A STUDY IN THE USE OF WOOD ASH IN CONE 07 LEAD FREE GLAZES

by

CAROLYN KAY RINGEL

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Approved by:

[Signature]
Major Professor
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ACKNOWLEDGEMENTS

The writer is especially indebted to Professor Angelo C. Garzio for his loan of written materials and his direction in this investigation.

Thanks are also extended to my fellow graduate students who were willing to give assistance whenever it was needed.
CHAPTER I

INTRODUCTION

The purpose of this investigation was to extend studies in the use of wood ash in stoneware and low-fire lead glazes (conducted by the author and others) to include the use of wood ash in lead and barium free, low-fire glazes. The results would determine the limits of composition with reference to specific materials and the general characteristics of the glazes developed.

It must be distinctly understood that the variables involved with glaze composition; i.e., varying temperatures, combinations and amounts of glaze materials, etc., do not allow for concrete conclusions which apply in every glaze situation. The conclusions drawn during this investigation apply only to that particular type of leadless glaze discussed.

HISTORICAL BACKGROUND

The use of wood or other vegetable ashes as glaze decoration or as glaze components is centuries old. The Oriental potters, notably the Chinese and later the Japanese used wood ash as a fluxing material in their stoneware glazes. The discovery of its practical use can only be deduced from the information supplied to us from this very early ware itself. The early potters probably discovered the practical use of ash by observing the melted ash deposits on the shoulders of some of the ware taken from a wood burning kiln. The idea or source of inspiration probably lies there.
Within the last century the introduction of wood ash as a flux was introduced to the Western world by Bernard Leach upon his return from extensive study in the Orient. His student Miss Katharine Pleydell-Bouverie has also done work in the comparison of various types of ashes.\(^1\) In the United States the most notable figure in the study and use of wood ash is Maija Grotell. Her student, H. L. Thurn has published a paper dealing with low-fire lead ash glazes.\(^2\) Leach, however is the only person to have published at any length and depth on the use of ash.

The literature available on the development of wood ash glazes is limited in detailed information. The descriptions given in these articles are confined to the resultant glazes and not detailed in their formation or variation of use. The information the author was able to obtain concerned itself primarily with ash glazes to be used at stoneware temperatures. H. L. Thurn's paper published in the Journal of the American Ceramic Society (1945) was the only source found dealing with the use of wood ash in a lead base at low-fire (cone 04-02) temperatures. The author was not able to obtain any published materials concerning the use of wood ash at temperatures below cone 04 whether in a lead or non-lead base.

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CHAPTER II

GLAZE FORMULATION AND TESTING

The glazes composing the test series were formulated from batch weights. This procedure is similar to the formulation of slip glazes, where the employment of an empirical formula is difficult and unreliable due to the inconsistencies in the clay or expense involved in obtaining an analysis. Problems with using ash as a glaze component are similar as a consistent chemical composition is virtually impossible. Formulation of glazes from the empirical formula require materials whose chemical compositions are fairly reliable in their basic composition.

It should be further explained that the ash of various parts of a single tree will differ in the quantity of silica and alumina their ashes contain; the more mature parts are higher in silica content. As so many variables make difficult a set chemical analysis, formulation from the batch weight was declared the solution. Here, changes to suit varying ashes could be quickly achieved without lengthy mathematical work which at best would be unreliable due to the nature of the ash.

All tests formulated were applied to bowl forms by brushing on the test glaze. Bowls were selected as the best form on which to test the glazes because they offered inclined surfaces allowing for the detection of glazes which were too fluid. It also offered the space necessary to apply several of the tests to be conducted at once, allowing all tests to be subjected to the same temperature. This offered a more accurate comparison within a glaze series.

\[3\text{Leach, Bernard H., op. cit.}\]
All tests were fired in a small 6½" x 6½" x 4" electric kiln designed for testing purposes. Due to its size and the desired low temperature, maturity could be reached in 15 to 20 minutes. Tests were withdrawn from the kiln upon maturity and submerged into shredded newspaper to smoke for five minutes. Smoking was initiated to allow the clay body to blacken between tests thus making the individual test more defined.

