A LABORATORY STUDY OF CALUMITE AS A MELTING AND FINING ACCELERANT

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ABSTRACT:

Calumite, a refined blast furnace slag, has long been used as a melting and fining accelerant in container glass melting and is finding wider use in float glass production. This laboratory melt study addresses the utility of Calumite through a series of hot-stage microscope experiments, and also attempts to quantify the beneficial compositional effects of Calumite addition to float glass batch. The results of this study were positive, and a plant trial of Calumite was recommended.

INTRODUCTION:

This report summarizes the details of a comprehensive evaluation of Calumite, refined blast furnace slag as a batch-added, melting and fining aid for a typical, clear, float glass. This laboratory study compared the melting, fining, chemical and physical properties, and the resistance to weathering of glasses made with and without Calumite as a batch ingredient. The additional issues of emissions and cullet compatibility were also considered. The experimental data indicated several positive benefits resulting from the use of Calumite as a batch material for clear float glass, and a plant trial was recommended.

Calumite®

BACKGROUND:

The use of blast furnace slag to increase glass productivity and lower energy costs is not a new concept. Many studies have been reported[1-5] on the use or proposed use of both unrefined and refined slag. The container industry has used slag as a melting and fining accelerant for years, but it is only recently that the sheet and float glass industry has attempted to capitalize on the benefits associated with this batch additive. The Japanese were the first to incorporate blast furnace slag as a float glass ingredient, and it is the author's impression that Ford Glass Division was the first U.S. glass manufacturer to use blast furnace slag in a float operation. The quality requirements placed on float glass necessarily demand the use of refined, blast furnace slag.

Calumite is a blended and refined form of blast furnace slag, with a representative composition as indicated in Table I. This beneficiated slag, previously melted in the steel-making process and only partially re-crystallized on cooling, is a source of calcia, alumina, magnesia, and silica. Also present are smaller quantities of iron, sulfur as both sulfate and sulfide, and elemental carbon; all of which aid fining. Calumite forms a low-melting eutectic with silica; and, since the silica content in Calumite is less than stoichiometric (and far less than that of the glass), the fusion reaction is driven toward the more rapid assimilation of sand grains into the glass melt.[6] This reaction, coupled with a low viscosity at glass melt temperature and a tendency to wet the sand grains, should significantly accelerate the melting process. Calumite is also weakly reducing; the sulfide and carbon act to lower batch redox, which in turn should lower retained SO_3 and aid glass refining.

TABLE I

TYPICAL CALUMITE COMPOSITION

Constituent	Weight %
SiO_2	37.42
TiO_2	0.44
Al_2O_3	7.68
Fe_2O_3	0.24
CaO	39.82
MgO	12.19
MnO	0.57
$S^=$	0.86
SO_3	0.25
$Na_2O + K_2O$	0.80
C	0.30
Total:	100.57
Oxygen Correction	0.43
Corrected Total	100.14

In order to be used as a batch ingredient in float glass manufacture, the composition of the blast furnace slag must be carefully controlled. The Calumite company achieves the necessary level of compositional control through their patented technology(7) called "blend piles." Through the statistically controlled placement of different lots of slag (which vary in composition), a storage pile is constructed which consists of a multiplicity of horizontal layers. Subsequent vertical "mining" of this inventory ameliorates the compositional variability inherent in different slag lots to a level consistent with float glass batch requirements. Additional beneficiation steps include drying, grinding and sizing, metals removal, and multiple chemical analyses to identify any problematic impurities and to guarantee compositional control.

EXPERIMENTAL WORK AND RESULTS:

Melt Studies:

A series of laboratory melts were made to assess the effect of Calumite on the melting rate of a typical, clear, float glass batch. All melts were made at 2650°F (1455°C) in platinum crucibles, utilizing a gas-fired furnace. Melt series were conducted for three levels of soda from salt cake: 1.15%, 2.3%, and 4.6%; while melting times were 30, 35, and 40 minutes. Transmitted-light photographs of the melts are shown as Figures 1-3, while stone and seed count data from those melts are graphed in Figure 4. Clearly, under the conditions of this study, the Calumite-containing melts are superior, in terms of their freedom from stones and seeds, to those melts made without Calumite. The solitary negative observation in this portion of the laboratory study was the formation of a surface scum on short-time melts containing low levels of salt cake. The surface scum was carefully isolated, analyzed by X-ray diffraction, and found to be entirely alpha-cristobalite. Since the scum disappeared with longer melting time and was completely siliceous, it was not considered to be a problem.

Hot Stage Microscope Studies:

A transmitted-light, hot-stage microscope was used to study the effect of Calumite addition on the fining of clear float glass melts. A description of the hot-stage microscope and ancillary equipment has been previously published.(8) This study was conducted for melts containing the same three levels of soda from salt cake (1.15%, 2.3%, and 4.6%) as the comparative melting series reported earlier.

