum free surfaces on the M-4 surfaces. The other addition percentages produced surface conditions on M-4 bars similar to those observed for R-4 except at cone 01 the glaze formation was less on the M-4 bars.

Color and surface conditions produced by the mono-basic ammonium phosphate additions are shown in Figure 5.

**Di-basic ammonium phosphate addition -- unfired state.** There was no noticeable stiffening of the shale until after the addition exceeded one percent. Additions in excess of one percent had the same forming characteristics as with mono-basic ammonium phosphate. See Figure 10. Again additions in excess of one percent caused surface deposits on drying.

**Di-basic ammonium phosphate addition -- fired state.** Again the one percent addition produced the cleanest surface on the R-4 bars. The one half and one percent addition produced the best results for the M-4 bars. A heavy coating of glaze was produced on the M-4 bars containing a two percent addition and fired to cone 01.

Color and surface conditions produced by the di-basic ammonium
phosphate additions are shown in Figure 6.

**Sodium ammonium phosphate addition -- unfired state.** Additions of one percent or less acted as a deflocculating material causing the shale to become extremely flabby when twenty five percent water of plasticity was used. Additions in excess of one percent caused the shale to stiffen, however, at three percent the shale was adjudged to have the same stiffness as with no addition. See Figure 10. Again, large amounts of addition caused surface salt deposits upon drying.

**Sodium ammonium phosphate addition -- fired state.** The one percent addition produced an R-4 bar free of surface scum deposits, however, it was badly strained by unequal deposition of soluble iron salts. Again, one half and one percent additions gave the best results with the M-4 bars. In all the bars having additions of one percent or more there was a cross sectional color variation due to the surface migration of iron salts. All scum free surfaces had a mottled finish. At cone 01, with both shales, there was a tendency to produce a spotty glazed coating. At cone 01 the color of the M-4 bars changed from the cone 07 salmon pink to a burnt brownish red.

Color and surface conditions produced by the sodium ammonium phosphate additions are shown in Figure 7.

**Ammonium nitrate addition -- unfired state.** Ammonium nitrate was hygroscopic and corrosive to the skin. Plastic shale reactions with the ammonium nitrate additions were similar to the previous mono-basic ammonium phosphate addition. Increasing the addition percent caused the shale to stiffen. See Figure 10. For additions in excess of one percent, salts were deposited on the surface during drying.
Figure 6. Effect of di-basic ammonium phosphate on color and surface condition.

Figure 7. Effect of sodium ammonium phosphate on color and surface condition.
Ammonium nitrate addition — fired state. The amount of scum formed on the R-4 bars increased as the percentage of ammonium nitrate increased. The effect on the M-4 bars was very similar except that at cone 01 there was a deepening of the red color.

Color and surface conditions for the ammonium nitrate additions are shown in Figure 8.

Ammonium chloride addition — unfired state. After the addition exceeded one quarter percent the shale stiffened very rapidly and with the two and three percent additions was very difficult to mold. See Figure 10. The ammonium chloride had a corrosive effect on the brass molds and the steel drying pallets. It was judged to be the poorest addition from the viewpoint of its effect on the working properties of the shale.

Ammonium chloride addition — fired state. As the amount of ammonium chloride added to the shale increased so did the amount of scum produced on both the R-4 and M-4 bars. At cone 01 there was an intensification of the red color in the M-4 bars. This was not noticed in the R-4 bars.

Color and surface conditions produced by the ammonium chloride additions are shown in Figure 9.

Validation of previous observations

To insure that these first results of the ammonium phosphates reducing the formation of surface scum were not accidental and were reproduced, a second set of bars was prepared. New samples of shale from the Rockford and Mason City shale pits were obtained. One half, three quarter and one
Figure 8. Effect of ammonium nitrate on color and surface condition.

Figure 9. Effect of ammonium chloride on color and surface condition.
Figure 10. Effect of additions on workability of shale tempered with twenty five percent water addition.
percent additions of mono-basic, di-basic and sodium ammonium phosphate were used. The bars were formed as described earlier.

The second sample of shales contained more soluble salts. The warmer summertime water also caused more of the soluble salt to be dissolved. The same relationship between percent addition and reduction of scum formation was observed in the second set of bars as with the first set. A reduction in the brightness of the fired color was the most noticeable difference. Chemical analysis showed that the second sample contained a higher calcia-magnesia content than the first samples. This would cause a bleaching of the red color and account for the reduction in brightness. The fired absorption values followed the same pattern as in the first test (vide infra).

Effect of an admixture of barium carbonate and ammonium phosphates on scumming

This study was done on the new samples of R-4 shales which had a higher carbonate content and showed severe scum formation. The bars were formed as previously outlined. Additions used were as follows: none, one pound per ton and three pounds per ton of barium carbonate. The barium carbonate amounts were mixed with one quarter and one half percent additions of mono-basic, di-basic and sodium ammonium phosphate. Bars were fired to cone 08, 04 and 01.

Results were as expected. The ammonium phosphate addition aided the barium carbonate in reducing the amount of scum formed. The best results obtained were with the high barium carbonate-high ammonium phosphate addition. The fired absorption was about the same as before
for the percent addition used.

It would seem that small additions of soluble ammonium phosphates could be made with the relatively insoluble barium carbonate to act as a scavanger to react with the sulfates that fail to react with the barium carbonate. Jackson (33) states that it is impossible to remove more than 85 percent of calcium sulfate from pure solution by barium carbonate in the aggregate condition. Sulfates in shales and clays are less likely to react completely with barium carbonate.

Color prints of the effects of the addition combinations are shown in Figures 11 through 13.

**Summary of effects of additions on surface conditions**

As is known, shales with a lower soluble salt content will require less chemical addition to prevent the formation of surface scum. For the M-4t shale the most beneficial addition of ammonium phosphates was one half percent, however, the R-4 shale required twice as much, one percent, for comparable results. The effects of the additions on the scum formation on R-4 and M-4 shale bars are summarized in Figures 14 and 15.

The most common ingredient causing white scum is calcium sulfate. When the ammonium bearing salt is added it reacts with the calcium sulfate to form ammonium sulfate and either a soluble or an insoluble compound. If the ammonium salt is added in excess a surface scum will be built up regardless of the solubilities of formed compounds. If an insoluble calcium compound is formed there exists an optimum range where no scum will occur on the surface. The ammonium sulfate formed is lost by volatization. If a soluble calcium salt is produced in the reaction
Figure 11. Scum reduction through the use of barium carbonate and mono-basic ammonium phosphate.

Pictured from left to right the shale treatments are:

None

1 lb/ton BaCO$_3$

3 lb/ton BaCO$_3$

1/4 % NH$_4$H$_2$PO$_4$ and 1 lb/ton BaCO$_3$

1/2 % NH$_4$H$_2$PO$_4$ and 1 lb/ton BaCO$_3$

1/4 % NH$_4$H$_2$PO$_4$ and 3 lb/ton BaCO$_3$

1/2 % NH$_4$H$_2$PO$_4$ and 3 lb/ton BaCO$_3$
Figure 12. Scum reduction through the use of barium carbonate and di-basic ammonium phosphate.

Pictured from left to right the shale treatments are:

None
1 lb/ton BaCO$_3$
3 lb/ton BaCO$_3$
1/4 % (NH$_4$)$_2$HPO$_4$ and 1 lb/ton BaCO$_3$
1/2 % (NH$_4$)$_2$HPO$_4$ and 1 lb/ton BaCO$_3$
1/4 % (NH$_4$)$_2$HPO$_4$ and 3 lb/ton BaCO$_3$
1/2 % (NH$_4$)$_2$HPO$_4$ and 3 lb/ton BaCO$_3$
Figure 13. Scum reduction through the use of barium carbonate and sodium ammonium phosphate.

Pictured from left to right the shale treatments are:

None
1 lb/ton BaCO₃
3 lb/ton BaCO₃
1/4 % NaNH₄HPO₄·bH₂O and 1 lb/ton BaCO₃
1/2 % NaNH₄HPO₄·bH₂O and 1 lb/ton BaCO₃
1/4 % NaNH₄HPO₄·bH₂O and 3 lb/ton BaCO₃
1/2 % NaNH₄HPO₄·bH₂O and 3 lb/ton BaCO₃
Figure 14. Effect of additions on formation of surface scum on shale R-1.
Figure 15. Effect of additions on formation of surface scum on shale H-4.
there is usually no reduction in the scum formation. The ammonium phosphates caused a reduction in the scum formation through the formation in insoluble calcium and magnesium phosphates as described previously.