The rapid maturing time and subsequent cooling period were carefully considered when analysing the tests. Small pinholes, excessive crazing and some incompletely healed surfaces were in some cases considered defects brought on by this method of firing. Such considerations are duly noted in the text.

The maturity of the kiln was determined by the use of small Orton 07 cones which indicated the achievement of 1787°F.
CHAPTER III

PREPARATION OF ASH

The wood ash used in these tests consisted of a mixture of hardwoods collected at one time from a common fireplace. It should be explained that ash, resulting from the burning of a single type of wood or other vegetable matter, when collected at different times or from various locations will have a different chemical makeup.\(^4\)

In other words, variations will occur among a common source (pine, hickory, grass clippings, etc.) due to soil, climate, season, age of source and parts of source used. For example, the ash of twigs of a tree vary, by chemical analysis from the ash of the trunk or of the bark.\(^5\)

It is therefore advisable to collect a large volume of ash and mix it very thoroughly so that it will be less subject to variation of chemical composition. Future collections of ash may require adjustments in the batch weights in order to duplicate the desired glaze effects obtained by the use of a previously gathered ash.

All literature dealing with the handling of ash suggest a screening through a 60 to 100 mesh sieve.\(^6\) The ash used for this testing was sieved four times through an 80 mesh sieve to remove all unburned or large carbonaceous material and allow a thorough mixing. Care should be taken not to breathe the fine particled ash and it is advisable to sieve the ash out-of-doors and to wear a mask as added protection.

\(^4\)Leach, op. cit., p. 160.  \(^5\)Leach, op. cit., p. 160.  
\(^6\)Leach, op. cit., p. 161.
References to ash preparation advise washing the ash from two\textsuperscript{5} to twenty\textsuperscript{6} times for the removal of all soluble salts, alkalies, chlorides and sulfates which allegedly cause variations in the glaze upon use and storage.\textsuperscript{7} From previous experience with the use of wood ash in stoneware glazes, which had been stored for a year and still remained reliable and consistant, this recommendation was ignored.

Caution must be observed however in using unwashed ash; when mixed with water the soluble alkalies cause the glaze to become caustic. Rubber gloves should be employed whenever contact with the skin is imminent.

The storage of an ash glaze must be in heavy plastic containers which can be tightly sealed to prevent moisture escape and infiltration of dust. Paper storage containers with wax linings are weakened or deteriorated by the ash glaze. Particular care should be taken in the storage of the dry sieved ash; it must remain dust and moisture free so that weight measurements are accurate.

\textsuperscript{5}Leach, op. cit., pp. 160.


\textsuperscript{7}Rhodes, Daniel, Clay and Glazes For The Potter, pp. 188, Philadelphia: Chilton Book Company, 1957.
CHAPTER IV
PRELIMINARY FLUX/ASH TESTS

The tests were prepared for this series primarily to determine if wood ash could be melted at cone 07 in combination with three fluxes: 1) colemanite (2CaO 3B₂O₃), 2) boric acid (B₂O₃ 3H₂O) and, 3) borax (Na₂O 2B₂O₃ 10 H₂O). Equal parts ash and each of the three fluxes were tested.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Ash</td>
<td>50*</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Borax (anhydrous)</td>
<td>50</td>
<td>50</td>
<td>*grams</td>
</tr>
<tr>
<td>Boric Acid</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colemanite</td>
<td></td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

The results showed that borax could melt the ash completely. Additional material would have to be added however to improve the quality of this test; a viscous agent to check the very fluid quality and an agent to improve the texture which was highly crazed; areas of glaze separation were sharp and raspy to the touch. Colemanite and boric acid performed identically concerning their melting abilities, in that both fluxes caused only a partial melt. Both tests (#2 and #3) were rough due to small unmelted particles which were suspended in a glassy transparent matrix. This did not eliminate the use of these materials, it only indicated that their proportions would have to be increased in order to obtain a complete melt.

A further comparison of the three fluxes in terms of their mobility in application is important to note. Borax proved to be a very difficult substance with which to work. This material had a very large particle size and did not break up when water was added. It remained granular even after
several minutes of hand grinding and could not suspend itself because of its weight. Therefore it was difficult to thoroughly mix the borax with the ash. Another difficulty prevailed in the application of a glaze containing borax in proportions large enough to melt the ash at this temperature; its granular quality did not allow it to be applied to ware by dipping or pouring. Hand grinding for ten minutes did not eliminate the problem.

