When producing pig iron it is common to charge a blast furnace with iron ore, coke and a fluxing material, usually limestone. The iron ore is then reduced to metallic iron, while the molten flux is drawn off and forms the slag. Approximately 30 million tons of slag per year are produced by the iron and steel industry in the United States. Most of this slag is used as a road material and by the building industry. To some extent, however, blast furnace slag is used as a raw material for glass melting.

Blast Furnace Slag as a Raw Material for Glass Melting and Refining

by Rune Persson, manager, Grangesberg Co.
Oxelosund Steelworks
Glass products, Technical Development

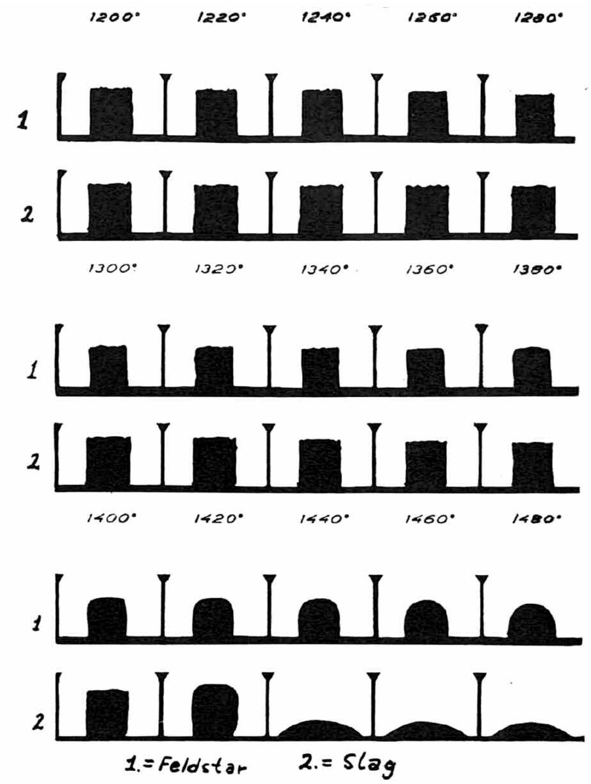


Fig. 1. *Cylinders of feldspar and blast furnace slag respectively heated in a hot stage microscope.*

The use of slag for glass melting was first mentioned in 1922 by Basore. It was then used in Germany for making colored bottles and chemical resistant glass. In 1925 two American patents were granted to Parsons[1]. In a detailed report, Basore[2] and Hull in 1934 described the production of opal glass, black glass, and chemical-resistant glass, using slag as a raw material. The chemical and physical properties of the glasses were tested and a plan for the production of slag glass on a commercial scale was discussed. They used up to 40 per cent of slag by weight of the batch and claimed to have obtained savings in the cost of raw materials and fuel and also to have produced glasses of superior qualities.

Two Russian glass technologists, Kitaigorodskii[3] and Karev dicussed the use of slag for glass melting in 1930. They used 30 per cent of slag in the batch and claimed that a high grade glass could be obtained at a considerable saving in cost. They could produce a clear glass when using sodium sulfate instead of soda ash for the introduction of sodium oxide.

In 1935, a manufacturer of glass containers in the United States began using slag in their amber production, limiting the quantities to approximately 5 per cent of the batch weight, excluding cullet. This limit was made necessary by high iron content of the slag and excessive variation of oxides.

The sheet glass factory of Oxelosund, Sweden, has used slag since 1935. The quantity added to the batch is ap-

1. C. E. Parsons, "Glass from Blast Furnace Slag," U.S. Pat. 1.522,697 (1925); "Slag in Glass Manufacture," U.S. Pat. 551,616 (1925).
2. C. A. Basore and L.H. Hull, "Technical and Economic Features in the Utilization of Blast Furnace Slag in Glass Manufacture" *Bulletin of Alabama Polytechnic Inst.*, No. 6, Vol XXIX (1934).
3. I. I. Kitaigorodskii and I. P. Karev, *Keram i Steklo*, 6.282 (1930) (Chem. Abstract 24.5954-1930), and *Keram. i Steklo* 6.465 (1930) (Chem. Abstract 25.1349-1931).

