

# Binary Silicate Glasses in the Study of Alkali-Aggregate Reaction

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Binary glasses of the oxides of sodium, potassium, lithium and lead with silica were tested as reactive aggregates with high- and low-alkali cements and with high-alumina cement and pressure-calcined gypsum plaster. It was found that the sodium- and potassium-silicate glasses acted as reactive aggregates, while the lithium- and lead-silicate glasses did not. The expansive reaction of the sodium-silicate glass could be inhibited by substituting pozzolan (finely ground opal) for relatively large portions of the cement.

● THE ALKALI-AGGREGATE REACTION between high-alkali cements and reactive aggregates, which frequently causes expansion of concrete, has been the subject of many investigations. The expansion has been shown to be affected by numerous factors, including the relative amounts of reactive and inert aggregates, the alkali content of the cement, the amount and quality of the mixing water and the nature of the water to which the hardened concrete is exposed, the minor constituents of the cement other than alkalies, the permeability of the cement paste, the particle size of reactive particles, and many others (1-14).

Many, if not most, of these studies have been conducted using natural aggregates and portland cement, materials of great complexity containing many components. The use of simpler cements and of aggregates consisting of only a few elements should aid in the study of the many variables. For example, the use of calcium-aluminate and calcium-sulfate cements containing little alkali and the use of a reactive aggregate in which the alkali is already present should reduce or remove the effect of the rate of release or diffusion of the alkali from the cement and permit the study of the action of the calcium hydroxide formed by hydration of the cements. With such an aggregate, the use of alkali-free cements would permit the study of the action of additives intended to control the alkali-aggregate reaction. Pyrex brand glass is used as a standard reactive aggregate for the study of this reaction; however, a simpler binary alkali silicate glass would supply both the alkali and the silica and itself be such a potentially reactive aggregate. Accordingly, experiments were undertaken in which these materials were tested, as well as other more conventional concreting materials.

## EXPERIMENTAL

Mortar bars, in which various binary glasses replaced 6 percent of the non-reactive graded Ottawa sand aggregate, were made and tested in accordance with ASTM Designation C-227-52T, Tentative Method of Test for Potential Alkali Reactivity of Cement-Aggregate Combinations. Measurements were made at  $\frac{1}{2}$ , 1, 2, 4, 8, and 16 months. High- and low-alkali cements, as well as high-alumina cement and a pressure-calcined plaster, were used. The last two contained insignificant amounts of alkali (as given in Table 1 where the composition of the cements is given). The aggregates tested for reactivity were eight soda-silica glasses containing from 50 to 90 weight percent of silica, six  $K_2O-SiO_2$  glasses containing from 60 to 90 percent of silica, ten  $Li_2O-SiO_2$  glasses containing 73 to 90 percent silica, four  $PbO-SiO_2$  glasses containing from 65 to

TABLE 1

Cement	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	FeO	CaO	SO <sub>3</sub>	MgO	Loss	Insol	Na <sub>2</sub> O	K <sub>2</sub> O	Li <sub>2</sub> O
Low-alkali	22.6	4.5	3.2	-	65.1	1.7	1.2	1.5	0.2	0.00	0.29	0.15
High-alkali	21.6	6.0	2.5	-	63.3	2.3	1.9	1.1	0.2	1.10	0.09	-
High-alumina	0.0	81.3	0.13	0.13	17.4	-	0.58	-	*	0.00	0.001	-
Pressure-calcined gypsum plaster					-	-	-	-	-	0.00	0.00	-

\*The insolubles were determined in accordance with Federal Specification SS-C-158 c. The high-alumina cement did not respond to the specified treatment—colloidal particles were formed which passed through extremely dense filter paper.

90 percent silica, and pure silica glass. The glasses were crushed and screened to pass a No. 20 and be retained on a No. 140 sieve.

The results of the measurements on mortar bars in which these glasses were used as aggregate are shown in Figures 1 to 7 where the expansions at various ages are plotted against the percentage silica in the glasses. A series of bars were made and measured using the glass containing 15 percent of soda, in which a finely ground pozzolan (opal passing the No. 325 sieve) was substituted for portions of the low-alkali cement. The results of measurements on these bars are shown in Figure 8.