Brushing was a feasible method of application if the surface to which the glaze was to be applied is flat and smooth. Great care had to be taken when brushing to obtain a smooth unstreaky application. Spraying was the only method of application which allowed for an even coating of the ware which was not flat and smooth. This too was the only method by which control over the thickness of the coating is possible.

Boric acid also had a granular nature but it was of much finer particle size than borax. It did not remain in suspension by itself. The ash/borax and the ash/boric acid combinations when combined with water resembled wet cement in texture. Both combinations were very heavy and granular and caused exceptional difficulties when applying them to the ware. Although brushing was the mode of application used during the testing to control the size of the test area, spraying was the only means of employing such mixtures with any degree of control.

Boric acid presented additional problems. It had an effervescent quality which caused the glaze to swell to twice its size when water was added to the mixture. A period of five or more minutes has to be allowed for this action to cease. If the glaze was applied before the effervescing had stopped, the boiling action took place on the ware itself leaving craters and bare spots which did not heal upon firing. The further use of boric acid was completely eliminated due to the above stated reasons.
Colemanite, a very fine particled material which remained in suspension with the ash, afforded the best glaze mixture. The glaze texture upon application was smooth and even. Pouring had to be done quickly to avoid excessive build up of the glaze but presented no other problems. Brushing could be done easily and spraying was without any problem. Due to those qualities the colemanite/ash (#3) combination was chosen as a base on which further experimenting would be conducted.
CHAPTER V

TEST SERIES A

Test glaze #3 (50/50 ash and colemanite) indicated that colemanite had the potential ability to melt the ash. A series of six tests were set up to determine the proportion of colemanite needed to cause a complete melt.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Ash</td>
<td>1*</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Colemanite</td>
<td>2*</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
</tr>
</tbody>
</table>

* parts by weight

Test A1 resulted in a completely melted glaze indicating that when using only these two components, colemanite must constitute twice the amount of ash in the batch weight. This particular test was very fluid and all further tests in this series were more exaggerated in the melt as the colemanite content increased. Test A1, a completely melted test was selected as a base for further work.

It is important that glazes contain some clay. Clay acts as a floatative helping to suspend the other ingredients and prevents rapid settling. Clay also furnishes the viscous agent, alumina, indispensible to any glaze and is also a compound containing silica. Clay also forms a more homogeneous bonding between the clay body and the glaze.

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8 Rhoads, op. cit., pp. 154.
Kaolin is the most pure form of clay; free from impurities or coloring oxides. In order to include clay in this glaze for the above mentioned reasons, kaolin (Al₂O₃, 2SiO₂) was chosen as the vehicle for introducing the viscous agent to the Al base to correct the fluid quality of the glaze. A short series of tests to determine the amount of kaolin necessary to correct the fluidity of the glaze and to note the effect of this compound on the melt were formed.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Ala</th>
<th>Alb</th>
<th>Alc</th>
<th>Ald</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Ash</td>
<td>1*</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Colemanite</td>
<td>2*</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Kaolin</td>
<td>.5*</td>
<td>1</td>
<td>1.5</td>
<td>2</td>
</tr>
</tbody>
</table>

* parts by weight

The results of these tests showed that tests Ala, one part by weight of kaolin added to the base, produced a glaze free from excessive fluidity. Test Ala did not correct the fault and tests Alc and Ald were too refractory to melt. It is important to note that Alb, with the inclusion of kaolin was very easily applied glaze when brushed onto the test bowl. It had a creamy and very smooth nature, suspended the ash well and caused no cracking or peeling during drying or firing, although the clay content was high and defects such as this could be expected.

Alb however, showed a high degree of crazing on the surface causing roughness to the touch. It was assumed that this heavy crazing was the result of an improper fit between the glaze and the clay body; the glaze contracted more than the body creating tension thus the crazing. As previously stated, some degree of crazing could be expected due to the circumstances of the rapid firing and cooling. The crazing evident in the Alb test
however, was too severe to be attributed only to the firing cycle thus the assumption of an improper fit would have to be remedied.