Blast Furnace Slag

proximately 1.5 per cent, or enough for the introduction of the full amount of alumina to the glass.

Today about 80 per cent of the amber glass being manufactured in the United States contains slag as one of its components. The use in amber container glass varies from partial replacement of the alumina-bearing component to a complete fulfillment of the dibasic oxides (calcium and magnesium). From 100 to 700 lb. per ton of glass is added to the batch. Slag is also used in emerald green glasses, the amount varying from 100 to 500 lb. per ton of sand. Blast furnace slag is also being used extensively as a batch component in fiber glass, where it comprises from 10 to 30 per cent by weight of the total batch.

In a recent American patent[4] it is claimed that an addition of 1.1 per cent of slag reduces the number of seeds by 65 per cent. For optimum improvement, it was found that the particle size should fall within the range 20 mesh to 100 mesh. As little as 0.01 per cent was found effective in lowering the seed count, and additions of up to 6.5 per cent were recommended. It was indicated that the improvements of the melting conditions were due to the finely divided sulfides in the slag.

General properties of blast furnace slag

According to a definition by the American Society for Testing Materials, blast furnace slag is "the non-metallic product consisting essentially of silicate and alumino-silicates of lime and other bases, which is developed simultaneously with iron in a blast furnace."

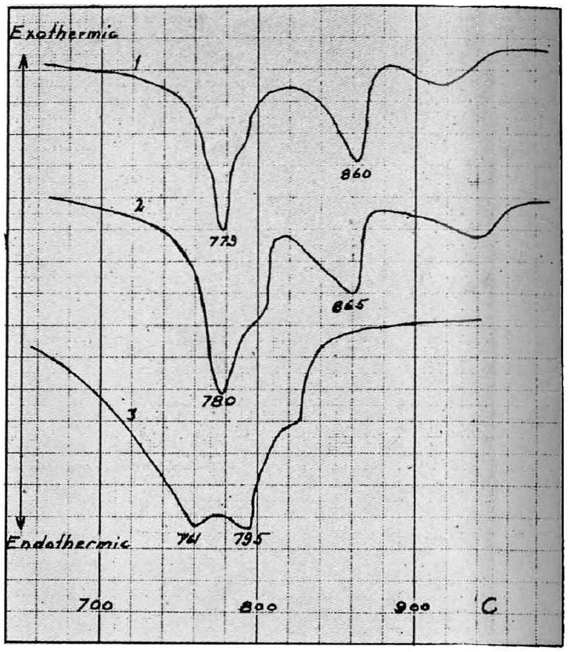
Depending on how the slag is cooled, it may be obtained in three different qualities—air-cooled, granulated, and expanded slag. All these forms may be used as a raw material for glass melting, although it is most common to use air-cooled and granulated slag. A typical chemical analysis of a blast furnace slag is shown in Table I.

It is seen that slag contains four major oxides which

TABLE I—Typical analysis of a blast furnace slag.

Oxide	%
SiO_2	38.1
TiO_2	0.6
Al_2O_3	9.4
Fe_2O_3	0.7
Cr_2O_3	0.006
CaO	42.8
MgO	5.4
MnO	1.2
Na_2O	0.1
K_2O	0.1
S	1.1

constitute about 95 per cent of the total composition. These oxides also are important components of ordinary soda-lime-silica glasses. There are some minor constituents, such as compounds of sulfur, manganese and iron with traces of other elements. From a glass melting point of view, the oxides of iron and manganese may be regarded as impurities. When so required, however, it is possible to choose slags low in these oxides. The iron in a slag exists as metallic iron as well as in an oxidized form. In granulated slag, the metallic iron usually contributes about



3.

4. J. R. Monks, Jr., U.S. Pat. 3,150,991 (1961), Glass melting method.
5. Private communication.

2.