The scum developed by the three percent addition of mono-basic ammonium phosphate was scraped off the unfired shale and the fired shale. X-ray and spectrographic analyses were made. The X-ray pattern of the unfired scum showed it to be mono-basic ammonium phosphate and shale. No ammonium sulfate was found, which was not surprising since a quantity of less than one percent in a mixture will be undetected unless it has an unusually strong X-ray peak.

No definite identification of the composition of the fired scum could be made. The X-ray equipment did not allow scanning below twenty degrees so that some of the identifying peaks were not obtained. Strong lines were obtained for quartz, alpha tridymite and alpha cristobalite. From the spectrographic analysis in Table 3 it appears that some form of calcium aluminum silicate should exist in the scum.

Two interesting things to note in the spectrographic analysis are the absence of the phosphorous line in the fired scum and the concentration of lead in the fired scum. The phosphorous can disappear in two ways, either by volatilization or migration into the fired shale.

Effects of Additions on Other Physical Properties

**Effect on fired absorption values**

Some of the additions had the annoying property of markedly increasing the porosity of the finished bars. The absorption determinations were made using the method outlined by the American Ceramic Society (34). One
Table 3
Spectrographic Analysis

<table>
<thead>
<tr>
<th>VS</th>
<th>S</th>
<th>M</th>
<th>W</th>
<th>T</th>
<th>FT*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Fe</td>
<td>Ti</td>
<td>Ba</td>
<td>Sn</td>
<td>Cu</td>
</tr>
<tr>
<td>Ca</td>
<td>Mg</td>
<td></td>
<td>Cr</td>
<td>Mn</td>
<td>K</td>
</tr>
<tr>
<td>Si</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ni</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Raw Shale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Si</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Unfired Scum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Ca</td>
</tr>
<tr>
<td>Si</td>
</tr>
</tbody>
</table>

* The letters refer to the intensity of the spectral lines of the elements: VS, very strong; S, strong; M, medium; W, weak; T, trace; FT, faint trace.

modification used was to evacuate the bars under vacuum instead of boiling them in water to remove the air from the pores. The percent absorption curves are shown in Figures 16 through 21.

The data obtained for cone 07 were used for comparative evaluation of the absorption figures since at cone 07 there was a minimum of glass formation. Additions of urea and sodium ammonium phosphate caused no change in the fired absorption. Additions of di-basic ammonium phosphate caused a slight increase in fired absorption. Additions of ammonium nitrate caused intermediate increases. Additions of mono-basic
Figure 16. Effect of urea on absorption.
Figure 17. Effect of mono-basic ammonium phosphate on absorption.
Figure 18. Effect of di-basic ammonium phosphate on absorption.
Figure 19. Effect of sodium ammonium phosphate on absorption.

PER CENT ADDITION

PER CENT ABSORPTION

R-4

Cone 01

Cone 07

M-4
Figure 20. Effect of ammonium nitrate on per cent absorption.
Figure 21. Effect of ammonium hydroxide on absorption.

PER CENT ADDITION

R-4

PER CENT ABSORPTION

Cone 0.1
Cone 0.7
M-4
ammonium phosphate and ammonium chloride produced the largest increase in fired absorption. The water of plasticity was held constant for all additions. There was a direct relationship between the increase in fired absorption and the decrease in workability or the ease with which the shale could be formed into a compact bar.

The Structural Clay Products Institute Research Foundation (30, p. 70) has reported that ammonium chloride additions in excess of three tenths of one percent caused a definite increase in the fired porosity. It was not stated whether this was found for an illitic or kaolinitic clay. The increase was attributed to the formation of a very fine pore system created by the loss of volatile compounds formed by the chloride. It is doubtful that this was the entire cause. Tables 4 and 5 are tabulations of the weight losses incurred while firing the shales to cone 07 with a two percent addition present, and the absorption changes brought about by this addition.

Note that urea, which is a volatile material but evidently very inert towards the clay mineral, has the third highest weight loss and had the least effect on the absorption. Mono-basic ammonium phosphate had a very small increase in weight loss but a very large increase in fired absorption. The presence of ammonium phosphate will cause some formation of high temperature compounds such as calcium and magnesium ammonium phosphates and calcium phosphates that are not volatile at cone 07. One should note that the addition of di-basic ammonium phosphate did not have the effect of increasing the fired absorption, even with more volatile ammonium present. For the above mentioned additions the only answer to
### Table 4
Fired Weight Losses and Absorption Changes for Shale R-4 at Cone 07

<table>
<thead>
<tr>
<th>Addition</th>
<th>Percent weight loss</th>
<th>Change in weight loss</th>
<th>Change in absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>12.33</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Urea</td>
<td>13.22</td>
<td>+0.89</td>
<td>-0.4</td>
</tr>
<tr>
<td>Mono-basic ammonium phosphate</td>
<td>12.70</td>
<td>+0.37</td>
<td>+5.3</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>12.61</td>
<td>+0.28</td>
<td>+0.6</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>12.33</td>
<td>0.00</td>
<td>+0.3</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>13.45</td>
<td>+1.12</td>
<td>+1.4</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>13.77</td>
<td>+1.14</td>
<td>+1.6</td>
</tr>
</tbody>
</table>

Their effects on the absorption lies in the reaction of these additions with the clay minerals. This will be further amplified by the viscosity curves in Figures 23 through 28.

The most plausible explanation is that the ammonium ion, and in the case of mono-basic ammonium phosphate, the hydrogen ion, act as floc- culation agents that cause the clay micelles to coalesce into loosely packed flocs. Hauser (35, p. 33) defines the term colloidal micelle as "a colloidal particle composed of its nucleus and all the ions and molecules which have been attracted to it." The nucleus would be a
Table 5
Fired Weight Losses and Absorption Changes for Shale M-4 at Cone 07

<table>
<thead>
<tr>
<th>Addition</th>
<th>Percent weight loss</th>
<th>Change in weight loss</th>
<th>Change in absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>10.73</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Urea</td>
<td>11.50</td>
<td>+0.82</td>
<td>-0.2</td>
</tr>
<tr>
<td>Mono-basic ammonium Phosphate</td>
<td>10.98</td>
<td>+0.25</td>
<td>+0.2</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>10.93</td>
<td>+0.20</td>
<td>+0.2</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>10.80</td>
<td>+0.07</td>
<td>+0.6</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>12.17</td>
<td>+1.14</td>
<td>+2.0</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>12.25</td>
<td>+1.52</td>
<td>+6.2</td>
</tr>
</tbody>
</table>

A single colloidal size clay particle. Surrounding ions and molecules would be the exchangeable or charge-counterbalancing ions and water molecules.

By varying the type and concentration of ions added to the shale the degree of coalescence into flocs may be varied. Large additions of ionizable salts will cause the flocs to agglomerate. During the formation of the flocs or agglomerates the colloidal clay particles are loosely packed causing an increase in the volume of the capillary pore system. This results in higher absorption values in the fired state.
Both the chloride and nitrate ion react with the impurities in the shale to form volatile chlorides and nitrates which are very soluble. Most of the formed soluble salt should concentrate on the surface and volatilize from there. Because of this high solubility according to the rules of crystallization it is possible for some of the chlorides or nitrates to crystallize within the shale. This could contribute some to the development of capillary pores, but not to the extent to produce the observed change in absorption. The reaction of the chemical salt with the clay mineral in the plastic state is the main cause of the formation of increased pore volume and absorption in the fired state.

**Effect on refractoriness**

Test pyrometric cones were prepared from the R-4 shale batches containing the three percent chemical additions. Cones were fired in a Denver Fire Clay P.C.E. furnace. Heat distribution in the furnace was checked before firing the test cones by firing a cone pat containing the same known cone in all locations. After a satisfactory heat distribution and heating schedule were worked out the test cones were fired.

Shale R-4, with no addition, had a P.C.E. somewhere between cone 6 and cone 8. It was difficult to bracket the P.C.E. any closer because of the fusion characteristics of the high carbonate shale. The glass formation was very rapid and of a low viscosity, causing the cone to slump and bloat instead of slowly bending over in a smooth arc.

The three percent addition of an ammonium phosphate salt decreased the refractoriness about one cone. This will vary with the shale depending upon the amount and composition of the glass originally formed.
in the untreated shale. The other ammonium salt additions had no apparent effect on the refractoriness. These observations are substantiated by the absorption curves in Figures 13 through 18. The decrease in refractoriness was caused by the fluxing action of the phosphorous oxide added. For shale R-4 additions under one percent will not affect refractoriness.