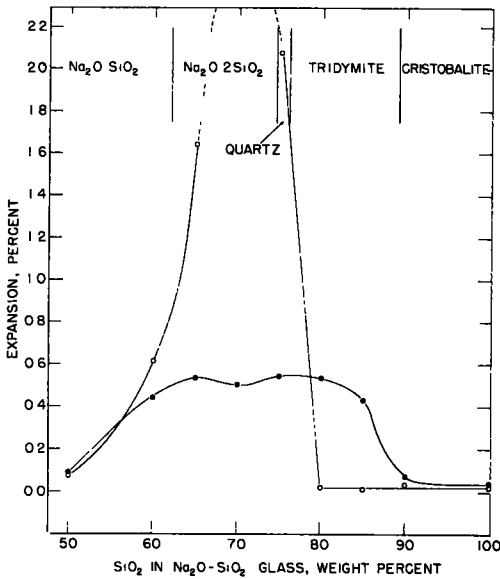


Figure 1. Expansion of mortar bars containing a series of  $\text{Na}_2\text{O}-\text{SiO}_2$  glasses. (Stored over water at 100 F—O with high-alumina cement, aged 8 months; O with gypsum plaster, aged 2 months.) Also shown are the primary phase regions for the system  $\text{Na}_2\text{O}-\text{SiO}_2$ .

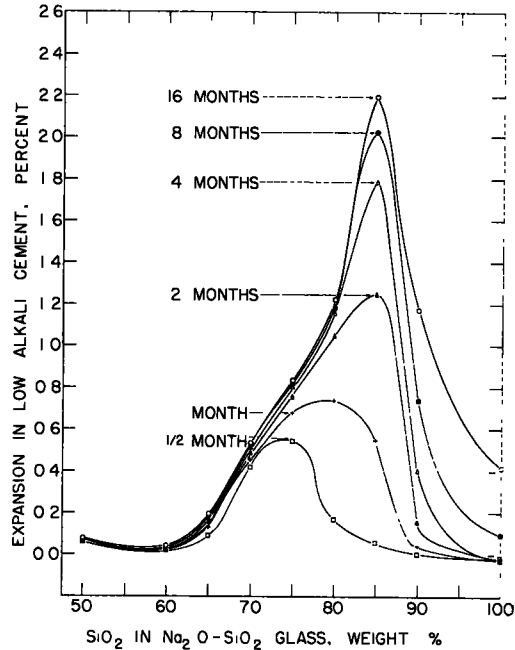


Figure 2. Expansion of mortar bars containing a series of  $\text{Na}_2\text{O}-\text{SiO}_2$  glasses in a low-alkali cement at various ages. (Stored over water at 100 F.)

Evidence that the glasses did indeed supply both the reactive silica and the necessary alkali for the alkali-aggregate reaction can be seen in Figure 1 showing expansions exceeding 0.55 and 2.0 percent obtained with high-alumina cement and gypsum plaster, respectively. Neither of these cements contained appreciable alkali. Because it has been found (16) that the properties of binary glasses vary with composition in some fashion connected with the potential primary phase on crystallization, the primary phase regions of the system  $\text{Na}_2\text{O}-\text{SiO}_2$  are shown in Figures 1 and 4 for comparison with the results of the expansion measurements.

