A Transparent Aluminum Glass From Blast Furnace Slag

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A TRANSPARENT ALUMINUM GLASS FROM BLAST FURNACE SLAG

ABSTRACT

The object of this investigation was to find an advantageous method for the disposal of blast furnace slag.

As a result of this investigation, a method was developed for the manufacture of a transparent glass from this material.

The method consisted of heating together slag, building sand, and soda. The sulphur was removed from the slag and transparency conferred upon the glass by the addition of a small amount of arsenic trioxide.

The optimum conditions for carrying out the various steps in the process were determined.

The physical properties of the glass were determined and uses were suggested for this material.

The production of the glass was carried out on a large laboratory scale and a brief study was made of the probable large scale equipment and cost of manufacture. The use of slag and inexpensive building sand effected a great saving in the cost of the raw materials, permitted the utilization of the waste heat of the melted slag, and gave a glass of superior quality.

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A Transparent Aluminum Glass from Blast Furnace Slag

Introduction.

In the production of pig iron, blast furnace slag is recovered in enormous quantities. In the untreated state it brings an extremely low price. There were reasons for thinking that slag could be converted into glass which seemed to be a worthwhile effort.

Bibliographical Review.

Several workers have attempted to make glass from blast furnace slag.

Parsons[1] digests the fine blast furnace slag with a solution of alkali metallic silicate to form calcium and magnesium silicates. The latter are separated by a centrifugal or thickener, and are mixed with other materials to form a glass making charge.

In order to utilize a basic slag (i.e., blast furnace slag) Parsons[2] converts the calcium sulphide of the slag into hydrosulphide by treating the slag with steam under a pressure of 150 pounds. The soluble calcium hydrosulphide is separated and the residue treated with sodium hydroxide to form a soluble sodium aluminate.

Enequist[3] employs a basic soda slag containing iron (Fe^{**}), plus sand and other glass making materials to form a black glass for use as glass or as a glaze.

Note: Apparently the above is not a blast furnace slag but is produced in the refining of copper and similar metals.

Since the glass developed from blast furnace slag necessarily is an aluminum glass, references pertaining to these glasses are included below.

The effect of aluminum on the annealing temperature is discussed by English and Turner[4]. They find that aluminum reduces the annealing temperature in most cases where this element replaces magnesium or calcium molecule for molecule.

English and Turner[5] find that the substitution of aluminum oxide for sodium oxide reduces the coefficient of expansion much more than the replacement of sodium by calcium or magnesium.

The density of glass containing aluminum, according to English and Turner[6], is generally less than that of other glass.

The uses for sodium-calcium-aluminum glasses are discussed by H. J. Powell[7]. A number of special uses were developed for these glasses before and during the war.

Springer[8] discusses the influence of aluminum oxide on the fusibility of glass. He finds that aluminum oxide decreases the fusibility of high alkali glass, but increases the fusibility of high calcium, low alkali glass.

The general properties of aluminum glass are discussed by Hodkins and Cousen[9].

A TRANSPARENT GLASS OF SUPERIOR QUALITY FROM BLAST FURNACE SLAG

Examination of the literature discloses the fact that little work has been done on the conversion of slag into glass. These results do not look very promising. Parsons attempted to dissolve certain constituents from the slag by chemical treatment. These substances were used for making glass. He also attempted to dissolve, by digestion with steam under pressure, the sulphur which is present as calcium sulphide in considerable quantities. Enequist worked primarily with a basic soda slag recovered as a waste or by-product, in the recovery of copper and similar metals from their ores. The nature of this slag, and the nature of the impurities present are quite different from blast furnace slag.

Analysis of blast furnace slag shows that it contains silica and lime, both of which are essential in making glass. It likewise contains alumina, which is allowed to remain since the literature showed that its presence is beneficial to glass. Since slag consists primarily of these three compounds, a study of the methods given above, suggested the conversion of all the slag into glass without any preliminary treatment whatever.

To carry out the conversion mentioned above it is necessary to consider the impurities present in the slag. These consist primarily of sulphur and iron, both of which are present in considerable quantities, together with small amounts of magnesium and titanium. It is necessary to remove the sulphur since it makes the glass opaque. Preliminary work showed that this could be done very advantageously by the addition of a small amount of arsenic trioxide to the charge. The sulphur escapes during the heating as the volatile arsenic trisulphide or pentasulphide. The arsenic trioxide, apparently, also oxidizes the iron to the ferric condition in which form it is least objectionable. The effects of the magnesium and titanium can be ignored.

The slag was mixed with other glass making materials—chiefly sand and soda—in such proportions that the resulting glass had good working properties. It was discovered that glass sand was not necessary. Ordinary building sand proved to be satisfactory.

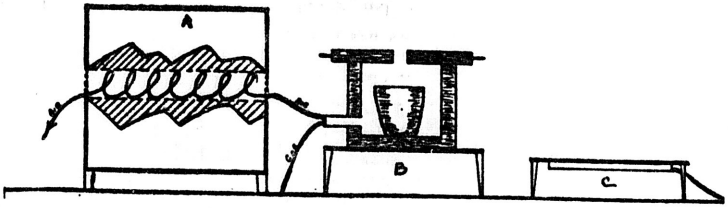
Unexpectedly good results were secured from the above mix and it soon became obvious that a method could be developed for the production of a glass of superior quality. The record of this investigation is presented below.

EXPERIMENTAL WORK

Preliminary work indicated that a temperature from 2500°F. to 2600°F. was necessary to fuse the mix and to carry out the necessary reactions between its constituents.

It appeared advisable to employ a gas fired furnace for this work. Accordingly, a small furnace was built from an old bucket. The furnace lining which was about one and one fourth inches thick consisted of an equal mixture of fire clay and sand. This lining proved to be very satisfactory. The experimental apparatus is shown in Fig. I.

The inside diameter of the furnace was 5 inches. Also the inside height was 5 inches. The furnace was provided with a large burner which entered one side near the bottom. The necessary compressed air for the burner was preheated by passing it through a coil of copper pipe heated in an



A—Electric Preheater
B—Gas Furnace
C—Pouring Plate
Scale: 1″ =12″

FIG. 1.—Experimental Apparatus

electric furnace. The burner was operated at an air pressure from 50 to 60 pounds per square inch. It was operated on natural gas.

The furnace was provided with a small fire clay crucible 2.25 inches in diameter and 2.50 inches high (inside dimensions). A crucible of this size gave a convenient quantity of glass (about 30 grams.) and still did not add the complications that a large laboratory scale or semi-plant operation would introduce. Later on, the work was carried out on a much larger scale.

The temperature of the furnace was determined by a Leeds and Northup optical pyrometer.

The melted glass was poured on a heated piece of sheet steel and rolled with a heated iron pipe. The sheet steel and the iron pipe were previously heated with a Bunsen burner.

In most cases, the rolled glass after it had cooled to a dull red was quickly transfered to an electric furnace, heated to a definite temperature, where it was annealed. The annealing consisted of the even and uniform cooling of the furnace whereby the strains set up in the solidification of the glass were relieved.

MATERIALS AND GENERAL PROCEDURE

Analysis of the various raw materials is given in Table I.

TABLE I

Analysis of Raw Materials Used.

Note: All results are reported as per cent by weight

	Gran. slag	Ungran. slag	*Sand	Brewer's Sand
H_2O	2.58	0.79	0.72	0.07
SiO_2	36.6	37.16	97.02	94.46
Fe_2O_3	1.37	3.54	1.09	0.32
Al_2O_3	11.09	13.45	0.64	4.18
TiO_2	——	0.47	——	1.02
CaO	45.11	43.33	0.65	0.38
MgO	0.22	Trace	Trace	Trace
S	1.20	1.0	——	——
Undetermined	1.83	——	——	——
Total	100.0	99.74	100.12	100.43

See page 29 for analysis of Meharg's sand.

The soda ash employed contained 85.72 per cent sodium carbonate and 14.77 per cent moisture.

The sodium sulphate employed in most of this work was of U. S. P. grade. A sample of crude sulphate employed in several runs was practically as satisfactory as the better quality.

The arsenic trioxide used contained 0.25 per cent non-volatile material, 0.20 per cent antimony trioxide, and .01 per cent iron. Since this compound is used in very small amounts, considerable variation in the composition should make relatively little difference.

Composition of Charge: Removal of Sulphur and Scum.

In the determination of the proper composition of the charge several considerations must be taken into account. In general[9], glasses usually contain from 65 to 75 per cent silica, from 8 to 18 per cent alkali, and up to 20 per cent calcium oxide, together with smaller amounts of other substances. Often considerable aluminum oxide is present. For verification of the above see Hodkin and Cousen—Textbook of Glass Technology published by D. Van Norstrand Co.