Each fining experiment was conducted as identically as equipment and experimental procedure would allow. Briefly, 20 grams of the experimental glass batch were melted in special platinum crucibles with sapphire window inserts in the crucible bottom. This crucible construction allowed the fining process to be visually followed and photographically recorded by viewing in the transmitted light of a mercury vapor lamp. All experiments were conducted at 2650°F (1455°C), and each batch was heated to the hold temperature at the same, controlled rate. Time zero, for fining observations, was defined as that time at which the melt reached the experimental temperature. Photographs of the melt were taken at five-minute intervals thereafter, to a total fining time of 60 minutes; and bubble counts were made using these photographic records. Plots of these seed counts are included as Figures 5, 6, and 7.

Figure 5 compares the fining action of melts which derive 1.15% of their soda from salt cake and which contain varying amounts of Calumite. The melts were all held at a fining temperature of 2650°F (1455°C); and, as would be expected, the number of bubbles decreases with time. However, the effect of Calumite on fining is readily evident, as the melts containing Calumite show a more rapid rate of bubble release, resulting in a more refined glass at the end of the experimental period. Interpretation of these data is complicated (and perhaps a bit dangerous), as the melts do not begin the experiment with the same number of bubbles. Rather than focus on the actual number of bubbles present at any time, one may reach a more valid comparison by noting the time at which refining begins and the rate at which refining takes place. At this low saltcake level, Calumite certainly appears to have a beneficial effect on fining.

Figure 6 displays a similar set of data for melts which derive 2.3% of their soda from salt cake. As in the previous data set, these melts also gain a fining benefit from the addition of Calumite. All three melts which contain Calumite have a lower bubble content at the end of the experimental period than does the melt without Calumite. Additionally, the rate at which the glasses release bubbles is higher for the melts containing Calumite. It was concluded that, at this intermediate saltcake level, the addition of Calumite helps fining.

Figure 7 is a graphical representation of the final set of experimental, hot-stage microscope data. These data compare the effect on fining of Calumite additions to glass melts which derive 4.6% of their soda from salt cake. Under these experimental conditions, no beneficial effect of Calumite addition is seen. All of the melts fine at essentially the same rate, and fine to the same level during the course of the experiment. The exception is a Calumite-containing melt which began the observation period with a higher number of seeds than did the other three melts. At this higher level of salt cake, it is postulated that the refining action of the salt cake predominates and obscures the relatively weaker fining effects of Calumite.

The ratio of weight percent Calumite to salt cake varied from 2:1 to 16:1 in these hot-stage microscope experiments. This is a higher ratio than was used in previous studies of more conventional fining agents such as As_2O_5, Sb_2O_5, CeO_2, and NaCl; all used in conjunction with salt cake. Therefore, it is concluded that Calumite, on a weight percent basis, is not a particularly strong fining agent.

Weathering Studies:

Calumite introduces alumina into the glass composition, and this alumina is in an easy-to-melt form. Alumina addition should improve the resistance to weathering of the glass, and this improved durability is one of the secondary benefits reportedly derived from the use of Calumite as a melting and fining accelerant.

A series of glass melts, with varying levels of Calumite, were tested for glass weatherability. By measuring the sodium leached, in a modified ASTM[9] test, it was possible to evaluate the effect of the alumina incorporated into the glass as various amounts of Calumite were added to the glass batch. As in all the previous tests, a standard clear, float glass batch composition was used for the experimental work.

The modified ASTM test used the following procedure: test glasses were ground to between 40- and 50-mesh particle size; 10 grams of ground glass were placed in a 250-ml Erlenmeyer flask filled with 50 ml of distilled water and autoclaved at 250°F (121°C) for 30 minutes; and the amount of alkali extracted from the 10-gram glass sample was determined by atomic absorption spectrometry and reported as concentration of sodium, in micrograms per cubic centimeter of solution.

The comparative results of these weathering tests are graphically displayed in Figure 8. This figure contains two data sets: (1) the relationship between the amount of alumina in the final glass melt and the amount of Calumite added to the glass batch, and (2) the relationship between the amount of sodium leached from the glass and the amount of Calumite added to the glass batch. The third relationship, that between the amount of sodium leached from the glass and the amount of alumina in the glass, can be readily deduced. An inspection of Figure 8 yields the presumed result: that sodium leaching of soda-lime-silica glass by water is indeed reduced by the incorporation of alumina into the glass. These experimental results also indicate that more alumina yields increased gains in glass durability; however, a region of diminishing returns is quickly reached. The leached sodium level decreases rapidly with the initial additions of Calumite, but then decreases more slowly with subsequent additions. The positive side of these results is that even relatively small increases is the alumina content of soda-lime-silica glasses, to the range of 0.3-0.5 weight percent, appear to have the potential to improve their weather and stain resistance.

