

Calumite* slag as a glassmaking raw material for the increase of furnace productivity†

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Various new ideas have been proposed, evaluated, and become established in recent years to improve furnace output. This paper discusses the relatively recent introduction into the UK of the use of blast furnace slag as a means of increasing furnace melting rates, lowering furnace temperatures, and improving refining. Also mentioned is the very recent introduction into the American glass industry of another slag product for use in amber glass allowing the complete removal of sulphates.

Various methods have been put forward recently for improved furnace output, among them batch pelletising, oxygen injection, modified burner angle, batch grain size, and new materials or use of additional materials at present not in use. This paper gives information regarding the use of blast furnace slag which is proving to be most valuable in helping to increase furnace productivity. Many of the ideas put forward require time and capital expenditure to introduce, whereas slag can be easily introduced into the system. Not only is it a help in melting but it is also an economic source of Al_2O_3 .

The use of slag in America began more than 25 years ago; it was initially limited to the manufacture of coloured glasses, but more recently it has been introduced into flint, fibre, and flat glass. This wider application has followed the production of a technically controlled product which is marketed under the registered Trade Mark or Brand Name Calumite.⁽¹⁾ It was introduced into the United Kingdom in 1965 for trials but full scale production did not commence until 1968. From first year sales of 7 500 t from the UK Plant, sales progressed last year to 61 000 t. Of this, 35% was exported throughout Europe and as far away as New Zealand, Kuala Lumpur, Singapore, Bangkok, and Greece. A production plant is now in operation in Germany supplying central and southern Germany, Austria, and Holland, while Calumite from England is still used in northern Germany.

Calumite has been widely accepted and, when used correctly and within its known limitations, can produce some very striking results.

Slag processing and composition

Some 70% of the Calumite used in the UK is composed of gehlenite, $2CaO \cdot Al_2O_3 \cdot SiO_2$, and akermanite, $2CaO \cdot MgO \cdot 2SiO_2$, in solid solution. These in turn form eutectic mixtures with the remaining main minerals present which are various forms of calcium silicate. They are therefore in a very desirable low melting form and as they are already in a glassy state are perfectly compatible with other glass making raw materials. The processing of blast furnace slag and its methods of use in the glass industry are covered by patents, with others pending, and it has been so successful throughout the world that there is a danger of the word Calumite becoming a generic name for this type of slag.

Unprocessed slag has been used with some slight improvements in glass melting but the glassmaker wishes to have a raw material which is much more consistent. It is for this reason that a large amount of capital has been laid out to supply a product of a composition which will normally lie within prescribed close limits. This is done by evaluation of blast furnace records, and selection, blending, and treatment to attenuate the various chemical components present.

The following steps are taken to improve the quality of Calumite made available to the glass industry: inspection and knowledge of the various blast furnace raw materials; review of the steel company's batch and analytical records; inspection of the blast furnace slag collection pits; selection of the correct slag; primary processing; blending; sampling of layers; plant and laboratory testing; analytical forecasting; further processing; quality control, with analysis of current shipments; statistical control; technical liaison with customers; and glass batch computations.

Effects of Calumite and sulphur compounds on refining and melting

First consider the effect of sodium sulphate.⁽²⁾ It has only a limited solubility in molten soda-lime-silica glass and therefore at temperatures above the first liquid phase, about 1040°C, the sulphate collects at

* The name "Calumite" is proprietary to and the registered trade mark of the Calumite Company, USA, when applied to refined blast furnace slag, whose chemical and physical properties are closely controlled.

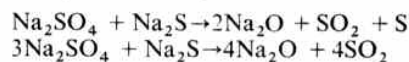
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the interfaces in the melt, between the particles of undissolved batch, the gas bubbles, and on the surface. It therefore acts as a surfactant and has the effect of increasing melt fluidity. At about 1288°C the thermal decomposition of Na_2SO_4 (in the presence of glass) becomes significant and this ultimately produces a stirring action at the interfaces which accelerates the dissolution of unmelted particles and allows bubbles to rise more rapidly through the melt.⁽³⁾

Sulphate has only a relatively low solubility in glass and therefore the residual excess sulphate, if still decomposing, can produce a large quantity of bubbles, resulting in foaming at or near the furnace hot spot.⁽²⁾ When sulphate is decomposed by a sulphide, as in the case of Calumite batch reactions, this begins at about 900°C, and the turbulence previously mentioned can occur earlier. In addition, the sulphate-sulphide reaction causes nearly all the sulphur in the batch to be ejected as SO_2 , thus reducing the possibility of foaming or reboil later in the melting process.^(4,5)

Sulphide alone will produce a refining action by reacting with free or nonbridging oxygen to produce SO_2 . However, to obtain full benefits in flint glass both the sulphide and sulphate should be used:



The use of elemental sulphur has been suggested⁽⁶⁾ and has proved effective, but the main problem here is getting an intimate distribution of a small quantity of sulphur throughout the batch. Using relatively large quantities of Calumite dependent on the colour of the glass being melted, the sulphide present is evenly and widely distributed.