Rhodes offers a list of comparisons of the expansion coefficients for common glaze oxides along with some possible remedies for the glaze flaws resulting from glazes containing oxides with high coefficients of expansion and contraction.\(^9\) Upon comparing those oxides contained in the Alb test with the check list, the calcium contributed by the colemanite was found to be the only possible oxide which could have been present in quantities high enough to cause the crazing.

One standard solution to correcting the problem of crazing is to increase the amount of silica in the glaze.\(^10\) Test series Ala through Ald had indicated that any addition of silica would have to be supplemented by a proportionate amount of flux to achieve a complete melt. An increase in the flux would mean a subsequent increase in the calcium, chief cause of the crazing. This direction was abandoned.

The check list indicated that zinc oxide has the lowest coefficient of expansion of the oxides.\(^11\) A series of tests were formed, designed to adjust the coefficient of expansion and thus the fit of the glaze by the introduction of zinc oxide (ZnO). This introduction would be made by additions to the batch weight by percentages in order to determine the effects of very small amounts of zinc to the base.

\(^9\) Rhodes, op. cit., pp. 154.  
\(^10\) Rhodes, op. cit. pp. 154.  
Alb base: 1 Wood Ash*  
2 Colemanite  
1 Kaolin  

Additions ZnO: 1% through 25%  
(Inclusive)  

* part(s) by weight

This series consisted of twenty-five separate tests, each successive test containing 1% more zinc oxide than the previous; zinc added by 1% through 25% inclusive, of the total batch weight. This series was labeled Alb-1 through Alb-25 inclusive, and indicated two qualities to be found by the use of zinc oxide at varying percentages. The following findings are peculiar only to the Alb-1 through Alb-25 series but many are not unlike the descriptions to be found throughout ceramic literature concerning the characteristics of zinc oxide.

Additions of zinc oxide of 1% through 9% of the total batch weight indicate that zinc oxide, at this temperature, acts as a powerful flux causing the glaze base (Alb) to once again become more fluid but had no effect on reducing the surface tension. These nine glazes are alike in that they are over fluxed (fluid), transparent and highly crazed. It is not until the level of zinc oxide reaches 10% of the batch weight that any indication of the lessening of surface tension becomes apparent. At this point and up to 20% the surface tension is lessened and at the point of 11% addition (test no. A2b-11) a satisfactory degree of the lessening of crazing, attributed to the composition of the glaze, was reached. Additions from 11% through 14% give identical responses; all glazes within this range show only a very light network of crazing (attributed to the firing cycle), some opacity, high gloss and are non-fluid. This indicated that 11% addition of the batch weight is the amount necessary to control the crazing. Additionally,
opacity is evident at 11% zinc oxide but is not of the same excellent value that true opaque glazes possess; i.e. glazes which employ tin oxide (SnO₂) as the chief opacifier. The opacity achieved by zinc oxide in this series is merely a clouding of the glaze.

At this point, having controlled the fluidity of the original base (Al) by the addition of Kaolin, correcting the crazing by the addition of 11% zinc oxide and having established some degree of opacity in the glossy base (Alb-11), it was desirable to improve the appearance of the base. This test as stated previously, had not achieved the desirable degree of opacity in that it was cloudy but not completely opaque. All other aspects of this test in respect to its physical properties were satisfactory. In order to complete the opacity, another effective opacifier was employed.

Tin oxide, the oldest and for many conditions the best opacifier was introduced to this (Alb-11) base.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Alb-11a</th>
<th>Alb-11b</th>
<th>Alb-11c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Ash</td>
<td>1†</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Colemanite</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Kaolin</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>11%*</td>
<td>11%</td>
<td>11%</td>
</tr>
<tr>
<td>Tin Oxide</td>
<td>.5%*</td>
<td>1%</td>
<td>1.5%</td>
</tr>
</tbody>
</table>

*parts by weight
*percent of total batch weight

Tin oxide because of the insoluability in most glazes¹² must be introduced to the Alb-11 base in very small amounts as zinc oxide has already provided a field of partial opacity which need only be supplemented

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by an opacifier as powerful as tin oxide.\textsuperscript{13} Tin oxide, when introduced into a high silica content glaze may impart a high lustre and increased fluidity; as little as 1\% or 2\% may improve the gloss.\textsuperscript{14} The above tests however, exhibit no change in the degree of gloss or fluidity, only the achievement of greater opacity.