Other Issues:

Several other factors were considered in our laboratory study, leading to the recommendation of a plant trial of Calumite. Lab melts of a typical production glass batch were made with and without Calumite. The Calumite-containing batches were modified to compensate for the composition of the slag.

Chemical compositions of the final glasses were nearly the same, except for an increased alumina content in the Calumite-containing glass. Retained SO_3 was lower in the Calumite-containing glass due to the lower batch redox.

The physical properties of the two glasses were also quite similar, with changes observed in the liquidus temperature and the density due to the increased alumina content. The high temperature viscosity behaviors of the two glasses were virtually identical from 2100°-2800°F (1150°-1540°C). Interestingly, production glass properties fell between those of the lab melts made with and without Calumite.

The effect of Calumite addition to the production glass batch on particulate and SO_2 emissions was projected using empirical models derived from extensive stack testing. While a simple addition of Calumite to the batch will certainly increase emissions (as more sulfur is being incorporated into the batch), the optimized batch formulations were projected to result in slightly lower SO_2 and particulate emissions.

Some concern existed about the handling of mixed-composition cullet during a transition to Calumite or when glass from a plant using Calumite was fabricated at a plant which had not yet incorporated Calumite as a batch ingredient. This concern was dismissed, when our U.S. plants began using glass manufactured by Ford's Canadian subsidiary without any problems due to mixing of cullet. The Canadian glass presently contains more alumina than would be introduced by using Calumite.

SUMMARY:

A comprehensive study of the effects of adding Calumite, refined blast furnace slag, to a typical Ford clear float glass batch was conducted. This study evaluated the melting, fining, weathering, chemical and physical properties, emissions, and system compatibility of glass made with Calumite. The melting study indicated a potential cost savings through decreased fuel use. Improved resistance to sodium leaching, resulting from the additional Al_2O_3 incorporated into the glass, was an accompanying benefit. Calumite was also determined to be a mild fining aid. Since the use of Calumite as a melting accelerant and fining aid holds the potential for fuel savings, while also improving the glass durability without introducing any deleterious chemical or physical changes into the finished glass product, a plant trial of Calumite was recommended.

EPILOGUE: A NOTE ON THE PLANT TRIAL

On July 7, 1983, Ford's Dearborn Glass Plant introduced the first Calumite batch into their clear float glass furnace. Over a period of two months, the level of Calumite was raised from the initial one percent of total sand weight to five percent of sand weight. Operational changes to the furnace were made as the effect of Calumite on the melting behavior of the batch became apparent. No operational difficulties were experienced during this trial, either during the introduction of Calumite or in implementing the process changes necessary to accomodate this melting and fining accelerant. Glass quality remained high, and savings were greater than projected by our laboratory studies. Dearborn's float operation continues to employ Calumite as a batch ingredient in their current operations.

ACKNOWLEDGEMENTS:

The author is grateful for the technical contributions of Howard G. Ross, presently retired from Ford Motor Company. The assistance in preparation of this manuscript by David D. Myers of The Calumite Company is also greatly appreciated.

# # #

FIGURES AND TITLES

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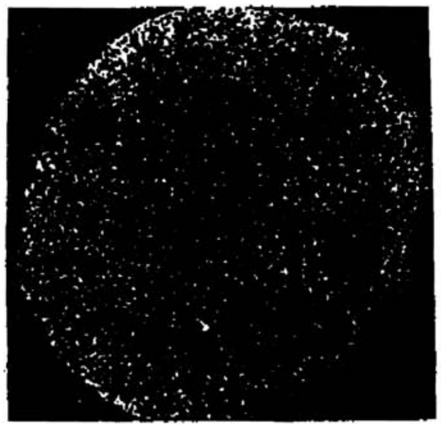
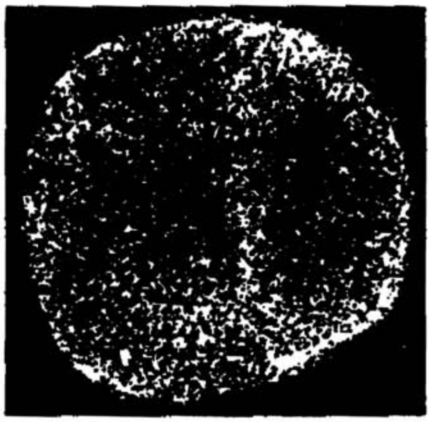
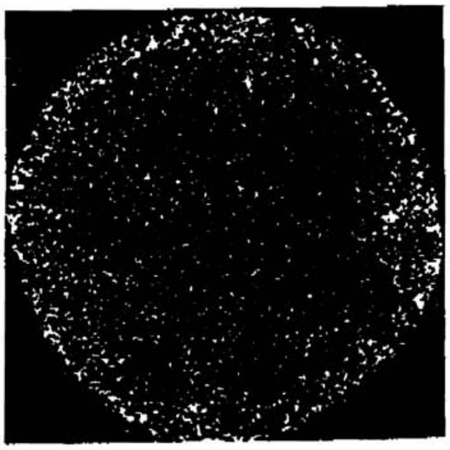
Figure 1 COMPARATIVE MELTING SERIES OF CLEAR FLOAT WITH AND WITHOUT CALUMITE
2650 °F