Effect on oxidation

Formation of nitrogen oxides. Ammonium salts are uniformly unstable with respect to heat. The nature of the thermal decomposition is dependent upon the anion present (36). Ammonium salts containing non-oxidizing anions (e.g. halides, CO$_3^{2-}$, S$^{2-}$) yield ammonia as one decomposition product. Ammonium salts containing oxidizing anions (e.g. NO$_2^-$, NO$_3^-$ and Cr$_2$O$_7^{2-}$) yield some oxidation product of ammonia, such as nitrogen or one of its oxides as one decomposition product.

After ammonia is formed it is possible for further combustion to take place. Barnett (37) lists the following oxidation equations for ammonia:

\[ \begin{align*}
\text{(1)} & \\
\text{(2)} & \\
\text{(3)} &
\end{align*} \]

Only the first reaction is of any commercial importance. A ferric oxide catalyst activated with bismuth oxide or with a mixture of bismuth and manganese dioxide is said to give a 95 percent conversion of ammonia-air mixtures at 700° C. into nitric acid. Such a catalyst is also effective at 300° C., but at this low temperature as much as 90 percent of the ammonia may be converted into nitrous oxide (N$_2$O).
Nitrous oxide is an oxidizing agent and Partington (38) states that it supports combustion more vigorously than air since on decomposition it yields a gas which is 33 percent oxygen by volume. With no catalyst present the decomposition begins at 520° C. and is complete at 900° C.

If any nitric oxide is formed it is immediately oxidized to nitrogen dioxide. Nitrogen dioxide has a strong pungent odor, an acid taste, and is extremely poisonous. During the firing of all test batches such conditions of smell and taste were noticed around the kiln during the oxidation period. Nitrogen dioxide is unstable and maintains an equilibrium condition with nitric oxide and oxygen:

\[ \text{NO}_2 \rightleftharpoons \text{NO} + \frac{1}{2} \text{O}_2 \]

According to Ephraim (39) colorless nitric acid had little or no effect on oxidizing sulfur, metals, etc. However if even a very little NO\(_2\) is introduced oxidation occurs immediately. In the ammonia equilibrium \[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \] there is a considerable quantity of free ammonia present in the range 300 to 500° C. If the decomposition of the ammonia is favored by the addition of a catalyst, the atomic nitrogen formed easily reacts with any oxygen present to form nitric oxide. However if any excess oxygen is present, nitric oxide can immediately pass into \text{NO}_2 and \text{N}_2\text{O}_4. Nitrogen dioxide yields at least one oxygen atom at fairly low temperatures and hence reacts under these conditions. Nitrogen dioxide has the ability to convert oxygen from its normal state into an activated state. The oxygen atom liberated reacts immediately and the energy released by its liberation serves to make the decomposition proceed more rapidly.
Nitrous oxide is the initial oxidation starter, probably followed by the effect of the nitrogen dioxide-nitric oxide equilibrium which converts ordinary oxygen atoms into energized oxygen atoms which are more reactive. All the materials necessary to form the catalyst are present in the shale, except the bismuth.

Oxidation conduct. An oxidation study was conducted for the addition of ammonium chloride, ammonium nitrate, mono- and di-basic ammonium phosphates at the one percent level. Test bars were machine formed. The bars were fired to 1200° F. and draw trials were made every 100° F. to check the oxidation progress. This was done by breaking the cooled bar and noting the loss displaced organic matter.

The one percent addition of ammonium chloride caused the oxidation to commence below 500° F., 200-300° F. lower than with no addition present. The oxidation began just below the surface and proceeded rapidly. At 700° F. the oxidation, or removal of dark material, appeared visually to be complete. None of the other additions showed any pronounced oxidation at this low temperature.

All shale bars containing the ammonium chloride addition showed two distinct color regions beneath the surface. Immediately below the surface existed a red band less than a quarter of an inch in thickness. The area inside of the band had the same buff color as the other bars. The red band formed below 500° F. and persisted during the remaining firing period. It was postulated that the red band was caused by the concentration of the ammonium chloride in the band region during the drying period. The reason why the low temperature oxidation should start just below the surface rather than at the surface can be explained
as follows. The ammonium chloride deposits on the surface have only one of their surfaces in contact with the shale material, which is catalyzing the ammonia breakdown and conversion into oxidizing nitrogen oxides. When ammonia is liberated from the surface it is liberated directly into the air without coming into contact with the catalytic material. If decomposition occurs beneath the surface the ammonia must work its way through the pore system of the shale and come into intimate contact with the catalytic material.

Up to 700° F. the ammonium phosphate additions caused no appreciable oxidation of the shale. Between 700° and 800° F. the shale appeared to become completely oxidized, at least the interior took on a uniform buff color.

The oxidation behavior of the ammonium nitrate addition was similar to that of the ammonium phosphates. Oxidation started slightly below 700° F. and appeared complete at 800° F. Ammonium nitrate has a melting point of 169.6° C. In the fused state the salt dissociates to give nitrogen dioxide and water. At this low temperature the oxidation reaction does not proceed rapidly and goes unnoticed. At 600° F. most of the ammonium salt is volatilized off and unable to react.

The oxidation began in the untreated shale shortly after 700° F. and was not completed until after 900° F.

All additions decreased the temperature range to bring about complete oxidation. Ammonium chloride was superior to all the other additions in oxidation conduct.

Loss of ammonia during firing. Using the standard Kjeldahl method (49, p. 538) the amounts of ammonia remaining in the shale at various
temperatures for the different additions were determined. The results
are shown in Figure 22. A blank run on the raw shale gave 0.03 percent
ammonia. At 900° F. all of the ammonia can be considered lost or com-
bined in such a manner as not to be released by this method of analysis.

Loss of sulfur during oxidation. To evaluate the effect of ammonium
compounds on the removal of sulfur the shale samples that had been fired
to 700° F. were analyzed for total sulfur content using the method out-
lined by Kolthoff and Sandell (40, p. 333). Seven hundred degrees was
selected because the ammonium chloride addition showed complete oxidation
but the others showed only the early stages of oxidation, if any. Each
addition had lost a large percentage of its ammonia content. The results
are shown in Table 6.

<table>
<thead>
<tr>
<th>Addition</th>
<th>Percent sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw clay (Unfired)</td>
<td>0.18</td>
</tr>
<tr>
<td>Raw clay (Fired)</td>
<td>0.17</td>
</tr>
<tr>
<td>1 % NH₄Cl</td>
<td>0.10</td>
</tr>
<tr>
<td>1 % NH₄NO₃</td>
<td>0.16</td>
</tr>
<tr>
<td>1 % NH₄H₂PO₄</td>
<td>0.24 (high)</td>
</tr>
<tr>
<td>1 % (NH₄)₂HPO₄</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Table 6
Sulfur Present at 700° F.
Figure 22. Ammonia content vs. temperature.
There appears to be no relationship between the total sulfur content and the loss of ammonia. There seems to be a definite relationship between the total sulfur content and the completeness of oxidation.

**Effect on viscosity of shale slips**

In the hand forming operation it was noted that different amounts of chemical additions varied the ease with which the shale could be formed into a satisfactory bar. An indication of the manner in which a chemical will affect a shale may be obtained by observing the viscosity changes an addition creates in the slip.

**Procedure.** Preliminary investigation showed that a slip prepared of 1000 grams of shale and 1000 mls. of distilled water was satisfactory; viscosity variations could be made over a wide range without changing the rotating speed of the Brookfield viscosimeter. The operation of this instrument has been reviewed by Oliver (41). The measurement observed and recorded was an apparent viscosity measurement. A definite operating procedure was outlined and rigorously adhered to. The procedure was as follows:

1. One thousand grams of shale, allowing for hygroscopic moisture, were weighed out to the nearest gram.
2. One thousand mls. of distilled water, allowing for hygroscopic moisture, were added to the shale.
3. The shale-water mixture was agitated and aged overnight to allow the shale-water system to approach equilibrium.
4. After aging, the slip was placed in a Hobart Kitchen
Aid mixer bowl, the chemical addition added and the slip was stirred with a wire whip beater at medium speed for five minutes. Ten and fifteen minutes were also tried. No advantage was found for the longer mixing times. An electric timing clock installed in the power circuit controlled the mixing time.

5. The chemicals were ground in a mortar and pestle to make them dissolve more easily in the slip. The additions were made in increments of one-tenth of one percent from zero to one percent or the viscosity range of the instrument's setting.