More recent work⁽⁷⁾ has shown that Calumite mixed with sodium carbonate can increase the reaction with silica by a factor of twelve compared to sodium carbonate alone. This effect was not dependent on the sulphide content and is another factor in favour of its use compared to other sources of sulphur or sulphide.

Comparisons have been made between the use of carbon and saltcake and the use of Calumite in flint glass. While the two materials improve refining, it is more difficult to blend them completely into the batch materials and also, at the point where refining is at a maximum, the glass becomes amber. Obviously as Calumite can be used to produce amber glass, too much Calumite, with incorrect proportions of other materials, can produce amber in flint glass. However, there is a wider safety margin with Calumite than with carbon because optimum refining is attained well before the Calumite addition is likely to produce an amber.

Calumite is an ideal source of alumina and melts at a lower temperature than either felspar or syenite; it has been shown to give less seedy glass than either of them.⁽⁹⁾

As Calumite contains between 45 and 50% of CaO plus MgO , it partly replaces limestone and dolomite. They are a little cheaper as sources of lime and magnesia but the Calumite does not have the problem

of the evolution of CO_2 . It is known that limestone and CaO are very poorly wetted by the primary melt and this can affect the melting rate of a soda-lime glass batch. The use of Calumite as a partial replacement for limestone reduces the endothermic effect which takes place between 740 and 840°C, and which is associated with the decomposition of carbonates.

Examples of the successful use of Calumite or slag

Normally 50–140 lb Calumite are used for each tonne of sand in flint glass, up to 400 lb in amber glass, and up to 250 lb in green glass. Details of batches for glass fibre, light bulbs, tubing, or flat glass are not given but in each case large quantities can be and have been used. The difference in refining following the use of Calumite in flint glass can be seen in Figure 1, and the batches used are shown in Table 1.

Table 1. Batch formulae of melts showing seed reductions with use of Calumite

	A/1	B/2	3
<i>Batch composition (lb)</i>			
Sand	2000	2000	2000
Soda	692	696	699
Limestone	555	500	463
Felspar	236	193	151
Calumite	—	50	100
Saltcake	18.3	16	16
<i>Theoretical glass composition (wt %)</i>			
SiO_2	72.82	72.81	72.80
Al_2O_3	1.76	1.76	1.75
Fe_2O_3	0.039	0.041	0.043
CaO	10.30	10.06	9.83
MgO	0.19	0.43	0.68
Alkali	14.68	14.68	14.68
SO_2	0.20	0.20	0.20
TiO_2	—	0.01	0.02
Seed count ratio	160	4	1

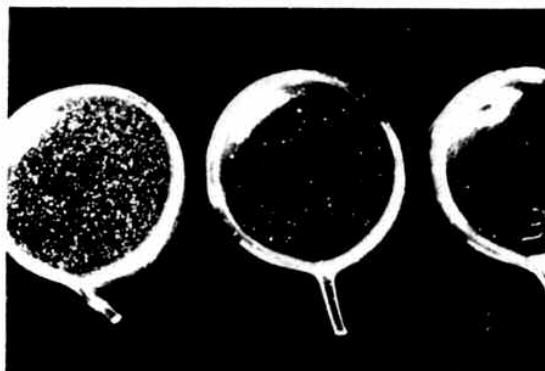


Figure 1. Samples showing decrease in seed count with use of Calumite

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Flat glass and containers in Russia

Work carried out by some Russian workers⁽⁸⁾ on the use of a slag in both containers and sheet glasses has been most encouraging. Using up to 10 wt% in sheet glass and 14% in container glass they found no changes in the main technological and physico-chemical properties, and suggested that the results indicated possibilities of a reduction in alkali oxide content.

From a sheet glass batch containing 8% slag, 1, 2, and 3% Na₂O were removed. A study of the melting of these glasses showed that the appearance of the liquid phase, dissolution of the sand grains, and also the final stages of melting and refining in compositions with Na₂O reduced by 2%, take place much more intensively than in a normal sheet glass. The degree of refining with 1–2% Na₂O removed is practically unchanged. With 3% Na₂O removed, the number of bubbles begins to increase but there are still less than in the original glass. It was found that with an optimum slag content and up to 2% Na₂O removed there was no effect on the viscosity between 1000 and 1400°C.