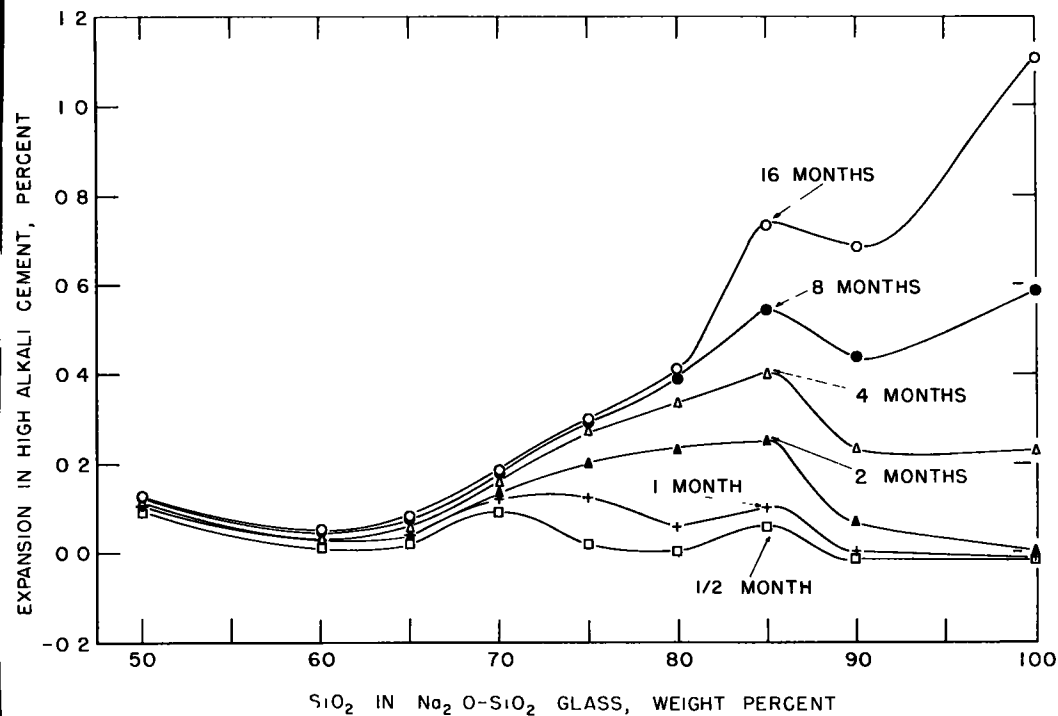


Figure 3. Expansion of mortar bars containing a series of  $\text{Na}_2\text{O}-\text{SiO}_2$  glasses in a high-alkali cement at various ages. (Stored over water at 100 F.)

Expansions obtained for bars containing a series of soda-silica glasses in low- and in high-alkali portland cements during a curing period of 16 months are shown in Figures 2 and 3. The top curves of these two figures are re-plotted in Figure 4 for easy comparison with the primary phase regions of the system  $\text{Na}_2\text{O}-\text{SiO}_2$ . Here it can be seen that for the low-alkali cement the greatest expansion occurs in the tridymite primary phase region, and for the high-alkali cement in the cristobalite primary phase region. However, because the cement contributes considerable  $\text{Na}_2\text{O}$  to the reaction, the aggregate becomes the equivalent of one containing more soda tested in a "no-alkali" cement. That is, for comparison with peaks in Figure 1, the peaks in Figure 4 should undoubtedly be shifted to the left in the direction of the sodium disilicate region.

Figures 5 and 6 show the expansions obtained with potash-silica glasses in low- and in high-alkali cements. The primary phase regions of the system  $\text{K}_2\text{O}-\text{SiO}_2$  are shown in these figures for easy comparison with the major features of the expansion curves. The expansions obtained with  $\text{PbO}-$  and  $\text{Li}_2\text{O}-\text{SiO}_2$  glasses are shown in Figure 7.

#### DISCUSSION

In general, less expansion occurred with the high-alkali than with the low-alkali cement. These observations are compatible with the following explanations; namely, (1) that the reaction product of the glass aggregate is made more fluid by the additional soda available from the high-alkali cement, or (2) that the high-alkali cement gives a higher concentration of electrolyte in the outer phase and thus reduces the osmotic pressure responsible for the expansion.

Very little expansion was obtained with the  $\text{Li}_2\text{O}-$  and  $\text{PbO}-\text{SiO}_2$  glasses. In fact, three out of the four series of measurements at 16 months (shown in Fig. 7) showed a slight shrinkage. The non-expansion of the  $\text{Li}_2\text{O}-\text{SiO}_2$  aggregates is what would be expected because lithium silicates are insoluble, and therefore would be non-reactive aggregates.

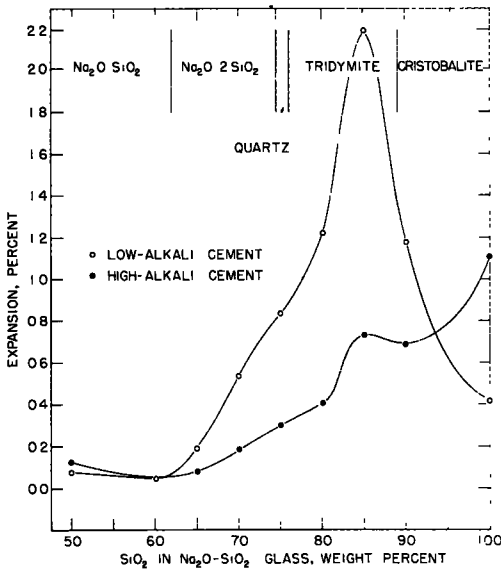


Figure 4. Expansion of mortar bars containing  $\text{Na}_2\text{O-SiO}_2$  glasses in low- and high-alkali cements, together with the primary phase regions of the system  $\text{K}_2\text{O-SiO}_2$ . (Stored over water at 100 F.)

The high expansion caused by the glass containing 15 percent of soda in the low-alkali cement could be largely eliminated or greatly delayed by the substitution of pozzolan for part of the cement. This effect is illustrated in Figure 8 showing the expansions obtained for bars containing various amounts of pozzolan. In this series, the bars containing no pozzolan expanded about 1.4 percent. This potential expansion was reduced to 0.2 percent by the substitution of 4 percent and to 0.02 percent by the substitution of 16 and 32 percent of the cement by pozzolan.