6. Immediately after mixing, the viscosity and pH measurements were made. Because of slight variations of viscosity measurements within the bowl, five readings, each in a different location, were taken and averaged. Spindle number four and rotation speed of six rpm were used.

The viscosity readings were obtained in the following manner. The first reading recorded was the maximum value at which the indicating needle started to rotate with the rotor. The second reading was arbitrarily selected as being the value indicated on the third revolution of the indicating needle. The difference between these two readings gave an indication of the thixotropic and dilatent properties of the slip. The values obtained were not reproducible to the absolute value, but the general nature of the curve produced was.

pH variations. A Leeds and Northrup pH meter was used for all pH
measurements. Only one addition, mono-basic ammonium phosphate caused any marked pH changes. An addition of one percent brought the pH to approximately 4.5. All other additions caused the pH to vary between 7 and 8 and all might be considered as neutral salts. The untreated shale slip had a pH of about 7.5 which would appear nominal for a high carbonate content shale. The pH curves are found with the viscosity curves in Figures 23 to 28.

**Effect of urea on viscosity.** The one percent addition had very little stiffening effect on the slip. Normally the untreated shale had a slight thixotropic tendency, that is, to become more fluid or decrease its viscosity when stirred. Urea caused the slip to become slightly dilatent or increase its viscosity while being stirred. This indicates the possibility that the untreated shale slip contains a small amount of surplus water loosely held to the charged clay particles. When the untreated slip was stirred and its structure changed from a closely packed one to a more loosely packed one these water molecules were released and became mobile water causing a decrease in the viscosity. However, when urea was added a very small amount of ammonia and NH$_4^+$ ions entered the water and became attached to the clay minerals. This reduced the tendency for the clay mineral to imbibe water. When any loosening of the structure occurred there was no reserve water to release and the increased friction of movement caused a viscosity increase.

The viscosity curve for urea is shown in Figure 23.

**Effect of mono-basic ammonium phosphate on viscosity.** There was no appreciable stiffening of the slip until after one-half percent addition. After one half percent, stiffening set in. The same dilatent property
Figure 23. Effect of urea on the viscosity of a shale slip and pH.
appeared as with urea. Additions up to one half percent should have little
effect on the workability of the shale.

The viscosity curve for mono-basic ammonium phosphate is shown in
Figure 24.

Effect of di-basic ammonium phosphate on viscosity. This addition
showed the typical rise and fall of the viscosity curve for a defloc-
culating material. After the addition exceeded two tenths of one percent
the viscosity remained constant until six tenths of a percent. This
would be the ideal working range for the addition. Beyond six tenths of
one percent the viscosity increased and the dilatent property of the slip
became more apparent.

The viscosity curve for di-basic ammonium phosphate is shown in
Figure 25.

Effect of sodium ammonium phosphate on viscosity. This addition
produced a typical sodium ion deflocculation curve. The initial region
of viscosity increase showed a thixotropic property, but the region of
minimum viscosity had a dilatent property. This addition would reduce
the amount of water required to produce a workable shale.

The viscosity curve for sodium ammonium phosphate is shown in
Figure 26.

Effect of ammonium nitrate on viscosity. A rapid increase occurred
in the viscosity after the addition exceeded three tenths of one percent.
The slip became extremely thixotropic. Significant readings on the
third revolution were difficult to obtain because a thin layer of water
gathered around the rotating spindle and almost any reading was possible.

The viscosity curve for ammonium nitrate is shown in Figure 27.
Figure 24. Effect of mono-basic ammonium phosphate on the viscosity of a shale slip and pH.
Figure 25. Effect of di-basic ammonium phosphate on the viscosity of a shale slip and pH.
Figure 26. Effect of sodium ammonium phosphate on the viscosity of a shale slip and pH.
Figure 27. Effect of ammonium nitrate on the viscosity of a shale slip and pH.

APPARENT VISCOSITY—POISES

Per cent addition

0.0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0

pH

300 400 500 600 700 800 900

1st Revolution

3rd Revolution
Effect of ammonium chloride on viscosity. The reaction was similar to that of ammonium nitrate except there was no noticeable formation of water around the spindle. Ammonium chloride caused extreme stiffening of the shale slip. Thixotropic properties were about the same as produced by ammonium nitrate.

The viscosity curve for ammonium chloride is shown in Figure 28.

Summary. When the concentration of lyophilic colloids is high in relation to the amount of water present it is possible for them to form gels. The nature of the anion present in the electrolyte will control the amount of water retained in the gel structure (10, p. 87). The salts affect this retention of water according to the Hofmeister anionic series: \( \text{SO}_4^{2-} \), \( \text{tartrate}^{2-} \), \( \text{citrate}^{3-} \) and \( \text{acetate}^{-1} \) inhibit the uptake of water whereas \( \text{Cl}^- \), \( \text{ClO}_3^- \), \( \text{NO}_3^- \), \( \text{Br}^- \), \( \text{I}^- \), and \( \text{CN}^- \) favor the retention of water in the gel formation, \( \text{Cl}^- \) having the least effect.

The thixotropic nature of the shale slip is controlled by the nature of the anion present. Anions which favor the imbibition of water, such as \( \text{Cl}^- \) and \( \text{NO}_3^- \), cause thixotropy. The phosphate ion (\( \text{HPO}_4^{2-} \)) inhibits the formation of gels and the imbibition of water as it produces dilatancy.

The presence of \( \text{NH}_4^+ \) flocculates the clay mineral. If one believes the hydration theory of deflocculation (25) the replacement of calcium and magnesium ions (hydrated radii 9.6 Å and 10.8 Å) by the ammonium ion (hydrated radius 5.37 Å) would cut the distance between adjacent clay mineral particles in half and thus reduce the deflocculated condition.

The writer firmly believes that ammonia (\( \text{NH}_3 \)) must be formed in the
Figure 28. Effect of ammonium chloride on the viscosity of a shale slip and pH.
water if an ammonium salt is to have a neutral or deflocculating effect. The only ammonium salt to have a deflocculant effect other than sodium ammonium phosphate was di-basic ammonium phosphate. This was the only ammonium addition to have the distinct odor of free ammonia at the forming temperature. Urea which slowly decomposes to form ammonia, water, and carbon dioxide had no appreciable effect on the viscosity.

**Effect on durability**

By durability one means how well the dry product will resist disintegration when constructed into a building and exposed to varying weather conditions. This has been the subject of much investigation (10, p. 854) but no one has yet arrived at conclusive tests that will evaluate this property. This work will not develop such a test either but it is believed that the following tests will give some indication as to how a fired product will perform.

1. Transverse strength.
2. Moisture expansion.
3. Absorption and C/B ratio.
4. Freezing and thawing tests.

**Preparation of test specimens.** All of the samples were prepared from the R-4 shale and all additions were at the one percent level. The water of plasticity was varied for the different additions to bring them to approximately the same working condition. The proper amount of water to add in each case was estimated by comparing the hand workability of the batches.

An attempt was made to evaluate the workability in terms of measured
values from a curve produced by a workability machine designed by Norton (h2). The machine uses a small hollow cylinder for a test specimen. When the chemical additions were present it was difficult to get the shale to join or knit back together after passing over the forming bridge in the die used to extrude the trial pieces. Failure to heal was especially noticeable with the additions that caused the shale to stiffen. When the cylinder was placed in the workability machine and torsion applied, the cylinder would split along the joint planes. The effect that certain ammonium salts had of decreasing the adhesion of the plastic shale should be given careful consideration if complex bridge designs are in use.

The measured water of plasticity used for the various additions is recorded in Table 7.

Table 7
Percent Water of Plasticity

<table>
<thead>
<tr>
<th>Addition</th>
<th>W.O.P.</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>22.2 %</td>
</tr>
<tr>
<td>NH₄Cl</td>
<td>27.4</td>
</tr>
<tr>
<td>NH₄H₂PO₄</td>
<td>25.3</td>
</tr>
<tr>
<td>NH₄NO₃</td>
<td>28.5</td>
</tr>
<tr>
<td>(NH₄)₂HPO₄</td>
<td>25.2</td>
</tr>
<tr>
<td>NaNH₄HPO₄·2H₂O</td>
<td>21.0</td>
</tr>
</tbody>
</table>
All shale batches were aged for twenty four hours before being formed into cylindrical bars. All bars were extruded using a modified Hobart Kitchen Aid meat grinder. No desairing was done. Twenty bars each, six inches long, were extruded for each addition and dried. Ten bars were fired at cone 07 and ten bars at cone 02. Cone 07 is about the normal firing of the shale, whereas cone 02 is about the maximum firing. The heating rate was the same as used previously for firing test bars.