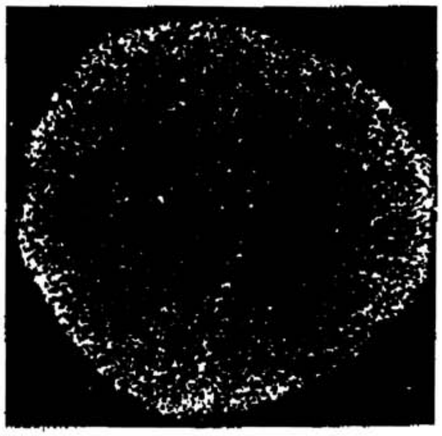
M1 1.15% SC No Calumite 30 Min.



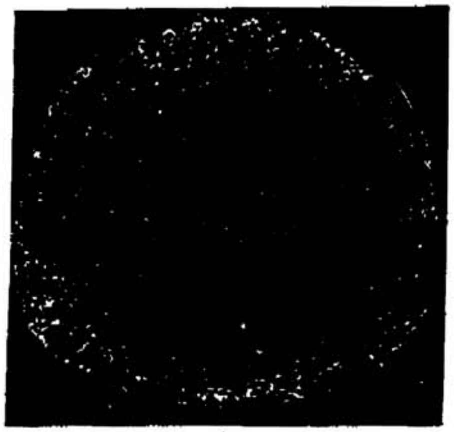
M2 1.15% SC 2.4% Calumite 30 Min.



M3 1.15% SC No Calumite 35 Min.



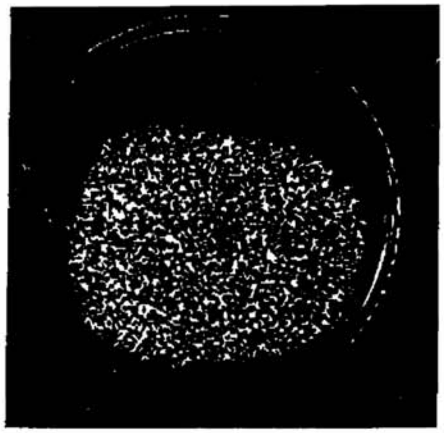
M4 1.15% SC 2.4% Calumite 35 Min.



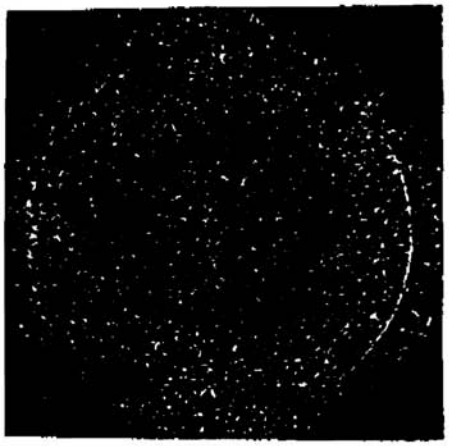
M5 1.15% SC No Calumite 40 Min.

M6 1.15% SC 2.4% Calumite [illegible] Min.

Figure 2 COMPARATIVE MELTING SERIES OF CLEAR FLOAT WITH AND WITHOUT CALUMITE
2650 °F

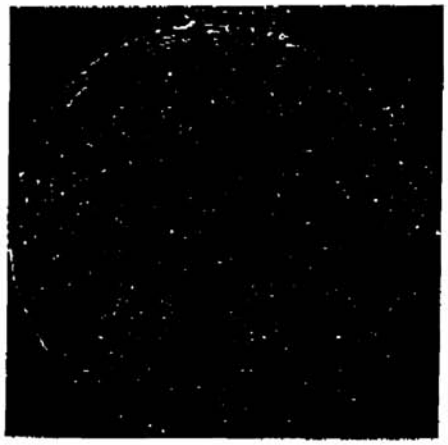


M7 2.3% SC No Calumite 30 Min.

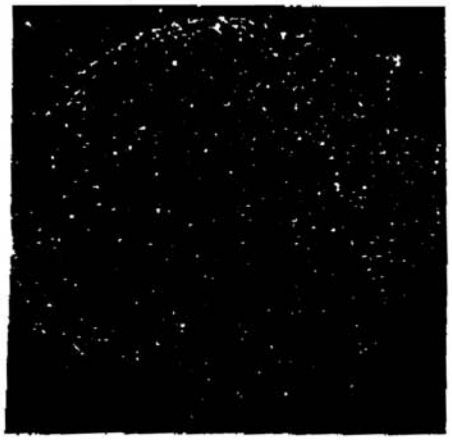


M8 2.3% SC 2.4% Calumite 30 Min.