From the analysis of the slag given above, it is obvious that the slag differs greatly from the desired composition. The calcium oxide content (45.11 per cent) is entirely too high, while the silica content (36.6 per cent) is much too low. A glass of this type would probably have a relatively high coefficient of expansion. Further, a glass of this type would stiffen very quickly on pouring[9], i.e., the product could be worked over a very limited temperature range. In many cases the upper limit is about 18 to 20 per cent

*This washed sand was employed for all of the small scale and most of the large scale work. It was secured from the Flomaton, Ala. plant of the Roquemore Sand and Gravel Co., and was considered to be representative.

calcium oxide. However, the presence of aluminum oxide would probably permit the use of more calcium oxide.

In order to secure a mix of the desired composition, sand was added to the slag. Ordinarily "glass" sand is used in glass making. This is sand of exceptional purity and uniform in size. However, recognizing that glass sand is not always found in districts where slag is available, an attempt was made to use a cheaper and more abundant sand. It was found that a good grade building sand was entirely satisfactory for this purpose. An additional advantage in using sand of this grade is that the usual screening plant is eliminated since the sand is ground to the desired size, all of the ground material being used. Note: In the work carried out later on a much larger scale, in some cases, "glass" sand of the usual degree of fineness was employed. Quartz and similar materials, if available, also might be used to advantage.

By employing 7 parts of slag to 8 parts of sand the calcium oxide was reduced to an amount corresponding approximately to the upper limit permitted for this material. Addition of a small quantity of alkali, (1.76 parts of soda ash) appreciably lowered the melting point of the mix and materially improved the working properties.

Addition of arsenic trioxide, as stated before, is essential in removing the sulphur of the slag and in oxidizing the iron. It is well known that arsenic trioxide is sometimes used in glass making as a fining agent. However, its use here depends upon an entirely different principle. As already stated it is used to combine with and remove the sulphur as the volatile arsenic trisulphide or pentasulphide and likewise to oxidize the iron, which is present in relatively large amounts, to the ferric condition. In this form the iron imparts lesser color to the glass. The determination of the proper quantity of arsenic will be discussed later. Suffice it to state at this time that one per cent was the usual amount used.

A mix consisting of 7 parts of slag, 8 parts of sand and 1.76 parts of soda ash, together with one per cent of arsenic trioxide worked very nicely except that a considerable amount of scum was formed. This was believed to be due to uncombined silica. It was obvious that increase of alkali should correct this condition. Since sodium sulphate is recommended by Hodkin and Cousen, for the correction of this condition, preliminary work was carried out whereby varying amounts of hydrated sodium sulphate were added to the mix until the scum disappeared. Five parts of sulphate to 40 parts of the mix proved effective.

The composition of the final charge follows:

(A) 7 parts of slag plus 8 parts of sand plus 1.76 parts of soda ash.
(B) To 8 parts of the above mix, add 1 part of hydrated sodium sulphate.
(C) Add 1 per cent arsenic trioxide.

On a percentage basis, we have the following:

Wet basis
(Per cent by weight)

37.21	slag
42.52	sand
9.37	soda ash
9.90	hydrated sodium sulphate
1.00	arsenic trioxide
Total 100.00	

NOTE: If anhydrous sodium sulphate is used, the slag amounts to about 40 per cent.

The above mix gave a pale green, transparent, glass of high luster, free from scum. The glass poured and worked very nicely, remaining soft for a considerable time. If this glass is desired for bottles, it is believed that it would work satisfactorily in automatic bottle machines. If it should harden too quickly for this purpose, increase of the alkali content should be beneficial.

It should be mentioned in this connection, that in special cases, the slag might be increased to a considerable degree and the sand reduced to a corresponding degree, without causing serious difficulty.

Fineness of the Charge.

As already stated, if the sand could be ground to a convenient size and all of the ground material used for glass, apparently it would be a distinct advantage. Further, such a procedure would eliminate a screening plant. An additional advantage would be a reduction in the period of heating, since the finely ground sand would combine more quickly with the alkali than a coarse grained sand. On the other hand, excessive fineness is believed to produce foaming of the charge.

With the above points in mind the sand was ground to a convenient size in a Broun pulverizer. Screen analysis of this material is as follows: None held by 40 mesh, 14.7 per cent held by 60 mesh and 63 per cent held by 100 mesh.

The slag was also ground in the Broun pulverizer, screen analysis being as follows: None held by 40 mesh, 34.5 per cent held by 60 mesh and 38 per cent held by 100 mesh.

The remaining constituents, with the exception of the sulphate, were already ground. The sulphate was ground to a fine powder. Screen analysis of this material was difficult to get, because of the hydrated character of this salt.

The soda ash and the arsenic trioxide were already ground to pass 100 mesh.

The above mix, ground as described, gave little trouble. The mix melted quickly, combination between the alkali and the sand being rather rapid. On heating, the charge swelled somewhat for a short time, but this was easily controlled by penetrating with a glass rod the crust which formed, whereupon the crust gradually subsided. Since coarse grained "glass sand" (none held by 20 mesh, all held by 40 mesh) likewise swelled and behaved in much the same way, no objection to the finely ground sand was observed.

Should the finely ground materials not prove to be satisfactory on a large scale, coarser grained materials could be used.

Course of a Run.

A large quantity of the mix was prepared and placed in a stoppered bottle.

As will be shown later, an attempt was made to utilize the waste heat of the slag, i.e., to convert melted slag directly into glass. The transfer of the charge to a heated crucible from a previous run seemed to be a step in this direction. Since this procedure also greatly reduced the time required for a series of runs, it appeared to be quite advantageous. Preliminary work having indicated that this procedure was entirely practical, this plan was adopted.

85 grams of the mix was placed in the hot fire clay crucible from a previous run. The average temperature of furnace and crucible at this time was about 1200°F. The crucible as it rested in the furnace was filled about two-thirds full of the charge.

The gas was then lighted, the air turned on, and the top placed on the furnace. The preheater was turned on, thereby gradually heating the air required for the combustion of the gas.

The temperature of the furnace rapidly increased. In 15 to 20 minutes, the charge began to swell. It was penetrated once or twice with a glass rod. Soon the charge subsided and quiet fusion took place.

As soon as the charge was placed in the hot crucible, arsenic vapors were noticed. During the first 20 or 30 minutes, vapors of arsenic sulphide passed from the crucible in large amounts. If desired these vapors could be collected by sticking a glass tube in the charge, the volatile sulphide condensing as a yellow precipitate in the upper part of the tube. When the furnace became hotter, sulphur dioxide was smelled readily. This continued for at least an hour.

The temperature of the furnace rapidly increased reaching 2500°F. in about 30 minutes. The temperature of the furnace was then slowly increased reaching 2600°F. in approximately one hour. It was maintained at this temperature, until the glass was poured.

At the end of approximately one and one-half hours, a sample secured by a Pyrex glass tube, showed that the glass was thoroughly fused, that transparency had been developed, that combination of the silica with the alkali was completed, that the glass was uniform in texture, and was reasonably free from bubbles. Consequently the glass was poured on a steel plate, previously heated by a gas burner, where it was rolled with an iron pipe. There were indications that the glass could be rolled, blown or moulded.

In most cases the glass was air-cooled to a dull red and quickly transfered to the electric annealing furnace which had been heated to the desired temperature (1100°F.) For further details see "Annealing".

Calculated Composition of the Glass.

An attempt was made to analyze the glass but so much difficulty was encountered, that it was decided that the composition could be more accurately calculated. The results calculated from the composition of the mix given on page 9 are as follows:

	Per cent by weight
SiO_2	64.90
CaO	20.18
Na_2O	8.75
Al_2O_3	5.17
Fe_2O_3	1.15
MgO	0.09
Total	100.24

In the above calculation, the theoretical yield of glass was 84.5 per cent, i.e., 15.50 per cent passed off as water or gas. It is assumed that there was no volatilization of the sodium. It is assumed further that the loss of sulphur is balanced by the arsenic remaining in the glass.

The actual amount of glass poured is from 65 to 75 per cent by weight.

Note: When a new crucible was used, since some of the glass was retained in the crucible, the yield was somewhat less. When the weight of the samples which are removed in the melting is added to the above, the yield is about 80 per cent which is not much below the theoretical yield.

Neither the crucible nor the furnace lining was corroded by the glass or by the chemicals added to the charge. This lining which consists of equal weights of fire clay and sand required little attention.