Randomization of bars. The bars used for each temperature were selected at random. This was done by placing twenty numbered balls in a jar, drawing out one ball at a time, recording the number, then replacing the ball in the jar before drawing the next ball. This was repeated until ten different numbers were drawn from the jar. These ten numbers were assigned to cone 07. The remaining ten numbers were assigned to cone 02. The procedure was repeated for each batch. After the kiln had cooled the bars were removed. Each batch was randomly divided into two groups and stored in desiccators. One group was broken in the dry state. The other group was broken after being autoclaved.

Transverse strength. All bars were broken on a Dillon testing machine using a five inch span and a 0.05 inch per minute rate of travel or 2000 lb./min. rate of loading.

An analysis of variance was performed on the transverse strength data obtained and the results are shown in Table 8. The recorded data and calculation methods are shown in Appendix B.

The analysis of variance table shows that for the shale R-14 only additions and temperature had any significant effect on the fired
Table 8  
Analysis of Variance for Transverse Strength for R-4

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>Variance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between additions</td>
<td>5</td>
<td>23,029,924</td>
<td>4,605,985</td>
<td>27.4*</td>
</tr>
<tr>
<td>Between temperatures</td>
<td>1</td>
<td>10,137,196</td>
<td>10,137,196</td>
<td>60 *</td>
</tr>
<tr>
<td>Between moistures</td>
<td>1</td>
<td>18,130</td>
<td>18,130</td>
<td>0.11</td>
</tr>
<tr>
<td>Interactions</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Addition x temperature</td>
<td>5</td>
<td>5,660,333</td>
<td>1,132,069</td>
<td>6.80*</td>
</tr>
<tr>
<td>Addition x moisture</td>
<td>5</td>
<td>1,314,620</td>
<td>262,924</td>
<td>1.57</td>
</tr>
<tr>
<td>Moisture x temperature</td>
<td>1</td>
<td>619,436</td>
<td>619,436</td>
<td>3.69</td>
</tr>
<tr>
<td>Addition x moisture x temperature</td>
<td>5</td>
<td>1431,967</td>
<td>86,393</td>
<td>0.54</td>
</tr>
<tr>
<td>Residual</td>
<td>96</td>
<td>16,113,197</td>
<td>167,845</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>119</td>
<td>57,324,813</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Significant at the 0.01 level. For the 0.01 level $F_{5,96}^{0.01} = 3.24$, $F_{1,96}^{0.01} = 6.94$. 
transverse breaking strength. The only significant interaction was between temperature and additions. The presence of moisture in the fired body had no effect on the breaking strength.

Since the analysis of variance shows that there was a significant difference between the additions the question arises as to which additions caused the difference. The average transverse breaking strengths are shown in Table 9.

The additions that caused the significant differences can best be evaluated by a comparison with the over-all addition average values using the no-addition average value as the comparison standard. Such a comparison would have a "t" distribution (see Appendix B). A slight bias may exist when numerous means are compared with a standard or control mean. It is possible, due to chance alone, to have a control mean that may be very high or very low. If this happens, the resulting calculated "t" value will either be accepted or rejected more often than it should. The probability of such an event occurring is usually quite small, so the application of the common "t" distribution is justified. If the calculated "t" value exceeds the tabulated "t" value the difference between the two means has usually not occurred because of chance variations but rather because of an assignable cause. The calculated "t" values are tabulated in Table 10.

Significant reductions in the transverse strength values were obtained for one percent additions of di-basic ammonium phosphate, ammonium nitrate and ammonium chloride.

It should be pointed out that in using the over-all condition averages in the comparison that in some cases increases and decreases
Table 9

Average Transverse Breaking Strength (psi) for R-4

<table>
<thead>
<tr>
<th></th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>No addition</td>
<td>Dry Auto-claved</td>
<td>Dry Auto-claved</td>
<td>Dry Auto-claved</td>
<td>Dry Auto-claved</td>
<td>Dry Auto-claved</td>
</tr>
<tr>
<td>Cone 07</td>
<td>1643</td>
<td>1593</td>
<td>1422</td>
<td>1372</td>
<td>1123</td>
</tr>
<tr>
<td>Cone 02</td>
<td>2125</td>
<td>2320</td>
<td>1633</td>
<td>2190</td>
<td>1671</td>
</tr>
<tr>
<td>Combined</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>temperature</td>
<td>1884</td>
<td>1957</td>
<td>1528</td>
<td>1782</td>
<td>1397</td>
</tr>
<tr>
<td>Over-all</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>conditions</td>
<td>1921</td>
<td>1655</td>
<td>1469</td>
<td>1909</td>
<td>980</td>
</tr>
</tbody>
</table>
Table 10

Values of "t" for Transverse Strength Comparisons

<table>
<thead>
<tr>
<th>Addition</th>
<th>&quot;t&quot; value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-basic ammonium phosphate</td>
<td>2.05</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>3.51*</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>0.09</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>7.30*</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>8.88*</td>
</tr>
</tbody>
</table>

* Significant values "t" (0.01) (96) = 2.64

have balanced each other out to give an over-all test of no significance for a main effect. For example, moisture conditions showed no significance yet in comparing the two average breaking strengths at cone 07 for the sodium ammonium phosphate addition it is apparent that the moisture reduced the average transverse breaking strength by almost fifty percent from a dry average strength of 1519 psi to a moist average strength of 860 psi. Other additions showed enough of an increase in their moist-strength values to mask this important difference.

Summation tables in Appendix B show that the total breaking strengths for dry bars and moist bars are almost equal.

Moisture expansion. The change in length due to moisture expansion was determined on half of the fired bars. After the moisture expansion data were obtained the bars were broken to obtain the transverse strength
values for moist or autoclaved bars, using the same equipment and procedure as with the dry bars.

Half the fired bars were autoclaved at 150 psi (gauge pressure) for one and one-half hours. There were too many bars for a single run so they were randomly split into two groups. After being autoclaved the bars were cooled overnight in the autoclave, then removed and placed in a humidity chamber until the moisture expansion measurements were determined.

Measurements were made with vernier Gaertener measuring telescopes. While in the plastic state the bars were marked with two parallel reference (+) marks. These were taken as the reference marks for the expansion measurements. Distances were measured in the dry fired state and in the moist fired state. The distance was measured from inside groove to inside groove. The dry length was used as the basis for all calculations. Considerable trouble was encountered with parallax and no degree of reliability will be placed on the measurements. The moisture expansion data, recorded as percent change in length, will be found in Appendix B.

The moisture expansion data were evaluated by the analysis of variance method. The results are shown in Table 11. Both temperature and additions had a significant effect on the moisture expansion. There also was a definite interaction between additions and firing temperature.

The average moisture expansion values are shown in Table 12. Applying the "t" test for comparing the average moisture expansion of the shale containing additions with the untreated shale the "t" values shown in Table 13 were obtained.
## Table 11

Analysis of Variance for Moisture Expansion for R-4

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>Variance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between additions</td>
<td>5</td>
<td>883</td>
<td>176.6</td>
<td>9.19*</td>
</tr>
<tr>
<td>Between temperatures</td>
<td>1</td>
<td>799</td>
<td>799</td>
<td>4.1 *</td>
</tr>
<tr>
<td>Temperature x addition</td>
<td>5</td>
<td>420</td>
<td>84</td>
<td>4.42*</td>
</tr>
<tr>
<td>Residual</td>
<td>48</td>
<td>920</td>
<td>19.2</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>59</td>
<td>3022</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Significant at the 0.01 level. For the 0.01 level $F_{5,48}^{5} = 3.44$, $F_{5,48}^{1} = 7.22$. 
Table 12
Average Percent Moisture Expansion for R-4

<table>
<thead>
<tr>
<th></th>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone 07</td>
<td>0.13</td>
<td>0.17</td>
<td>0.11</td>
<td>0.24</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>Cone 02</td>
<td>0.05</td>
<td>0.03</td>
<td>0.06</td>
<td>0.10</td>
<td>0.11</td>
<td>0.04</td>
</tr>
<tr>
<td>Combined average</td>
<td>0.09</td>
<td>0.10</td>
<td>0.085</td>
<td>0.17</td>
<td>0.115</td>
<td>0.045</td>
</tr>
</tbody>
</table>
Table 13

Values of "t" for Moisture Expansion Comparisons

<table>
<thead>
<tr>
<th>Addition</th>
<th>&quot;t&quot; value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-basic ammonium phosphate</td>
<td>2.19</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>1.70</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>19.4*</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>5.5*</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>12.0*</td>
</tr>
</tbody>
</table>

* Significant values  "t" (0.01) (t8) = 2.68

Ammonium nitrate and sodium ammonium phosphate caused an increase in moisture expansion, but ammonium chloride caused a decrease in moisture expansion.