M9 2.3% SC No Calumite 35 Min.



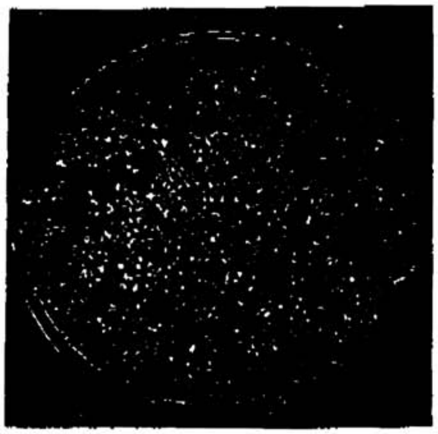
M10 2.3% SC 2.4% Calumite 35 Min.



M11 [illegible].3% SC No Calumite 40 Min.

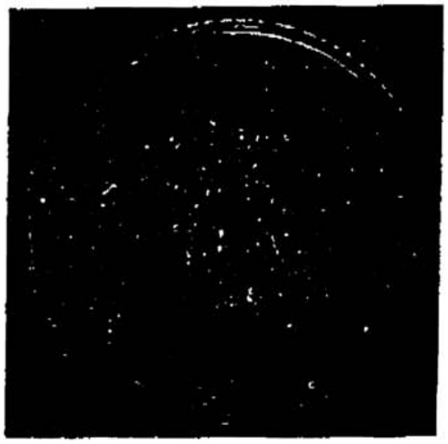
M1[illegible] [illegible].3% SC [illegible].4% Calumite [illegible] Min.

Figure 3 COMPARATIVE MELTING SERIES OF CLEAR FLOAT WITH AND WITHOUT CALUMITE
2650 °F



M13 4.6% SC No Calumite 30 Min.

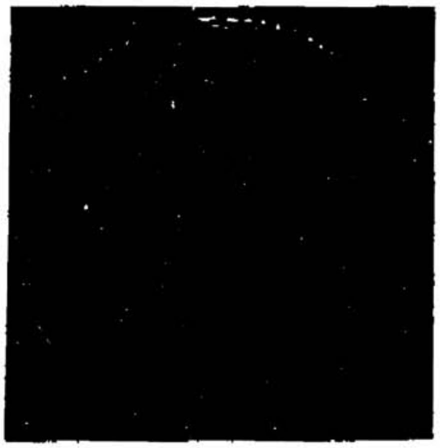
M14 4.6% SC 2.4% Calumite 30 Min.



M15 4.6% SC No Calumite 35 Min.

M16 4.6% SC 2.4% Calumite 35 Min.

M17 4.6% SC No Calumite 40 Min.



M18 4.6% SC [illegible] Calumite [illegible] Min.