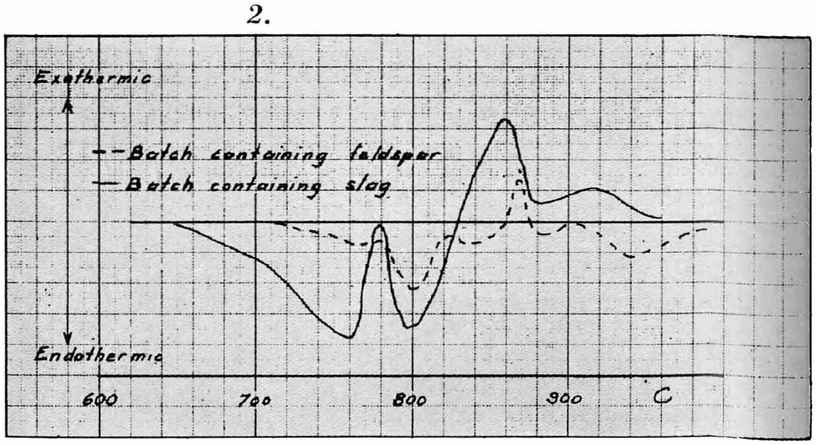


Fig. 2. *Melting reactions studied by means of a DTA-method.*

Fig. 3. *DTA-curves for batches containing feldspar and slag respectively after having subtracted the values for an alumina free batch.*

Fig. 4. *A recommended grain size distribution for blast furnace slag.*

TABLE II—Chemical compositions of the experimental glasses.

Oxide	Fourcault glass %	Container glass %
SiO_2	72.0	73.0
Al_2O_3	0.5	1.5
Fe_2O_3	0.15	0.15
CaO	8.0	11.5
MgO	4.0	—
Na_2O+K_2O	15.3	13.8

one third of the total iron, and this can be removed by magnetic separation.

The chemical and physical structure of slag is stable and is unaffected by weathering conditions. Its components are combined uniformly, and volatile matter is eliminated. Granulated slag is in a glassy condition, while air-cooled slag is mostly crystalized, frequently as gelenite and mervinite. The melting point of slag is 1300-1320°C.

A comparison between the behavior of slag and that of feldspar under a hot-stage microscope is shown in Fig. 1. The two materials were ground to less than 200 mesh, and cylinders of about 3 mm. diameter and 3 mm. high were pressed and placed under the hot-stage microscope, then heated to 1100°C in 50 min. The temperature was increased 4°C per min., and pictures of the cylinders were taken at 20°C intervals.

As can be seen from the figures, deformation starts at about 1300°C for the feldspar, and at 1400°C for the slag. The melting was completed at 1440°C for the slag and at 1520° for the feldspar. It is seen that the molten slag has quite a low viscosity compared to that of feldspar.

Laboratory meltings

Glasses of two different compositions were melted in an electric laboratory furnace—one, a typical Fourcault sheet glass and the other, a semi-white container glass. Their chemical compositions are shown in Table II.

4.

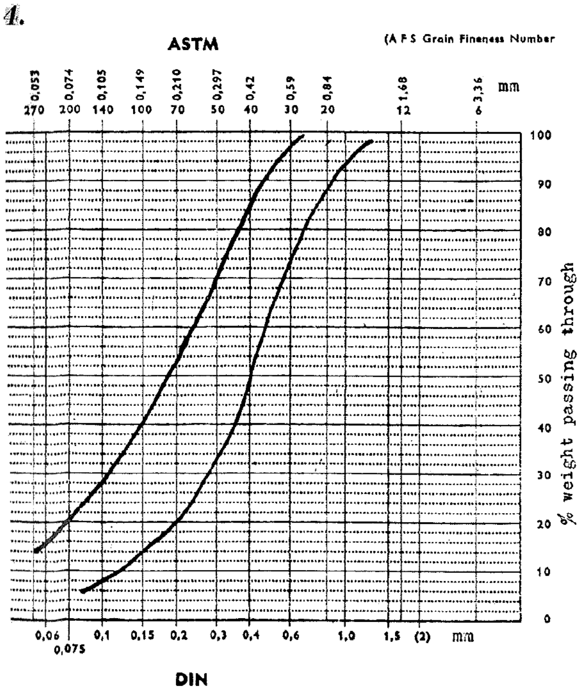


TABLE III—Chemical compositions of raw materials.