Examination of the above table shows that the calcium oxide content is relatively high. In spite of this fact, it is believed that the glass is sufficiently workable. Should experience show this is not the case, an increase in alkali should correct this condition.

DETERMINATION OF OPTIMUM CONDITIONS

Amount of Arsenic Trioxide.

As already stated the object of the arsenic trioxide is to combine with and remove the sulphur, and to oxidize the iron and keep it in that condition.

The amount of sulphur is fixed for a given slag, but the amount of oxidizing agent necessary to oxidize the iron and keep it in that condition depends upon the amount of iron in the slag and sand and somewhat upon the reducing effect of the furnace gases. It follows that in general the amount of arsenic trioxide required will vary considerably. For example, in the work outlined it will be shown that one per cent is satisfactory, while, as seen later, on a larger scale, using the same mix, 1.5 to 2.0 per cent is required for a light green glass. The increase is probably due to the greater quantity and effectiveness of the furnace gases. On the other hand, in the larger scale work it is shown that by using a pure "glass" sand found in large quantities in at least one locality in Alabama, an almost colorless glass could be secured with 0.3 per cent arsenic trioxide.

The amount of arsenic trioxide required in the small scale work already outlined, was determined as follows: Preliminary work indicated that 2.0

TABLE II

Glass Made with Different Amounts of Arsenic Trioxide.

	Appearance in diffused daylight.		Appearance under 60 watt frosted globe.		
Per cent As 203	Thickness of section 1/8 inch.	Thickness of section 1/4 inch.	Thickness of section 1/8 inch.	Thickness of section 1/4 inch.	Color
2.0	Very transparent	Transparent	Very transparent	Transparent	Light green
1.0	Very transparent	Transparent	Very transparent	Transparent	Light green
0.50	Transparent	Transparent	Transparent	Transparent	Green to brown
0.25	Transparent	Somewhat transparent	Transparent	Transparent	Dark brown
None	Pract. Opaque	Opaque	Slightly transparent	Opaque	Dark brown to black

per cent gave satisfactory results. To determine if this was the least amount that could be employed, a series of runs was made employing 2.0, 1.0, 0.5 and 0.25 per cent of arsenic trioxide. The other conditions were the preliminary conditions which have been used up to this time. These are as follows: Temperature 2500-2600°F.; length of heating 90 minutes; rate of heating, rapid, (see p. 15), charge placed in a hot crucible from a previous run.

The results of this work are given in Table II.

Examination of the table shows that with no arsenic trioxide, the glass is opaque. With more than 0.5 per cent green glass is secured, while with less than 0.5 per cent, the glass is brown. It follows that either brown or green glass can be made as desired by merely making a slight adjustment in the amount of arsenic trioxide.

In the selection of the proper amount of arsenic trioxide, it is desirable to avoid 0.5 per cent since both green and brown glass is secured at this point. It is necessary to go definitely on one side or the other of 0.5 per cent. Consequently, if a brown transparent glass is desired, the arsenic trioxide can be kept at a very low figure. However, it is believed that the pale green glass would have many more uses than the brown glass. Consequently, more than 0.5 per cent arsenic trioxide is desired. To insure a reasonable margin of safety, i.e., to prevent the reduction of the iron by the furnace gases, 1.0 per cent arsenic trioxide was selected. This amount was used in all remaining work carried out on a small laboratory scale.

Temperature of Heating.

In the preliminary work, a temperature from 2500°F. to 2600°F. was employed. This temperature was determined by a Leeds and Northrup calibrated optical pyrometer made by the Hickok Electrical Instrument Company. This temperature was satisfactory, the glass being quite liquid and flowing readily from the crucible. At 2600°F. the bubbles were removed readily.

In order to determine if from 2500°F. to 2600°F. is the best temperature range, a series of runs was made at a somewhat lower temperature (2400°F.) and at a higher temperature (2700°F.). In this work, the amount of arsenic trioxide employed was one per cent, the remaining conditions being the preliminary conditions discussed on page 13.

The results secured at the various temperatures are summarized in Table III.

TABLE III

Glasses Made at Various Temperatures

Temperature of furnace	Fusion of the glass	Bubbles in glass	Pouring of glass	Condition of crucible and furnace lining
2400°F.	Somewhat incomplete	Numerous	Rather unsatisfactory	Good
2500°F.-2600°F.	Complete	Many less than at 2400°F.	Entirely satisfactory	Good
2700°F.	Complete	Relatively few	Fairly satisfactory Some crucibles soft	Fair to poor

On examination of Table III, it is evident that 2400°F. is too low. A this temperature, the glass is somewhat unevenly melted, it is too viscou to flow readily from the crucible, and it contains many bubbles. At th highest temperature (2700°F.) the melted glass flows readily from the cru cible and is relatively free from bubbles. However, difficulties were en countered with the crucibles and furnace lining. Some of the crucibles wer soft at the end of the run and in some instances were somewhat corroded The furnace lining made from an equal weight of fire clay and sand, wa partly fused at this temperature. Temperatures above 2700°F. were not trie because it was practically impossible to secure higher temperatures with th equipment available.

Since 2400°F. was too low, and 2700°F. too high, it is obvious tha from 2500°F. to 2600°F. is the correct temperature. At this temperature fusion of the glass is complete, the glass pours readily from the crucible an the bubbles are readily eliminated. The furnace lining is not appreciabl softened or corroded at this temperature.

Consequently this temperature was adopted for all future work.

Length of Heating.

The length of heating must be sufficient to permit the completion of th following:

(1) Fusion of the mix or charge.
(2) Combination of the arsenic with the sulphur and the complete volitizatio of the arsenic sulphide.
(3) Reaction of the alkali with the silica to form complex silicates.
(4) Fining of the glass and removal of bubbles.

In the small scale work all of these steps with the exception of numbe four are completed within 40 minutes. In the heating of the mix the charg soon begins to swell due to escaping gases. As the temperature increase the charge subsides. Within a few minutes more fusion is practically com pleted. At this time the glass is practically opaque. Within 20 to 30 minute the glass has become transparent indicating that the first three steps hav taken place but the glass is still full of bubbles. Consequently, it is necessar to heat for a longer period in order to remove them.

Preliminary work indicated that sulphur dioxide comes off for at leas one hour. Since this would produce bubbles, it does not appear necessary t try a period as short as one hour. Consequently, the results secured at on hour were not accurately determined. However, one or two runs for th duration of one hour gave glass with many bubbles.

TABLE IV

Length of Heating.

Time (minutes)	Color	Degree of transparency	Bubbles	Additional
100	Pale green	Very transparent	Fair number	Practically no SO_3 comin off
140	Pale green	Very transparent	Possibly a few less than at 100 minutes	Little if any SO_3 coming of

In order to allow time for the bubbles to escape a series of runs was carried out during a period of heating (100 minutes) appreciably longer than one hour. In order to determine if this time was sufficiently long, a series of runs was carried out at a still longer time (140 minutes). In all this work the amount of arsenic trioxide was one per cent, and the temperature was from 2500°F. to 2600°F. For other conditions see the preliminary conditions discussed on page 13.

The results of the above work, are summarized in Table IV.

An examination of the above table indicates that after heating for 100 minutes the bubbles were relatively few. Since the results secured at 140 minutes were not a great deal better than those secured at 100 minutes, a period of heating of 100 minutes was adopted for the remainder of the small scale work.

At this point, attention should be drawn to the fact that no particular importance was attached to the removal of the last few bubbles. It is difficult to employ on a small scale, the devices that are employed to advantage for the removal of bubbles on a large scale. It is well known that on a large scale removal of bubbles can be accomplished in a satisfactory manner. In all probability the period of heating on a larger scale would be much longer than on a small scale.

Rate of Heating.

In the preceding work, the charge was placed in a crucible previously heated to a dull red. The gas and air were then turned on and the furnace was heated as rapidly as possible. As already mentioned (see page 10) this plan is advantageous on both a laboratory and a plant scale.

There is no reason for thinking that better results can be secured by a slower rate of heating. For the sake of completeness however, a series of runs was carried out at an appreciably slower rate. So that any possible variation in quality due to the rate of heating might be brought out, the charge was placed in a cold crucible and furnace. In case any difference in quality was noted at the slower rate, it would then be necessary to de-

FIG. II.—Rate of Heating

termine whether it was due to the cold crucible and furnace or to the slower rate of heating.

In order that the length of heating in the two cases might be the same, the time in each case was calculated from the point where the heating curve became essentially horizontal (2400°F.

In these runs, the amount of arsenic trioxide was one per cent, the temperature from 2500 to 2600°F., and the length of heating 100 minutes, or 70 minutes after reaching 2400°F. Note: When the usual rate is employed, it requires 30 minutes to reach 2400°F.