FIGURE 4

MELTING COMPARISON - WITH AND WITHOUT CALUMITE

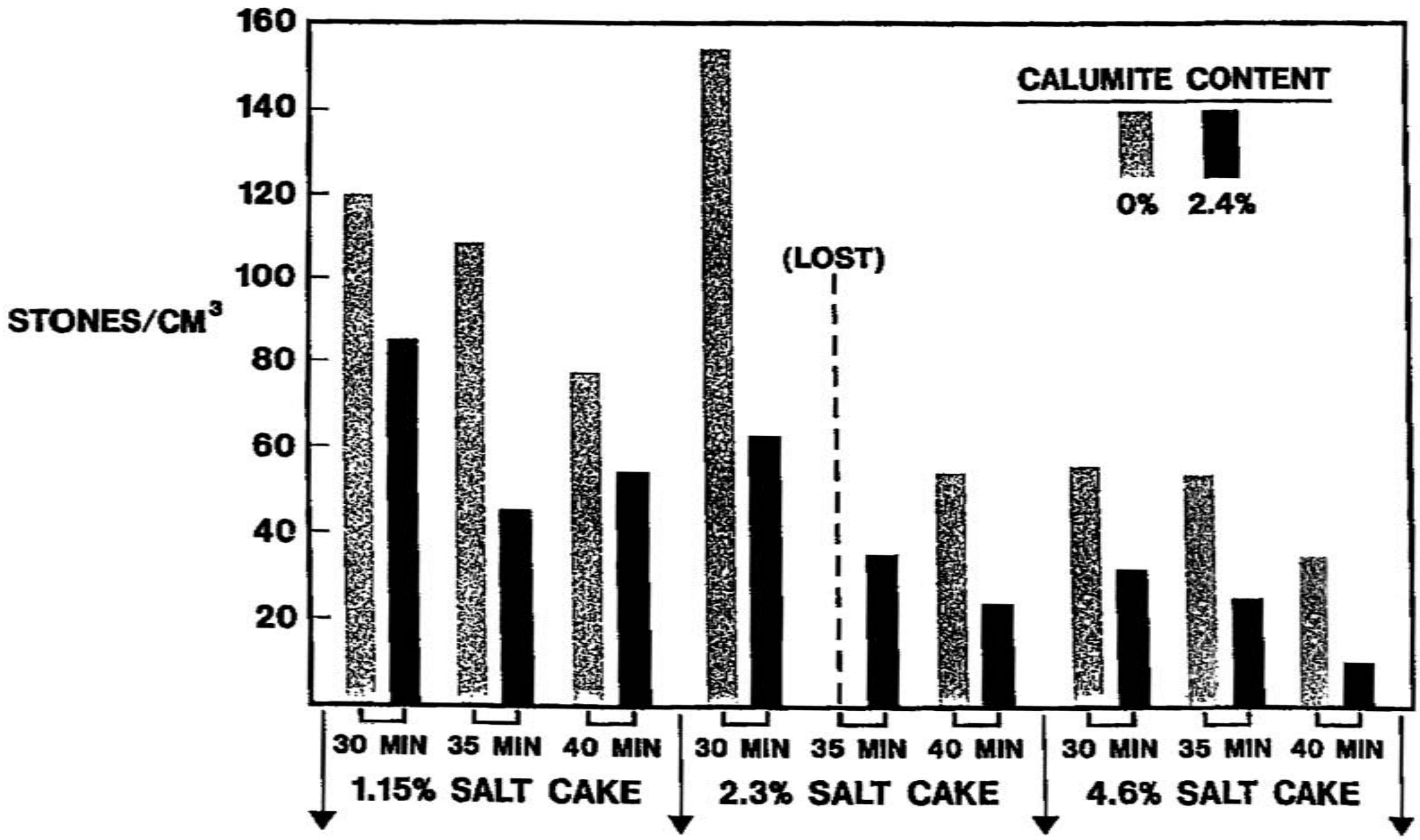


FIGURE 5

FINING EFFECT OF CALUMITE

(1.15 PERCENT SODA FROM SALT CAKE - 2650°F)