Oxide	Feldspar %	$Al(OH)_3$ %	Blast furnace %
SiO_2	74.0		34.1
TiO_2	—		0.5
Al_2O_3	15.1	65.0	15.7
Fe_2O_3	0.3		0.4
CaO	0.7		39.2
MgO	—		7.1
MnO	—		0.5
Na_2O	4.3		—
K_2O	4.5		—
S	—		1.6

Three different raw materials (Table III) were used in order to introduce the alumina in the glass: feldspar, aluminium hydroxide, and blast furnace slag.

Glass samples of about 200 gm. were melted in clay crucibles at 1400°C for 4 hr. A seed count of the different samples is given in Table IV.

TABLE IV—Number of seeds per 10 gm. of glass.

Type of glass	Feldspar	$Al(OH)_3$	Slag
Sheet glass	10	18	8
Container glass	60	69	3

The lowest seed count was found in the container glass when introducing alumina by the slag. With less slag, a higher seed count was obtained (Fig. 8) for the sheet glass. The alumina content is only 1/3, compared to that of the container glass. An opposite effect was found when introducing the alumina by feldspar and aluminum hydroxide.

Similar results have been found by the Glass Research Institute of Sweden[5]. While the above-mentioned results indicate that the number of seeds in a glass using slag as one of the raw materials is approximately 80 per cent of the seed count in a "feldspar glass," the results from the Glass Institute indicate a reduction of 45 per cent. These results refer to a sheet glass.

The three batch reactions were studied by means of differential thermal analysis methods. The first batch contained no raw material by which alumina was introduced; another batch contained feldspar; and the third one, blast furnace slag. In the alumina-free batch, there are two main endothermic peaks, one at 779°C and one at 860°C, as shown in Fig. 2. These peaks are also present in the batch containing feldspar. In addition, this batch has a more marked endothermic region from 780°C to 860°C. In the batch containing slag, the endothermic region starting at 640°C is quite marked. There is one peak at 761° and one at 795°C.

Plotting the figures for the feldspar and the slag-containing batches, after subtracting against those of the pure batch, shows (Fig. 3) that the endothermic region starts at about 60°C lower temperature in the batch containing slag. The two endothermic periods at 780°C and at 800°C appear more marked in the batch containing slag. Both batches have an exothermic peak at 860°-870°C. The exothermic region is much more marked, however, for the batch containing slag. It is seen from these curves that slag gives rise to more marked reactions in a glass batch than does feldspar.

(*Continued on page 582*)

INVENTIONS . . . *from page 579*

position to again draw the filming tube. A second pause then permits the new drawing operation to continue for a short time to allow the filming tube to develop uniform wall thickness and the flake product to thereby attain uniform standard grade. Thereafter the collection fan is restarted and the product is again collected (6 claims and the following references).

United States Patents

2,251,726	8/1941	Welech et al.	65-142 X
2,339,590	1/1944	Thomas et al.	65-11 X
2,780,889	2/1957	Fulk	65-181 X
2,884,531	4/1959	Bosch	18-2 X
2,972,210	2/1961	Broman et al.	65-160 X
3,035,371	5/1962	Mouly et al.	65-161

Other Patents

Sized Glass Fabric and Method. Pat. No. 3,227,192. Filed Apr. 2, 1962. Issued Jan. 4, 1966. Assigned to Pittsburgh Plate Glass Co. by David H. Griffiths (11 claims).

REFRACTIVE INDEX . . . *from page 563*

therefore governed by the change in polarizability and thus index decreases as hydrostatic pressure increases. This finding verifies Mueller's physical theory of photo-elasticity.

Temperature vs. Pressure

During this study the effect of temperature on the refractive indices of the same materials was also investigated. The change in index with change in temperature may be attributed to three factors:

1. A change in the number of scattering centers per unit volume.

2. A change in polarizability resulting from density change.

3. A change in polarizability caused by temperature change exclusive of density change.

Generally, refractive indices that decreased with pressure, increased with temperature, and vice versa. For glasses, however, the refractive indices increased with both pressure and temperature. This result is attributed to a large temperature coefficient of polarizability coupled with a low coefficient of thermal expansion.