The two rates, are shown graphically in Fig. II.

The results secured at the two rates differed little if at all. No difference was noted in the general appearance, degree of transparency, or color of the glass. The number of bubbles was about the same in the two cases. Since no clear cut advantage was derived at the slower rate, the rapid rate was adopted.

In summing up the above results, it may be stated that the most favorable conditions for the production of glass from granulated blast furnace slag have been shown to be: (1) Amount of arsenic trioxide, one per cent. Note: employing ungranulated slag, and glass sand, 0.3 per cent was satisfactory. See pages 31 and 32. (2) Temperature of heating, 2500°F. to 2600°F. (3) Length of heating, 100 minutes. (4) Rate of heating, rapid. See page 15.

ANNEALING OF THE GLASS

The object of annealing is the removal or prevention of strain which develops when the glass is suddenly cooled. When a piece of glass is heated to a point known as the "upper annealing temperature" or "annealing temperature", the strain is quickly relieved. Then, if the glass is slowly cooled, it will be relatively free from strain.

The upper annealing point has been defined[9] as the point where 95 per cent of the strain is relieved in three minutes. It is frequently defined as the temperature above which there is danger of loss of shape. In other words the glass is appreciably soft at this temperature.

Two methods of annealing are known. One method consists of annealing quickly at a relatively high temperature and cooling slowly. The other method consists of annealing slowly at a relatively low temperature, and cooling quickly.

According to Adams and Williamson (Jr. of Franklin Inst. Vol. 190 p. 838) the second method has many advantages. According to these men, glass anneals throughout a range known as the annealing range which begins at the upper annealing point and extends 150°C. below this point. At this temperature the glass anneals very slowly. The advantages of the second method given by Adams and Williamson are as follows:

(1) It is easier to hold an annealing kiln at a constant temperature than to cool the kiln at a given rate.
(2) The cooling takes place in a short time and does not need careful control.
(3) The danger of over heating the glass is minimized.
(4) The danger of devitrification is less when the glass is annealed at a low temperature.

Because of the advantages mentioned above, the second method was

adopted for annealing of the slag glass. The following work is yet to be completed in connection with annealing:

(1) Determination of the upper annealing temperature.
(2) The selection of a point **below** the upper annealing temperature for the annealing of the glass.
(3) Determination of a satisfactory rate of cooling.
(4) The selection of a method for determining **when** the glass is properly annealed.

Determination of the Upper Annealing Temperature.

This point was determined by supporting sheets of glass 2.5 inches long and one-eighth of an inch thick on two fire clay supports set horizontally two inches apart in an electric furnace. The furnace was then slowly heated, the temperature being measured by a calibrated base metal thermo-couple. The temperature where the glass begins to sag was recorded as the upper annealing point. Careful examination showed that this was 1200°F. The upper annealing point of a glass of somewhat the same composition (17.38 per cent calcium oxide) is reported by Hodkin and Cousen, p. 49, as 613°C. (1135°F.).

Selection of a Suitable Annealing Temperature.

It was believed that a temperature 100°F. below the upper annealing temperature would avoid the dangers mentioned by Adams and Williamson, and still permit rapid annealing of the glass. This temperature proving to be very satisfactory, it was adopted for this work.

Experimental work was carried out to determine how long it was necessary to maintain the glass at this temperature. With pieces of glass several inches long, two inches wide, and from one-eighth to one-fourth of an inch thick, ten minutes proved to be sufficiently long. For larger pieces of glass a much longer time would probably be necessary.

Rate of Cooling of the Glass.

As stated before slow cooling of the glass is necessary to prevent the development of strain. This rate of cooling would depend no doubt upon the dimensions of the glass. Consequently, this rate must be redetermined whenever the dimensions of the glass are changed.

The proper rate of cooling for sections of slag glass of the dimensions already discussed was determined as follows: It is advantageous that this rate be as rapid as possible. The most rapid rate of cooling readily obtainable would be secured by cutting off the electric current and allow the furnace to cool. This procedure would require no attention whatever.

(1) The average rate of cooling of the furnace when this was done was as follows:

	Temperatures, °F.		
	Original temperature, 1100°		
10 minutes	987°	70 "	595°
20 "	900°	80 "	580°
30 "	810°	90 "	545°
40 "	765°	100 "	500°
60 "	665°	110 "	470°

The glass was allowed to remain in the furnace overnight or until it had cooled to room temperature.

(2) Results secured by transfering the hot (dull red) glass to the furnace heated to 1100°F. maintaining this temperature for 10 minutes, cutting off the electric current and allowing the furnace to cool, proved to be very satisfactory. Consequently, this procedure was adopted.

Selection of a Method for Determining When the Glass is Annealed.

According to Hodkin and Cousen, p. 43, the fact that unannealed glass is under strain is very conveniently shown by the use of polarized light. Strained glass turns the plane of vibration of plane polarized light which passes through it. Consequently, all that is necessary is to adjust the Nicols in a polarizing microscope until the field is dark i.e., "cross" the Nicols. If a piece of annealed glass is then placed upon the stage, the field remains dark. However, if strained or unannealed glass is placed upon the stage, the field is relatively light (sometimes green) due to the rotation of the plane of polarized light which permits some of it to pass through the upper Nicol.

When the above method was applied to the slag glass, heated and cooled as already explained, the field was dark showing that the glass was properly annealed.

METHODS AND RESULTS OF TESTING THE GLASS

The most important physical properties of the glass include the luster, hardness, specific gravity, tensile strength, crushing strength, coefficient of expansion, electrical conductivity, thermal endurance, and the resistance to corrosion by water, acids and alkalies. The details and results of the various tests to which the glass was subjected are given below.

Luster.

Glass made from both granulated and ungranulated slag (see a later section, page 30) possessed a high gloss or luster quite different from the inexpensive glass ordinarily used for bottles and similar purposes, table ware and the like. This property suggested the use of the glass not only for bottles, but also for table tops, tiles, and for decorative purposes.

Hardness.

The hardness of the glass made from both the granulated and ungranulated slag is from 6 to 6.5 on Moh's scale of hardness. Window glass is given as 5.5 by Kraus and Hunt's Mineralogy.

Specific Gravity.

The specific gravity was determined in the usual way by submerging the annealed glass in water and recording the loss in weight. The results of this work are given in Table V.

The values below are probably a little low due to a few bubbles in the glass. This somewhat high value is probably accounted for by the high calcium oxide content and by the presence of considerable alumina. According to Hodkin and Cousen both compounds impart a high density to glass.

TABLE V

Specific Gravity of Slag Glass.

		Weight in air	Weight in water	Specific gravity
Glass from granulated slag	(1)	15.1234	9.3500	2.61
	(2)	10.2210	6.3061	2.60
	(3)	17.1502	10.5872	2.60
	(4)	11.7424	7,2132	2.583
Glass from ungranulated slag	(1)	20.4470	12.6300	2.606
	(2)	7.2762	4.4936	2.605
	(3)	10.210	6.301	2.602

Average of glass from granulated slag 2.598
Average of glass from ungranulated slag 2.603
General average 2.600

Tensile Strength.

Acocrding to the same authorities, page 23, the tensile strength of glass is of great importance since the mechanical stability of glass-ware depends in large measure upon it. This property is measured by the smallest weight which will cause the breakage of a rod of glass of unit area cross section. According to Hodkin and Cousen (page 23) Trautwine reports from one to four tons per square inch for glass.

The same authorities quote Winkelmann and Schott to the effect that Jena glass varies between two and five and one-half tons per square inch. Kowalski's results vary from 5 to 6 tons per square inch.

The tensile strength of the slag glass was determined by means of a thread breaking machine belonging to the Textile Department. The method as finally developed consisted of drawing rods of glass several inches long, so that the rods were of greater diameter at either end. Near each end where the diameter of the rod begins to increase, a small rubber lined screw clamp was lightly clamped on the rod. Each of the screw clamps was attached to the thread breaking machine by a stiff loop of steel wire. By this procedure slipping and twisting of the glass when the pressure was applied, was practically eliminated. A uniform vertical "pull" was secured, the glass breaking with a circular cross section.

The breaking force was measured on the dial of the thread testing machine, and the diameters of the rods at the point where they broke, or at the smallest place was accurately determined by a thickness gauge made by Randall-Stickney Co., of Waltham, Mass. The diameters of the rods varied from .025 to .035 inches.

The results of the tests made on glass from both granulated and ungranulated slag are given in Table VI.