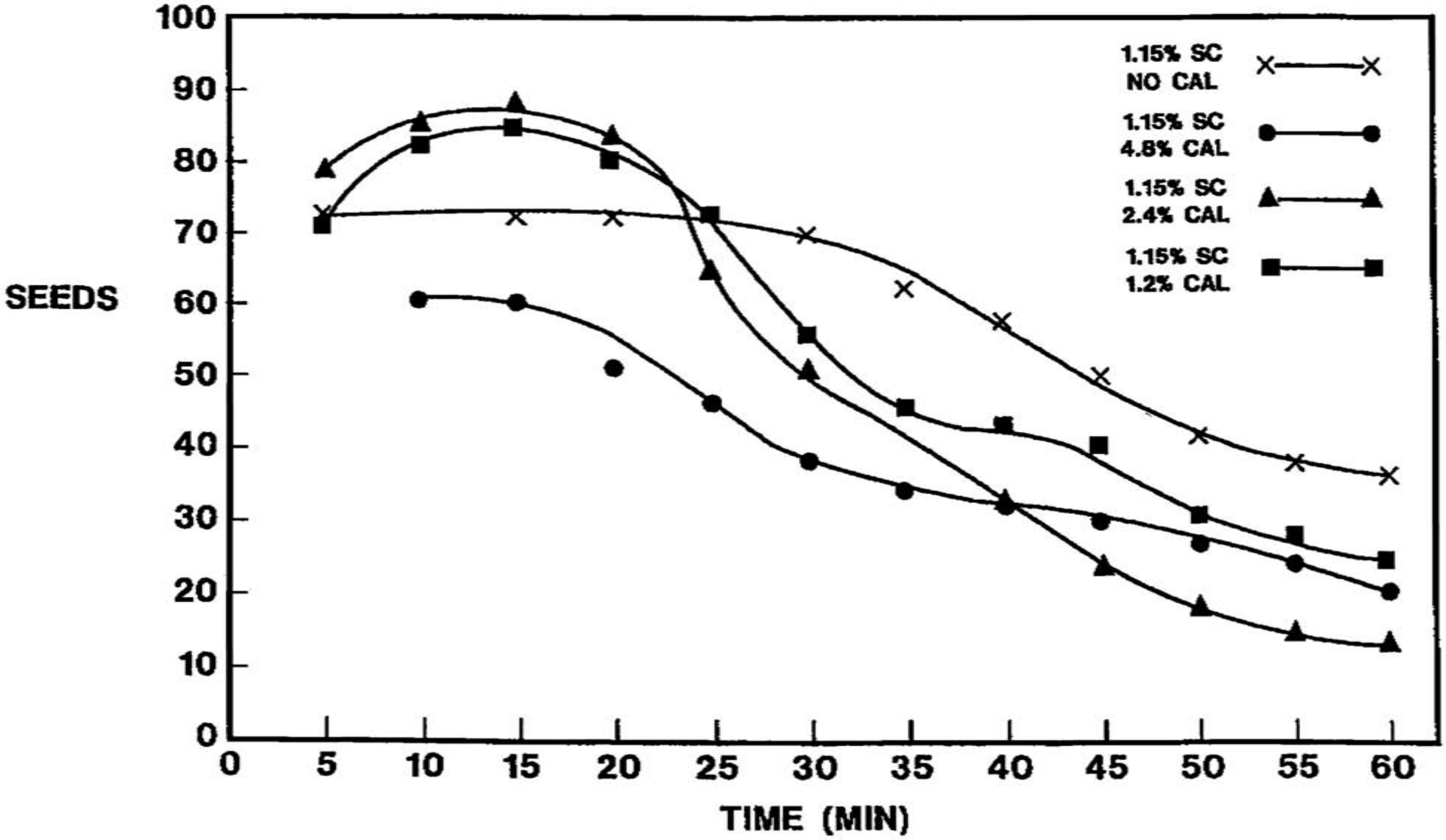


FIGURE 6

FINING EFFECT OF CALUMITE

(2.3 PERCENT SODA FROM SALT CAKE - 2650°F)