Test Alb-1lb has a very dense opacity, is glossy, non-fluid and very smooth. Because of the denseness of the opacity it is difficult to discern any crazing without very close inspection of the test. The crazing was limited to a multitude of very fine hairline cracks which were not discernible to the touch. Test Alb-1lc was unmelted indicating that the glaze was supersaturated with tin oxide; the fluxes were not able to react with this abundance of refractory material causing an unmelted surface.

Test Alb-1lb satisfied all the requirements set up for glaze development in this series: 1) it achieved a complete melt with the use of colemanite, 2) the excessive fluidity had been checked by the use of kaolin, 3) the excessive crazing had been arrested by the use of zinc oxide with its low coefficient of expansion and contraction and, 4) a dense opacity had been achieved with the combination of zinc oxide and tin oxide.

Alb-1lb is a glossy glaze and is very white in color. Its texture and appearance resemble a stoneware ash glaze in its segregated areas of fluidity or streaky appearance. This glaze works well on rough or smooth textures giving a complete and very stony opacity.


\textsuperscript{14}Rhodes, op. cit., pp. 124.
CHAPTER VI

TEST SERIES B

The tests in Series B were formulated to produce a semi-matte opaque glaze. Colemanite was used as the chief flux. Wood ash and kaolin supplied the major proportion of the silica and alumina.

Cryolite ($\text{Na}_3\text{AlF}_6$) a powerful auxiliary flux and opacifier, is particularly compatible with its addition to colemanite.\(^{15}\) Cryolite is a compound containing alumina and a natural source for insoluble sodium. Although sodium tends to promote gloss, the refractories (particularly alumina) contained in these glazes were very likely to promote a semi-matte surface.

Another compound, Nepheline syenite ($\text{Na}_2\text{Al}_2\text{O}_3$) was added to this glaze test series. Nepheline syenite begins to sinter at approximately cone 08.\(^{16}\) Due to the amount of alumina and silica contained in this material and its ability to begin sintering at a very low temperature, Nepheline syenite seemed a likely compound to help promote the semi-matte surface.

In the twelve tests which comprised this series, kaolin was the only material which remained at a constant proportion. All other components were added in varying amounts to determine the most satisfactory combination to produce the desired glaze effects.


<table>
<thead>
<tr>
<th></th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
<th>B5</th>
<th>B6</th>
<th>B7</th>
<th>B8</th>
<th>B9</th>
<th>B10</th>
<th>B11</th>
<th>B12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Ash</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Nepheline</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>syenite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colemanite</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Cryolite</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Kaolin</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Tests B1, B2, B3, B4, B5, B6, B7, B8 and B12 were melted, semi-glossy, semi-opaque with some crazing. All other tests were unmelted or only partially melted. Of those tests which were melted, B3 and B4 were by far the superior tests. They were well melted, semi-gloss, semi-opaque with no running and their texture was very smooth. The tests did exhibit some crazing but did not cause a roughness of texture.

Test B4 was a well melted test which was quite fluid. Compared with test B3 which contained only half as much cryolite; it can be determined that cryolite is indeed a powerful flux at this temperature when in combination with colemanite. B4 was unlike all other tests in that white opaque discs, the largest measuring 3/16 inch, were suspended at the upper surface of the otherwise transparent glossy glaze. The discs themselves were matte and dry. A comparison of B4 with the formulae of all other tests in the series indicates that the over abundance of cryolite in the glaze caused the formation of these discs. During the melting the cryolite which could not be taken into chemical solution segregated itself, forming these pools or islands of white matte discs. Test B12, the only other test in the series containing two parts by weight of cryolite in a similar formula, with the exception of the amount of colemanite, did not contain these isolated discs. The apparent explanation is that the right combination of colemanite cryolite was not reached in this test and could not produce the white matte discs found in the B4 test.
Cryolite is thought to be responsible for the semi-opaque quality found in all melted tests. It should be explained that this opacity is caused by small fish scale crystals which are held in suspension beneath the surface of the glaze. Test B4 is the only test to not contain these crystals. A more dense accumulation of crystals are found in that section of the test bowl where there was a thicker application of the glaze; more opacity was achieved in those areas.

