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Stanley A. Long
Iowa State University

Thomas D. McGee
Iowa State University

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Stabilization of Lime with a Protective Glass Coating¹

STANLEY A. LONG AND THOMAS D. MCGEE²

Abstract. The persistent hydration of lime has severely limited its use as a refractory material. Its hydration is somewhat retarded, but not prevented by heat treatment. A number of investigators have attempted to stabilize lime with chemical additions and have met with limited success. In this investigation an attempt has been made to stabilize lime by introducing a protective coating of glass and by hot pressing to reduce the porosity. Powdered refractory glasses and granular lime were hot pressed in a graphite mold at temperatures ranging from 1250 to 1450°C. The glasses were: 1) calcium-aluminate, 2) alumino-silicate and 3) alumino-phosphate. Samples pressed with the alumino-silicate glass showed poor bonding and disintegrated when removed from the mold. Samples made with the calcium-aluminate and the alumino-phosphate glass showed good resistance to hydration when exposed to the atmosphere. Samples pressed with the calcium-aluminate glass at 1450°C withstood immersion in water at room temperature for 72 hours without disintegration.

Calcium oxide, or quicklime, has a melting point of 2572°C. Next to magnesite, it is the most refractory commercial oxide (11). Unlike magnesite, it is widely distributed in deposits of great purity (limestone). If these were the only considerations, CaO refractories would be valuable for a number of applications. However, little success has been had with this material as a refractory, for it hydrates readily in both air and water. This hydration results in a large volume increase and in the disintegration of any CaO article.

The hydration tendency of CaO decreases with increasing firing temperature, but no matter how it is heat treated it is impossible to convert it to a stable form (13). Lime which has been heated below 1000°C reacts with water immediately to form Ca(OH)₂ with the evolution of a large amount of heat, while lime burnt at a higher temperature reacts more slowly. A lump of crystalline lime placed in water is dissolved very slowly at the surface, the hydration being so gradual that there is no apparent rise in temperature. There is no change in the

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² Ceramic Engineering Department, Iowa State University.

crystal structure of lime with increasing firing temperature. Shrinkage does occur, however, so the decrease in hydration tendency is probably due to the consequent reduction in surface area (12).

Searle and Grimshaw (13) give the following possible explanation for the greater hydration of lime than magnesia. Both CaO and MgO may be represented by a cubic structure with 6:6 co-ordination. This is an idealized structure and represents oxygen atoms in a form of packing which exists only in a few oxides. Each cation is bonded to 6 oxygen atoms. Each receives one-third valency share. Each oxygen atom is bonded to 6 cations. MgO forms a stable oxide which is not liable to hydration under normal atmospheric conditions. Consideration of the ionic radius ratios shows that Mg:O (0.58) is well within the limits of 6-fold co-ordination (0.414-0.732), but Ca:O (0.76) is too large. The resulting octahedral configuration of oxygen about each calcium must, therefore, be highly distorted. The close-packed idealized structure may be replaced by a more open structure, permitting the free access of water molecules and the consequent ease with which CaO can be hydrated. Gregg (4) theorizes that "the fall in reactivity of CaO and MgO at higher firing temperatures is due to a decrease in specific surface and a decrease in lattice strain."

Many attempts have been made to stabilize lime by sintering. Whittemore (16) compacted the lime with kerosene and fired for 3 hours at 1750°C, obtaining a dense, strong, smooth body. Ancetti (2) bonded lime with 2-10% CaF₂ and fired as high as 1800°C. Keller et. al. (6) fired lime to 1750°, ground to 200 mesh and refired at temperatures ranging from 1850-2100°C. Allendorfer (1) used CaH₂ as a binder in the unfired state. Norton (11) states that "If lime is heated to 1800°C in an oxidizing atmosphere, it may be crystallized and in this form has a considerable resistance to slaking." Although sintering greatly reduces the hydration tendency, it does not eliminate it.

Another approach to the stabilization of lime is the use of chemical additions. Many attempts have been made in this area, but none has proved entirely satisfactory. Fisk (3) has made lime crucibles bonded with a maximum of 10% TiO₂ which have "a relatively good stability to the slaking action of the atmosphere." McAllister (8) made lime blocks which survived 13 months service in the hot zone of a lime kiln. His composition consisted of 85-97% CaO, 1-10% Fe₂O₃, and 2-5% MgO. He also proposes (9) a lime refractory bonded with as much as 35% clay. Hathaway (5) used both TiO₂ and ZrO₂ as stabilizers to produce lime refractories which had "excellent" resistance to the

atmosphere. Kuhn and Bellosa (7) produced dense CaO bodies with the addition of 5 to 10% ZrO₂.