It is noted that there is little difference between the glass from the granulated slag and ungranulated slag and that the results from both types are quite high.

It is true that the diameters of the glass rods tested were small. This of course leads to a high conversion factor. However, the diameters were carefully determined and it is not believed that serious error was introduced in this way. The tensile strength of a number of samples of laboratory

TABLE VI

Tensile Strength of Slag Glass.

Number	Glass from granulated slag lbs. per sq. inch) (Tensile strength	Glass from ungranulated slag lbs. per sq. inch) (Tensile strength
1	10.815	21.875
2	14.726	19.270
3	7.897	8.000
4	23.331	19.875
5	11.679	9.365
6	18.887	
7	19.375	
Average	15.257	15.677

glass roding determined with exactly the same apparatus was from 10,000 to 12,000 pounds per square inch.

The high tensile strength of the slag glass is accounted for by the relatively high content of calcium oxide and by the considerable content of aluminum oxide. Both of these compounds impart a high tensile strength to glass. See Hodkin and Cousen, pp. 100 and 107.

Crushing Strength.

According to Hodkin and Cousen, p. 24, the crushing strength does not play such an important part in the mechanical stability of glass as the tensile strength. However, the crushing strength is said to be much higher than the tensile strength.

The crushing strength of small sections of the slag glass from one-eighth to three-sixteenths of an inch thick, was determined by a small hydraulic press. In order to take care of irregularities of the glass, the latter was placed between small boards secured from a cigar box. The results of this work are given in Table VII.

TABLE VII

Crushing Strength of Slag Glass

Glass	Area of glass (sq. inches)	Lbs. pressure employed	Crushing strength (lbs. per sq. in.)
1. From gran. slag	0.20	10.000	50.000
2. " " "	0.137	7.000	51.000
3. " " "	0.07	10.000	143.000
4. " " "	0.125	8.000	88.000
5. From ungran. slag	0.125	8.000	64.000
6. " " "	0.1369	7.000	61.100
7. " " "	0.125	8.000	64.000

The testing of sections of small area was necessary because of the limited capacity of the press available for crushing the samples. Considerable difficulty was encountered in preventing the cracking of the glass when the pressure was applied. As a whole the above results are not considered highly accurate, but are believed to be approximately correct. Due to the presence of a few bubbles, and to the fact that the pressure was not applied entirely in a vertical direction, the above results are believed to be low. Several of these results are comparable to the results for Jena glass given by Hodkin and Cousen p. 24.

Coefficient of Linear Expansion.

The importance of the coefficient of expansion for bottles that are to be heated, for chemical glass ware, etc., is too well known to require discussion. The coefficient of expansion of the slag glass was determined in the usual way by slowly heating a long rod of glass and recording the increase in length. The glass rod was firmly attached to an iron bar which was surrounded by a jacket through which hot air was passed. The increase in the temperature of the rod was determined by a thermometer while the increase in the length of the rod was determined by means of a micrometer.

In order that the rods might be representative they were made by melting together glass from each series of runs. The results secured in this work are given in Table VIII.

TABLE VIII

Linear Coefficient of Expansion.

	Original length of rod (mm.)	Increase in length of rod (mm.)	Increase in temp. °C.	Linear coefficient of expansion
Glass from granulated slag	787.5	0.44	69.5	.00000803
	787.5	0.42	69.5	.00000767
	787.5	0.43	69.5	.00000785
	786.5	0.43	67.0	.00000816
	786.5	0.44	67.0	.00000835
	786.5	0.44	68.0	.00000824
	786.5	0.44	68.0	.00000824
		Average		0.0000081
Glass from ungranulated slag	786.0	0.46	66.0	.00000887
	786.0	0.46	66.0	.00000887
	786.0	0.45	69.0	.0000083
	786.0	0.48	68.0	.0000089
		Average		0.00000873
		General Average . .		0.00000841

It is noted that the results for glass made from ungranulated slag are slightly higher than those secured from granulated slag. This is probably accounted for by the fact that in the former case an attempt was made to utilize the waste heat of the melted slag. The method employed for this did not permit quite as accurate control of the composition as the other method.

The tendency was toward a little too much slag. This would make the results run high. See page 30. The higher iron content of this slag would have the same effect.

The coefficient of expansion secured above compares favorably with that of other glasses. According to Hodkin and Cousen, soda lime glass varies between .000011 and .000008, while laboratory glass-ware varies from .0000055 to .0000075. Consequently the slag glass has a lower coefficient than most of the soda lime glass and is but little higher than the maximum reported for the chemical glass.

Electrical Resistance.

The electrical resistance of the slag glass is not considered of particular importance. However, for the sake of completeness, several preliminary determinations of this property were made. It is well known that an accurate determination of electrical resistance is highly complicated. No claim for great accuracy is made in this work.

The small samples of glass were compressed between two conducting surfaces. The set up consisted of a galvanometer, a standard shunt, and a resistance. The apparatus was connected and the voltage applied. The deflection of the galvanometer was noted. This instrument was of the portable type with a megohm sensitivity of 10^8, made by Leeds and Northup. Knowing the constant of the galvanometer the resistance can be calculated. The formula for this together with a typical calculation is given below:

$$R = \frac{KE}{Md} = \frac{90{,}000{,}000 \times 100}{5 \times 2} = 900 \text{ Megohms}$$

In the above formula, K is the galvanometer constant (90 megohms) M the shunt constant (5), d the deflection in mm. (2), and E the volts supplied (100).

K was determined by substituting a known resistance in place of the unknown.

The results secured on the slag glass varied from 300 to 900 megohms per cubic centimeters. The temperature when this work was done was 90°F.

Note: The writer is much indebted to Professor Carlovitz of the Department of Electrical Engineering for his assistance in this work.

Thermal Endurance.

According to Hodkin and Cousen (p. 28), the power of glass to withstand sudden temperature changes without breaking is known as its thermal endurance. This property is said to depend upon several physical properties the most important of which are (1) Thermal conductivity (2) Thermal expansion and (3) Tensile and crushing strength.

A high thermal conductivity, a low coefficient of expansion, and a high tensile and crushing strength favor a high thermal endurance.

It will be remembered that the slag glass has a high tensile strength and a relatively low coefficient of expansion. Both properties imply a high thermal endurance. The thermal conductivity was not determined due to lack of suitable equipment. However, this factor can be calculated from the composition of the glass. (see Hodkin and Cousen, p. 26). Because of the high calcium oxide content this value should be high. It follows that a high thermal endurance is to be expected in the case of the slag glass.

Hodkin and Cousen (p. 29) more or less definiely classify glass according to its thermal endurance. Bottles are tested for thermal endurance by heating them in water and suddenly submerging them in cold water. Where thermal endurance is good, 75 per cent should withstand temperature changes of 50°C. or more.

The thermal endurance of glass for miners lamps is determined by heating the glass in water to 100°C. and plunging it in water at 15°C., (a temperature difference of 85°C.) when not more than 50 per cent should break.

The slag glass was tested for thermal endurance by the methods outlined above. Pieces of annealed glass, three to four inches long, two inches wide, and from one-sixteenth to one-fourth inch thick (this thickness is comparable to bottles) were heated to 82°C. and submerged in water at 32°C. Other pieces of similar size were heated to 100°C. in boiling water and submerged in water at 15°C. It is recognized that testing sections of glass several inches long by this process, would not necessarily give the same results as the testing of bottles. In order to secure a direct comparison, a number of pieces of brown and white bottle glass were secured which had approximately the same dimensions as the slag glass. They were tested in exactly the same way. The results secured in this work are given in Table IX.

TABLE IX

Thermal Endurance of Slag Glass

	Temp. heated	Temp. of the cold water	Temp. difference	Result	
Glass from granulated slag	82°C.	32°C.	50°C.	No change No change No change	No change No change No change
Glass from ungranulated slag	82°C.	32°C.	50°C.	No change No change No change	No change No change No change
Bottle glass (brown and white)	82°C.	32°C.	50°C.	No change No change No change	No change No change No change
Glass from granulated slag	100°C.	15°C.	85°C.	No change No change Cracked	No change No change No change
Glass from ungranulated slag	100°C.	15°C.	85°C.	No change No change Badly cracked	No change No change No change
Bottle glass (brown and white)	100°C.	15°C.	85°C.	No change No change Badly cracked	Badly cracked No change No change

On examination of the above tables the conclusion is reached that the thermal endurance of the slag glass by direct comparison is at least as good and probably somewhat better than bottle glass. It will be remembered that there are theoretical reasons for expecting the slag glass to have a good

thermal endurance. According to the data given by Hodkin and Cousen, which has been mentioned, the slag glass is better in this respect than the bottle glass and is probably about as good as the glass for miner's lamps.