Test glaze B3, because of its superior physical properties was chosen from this series for further experimentation in an attempt to produce complete opacity and to achieve a more matte surface.

Zinc oxide was eliminated from consideration as an opacifier because of its performance in the A series; it was found to add fluxing power and gloss which, in this case, was not desirable.

Tin oxide which in Series A had proven to be an effective opacifier when used in small quantities was selected once again to serve this role.

<table>
<thead>
<tr>
<th></th>
<th>B3a</th>
<th>B3b</th>
<th>B3c</th>
<th>B3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3 base + additions:</td>
<td>$\frac{1}{2}$% SnO$_2$</td>
<td>1% SnO$_2$</td>
<td>$1\frac{1}{2}$% SnO$_2$</td>
<td>2% SnO$_2$</td>
</tr>
</tbody>
</table>

All tests in this series were unmelted. Tin oxide added to this bases caused it to be too refractory. Another short series was tested in which tin oxide was held below $\frac{1}{2}$ of total batch weight.

<table>
<thead>
<tr>
<th></th>
<th>B3e</th>
<th>B3f</th>
<th>B3g</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3 base + additions:</td>
<td>1/8% SnO$_2$</td>
<td>$\frac{1}{2}$% SnO$_2$</td>
<td>3/8% SnO$_2$</td>
</tr>
</tbody>
</table>

Test B3e was partially melted, in that its surface was beginning to fuse. B3f and B3g were completely unmelted.
A study of the components of the B3 base would suggest that the kaolin content was most likely to contribute to the difficulty in melting any tin oxide additions. All other components have a lower melting point than kaolin (cryolite having already proved to form a eutectic with Colemanite thus lowering what would normally be a high melting point). Therefore in the next series the kaolin content was cut by half and the tin oxide was added in increasing increments.

<table>
<thead>
<tr>
<th></th>
<th>B3h</th>
<th>B3l</th>
<th>B3l</th>
<th>B3k</th>
<th>B3l</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Ash</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Nepheline Syenite</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Colemanite</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Cryolite</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Kaolin</td>
<td>.5</td>
<td>.5</td>
<td>.5</td>
<td>.5</td>
<td>.5</td>
</tr>
<tr>
<td>Tin Oxide</td>
<td>1/8%</td>
<td>1/4%</td>
<td>1/4%</td>
<td>1%</td>
<td>1.5%</td>
</tr>
</tbody>
</table>

All tests were well melted, smooth, non-fluid and not crazed. Test B3h was more opaque than the preceding tests and the opacity of this series continued to improve through test B3k (1% SnO₂). B3k is an opaque glaze which is semi-matte. Test B3k and B3l are identical in opacity, indicating that any additional amount of SnO₂ added over 1% was unnecessary to achieve the objective: an opaque, semi-matte glaze.

Test glaze B3k is easily handled and applied to ware by pouring, brushing or spraying. A moderate to heavy coating is required in order to achieve maximum opacity. Too thin an application results in only partial opacity.
CHAPTER VII

TEST SERIES C

The preliminary tests Nos. 1 through 3, indicated that anhydrous borax was the most potent of the three fluxes tested. Previously stated, borax was an extremely difficult substance to work with in terms of mixing and application when used in the amounts necessary to cause a melting of the ash. With the knowledge that the only mode of application which presented any satisfactory results was spraying, a series of tests was prepared employing borax as the chief flux.

Previous experience in the use of borax in stoneware glazes, when used in substantial amounts (15% of the batch weight) resulted in a very mottled surface effect which, when coloring metallic oxides were introduced, gave varying hues and multiple colors. This was due to the concentration of borax in the glaze because of its particle size. As the large particles could not be dissolved or reduced they remained in concentrated areas having a decided effect upon the coloring metallic oxides.

The objective of this series was to develop a workable glaze which would employ borax as its chief flux in order to produce a glaze whose surface is mottled in color and if possible texture.