Small chemical additions do not alter the crystalline form of the bulk of the CaO. Therefore, any reduction in the hydration tendency resulting from chemical additions may be attributed to the "shielding" provided by the matrix which is formed. Fisk (3) analysed his product and found that the crystalline matrix consisted of 3 CaO · 2TiO₂. This material surrounded the lime grains and helped protect them from hydration. The success of others is probably also due to this mechanism. If it is the shielding which is important and not the chemical reactions which occur, stabilization should be possible by the addition of a glass. Upon firing above its softening point, the glass could be forced to flow around the lime particles. Upon cooling each lime particle would then be encased in a thin file of glass, which would protect it from hydration.

THEORETICAL ASPECTS

There are several difficulties which would be encountered in an attempt to fabricate glass-coated lime. One of these is the difference in the thermal expansion of the two materials. Glasses generally have lower coefficients of thermal expansion than crystalline solids. CaO, being an ionic crystal, has a high coefficient (128×10^{-7} per °C at 900°). If the body is formed at a high temperature and cooled, the lime will contract faster than the glass, leaving the glass in compression. Since glass is much stronger in compression than tension, this may not be too detrimental.

The softening point and chemical nature of the glass are of prime importance. If the glass-coated lime is intended for use as a refractory, the glass should have a high softening temperature and high viscosity at the service temperature. There should be as little reaction as possible between the lime and the glass in order that the "shielding" will not be adversely affected. Such reaction is difficult to predict, but the possibilities of reaction may be limited by using a glass, 1) with a high lime content, 2) with a minimum number of components and, 3) with a minimum of "acid" constituents.

With these considerations in mind three glasses were selected for use in the investigation. A calcium-aluminate glass (Glass A) was selected primarily because of its favorable chemical nature. This glass was composed of 44.8% (weight) CaO, 48.6% Al₂O₃ and 6.6% SiO₂. Stanworth (15) attributes it with a deformation temperature of 860°C and an average linear coefficient of thermal expansion of 75×10^{-7} per °C and 0° to 900°C. He melted the

glass at 1500°C and formed 1 and 2 inch diameter discs from it with no evidence of devitrification.

Glass B was modified from that given by Stanworth (14). CaO was substituted for BaO to give a composition of 13.1% CaO, 29.2% Al₂O₃, 40.6% P₂O₅ and 17.2% B₂O₃. Stanworth melted the original glass at 1500° and reports a deformation temperature of greater than 600°C. He gives no data on thermal expansion.

Glass C was also modified from that given by Stanworth (14). CaO was substituted for 8% BaO and 4% MgO to give a composition of 21.2% CaO, 24.9% Al₂O₃ and 54.0% SiO₂. He also melted this glass at 1500°C. It had an expansion coefficient of 50.1×10^{-7} per °C from 0 to 900°C. Stanworth reports a viscosity of 10¹³ poises at 760°C for the unmodified glass.

EXPERIMENTAL PROCEDURE

Batch weights were calculated for 100 g. of each glass. The CaO was added as CaCO₃ and the P₂O₅ as (NH₄)₂ HPO₄. All other constituents were added as the oxides. The glasses were then melted in carbon crucibles with an induction furnace. A temperature of 1525°C was maintained for 10 minutes after which the glasses were quenched in water. Glasses B and C wetted the crucible and were not completely removed in the pouring operation. Their smoky gray color indicated the presence of carbon. Glass A did not wet the crucible, the frit being a grayish white color.

The fritted glasses were ground in a steel ball mill with steel balls. Glasses A and B were ground approximately 1½ hours until less than 5% was retained on a 200-mesh sieve. Glass C was inadvertently ground for 15 hours. As much of the resulting iron contamination as possible was removed by sifting the material through a labyrinth magnetic filter. Powder X-ray diffraction tests of the ground materials showed no evidence of crystallinity.

Technical grade lump CaO was crushed in a Plattner mortar. The -14 +28-mesh fraction was used for sample preparation. Sufficient glass was added to obtain 25 volume percent. The specific gravities of the lime and the glasses were taken as 3.32 and 2.50 respectively. The materials did not mix well, so a small amount of absolute methanol was added to wet the lime grains prior to the addition of powdered glass.

The samples were hot pressed in order to reduce the porosity and to insure flow of the glass around the lime particles. Murray et. al. (10) hot pressed CaO alone in a graphite pressing mold. They found no reaction between the lime and the mold below 1700°C. A simple, double-plunger, cylindrical graphite mold

was used which fit loosely in the susceptor crucible of an induction furnace. Two small spacing wafers of carbon were used so that three samples could be hot pressed at one time to produce $\frac{1}{2}$ inch diameter by $\frac{1}{4}$ inch high specimens.