The conductivity of heat and modulus of elasticity were not determined due to lack of suitable equipment. A method for calculating these results from the composition is given by Hodkin and Cousen pp. 26 and 24.

RESISTANCE OF SLAG GLASS TO CORROSION

The importance of the durability of glass, or its resistance to corrosion by water, acids and alkalis is obvious. This property is important in almost any type of glass. It is particularly important in the case of bottle glass, glass for building purposes, and for chemical glass. It follows that this property is of much importance as far as slag glass is concerned since suggested uses for the slag glass include those mentioned above.

In most cases, the corrosion of glass is tested by a study of the action of boiling water, boiling hydrochloric acid and hot alkali solution upon it. A table showing the action of these reagents upon two grades of chemical glassware is given by Hodkin and Cousen (p. 56). A number of samples of slag glass were tested by the method suggested above. For the sake of comparison, these results were tabulated by the side of the data given by Hodkin and Cousen. The results are given in Table X.

TABLE X

Resistance of Slag Glass to Corrosion.

Note: Glass "A" mentioned by Hodkin and Cousen refers to a high grade chemical glass, while "B" is of somewhat inferior quality.

	Chemical Glass		Slag Glass	
	Loss in weight in milligrams per sq. decimeter		Loss in weight in milligrams per sq. decimeter.	
Water Test:	A	B	C	D
300 c.c. of distilled water boiled to 100 c.c. in 2 hours	0.6	6.2	None	None
Alkali Tests:				
(1) 2 N caustic soda (100°C.) for 3 hours	283.8	364.0	6.50	17.58
(2) N/10 caustic soda (100°C. for 3 hours)	61.8	111.3	0.83	——
Hydrochloric Acid Tests:				
(1) 250 c.c. constant boiling acid evaporated to 100 c.c. in 1.5 hours.	8.3	5.4	0.50	4.12

C refers to glass from granulated slag while D has reference to glass from ungranulated slag.

Examination of Table X indicates that the slag glass offers an excellent resistance to the corrosive action of boiling water, alkali, and hydrochloric acid. No loss whatever was observed after treating with boiling water. The loss after heating in 2 N sodium hydroxide at 100°C. was almost negligible.

This loss is less than one-fifteenth that reported by Hodkin and Cousen for the better quality of chemical glass. A sample of brown bottle glass placed in the 2 N alkali solution with the slag glass, lost 23.1 mg. per decimeter. This is twice the average loss of the slag glass. The loss in hydrochloric acid is also much less than that of the chemical glass. After successive treatment of the slag glass with boiling water, alkali and acids, it was not dulled, but retained most of its original luster. This is not true in the case of low grade glass.

In general it would appear that the slag glass possesses excellent resistance to corrosive agents. This is probably due to the high calcium oxide content and to the presence of considerable aluminum oxide. The somewhat greater loss of the glass from the ungranulated slag is probably due to the fact that this glass contained somewhat more slag than the glass from the granulated slag. This is due to a detail in the manufacture which on a relatively small scale could not be controlled accurately. See p. 30. The increase in the iron content of this glass, likewise may explain the increase in the corrosive action.

SUMMARY OF THE PROPERTIES OF THE SLAG GLASS

In summing up the above results, the slag glass is characterized by a high luster, pale green (if desired the glass can be made almost colorless), to dark green color, a high specific gravity, a high tensile strength, a relatively low coefficient of expansion, a good thermal endurance, and a remarkable resistance to corrosion by boiling water, hot sodium hydroxide (100°C.) and boiling hydrochloric acid. The glass is further characterized by its elasticity, which in the drawn rods is very noticeable, and by it toughness. Under the present conditions no satisfactory method has been devised for securing quantitative data on these two properties.

POSSIBLE USES FOR THE SLAG GLASS

The relatively low coefficient of expansion, the high tensile strength, the good resistance to shattering on heating and submerging in water, and the excellent resistance to corrosive agents such as boiling water, hot sodium hydroxide solution, and boiling hydrochloric acid suggest the use of the glass for bottles, jars and similar purposes and also as a lining for kettles, tanks, and other pieces of chemical equipment.

A glass with the above properties should be suitable for building and construction purposes, such as glass floors, glass tiles and the like. The high gloss of the glass is of importance in this connection.

The glass is also suggested for decorative purposes. This glass when in the form of a fluted cylinder or in irregular hair like masses is quite attractive and might be used for vases, table tops, cheap jewelry and for similar purposes.

The aluminum content of the glass suggests that it might be used for some of the purpose which have been suggested[7] for sodium-calcium-aluminum glasses. This glass is used for mine horns, x-ray bulbs, thermometers, lamp shades, and airman's goggles.

PRODUCTION OF THE GLASS ON A LARGE LABORATORY SCALE

It was desirable to produce the glass on a larger scale in order to verify the small scale results and develop new information of value. A scale was adopted which was large enough to give much information of value, but still small enough to be within the capabilities of the equipment available for this purpose.

Apparatus.

The small scale appartus was duplicated on a much larger scale. A gas fired furnace was built 8.5 inches inside diameter (11 inches outside) and 10.5 inches high inside diameter (twelve inches outside). The walls of the furnace consisted of approximately equal weights of fire clay and sand. They were about one and one-half inches thick. Two gas burners were introduced near the bottom of the furnace. These burners made an angle of 90 degrees with each other. With this arrangement, the flames rotated around and around the crucible before passing out through an opening in the top of the furnace. This led to the regular and even heating of the furnace. The top of the furnace was built from equal weights of fire clay and sand. It was provided with an opening for the discharge of the furnace gases. It contained a long iron bar which passed horizontally through the top and projected on either side. The ends of this bar served as handles. A drawing of the apparatus is shown in Fig. III. (p. 27).

Each burner was provided with a coil of pipe which was placed in an electric furnace. The electric furnaces served for preheating the compressed air for the burners. The glass was poured on a heated electric hot plate where it was rolled with a piece of pipe which had been heated. The glass was annealed in an electric furnace.

Fire clay crucibles of two different sizes were used in this work. The larger size was 5.4 inches in diameter (outside) and 8 inches high (outside). Since the breakage of these crucibles was high under the conditions under which the furnace was operated, a smaller size 3.5 inches in diameter and 5.25 inches high (outside) was used for most of the work, the larger size being used only enough to check the results secured on the smaller scale.

The granulated slag and sand employed for the small scale work was used for this work also. As a matter of fact some of the same mix used in the small scale work was used for this work.

The process itself was exactly the same as that employed on the small scale. The results secured in this work are given in Table XI.

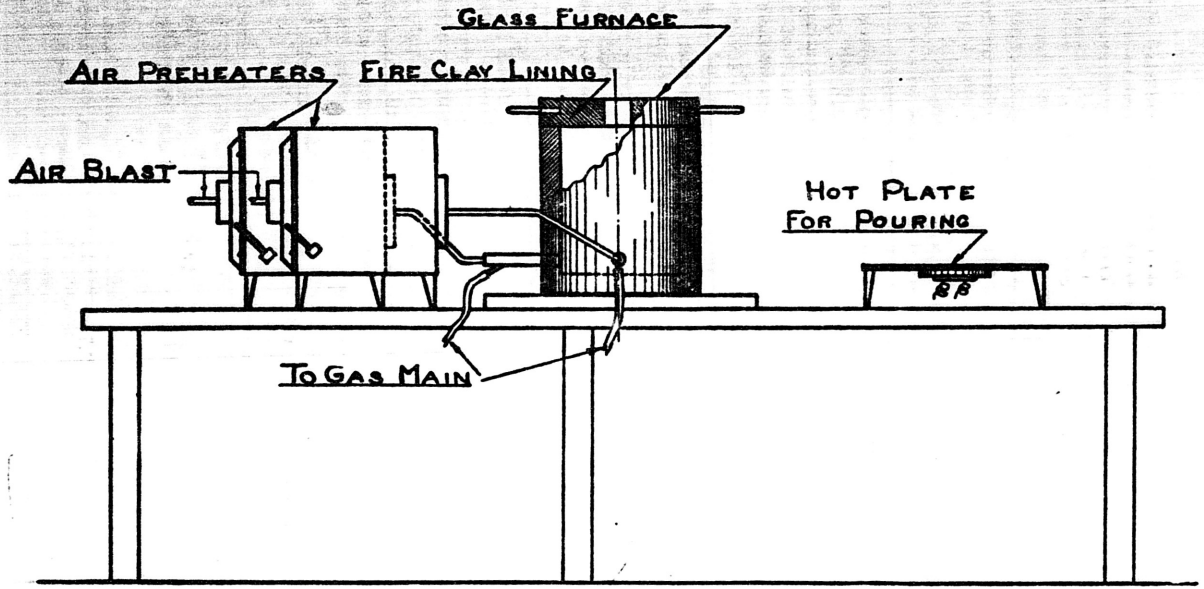


FIG. III.—Large Laboratory Scale Production of Slag Glass
Scale 1" = 12"