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood Ash</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Borax</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Zinc Oxide</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
</tr>
</tbody>
</table>

All tests with the exception of C7 were melted. C7 was partially melted but had a rough surface. Tests C1 through C6 are all mottled in
texture and have a cratered surface which is pleasant to the touch. Tests C3 and C4 are the most outstanding in their cratered and mottled appearance.

Zinc oxide constitutes 25% (2 parts by weight) of the batch in the C3 test and 33 1/3% (3 parts by weight) in test C4. This is a supersaturation of the oxide and is at too high a percentage to contribute to the glaze as a flux. Its refractoriness at this point causes a dense but mottled opacity. Areas of zinc concentration are opaque and areas of high borax concentration are transparent. The effect is very much like that obtained in salt glaze firings; an orange peel texture. In terms of the most effective texture, test C4 is superior.

The simple nature of this glaze (C4) causes the same difficulties in application as did test #1 in the initial series. The only reliable method of application is by spraying unless the surface of the ware is flat and smooth. Brushing can then be used to apply the glaze. Best results are obtained when the application is moderate. There are no problems in cracking or peeling of the glaze during drying or firing. The mottled texture is consistant throughout and increases in intensity as the glaze is more thickly applied. Too thick a glaze coating will, however, result in isolated areas of running on a vertical surface due to the concentration of borax.
CHAPTER VIII

CONCLUSION

The tests of the preliminary series and series A, B and C readily prove the original theory that wood ash can be made to melt without the use of lead or barium at cone 07, 1787°F. It has been proved that it is possible to combine certain materials with wood ash so as to form a readily fusible glaze. This then, shows the versatility of the wood ash in that it can be employed for both low-fire as well as high-fire glazes successfully.

The great proportion of fluxes required to produce the necessary fusibility and fluidity makes it almost impossible to avoid a glaze which can sustain, without running, any applied (or painted on) coloring oxide. It is necessary to note that any attempt by the author to apply such colorants resulted in a running or smearing of the color(s). Coloring oxides combined with the glaze causing the whole glaze to be colored, cause no problems.

It is important to note that when making additions to the batch formula, care should be taken to add ingredients which are known to form eutectics with other employed glaze materials. The percentages of these ingredients can be varied within their natural limit of fusibility with one another. What these limits are can only be determined by experimentation with the chemicals used and at a specifically desired temperature. This is illustrated in Series B1 through B12 where colemanite and cryolite are purposely combined so that the very refractory cryolite which could lend opacity to the glaze is allowed to form a eutectic causing it to melt well below its normal melting temperature. Another eutectic formation is found in Series Alb-1 through
Alb-25 where, when introduced in small proportions, zinc oxide could be made to act as an auxiliary flux. Greater amounts caused opacity; the zinc became a refractory. It is also of great importance to restate that the silica furnished by the wood ash has formed a eutectic with the other chemical components of the ash allowing it to melt far below the temperatures required to melt quartz or flint. This points up another value in the use of ash in low-fire glazes.

Within the different series (A, B and C) the same components with occasional minor additions, are used to develop matte glazes as are used for glossy ones. The proportions, however are altered. One component may be reduced and replaced by another, or if this causes flaws, further adjustments of component proportions can be accomplished. As noted in series Alb-1 through Alb-25 and series C, zinc oxide, according to the make-up of the glaze, can be used in glossy or matte, transparent or opaque glazes with surfaces either crazed or smooth. Cryolite in like manner has the ability to act as an auxiliary flux or as a refractory opacifier.

The application of these glazes and the limitations thereof are important to define. Glazes, whether they be high-fire or low-fire, that contain ash require special handling because of their physical nature. Glazes containing ash are difficult and often impossible to apply to ware by pouring or dipping as the glazes will adhere immediately and will not flow along the surface of the ware giving an even coating. The excessive build up of glaze when applied in this matter, can be expected to crack and peel from the ware during drying and firing. Another frequent flaw is the tendency of thickly accumulated glazes to remain immature. As a rule, the higher the ash content of a glaze the more difficulty in application.
Brushing of an ash glaze onto the ware is a suitable means of application if the area is small, smooth and flat. Textured surfaces will not receive an even coating and will be spotty in texture and color after firing. This manner of application is extremely difficult if the ash content is high (30%+) or if the fluxes employed are of a granular nature such as borax or boric acid or the carbonates of the alkalies. This granular form causes a streaky and uneven application as the particles are dragged along the surface by the brush.