This decrease in expansion with addition of pozzolan indicates that some factor other than the relative migration rates of sodium and calcium (as has been suggested by others (14)) is responsible for the effectiveness of pozzolan in controlling expansion. This conclusion is evident because the sodium is already in the aggregate, ready to react and swell, before the calcium could possibly reach the aggregate to control the expansion.

#### SUMMARY

It has been shown that synthetic binary sodium and potassium silicate glasses as

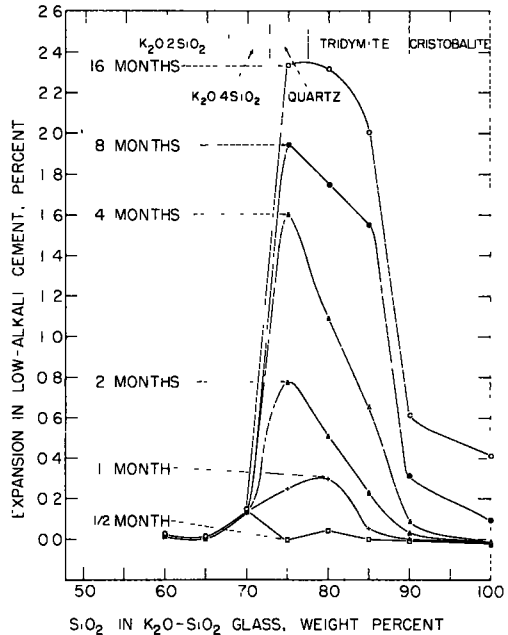


Figure 5. Expansion of mortar bars containing a series of  $\text{K}_2\text{O-SiO}_2$  glasses in low-alkali cement at various ages, together with the primary phase regions of the system  $\text{K}_2\text{O-SiO}_2$ . (Stored over water at 100 F.)

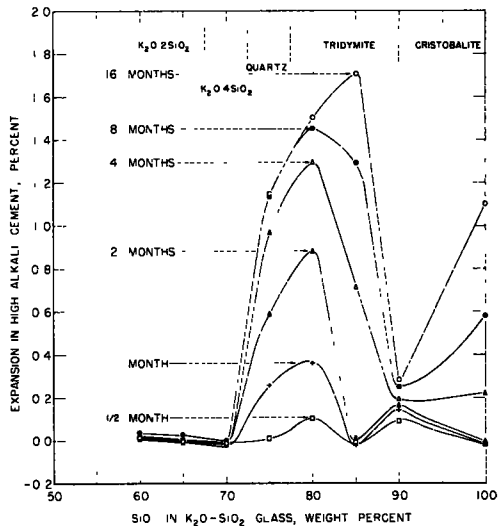


Figure 6. Expansion of mortar bars containing a series of  $\text{K}_2\text{O-SiO}_2$  glasses in high-alkali cement at various ages, together with the primary phase regions of the system  $\text{K}_2\text{O-SiO}_2$ . (Stored over water at 100 F.)

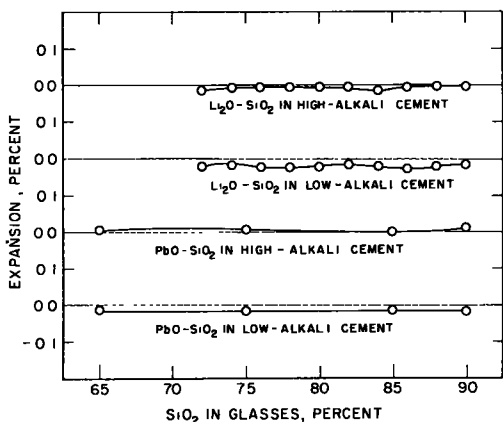


Figure 7. Expansion of mortar bars containing the indicated PbO-SiO<sub>2</sub> or Li<sub>2</sub>O-SiO<sub>2</sub> glasses. (Stored over water 16 months at 100 F.)

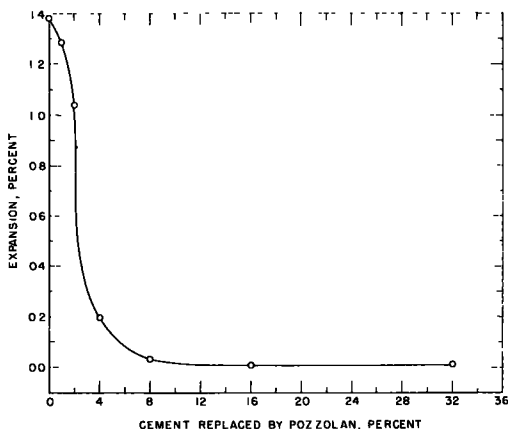


Figure 8. Reduced expansion of mortar bars containing a 15 percent Na<sub>2</sub>O—85 percent SiO<sub>2</sub> glass caused by replacement of part of the low-alkali cement with pozzolan (opal passing #325 sieve). (Bars stored over water 4 months at 100 F.)

aggregates cause expansion by the alkali-aggregate reaction in cements containing no alkali, and that this expansion can be inhibited by the addition of pozzolans.