TABLE XI

Larger Scale Production of Glass from Granulated Slag

Run	Weight of charge (gms)	Amount of arsenic (per cent)	Rate of heating	Time of heating (hrs.)	Yield (per cent)	Color	Comments
1.	700	1.0	See "Remarks"			green	Charge foamed over top of crucible. Run discontinued.
2.	600	1.0	"	3.0	80. (see below)	Dark green	Relatively few bubbles
3.	600	1.0	"	3.0	80.4 (see below)	Dark green	Nearly free of bubbles. Darker green than small scale.
4.	606	1.0	"	3.0	82.0	Dark green	Few bubbles Darker than small scale.
5.	229	2.0	"	3.33		Light green	Inc. in As_2O_3 gives a much lighter colored glass. Few bubbles
6.	228	1.5	"	1.5	71.5	Light green	Inc. in As_2O_3 give a lighter colored glass.
7.	606	2.0	"	2.17	81.0	Light green	Many bubbles
8.	612	2.0	"	2.5	80.0 est.	Light green	Crucible broke at 2.5 hrs. Not many bubbles.
9. see below	202	1.0 (also $NaNO_3$)	"	2.66	80.0 est.	Light brown	Bubbles.
10. see below	202	1.5	"	1.83	70.0	Very pale green almost colorless	Lightest color made up to this point.
11. see below	203	1.5	"	2.75	—	Almost colorless	

Remarks.

In runs one to four inclusive a dark green glass was secured which was much darker than that secured on the small scale. Apparently this was due to the fact that the iron was reduced to the ferrous condition. This could readily be since the gas burners were so constructed that there was an excess of gas rather than air. Probably this was responsible for a strong reducing action.

In runs 5 to 8 inclusive, the arsenic trioxide was increased in order to retain the iron in the ferric condition. It will be noted that this gave a light colored green glass which was the equal of that made on the small scale.

In runs 9, 10, and 11 a very high grade sand secured from property owned by Dr. Meharg of Anniston, Alabama was used. The remainder of the charge was the same as usual. A very pale green, almost colorless glass was secured in these runs. The above sand is said to run 99.57 per cent silica, and 0.03 per cent iron. This sand was used in the coarse form in which it was delivered. Screen analysis showed none held by 20 mesh, all held by 40 mesh. 1.5 per cent arsenic trioxide was sufficient to give an almost colorless glass. This is an excess since on page 31 it is shown that 0.3 per cent is sufficient.

In general the above runs duplicated the small scale runs. As the mix began to melt, it swelled. The charge was penetrated once or twice with a glass rod to take care of this. The fineness of the sand appeared to make no difference in the degree of swelling. The coarse grained sand used in runs 9, 10, and 11 apparently brought about as much swelling as in the runs where the ground sand was employed.

The light green glass made on this scale apparently was fully the equal of that made on the smaller scale. For the methods and results of testing this glass, see page 18.

The rate of heating was approximately the same in the various runs. This rate in typical runs is given below.

	Begin	20 min.	40	60	80	100	120	140	160	180
Run 2	cold furnace	2090°F.	2436	2530	2575	——	2530	2575	2530	2530
Run 7	cold	2160	2337	2515	2560	2590	2590	2590		
Run 10	cold	1906	2305	2452	2500	2500	2540			

In this work it was found that the crucibles could be used only once. In commercial work the crucible or tank furnace could be used many times. Consequently in calculating the yields, the glass left in the crucible was added to that recovered on pouring. If this was not done the yield would be reduced to 60 to 65 per cent of the net weight of the charge.

In conclusion, a study of the larger scale runs, indicated that exactly the same results were secured as on the small scale. It is true that more arsenic trioxide was required to give a light green glass. However, in the next section, when the burners were corrected to use more air and less gas, good results were secured with much less arsenic trioxide. For example, with the high grade sand previously mentioned only 0.3 per cent was neces-

sary to give an almost colorless glass. In this connection, one or two runs have been made where part of the arsenic trioxide was replaced by sodium nitrate. The results were good. One sample of technical sodium sulphate which apparently contained nitrate, gave a transparent glass without the addition of arsenic trioxide.

UTILIZATION OF WASTE HEAT OF THE MELTED SLAG

It would be quite desirable if the waste heat of the melted slag, when it is discharged from the blast furnace, could be utilized. This would necessitate the conversion of the melted slag directly into glass without allowing it to cool.

Small scale work carried out to determine this point involved melting the slag, adding the other materials which are necessary, and heating until the necessary reactions are accomplished and the slag has been converted into glass. For this work it is obvious that ungranulated slag should be used. Analysis of this slag is given on page 8.

The sand employed for this work was the building sand used in the small scale work. Its analysis is given on page 8.

The sand was ground as usual. Screen analysis showed none held by 20 mesh, 36 per cent held by 60 mesh, and 63 per cent held by 100 mesh. The sand was then mixed with all the other constituents except the slag, in the same proportions as used in the small scale work. (See page 9). The apparatus employed is the same as that described in Fig. IV.

The course of a run was then as follows:

A weighed amount of coarsely ground slag was placed in a crucible, which was heated in the furnace until the slag had melted. The hot slag was then poured on top of the proper weight of sand-soda mixture which was contained in a cold crucible. The quantities of slag and sand-soda mixture were so calculated that the final mix had the usual composition. Some of the slag remained in the slag crucible after pouring. It is necessary to estimate what allowance must be made for this, since the crucible could not be weighed before and after using since its bottom becomes covered with melted glass from the furnace bottom.

After the melted slag was poured on the top of the sand-soda mixture, the crucible was placed in the furnace, still hot from melting the slag, where it was heated in the usual way. Within 20 to 30 minutes the entire charge is melted, when it is stirred with a glass rod. If necessary the contents of the crucible are stirred again about 15 minutes later. Not much stirring is necessary since the gases from the soda, sulphate and arsenic trioxide are forced to pass upward through the melted slag. The run was then continued in the usual way until the glass became transparent and relatively free from bubbles.

The above method worked very nicely. It has one distinct advantage over the old method which is that there is no swelling of the charge on heating.

The rate of heating in a typical run is given in Fig. III b.

The results of the various runs are given in Table XII.

TABLE XII

Conversion of Ungranulated Slag Directly into Glass.

(Utilization of Waste Heat of the Melted Slag)

Run	Weight of slag (Gms.)	Weight of total charge (gms.)	Amount of arsenic trioxide (per cent)	Rate of heating	Time of heating after melting slag (hrs.)	Yield	Color	Comments
12.	75	200	1.5	See below	1.75	70.	Light to medium green	Many bubbles
13.	75	200	1.5	See below	1.50	75	Medium green	Some bubbles. Some brown in glass.
14.	85	200	2.0	"	2.25	71	Green	Somewhat lighter color than in run 13 Too much slag by mistake.
15.	75	200	2.0	"	2.08	70	Medium green	Slightly darker than glass made in usual way.
16.	75	200	2.0	"	2.0	68	Medium green	Darker than glass made in usual way.
17.	225	600	2.0	"	1.0 (crucible broke)		Medium green	The larger crucibles frequently break.
18.	225	600	1.5	"	2.33		Light green	Special care to secure oxidizing gas flame Crucible broke run discontinued.
19.	75	200 (see below)	0.30	"	2.0	75	Very pale green	Meharg sand caused big reduction in arsenic trioxide.
20.	75	200 (see below)	0.30	"	2.25	70	Almost colorless	Considerable bubbles.
21.	275	600 (see below)	0.30	"	1.67		Pale green	Crucible broke.
22.	75	200 (see below)	0.50	"	2.0	72	Almost colorless	Sand owned by Judge Brewer, Opelika, Ala.
23.	75	200 (see below)	0.30	"	2.33	71	Almost colorless	Same sand as in No. 22

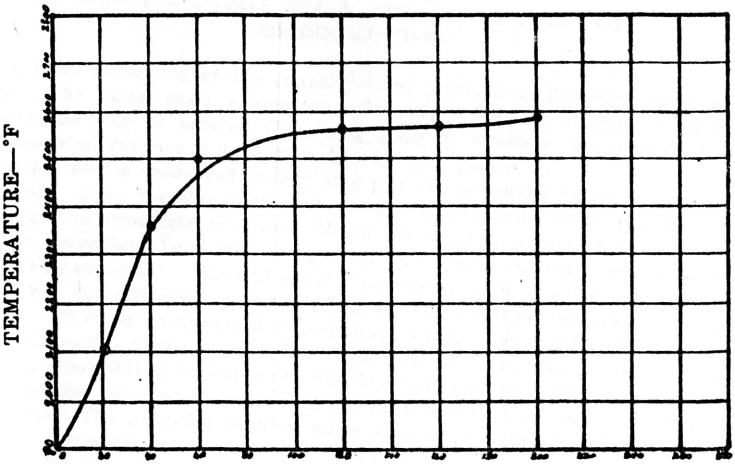


FIG. III B.—Rate of Heating

Remarks.