The shale fired to cone 07 containing one percent sodium ammonium phosphate showed a moisture expansion almost twice that of the untreated shale. At cone 02 the expansion decreased but was still greater than for the untreated shale. This was attributed to the fact that at cone 07 a small amount of simple sodium silicate glass formed acting as part of the bonding matrix. The sodium silicate hydrated in the presence of moisture, causing slight expansion and weakening of the glassy bond. Firing to cone 02 formed a complex silicate glass which resisted hydration. Such a postulation helps explain the loss in transverse strength observed between the dry and moist conditions for the sodium
ammonium addition fired at cone 07.

**C/B ratio.** The C/B ratio test was designed to give some estimation of the reserve volume of pore space in a bar. The C/B ratio is the ratio of the absorption obtained by soaking for 24 hours in water at room temperature to the absorption obtained by soaking in boiling water for five hours. The C/B values were obtained for the unautoclaved bars. The recorded data may be found in Appendix B. An analysis of variance was made on the data and the results are shown in Table 14. Both temperature and additions had a significant effect on the C/B values. There was no significant interaction between temperature and additions.

The average C/B ratios are shown in Table 15. Applying the "t" test for comparing the average C/B ratio for the shale containing additions with the untreated shale the "t" values shown in Table 16 were obtained. All additions except sodium ammonium phosphate significantly reduced the C/B ratio.

**Freezing and thawing.** The unautoclaved bars, on which the C/B ratios were obtained, were subjected to a freezing and thawing test. The bars were thoroughly dried because they had been previously saturated with boiling water. The boiling water fills the smaller pores not normally filled by soaking in room temperature water. Frost resistance is believed to be due in part to a reserve volume of empty small pores into which the ice can expand. After being thoroughly dried the bars were soaked for 48 hours in water at room temperature. The saturated bars were placed vertically in enameled pans. About one inch of water was placed in the pan with the bars. The pan and its contents were placed in a General Electric deep freezer. The freezing-thawing cycle
### Table 14

**Analysis of Variance for the C/B Ratio for R-4**

<table>
<thead>
<tr>
<th>Source</th>
<th>Degrees of freedom</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>Variance ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Between additions</td>
<td>5</td>
<td>84.8</td>
<td>169.6</td>
<td>16.3%</td>
</tr>
<tr>
<td>Between temperatures</td>
<td>1</td>
<td>47.6</td>
<td>47.6</td>
<td>45.9%</td>
</tr>
<tr>
<td>Temperature x additions</td>
<td>5</td>
<td>151</td>
<td>30.3</td>
<td>2.93</td>
</tr>
<tr>
<td>Residual</td>
<td>48</td>
<td>498</td>
<td>10.4</td>
<td></td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>59</strong></td>
<td><strong>1973</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Significant at the 0.01 level. For the 0.01 level $F_{5,48}^0 = 3.44$, $F_{1,48}^1 = 7.22$.\*
Table 15
Average C/B Ratio for R-1

<table>
<thead>
<tr>
<th></th>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>One percent</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone 07</td>
<td>0.964</td>
<td>0.882</td>
<td>0.905</td>
<td>0.944</td>
<td>0.932</td>
<td>0.898</td>
<td></td>
</tr>
<tr>
<td>Cone 02</td>
<td>0.932</td>
<td>0.828</td>
<td>0.826</td>
<td>0.938</td>
<td>0.828</td>
<td>0.824</td>
<td></td>
</tr>
<tr>
<td>Combined average</td>
<td>0.948</td>
<td>0.855</td>
<td>0.865</td>
<td>0.941</td>
<td>0.880</td>
<td>0.866</td>
<td></td>
</tr>
</tbody>
</table>
Table 16
Values of "t" for C/B Ratio Comparison

<table>
<thead>
<tr>
<th>Addition</th>
<th>&quot;t&quot; value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mon-basic ammonium phosphate</td>
<td>7.1*</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>6.4*</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>0.54</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>5.1*</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>6.2*</td>
</tr>
</tbody>
</table>

* Significant values "t" (0.01) (6) = 2.68

consisted of twenty hours of freezing at a temperature of -15° F., and four hours of thawing by submersion in a tank of running water. The procedure was repeated for fifty cycles. No cracking of the bars appeared until after forty cycles had been completed. Small chips started to spall off after the seventh cycle. A summary of the effect of the freezing and thawing test is given in Tables 17 and 18.

None of the bars fired to cone 02 showed any visible spall marks. For some additions the weight loss at cone 02 recorded in Table 18 was as high as the weight loss for cone 07. The hydration of the free lime in the cone 07 bars would decrease the apparent weight loss. Bars containing the sodium ammonium phosphate addition and fired to cone 07 showed a net weight gain. This helps to substantiate the hypothesis that the sodium present formed a simple silicate glass which hydrates.
Table 17
Visual Comparison of Disintegration of Bars at End of Freezing and Thawing Test

<table>
<thead>
<tr>
<th>Addition</th>
<th>Cone 07</th>
<th>Cone 02</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Splitting and spalling</td>
<td>No damage</td>
</tr>
<tr>
<td>Mono-basic ammonium phosphate</td>
<td>Spalling</td>
<td>No damage</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>Splitting and spalling</td>
<td>No damage</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>Splitting, No spalling</td>
<td>No damage</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>Moderate spalling</td>
<td>No damage</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>Severe spalling on one bar. None on remaining.</td>
<td>No damage</td>
</tr>
</tbody>
</table>

Table 18
Weight Change in Grams for Five Bars at the End of the Freezing and Thawing Test

<table>
<thead>
<tr>
<th>Addition</th>
<th>Cone 07</th>
<th>Cone 02</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>-2.52</td>
<td>-1.38</td>
</tr>
<tr>
<td>Mono-basic ammonium phosphate</td>
<td>-3.03</td>
<td>-1.38</td>
</tr>
<tr>
<td>Di-basic ammonium phosphate</td>
<td>-1.22</td>
<td>-1.27</td>
</tr>
<tr>
<td>Sodium ammonium phosphate</td>
<td>+1.44</td>
<td>-0.88</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>-2.04</td>
<td>-2.00</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>-3.42</td>
<td>-1.57</td>
</tr>
</tbody>
</table>
All of the spalling started below the frozen water level. The spalling behavior was the same on all spalled bars. The surface skin of aligned clay mineral particles peeled off as though there was a plane of weakness present in the bars fired to cone 07. Areas of heavy salt concentration were more susceptible to spalling than the clean surfaces. Some of the spalling of the bars fired to cone 07 was due to the expansion of free lime beneath the surface.

The only generalization is that high strength, low C/B ratio and good reaction between free lime and the shale material are necessary to produce a frost resistant fired product. For the shale R-4 this can best be accomplished by increasing the firing temperature to about cone 02.

**Effect on hydration of free lime**

From the visual inspection of the bars that were autoclaved and those subjected to the freezing and thawing test no difference could be observed in the reduction of hydrated lime spots. Ammonium additions did not reduce the ability of the free lime to hydrate. Increasing the degree of shale maturity from cone 07 to cone 02 substantially reduced the reaction occurring between free lime and water vapor.
SUMMARY AND CONCLUSIONS

The effects of additions of urea, mono-basic ammonium phosphate, di-basic ammonium phosphate, sodium ammonium phosphate, ammonium nitrate and ammonium chloride on a high carbonate content illitic shale (with chlorite) were investigated. The following conclusions have been drawn:

1. Additions of ammonium phosphate compounds of one-half to one percent were able to reduce the formation of surface scum.

2. Ammonium phosphates have a definite possibility for use as a scavenger material to aid barium carbonate in reducing surface scum formation.

3. Additions of urea, di-basic ammonium phosphate or sodium ammonium phosphate which have a neutral or deflocculating effect on the clay minerals have the least effect on fired absorption.

4. Additions of mono-basic ammonium phosphate, ammonium nitrate or ammonium chloride which flocculate the clay minerals cause an increase in the fired absorption.

5. Mono-basic ammonium phosphate has the ability to reduce the plasticity of an illitic shale without producing a surface scum problem.