Spraying of an ash glaze is the recommended means of application. By this method a smooth, even application of any desired thickness is possible. The granular nature of the ash as well as many of the standard glaze compounds will not impede the method of application. An even dispersion of the glaze components is then possible eliminating segregated areas of certain components which would cause an uneven melt.

Low-fire ash glazes which do not contain lethal compounds are easily developed and with little inconvenience employed. The use of such a readily available compound as ash, whose cost involves only the potter's time to collect and prepare, invites itself to be used in all types of firing and at all temperatures. The employment of ash as a major part of a glaze can reduce the cost substantially. The fluxes needed to melt the ash are not exotic nor expensive. It is the author's firm conviction that ash glazes of any type or description can be formulated for any desired temperature.
COLOR TEST RESULTS

Color tests for both oxidation and reduction atmospheres were run on three of the developed glazes representing one glaze from each of the major series.

1. ½% Copper Oxide (black)  Alb-11b  Oxidation – turquoise to green
   Reduction – bright copper
   B4k  O – dark turquoise
        R – bright copper
   C4  O – mottled mint green
        R – mottled copper/purple

2. 1% Copper Oxide (black)  Alb-11b  O – dark turquoise
   R – bright copper
   B4k  O – very deep turquoise
        R – bright copper
   C4  O – deep mottled turquoise
        R – mottled copper/red

3. 1% Chromium Oxide  Alb-11b  O – bright green
   R – light brown
   B4k  O – bright green
        R – green
   C4  O – mottled light brown
        R – mottled dark brown

4. 1% Manganese Dioxide  Alb-11b  O – light purple
   R – muddy brown
   B4k  O – muddy purple
        R – muddy brown
   C4  O – light olive
        R – mottled green/brown

5. 3% Manganese Dioxide  Alb-11b  O – muddy purple
   R – brown
   B4k  O – muddy purple
        R – dark brown
   C4  O – deep mottled brown
        R – deep mottled dark brn.
6. ½% Cobalt Carbonate

<table>
<thead>
<tr>
<th></th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alb-11b</td>
<td>intense blue</td>
<td>intense blue</td>
</tr>
<tr>
<td></td>
<td>intense dark blue</td>
<td></td>
</tr>
</tbody>
</table>

|        |                    |                    |
| B4k    | O                  | Rumberg            |
|        | intense blue       | intense dark blue  |

|        |                    |                    |
| C4     | mottled sky blue   | mottled medium blue|
|        |                    |                    |

7. 1% Cobalt Carbonate

<table>
<thead>
<tr>
<th></th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>intense blue</td>
<td>blue/black</td>
</tr>
</tbody>
</table>

|        |                    |                    |
| B4k    | O                  | Rumberg            |
|        | intense blue       | blue/black         |

|        |                    |                    |
| C4     | mottled dull navy blue | mottled deep navy |
|        |                    |                    |

8. 1% Red Iron Oxide

<table>
<thead>
<tr>
<th></th>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O*</td>
<td>R*</td>
</tr>
</tbody>
</table>

|        | O*        | R*        |
| B4k    | O*        | R*        |

|        | O*        | R*        |
| C4     | O*        | R*        |

*tests proved too refractory to melt
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A STUDY IN THE USE OF WOOD ASH IN CONE 07 LEAD FREE CLAZES

by

CAROLYN KAY RINGEL

B. A., Kansas State University, 1971

AN ABSTRACT OF A MASTER’S THESIS

submitted in partial fulfillment of the requirements for the degree

MASTER OF ARTS

Department of Art

KANSAS STATE UNIVERSITY

Manhattan, Kansas

1973
The purpose of this investigation was to extend studies in the use of wood ash in stoneware and low-fire lead glazes (conducted by the author and others) to include the use of wood ash in lead and barium free, low-fire glazes. The results would determine the limits of composition with reference to specific materials and the general characteristics of the glazes developed.