In runs 12 to 18 inclusive little reduction in the arsenic trioxide was possible if a light green glass was desired, in spite of the fact that the gas burners had been adjusted to give a more oxidizing flame. This no doubt is explained by the very high (3.54 per cent) iron oxide content of the ungranulated slag.

In runs 19, 20 and 21 sand from near Anniston, Alabama belonging to Dr. Meharg of Anniston was used. This sand not only permits the reduction of the arsenic trioxide to 0.3 per cent, but also gives an almost colorless glass. It is reported that large quantities of this sand are available. Analysis is reported to show 99.57 per cent silica and 0.03 per cent iron. Screen analysis is given on page 29.

In runs 22 and 23, a sand owned by Judge Brewer of Opelika, Ala. was used. This sand also permitted the reduction of the arsenic trioxide to 0.3 per cent and gave a nearly colorless glass. Analysis of this sand is given on page 8. None of this sand was held by 20 mesh, while all was held by 40 mesh.

Examination of the above table shows that the melted slag can be readily converted directly into glass. The glass itself is very comparable to that made from granulated slag in the usual way. (See page 18 for the methods of testing and a comparison of the two types).

This method not only utilizes the heat of the melted slag but also eliminates the mining, grinding and screening of the slag. The swelling of the charge during heating is also eliminated. The melted slag has a somewhat corrosive action on the clay crucibles. However, neither the glass nor the chemicals added to the charge had any effect on the crucibles or the furnace lining. The latter required very little attention.

PROBABLE LARGE SCALE APPARATUS AND COST CONSIDERATIONS

A brief discussion of the considerations involved in this work is given below. The large scale equipment will vary somewhat depending upon whether the slag is secured from slag piles or whether the melted slag from the blast furnace is converted directly into glass.

If the slag is recovered from a slag pile the following process might be employed: Mine the slag with a steam shovel and grind it in a series of course and intermediate crushers. Store the coarsely ground slag and the sand in convenient hoppers. Weigh out the proper amounts of coarsely ground slag and sand. Mix and grind these materials in a pulverizer or ball mill. Store this mixture in a suitable hopper. Convey this mixture to a tank furnace. There is no apparent reason why this type of furnace should not be satisfactory. Convert the glass from the tank furnace directly into bottles or other objects by automatic blowing machines, by pressing, or moulding. Transfer the shaped articles to an annealing furnace which is of the usual type. The annealed articles when discharged from the furnace are ready for shipment.

Hot slag from the furnace might be "granulated" i.e., poured into cold water. This would eliminate the mining and coarse grinding of the slag. The granulated slag might be stored in a suitable hopper, and added directly to the sand and other materials. The mixture might be finely ground and mixed in a suitable pulverizer or ball mill as before.

Should it be desired to convert the melted slag as delivered from the blast furnace directly into glass, the following process might be used: Discharge the melted slag into a gas heated, brick lined mixer. Deliver the other materials from a hopper into the cold end of a tank furnace. Pour a measured amount of the melted slag directly upon the sand and other materials. The hot gases from the soda, sulphate, and arsenic trioxide should then pass directly upward through the melted slag. This reduces the mixing to a minimum. Probably a mixer of some sort would be necessary, however. It may be that the use of large fire clay crucibles provided with a fire clay or graphite stirrer could be used advantageously. The remainder of the process is exactly like the one already described. A flow sheet of this process is given in Fig. IV.

Cost Considerations.

As already explained two or more processes are available for the production of the slag glass. There is also a considerable variation of the cost of the sand and other materials in various parts of the country. The composition of the sand itself varies considerably in different localities. Under the circumstances, it appeared to be preferable not to attempt to give a numerical value for the estimated cost of production, but rather to compare the processes for slag class with the standard process for soda lime glass, showing the advantages to be derived in utilizing the slag for glass manufacture.

The advantages derived from the use of the slag are as follows:

(1) The slag supplies all the bases (calcium oxide and aluminum oxide) necessary with the exception of the soda.

(2) The slag furnishes a considerable part of the silica (sand) necessary.

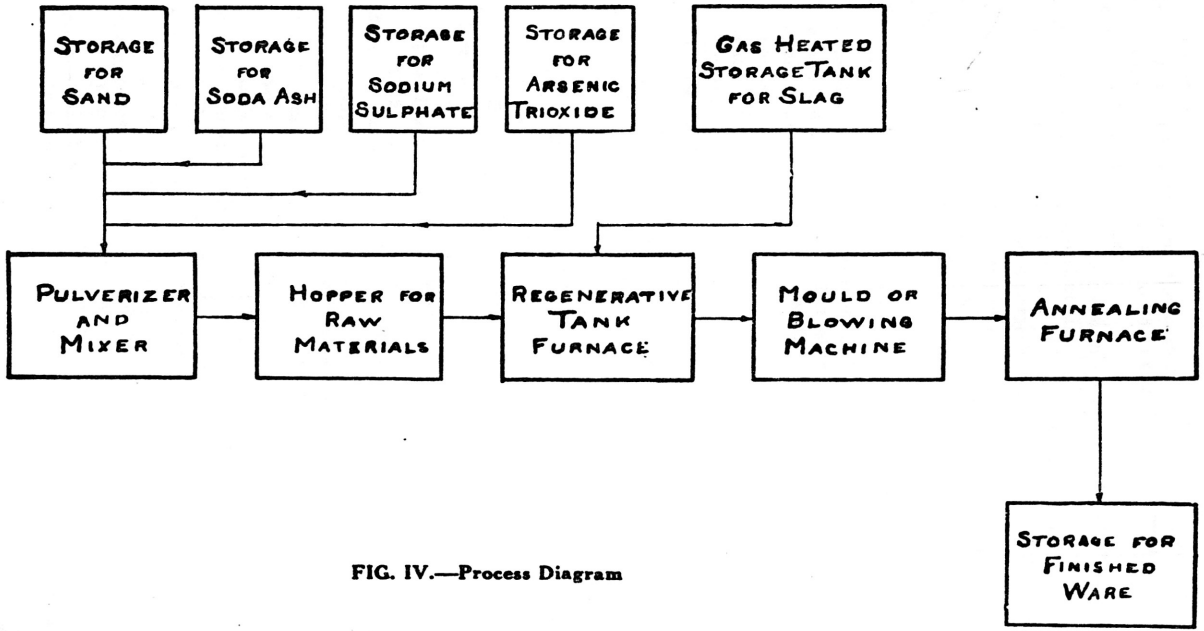


FIG. IV.—Process Diagram

(3) The remaining sand is building sand and not glass sand. Assuming that glass sand costs $2.50 per ton delivered while building sand costs 50 cents per ton, where $2.50 is spent for sand in soda lime glass manufacture, the cost of the sand for the slag glass would be only 39 cents, or about one-sixth the above cost.

(4) Since all of the ground sand is utilized, the cost of a screening plant and the cost of screening and grading the sand is eliminated. Further, the sand itself is more efficiently utilized.

(5) The process for slag glass is more flexible since in all probability quartz or sandstone could be ground and substituted for the sand.

(6) The heat of the melted slag from the furnaces can be utilized. In other words the melted slag can be converted directly into glass. This should appreciably reduce the amount of fuel required.

(7) The glass itself is of superior quality though made by an inexpensive process. Because of this reason the glass should bring a better price than soda lime glass.

SUMMARY

A process for the production of a transparent glass from blast furnace slag has been outlined and studied in detail. The effect of variations in the process has been studied and the optimum conditions for the process determined. The glass has been made on both a laboratory and a large laboratory or small semi-plant scale.

The probable large scale installation has been outlined and the cost of manufacture of the glass discussed.

The results of the experimental work indicate that by the proposed process a glass of superior quality can be produced from the slag at a low cost. This glass has many interesting properties. It should have many important uses.

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