6. The increase in fired porosity caused by mono-basic ammonium phosphate, ammonium chloride and ammonium nitrate was mainly due to the clay mineral-ammonium
salt reaction, nor to the loss of volatile compounds.

7. One percent additions of ammonium chloride, ammonium nitrate or di-basic ammonium phosphate cause a decrease in dry fired strength.

8. Ammonium chloride causes oxidation to begin around 500°F, due to the formation of nitrogen oxides that react with the sulfides and organic matter.

9. All the ammonium additions shorten the time and reduce the temperature required for the oxidation to become complete.

10. A one percent addition of any of the chemicals used had no effect on reducing the hydration of free lime in bars fired to cone 07.

11. Firing to cone 02 reduces the formation of free lime spots. The mature firing fosters a better reaction between the lime and the constituents of the shale.

12. Bars of R-4 shale fired to cone 02 withstand fifty cycles of freezing and thawing without any disintegration. Bars fired to cone 07 show cracking and spalling. Only the one percent addition of ammonium chloride shows any improvement in frost resistance at cone 07.

13. For the ammonium salts studied the nature of the anion present controls whether the slip will have a thixotropic or dilatent property.

The following conclusions are believed to have some justification
but more work would be necessary to substantiate them.

1. It may be harmful to add a sodium deflocculant to a shale
   that has a minimum of glass bonding material present.
   The sodium present reacts to form a simple sodium silicate
   glass which will decompose in the presence of moisture and
   reduce the fired strength of the shale.

2. Deflocculation with ammonium salts is brought about by the
   presence of ammonia (NH₃), not the ammonium ion (NH₄⁺).

3. Ammonium salts reduce the adhesion power between plastic
   shale particles.
BIBLIOGRAPHY

1. They have reduced black coring with ammonium chloride; Alton Brick Co. Brick and Clay Rec. 126: (2) 40-41. 1955.


ACKNOWLEDGEMENTS

The author wishes to thank The Edward Orton Jr. Ceramic Foundation, Columbus, Ohio for granting the fellowship which supported the work; the Mason City Brick and Tile Company and the Rockford Brick and Tile Company for supplying the shale samples; Professor G. M. Dodd for his direction and encouragement of the work and Wayne Calderwood for his assistance in obtaining X-ray and spectrographic data.
APPENDICES
APPENDIX A

Rapid Determination of Calcium and Magnesium in Shales

Elaborate or expensive equipment is not actually necessary to carry out this method of analysis. Chemical solutions of known strength may be purchased from chemical supply houses. For routine quality control work a good side balance will be accurate enough for weighing out the samples of shale. The following is a list of the standard solutions needed and how to prepare them.

Preparation of solution used

**Indicator (F2hl).** Weigh out 0.1 gm. of reagent-grade Erichrome Schwartz T(F2hl) and dissolve in 20 ml. of alcohol. This indicator is rather unstable in the liquid form and should be prepared frequently. When an excessive amount of indicator is required to produce an end point color change the indicator is starting to decompose and should be replaced.

**Buffer solution.** Dissolve 6.75 gm. of NH₄Cl in 57 ml. of concentrated NH₄OH and dilute to 100 mls. The pH should be just above 10. This solution should also be prepared in small quantities to insure freshness. If the pH falls below 10 the end-point reaction will not be sharp, but rather a foggy transition of color.

**Standard calcium carbonate solution.** Dissolve 1.000 gm. of high purity\(^1\) CaCO\(_3\) (c.p. is not pure enough) in a little dilute HCl. Dilute

---

\(^1\)Available from Merick Chemical Company.
to exactly one liter and store in a stoppered bottle. One ml. of this solution will contain 1.00 milligram of CaCO₃.

Standard sodium versenate solution. Dissolve 5.00 gms. of versenate¹ and 0.125 gm. of MgCl₂·6H₂O in one liter of water and mix well. If the distilled water is slightly on the acid side, pH 5-6, it is advisable to add enough sodium hydroxide to the water to bring the pH up to 7, otherwise the sodium versenate will revert to a hydrogen versenate which is insoluble in water.

Murexide indicator. Mix 40 gms. of powered potassium sulfate and 0.2 gm. of murexide.² This indicator is used in the dry condition.

Standardization of versenate solution. Put into a glazed white casserole pipette 25.00 mls. of standard calcium carbonate solution, add 2.0 mls. of buffer solution and 6 drops of F2H4 indicator. Titrate with the versenate solution to the light blue end-point. Dividing the 25 mg. of calcium carbonate by the number of ml. of versenate required for the titration give the equivalent of calcium carbonate in terms of one ml. of versenate. It is easier to calculate the equivalent of magnesium carbonate than to prepare a standard solution. The calculation is done as follows:

\[
\text{Equivalent of CaCO}_3 \times \frac{83.34}{100.09} = \text{Equivalent of MgCO}_3.
\]

¹Available from Hach Chemical Company, Ames, Iowa.

²Source, Eastman Kodak Company.
Digestion of shale

1. Weigh out 0.5 grams of shale.
2. Digest with 25 mls. of 1:1 HCl and evaporate to dryness.
3. Add 25 mls. of distilled water and redissolve the soluble salts.
4. Add a few drops of 1:1 NH₄OH to bring the pH to 7. This will precipitate most of the soluble iron as iron hydroxide.
5. Filter the solution through a double layer of No. 40 Whatman filter paper using a Buchner filter.
6. Wash the precipitate and filter paper with 1 percent NH₄NO₃ solution.
7. Dilute the filtrate to a convenient amount, usually 250 mls.

Determination of calcium carbonate

1. Pipette out 25 mls. of solution.
2. Add 2 mls. of 20 percent NaOH.
3. Add 20-30 mg. of prepared murexide indicator.
4. Titrate with standard versenate to violet end-point.
5. Calculate percent calcium present as calcium carbonate as follows:

\[
\frac{(\text{CaCO}_3 \text{ eq. of versenate}) \times (\text{mls of versenate})}{10} \times 100
\]

Determination of magnesium carbonate

1. Pipette out 25 mls. of solution.
2. Add 3 mls. of buffer solution, bringing pH above 10.
3. Add 10 mg. of NaCN to tie up any remaining soluble iron.
4. Add 6 drops F241 indicator.
5. Titrate with standard versenate solution to a light blue end-point.

6. Calculate percent magnesium present as magnesium carbonate as follows:

Since the F2H1 indicator does not change color until all of the calcium and magnesium have reacted with the versenate it will be necessary to subtract the number of mls. of versenate used to determine the calcium found in the previous section.

Total mls. required for the F2H1 end-point minus the mls. required for the murexide end-point gives the mls. reacting with the magnesium.

\[
\frac{(\text{MgCO}_3 \text{ eq. of versenate}) \times (\text{mls. of versenate}) \times 10}{\text{weight of sample}} \times 100
\]

The amounts found by this method may be slightly lower than those found by the regular fusion method for shale. This method does not react with the calcium or magnesium ions that may be tied up internally in the clay minerals structure. It does, however, give a very reliable estimate of the quantity of magnesium and calcium present as accessory minerals or impurities.
APPENDIX B

Data and Sample Calculations

The transverse breaking strength was determined on cylindrical bars. Distance between supports was five inches. Transverse strength in psi was calculated according to the following formula:

\[
M = \frac{8PL}{\pi d^3}
\]

\[M = \text{modulus of rupture psi}\]
\[P = \text{load in pounds at rupture}\]
\[L = \text{distance between supports in inches}\]
\[d = \text{diameter of specimen in inches}\]
\[\pi = 3.14\]

The calculated transverse breaking strength data are recorded in Table 19.