The samples were placed in the mold and compacted with a hydraulic press prior to the hot pressing operation. Then the mold was inserted in the induction furnace and a $\frac{1}{4}$ inch graphite "lid" was placed over the top with a hole provided for the top plunger. The bottom plunger contacted the bottom of the susceptor crucible. A $\frac{1}{4}$ inch hole extended thru the lid and halfway thru the pressing cylinder so that the temperature could be determined with an opical pyrometer. A pressure of 1000 p.s.i. was applied with a simple lever arrangement. Shims were used to keep the lever arm as nearly perpendicular to the plunger as possible. Power was applied rapidly until deformation began and then more slowly until no further deformation was apparent.

Initial hot pressing experiments revealed an excessive temperature gradient in the mold. External appearance indicated and microscopic examination confirmed that the cooler upper portion was incompletely compressed. The temperature gradient was reduced to an acceptable amount by insulating the $\frac{3}{8}$ " space between the mold and the lid with carbon black.

Two experiments were made with glass A. Deformation began at about 1275°C . Deformation was complete at 1375°C and the first pressing was discontinued at this point. The second group of samples (only two) were fired until the temperature reached 1450°C . These samples were difficult to remove from the mold as the glass had been fluid enough to flow out around the plungers.

Only one group of samples was made with glass B. Deformation began at 1100°C and was complete at 1250°C . All three samples were well compacted. No more samples were made because the glass was not refractory enough.

Two unsuccessful pressings were made with glass C. Deformation began at 1260°C . One group was fired at 1350° and the other to 1435° . The glass did not bond the lime grains, as the samples disintegrated when removed from the mold. Microscopic examination showed that the lime grains had been destroyed (no sharp angular grains) and the glass had formed globules. Apparently there had been some type of reaction between the two materials.

RESULTS

The successfully pressed samples (5 with glass A, 3 with glass

B) were placed in loosely covered sample jars. After two months time they were unaltered. All the samples were then immersed in water. The three samples formed with glass B were completely disintegrated after 20 hours. All but one of the samples formed with glass A at 1375°C were also completely disintegrated after 20 hours. The third was destroyed after 28 hours. The samples formed with glass A at 1450°C were substantially unchanged after 20 hours immersion, although the water became milky. After 72 hours they were still whole but the outer surfaces had begun to disintegrate.

DISCUSSION OF RESULTS

The experiment was successful in that high-lime bodies "shielded" by glass were produced which showed considerable resistance to slaking. Further slaking tests with more closely controlled conditions are needed in order to compare these results with those of other investigators. The actual significance of the investigation is also dependent upon further data concerning the properties of glass-bonded lime under refractory service conditions. It is possible that lime refractories of this nature would find application in industry.

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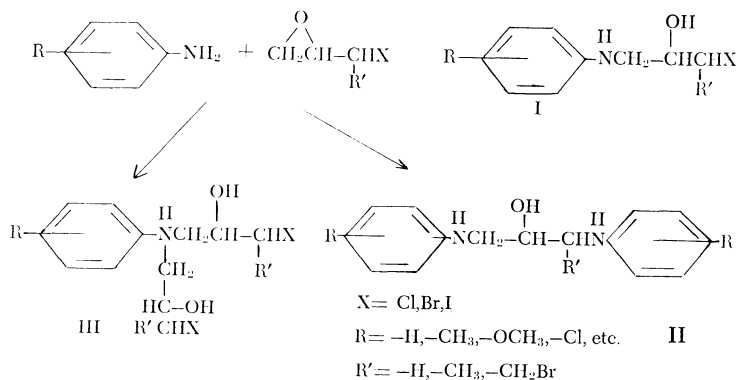
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Reaction of Aromatic Amines with Epihalohydrins¹

ORM ANILINE AND
F. C. PENNINGTON²

Abstract. Published procedures for the reaction of primary aromatic amines with epihalohydrins to give 1:1 addition compounds are not generally applicable, and we have found that they frequently lead to impure products. The reactions were investigated in water, alcohol and bromobenzene solutions. A number of techniques were used to follow the reaction. Infrared spectroscopy gave qualitative data since significant changes occur in the $2.5 \mu - 3.0 \mu$ and the $10 \mu - 11 \mu$ regions of the spectrum. Thin layer chromatography made it possible to detect the formation of by-products and to determine the purity of the addition compounds. The best quantitative measure of the rate of the reaction was obtained by means of an oxirane titration with HBr. The reaction of epichlorohydrin with p-anisidine, p-toluidine and aniline in bromobenzene solution exhibited an induction period believed to be due to the catalytic effect of HCl split out from the addition compound by unreacted amine.

The reaction of primary aromatic amines with epihalohydrins may give addition compounds (I, II, III) in which the ratio of amine to halide is 1:1, 2:1, or 1:2. We have been interested in 1:1 addition compounds



(I) since it has been shown that they can be cyclized and the

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² Coe College, Cedar Rapids, Iowa.