Lithium- and lead-silicate glasses as aggregates did not cause expansion, thus demonstrating the effect of differing ions on the alkali-aggregate reaction and the necessity for the presence of sodium or potassium or both for the reaction to occur.

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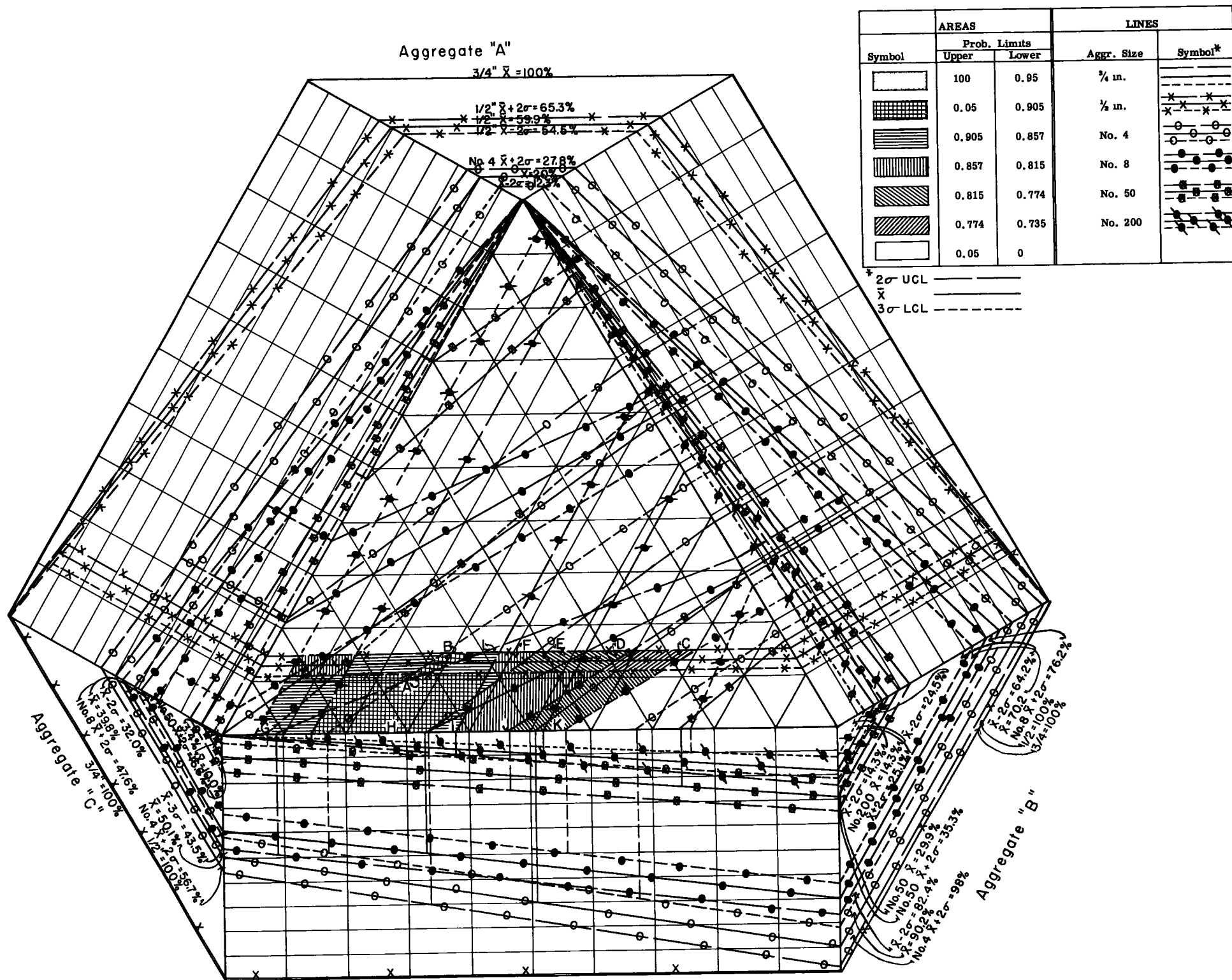


Figure A-5. Example IV; aggregate blending on the basis of the probability of test results