To apply the analysis of variance it is necessary to calculate the sum of squares for the various effects and their combinations. It helps to visualize the calculations for the sum of squares if sub-tables of the main table are constructed. Sub-table 19-a for addition was formed by summing all the data for each addition and recording it in the proper column. Sub-table 19-b for temperature was formed by summing all the data for each temperature. Sub-table 19-c for moisture condition was formed by summing all the data for each moisture condition. Sub-table 19-d for temperature-additions was formed by summing the proper temperature-addition combinations. Sub-table 19-e for addition-moisture condition was formed by summing the proper temperature-moisture condition
Table 19

Transverse Breaking Strength – psi

<table>
<thead>
<tr>
<th>Firing cone</th>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Auto-claved</td>
<td>Dry</td>
<td>Auto-claved</td>
<td>Dry</td>
<td>Auto-claved</td>
</tr>
<tr>
<td>Cone 07</td>
<td>1560</td>
<td>1601</td>
<td>1630</td>
<td>1242</td>
<td>1241</td>
<td>1301</td>
</tr>
<tr>
<td></td>
<td>2020</td>
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<td>895</td>
<td>1359</td>
<td>866</td>
<td>606</td>
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<td>1644</td>
<td>1358</td>
<td>1271</td>
<td>1604</td>
<td>2193</td>
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<td>1616</td>
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<td></td>
<td>1617</td>
<td>1674</td>
<td>1493</td>
<td>1372</td>
<td>910</td>
<td>1113</td>
</tr>
<tr>
<td>Cone 02</td>
<td>1140</td>
<td>2568</td>
<td>1530</td>
<td>2093</td>
<td>1995</td>
<td>2365</td>
</tr>
<tr>
<td></td>
<td>1939</td>
<td>1301</td>
<td>1662</td>
<td>2730</td>
<td>1316</td>
<td>1933</td>
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<td>1490</td>
<td>2740</td>
<td>1662</td>
<td>2280</td>
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<td>2660</td>
<td>2611</td>
<td>1802</td>
<td>1674</td>
<td>1360</td>
<td>856</td>
</tr>
<tr>
<td></td>
<td>2225</td>
<td>2220</td>
<td>2083</td>
<td>1718</td>
<td>2024</td>
<td>1890</td>
</tr>
</tbody>
</table>

Grand Total = 174,027
### Sub-table 19-a

**Summation for Additions**

<table>
<thead>
<tr>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>38,040</td>
<td>29,285</td>
<td>38,171</td>
<td>19,597</td>
<td>15,480</td>
</tr>
</tbody>
</table>

### Sub-table 19-b

**Summation for temperature**

- Cone 07: 67,575
- Cone 02: 10,552

### Sub-table 19-c

**Summation for Moisture Condition**

- Dry: 86,276
- Autoclaved: 87,751
### Sub-table 19-d

**Summation for Temperature x Addition**

<table>
<thead>
<tr>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone 07</td>
<td>16,180</td>
<td>13,968</td>
<td>11,624</td>
<td>11,893</td>
<td>8,258</td>
</tr>
<tr>
<td>Cone 02</td>
<td>22,224</td>
<td>19,122</td>
<td>17,661</td>
<td>26,278</td>
<td>11,339</td>
</tr>
</tbody>
</table>

### Sub-table 19-e

**Summation for Additions and Moisture Condition**

<table>
<thead>
<tr>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>18,837</td>
<td>15,275</td>
<td>13,974</td>
<td>21,168</td>
<td>9,641</td>
</tr>
<tr>
<td>Autoclaved</td>
<td>19,567</td>
<td>17,815</td>
<td>15,311</td>
<td>17,005</td>
<td>9,956</td>
</tr>
</tbody>
</table>
Sub-table 19-f

Summation for Temperature x Moisture Condition

<table>
<thead>
<tr>
<th></th>
<th>Dry</th>
<th>Autoclaved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone 07</td>
<td>36,575</td>
<td>33,000</td>
</tr>
<tr>
<td>Cone 02</td>
<td>49,701</td>
<td>54,751</td>
</tr>
</tbody>
</table>

Sub-table 19-g

Summation for Temperature x Addition x Moisture Condition

<table>
<thead>
<tr>
<th></th>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dry</td>
<td>Autoclaved</td>
<td>Dry</td>
<td>Autoclaved</td>
<td>Dry</td>
<td>Autoclaved</td>
</tr>
<tr>
<td>Cone 07</td>
<td>8213</td>
<td>7917</td>
<td>7108</td>
<td>6860</td>
<td>5617</td>
<td>6007</td>
</tr>
<tr>
<td>Cone 02</td>
<td>10624</td>
<td>11600</td>
<td>8167</td>
<td>10955</td>
<td>8357</td>
<td>9304</td>
</tr>
</tbody>
</table>
combinations. Sub-table 19-g for addition-temperature-moisture condition was formed by summing the addition-temperature-moisture condition combinations. All the numerical results of the calculations for the sum of squares are in the analysis of variance Table 8, page 69. All summations in the calculations of the sum of squares are divided by the number of terms that formed the sum of the numbers in the table used.

Total sum of squares is calculated from the data in the Table 16.

\[(1506)^2 + \ldots + (664)^2 - \frac{(174,027)^2}{120} = \text{TSS}\]

The term \(\frac{(174,027)^2}{120}\) is a correction for the mean. It appears in all sum of squares and hereafter will be called C.

Addition sum of squares using the data in Sub-table 16-a.

\[\frac{(38,404)^2 + \ldots + (15,480)^2}{20} - C = \text{SSA}\]

Temperature sum of squares using the data in Sub-table 16-b.

\[\frac{(69,575)^2 + (104,452)^2}{60} - C = \text{SST}\]

Moisture condition sum of squares using the data in Sub-table 16-c.

\[\frac{(86,276)^2 + (87,751)^2}{60} - C = \text{SSM}\]

Temperature x addition interaction sum of squares using the data in Sub-table 16-d.

\[\frac{(16,180)^2 + \ldots + (7828)^2}{10} - C = \text{SST - SSA} = \text{SST x A}\]

Addition x moisture interaction sum of squares using data in Sub-table 16-e.

\[\frac{(18,837)^2 + \ldots + (8,097)^2}{10} - C = \text{SSA - SSM} = \text{SSA x M}\]
Temperature x moisture interaction sum of squares using date in Sub-table 16-f.

\[
\frac{(36,575)^2 + \ldots + (54,751)^2}{30} - C - \text{SST} - \text{SSM} = \text{SS M x T}
\]

Addition x moisture condition x temperature interaction sum of squares using data in Sub-table 16-g.

\[
\frac{(8213)^2 + \ldots + (3953)^2}{5} - C - \text{SSA} - \text{SST} - \text{SSM} - \text{SS A x T} - \\
\text{SS A x M} - \text{SS M x T} = \text{SS A x T x M}.
\]

The residual sum of squares was found by difference. All the sub-group sum of squares are totaled and subtracted from the total sum of squares.

The mean squares values were formed by dividing the sum of squares by its degrees of freedom.

The variance ratios for this particular case were formed by dividing the mean square of the attributal factor by the mean square of the residual. The variance ratio has an F distribution with corresponding degrees of freedom. A more detailed explanation of statistical methods may be found in statistical analysis and methods textbooks (43).

The "t" test was used earlier as a method of testing whether an addition had caused a significant change in the observed values. The formula used was

\[
"t" = \frac{X_a - X_b}{S\left(\frac{1}{n_a} + \frac{1}{n_b}\right)^{1/2}}
\]

- \(X_a\) mean of values of a
- \(X_b\) mean of values of b
\[ n_a \text{ number of observations of a} \]
\[ n_b \text{ number of observations of b} \]
\[ S \text{ standard deviation} \]

The best estimate of the standard deviation is the square root of the residual mean square.

For example, it was suspected that a mono-basic ammonium phosphate addition of one percent would cause a significant difference in the transverse breaking strength. Using the over-all condition means listed in Table 9 and the residual mean square from analysis of variance Table 8 the following "t" value was calculate.

\[
\bar{y}_{\text{no addition}} = 1921 \\
\bar{y}_{\text{mono-basic}} = 1655 \\
\begin{align*} 
  n_a &= 20 \\
  n_b &= 20 \\
  S &= 409.7 \\
  "t" &= \frac{1921 - 1655}{\frac{409.7}{(0.316)}} = 2.05
\end{align*}
\]

Since this value is less than the value "t"(0.01) (96) = 2.69 there is no justification in saying that the mono-basic ammonium phosphate had any effect on the transverse breaking strength.

The data for moisture expansion Table 20 and C/B ratio Table 21 were analyzed by the same methods used on the transverse strength data.
Table 20

Percent Moisture Expansion x 100

<table>
<thead>
<tr>
<th>Firing cone</th>
<th>No addition</th>
<th>Mono-basic ammonium phosphate</th>
<th>Di-basic ammonium phosphate</th>
<th>Sodium ammonium phosphate</th>
<th>Ammonium nitrate</th>
<th>Ammonium chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cone 07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>17</td>
<td>30</td>
<td>18</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>23</td>
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<tr>
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<td>11</td>
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</tr>
<tr>
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</tr>
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<td>12</td>
<td>30</td>
<td>11</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Cone 02</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
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Table 21

**C/B Ratio x 100**

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