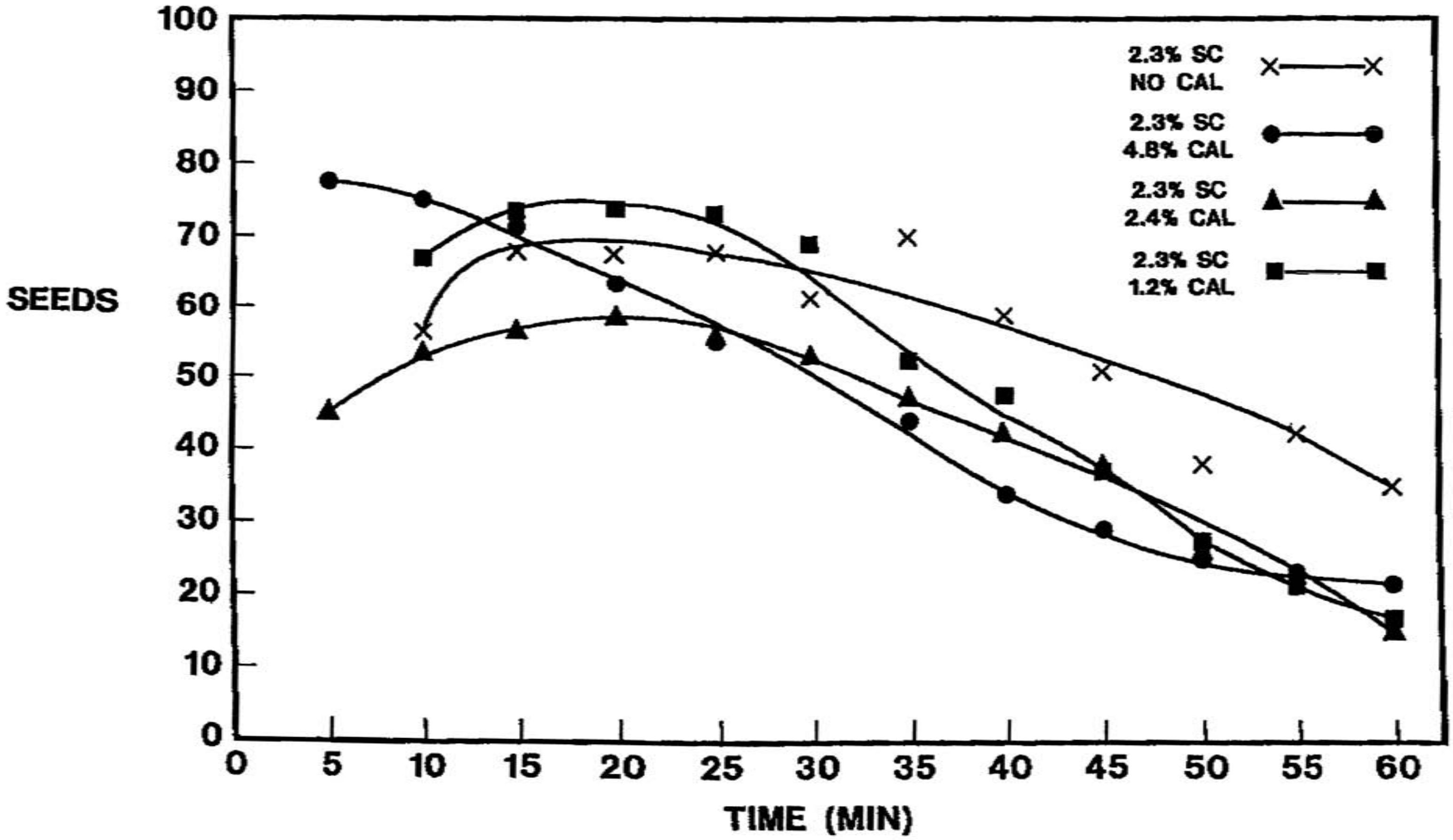


FIGURE 7

FINING EFFECT OF CALUMITE

(4.6 PERCENT SODA FROM SALT CAKE - 2650°F)

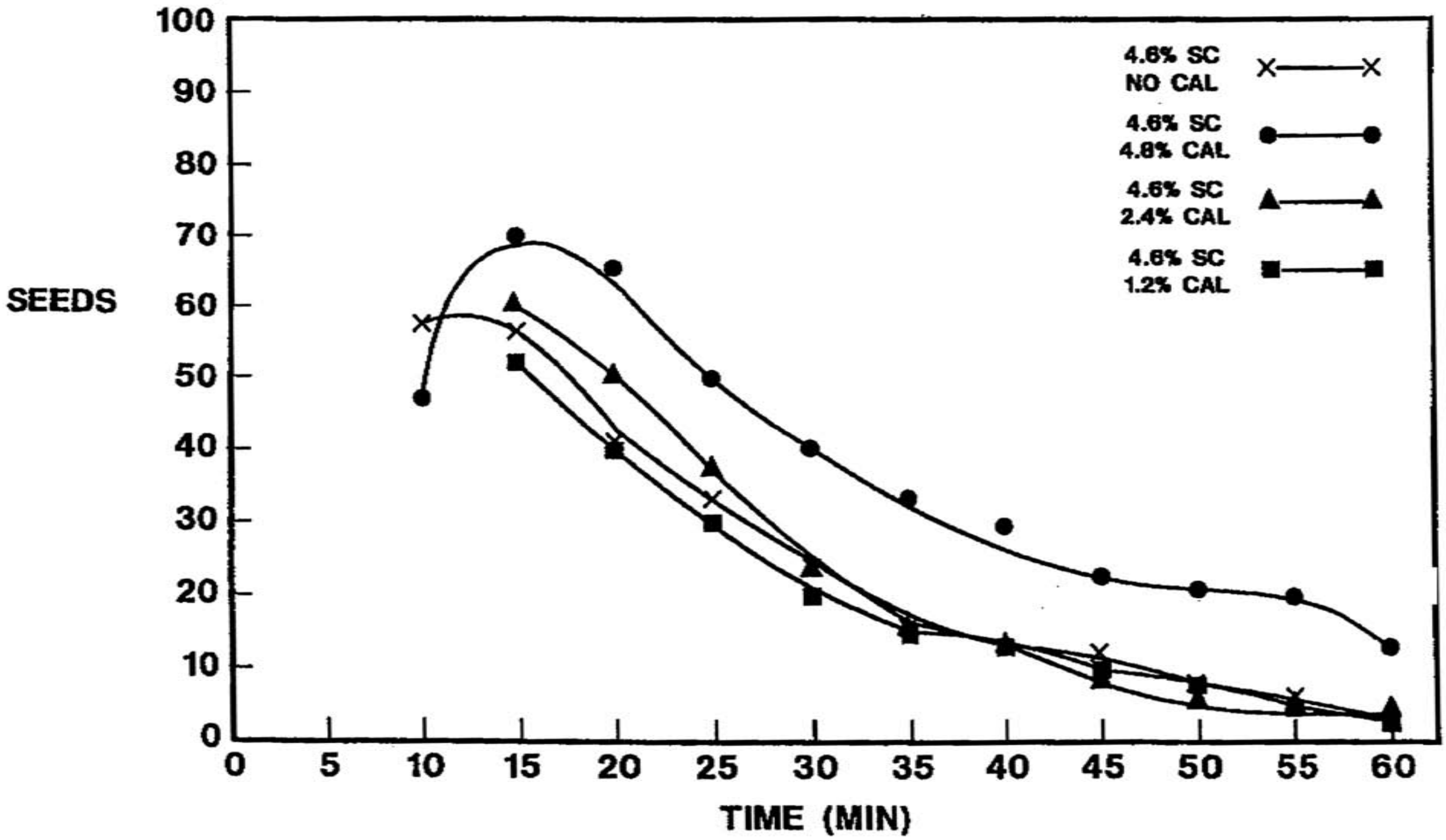


FIGURE 8

WEATHERING OF CALUMITE-CONTAINING GLASSES