BLAST FURNACE SLAG . . . *from page 539*

Full scale experiments

Experiments have been carried out in a regenerative tank furnace (500-ton capacity) for melting sheet glass. At a temperature of 140°C, a good quality glass with a low seed count was obtained when the alumina was introduced by slag. When changing to feldspar instead of slag, the number of seeds increased by about 60 per cent (Table V). The composition of the sheet glass is shown in Table II.

These results are in good correlation with the laboratory findings. When melting the batch containing feldspar, an attempt was made to decrease the number of seeds by increasing the temperature. For various reasons, it was not possible to increase the temperature more than 20°C to 1470°C. Even then, however, the number of seeds was

Calumite®

higher than when adding slag to the batch. The difference in seed counts was in fact so marked that it was impossible to carry on using feldspar in the batch for this particular furnace. Experience from some American glass manufacturers indicates that the furnace temperature has to be

TABLE V—Number of seeds in sheet glass.

ALUMINA INTRODUCED BY Slag	Feldspar	No. of seeds/kg. glass
100	0	19
50	50	25
0	100	30

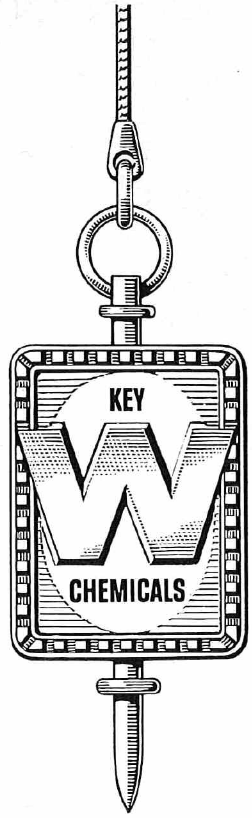
increased by approximately 40°C in order to get the same seed count when using feldspar, compared to when using slag. Practical experience has shown that the furnace output can be increased by about 20 per cent when slag is used instead of feldspar.

Quality recommendations

The chemical analysis of a slag from a blast furnace varies from time to time. In order to get a slag that is acceptable as a raw material for glass melting it is therefore necessary to process the slag in different ways. Air-cooled or granulated slag may be used. The slag processor usually must have enough quantity in order to blend slags of different chemical analyses so as to obtain a final product with a composition that lies within certain predetermined limits. It also has to be crushed and screened to fall within a certain grain size range. The processing involves a magnetic separation as well.

At Oxelosund it has been found that the limits of chemical analysis (Table VI) are acceptable for a slag for sheet glass manufacturing. The sheet glass has an alumina content of 0.6 per cent and an iron content of about 0.12 per cent Fe_2O_3. When using the slag for a glass with a higher alumina content, it may be necessary to reduce its iron content, since the color of the glass otherwise may be objectionable. It is possible to decrease the iron content to about 0.3 per cent. From a quality point of view, it is

(Continued on next page)



(Continued from page 583)
often required to have a high ratio of alumina to iron oxide. For types of glasses other than sheet glass it may be necessary to keep narrower ranges of the chemical analysis.

TABLE VI—Recommended analysis of a blast furnace slag.

Oxide	%
SiO_2	35 - 37
Al_2O_3	10 - 12
Fe_2O_3	max. 0.65
CaO	42 - 44
MgO	4 - 6
MnO	max. 0.60
TiO_2	max. 0.60
S	max. 1.5

The grain size of the slag should be within 20 to 200 mesh, which is similar to that of sand. A suitable grain size distribution is shown in Fig. IV.

Conclusion

After certain treatments, blast furnace slag can be a cheap and valuable raw material for the glass industry. In the American glass industry today, more than 250,000 tons* are used annually. With the raw material available in a great many nations, it seems quite likely that its use will be extended considerably in the future.

*Trademarked as Calumite.

Acknowledgment

The author is indebted to Robert W. Hopkins, president, the Calumite Co., Morrisville, Penna., for interesting discussions and valuable information.