Flint glass

In one glassworks in America the use of 8.6% Calumite in a flint glass container tank has saved 20% fuel, reduced the seed to practically zero from 400/100 g, and reduced the melting temperature by 66 deg C. The average pull is now 3.25 t/m² at 1540°C. In another American glassworks, again in a flint tank, they were pulling 2.26 t/m² at a temperature of 1540°C and a seed count of 80–120/100 g with no Calumite. With the introduction of 3.75% Calumite they were able to drop their temperature by 38 deg C and lower the seed count to 4–10/100 g. Without further batch or temperature changes the

pull was increased to 2.46 t/m² and the average seed count increased to only 14/100 g; a further increase in pull to 2.96 t/m² gave an increased seed count of 25/100 g. Summarising, with 3.75% Calumite this manufacturer was able to lower his furnace temperature by 38 deg C, increase his pull by 31%, and reduce his seed count by 75%.

Table 2. Typical flint container formulae

	A	B
<i>Batch composition (lb)</i>		
Sand	2000	2000
Soda Ash	736	746
Limestone	508	423
Felspar	244	206
Calumite	0	100
Saltcake	16	16
Carbon	1.5	0
Decoloriser mix	0.75	0.75
<i>Theoretical glass composition (wt %)</i>		
SiO ₂	72.86	72.86
Al ₂ O ₃	1.63	1.63
Fe ₂ O ₃	0.037	0.044
CaO	9.53	9.15
MgO	0.19	0.61
Alkali	15.55	15.55
SO ₃	0.20	0.15
TiO ₂	0.003	0.02
MnO		0.02

Table 2 shows a typical flint container formula both with and without Calumite. As may be seen, the major ingredients are reduced, whereas the oxide content and glass properties remain the same. Some concentrated reducing agents such as the carbon in batch A or sulphur are used today in the production of oxidised glasses. The proper mixing and dispersion of these concentrates in the batch is most difficult due to the small amounts used. Calumite, on the other hand, is in essence a high temperature, fritted, dilute reducing

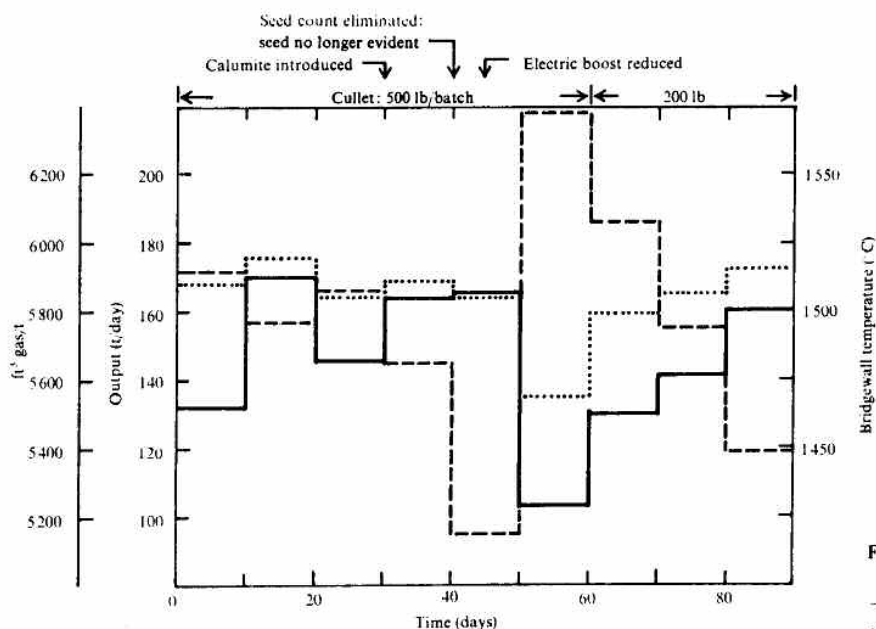


Figure 2. Furnace data for flint tank
 — output
 --- gas consumption
 bridgwall temperature

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agent. Its low sulphide content demands that a substantially larger amount be added to the batch than would be added when using the concentrated reducing agents—in this example 100 lb of Calumite compared with 1.5 lb of carbon. This larger amount ensures a more uniform and intimate mix, and thereby a more efficient reaction.

It is also interesting to note that the Calumite delays the reaction time due to the size of the particles. This allows for the sulphur in the Calumite to be oxidised at different times in the melt thereby improving the efficiency of the reaction. This reaction produced an evolution of sulphur dioxide bubbles in the melt thereby enhancing the homogeneity of the glass as well as removing seeds from it.

The overall efficiency of this reaction provides benefits not previously possible with concentrated reducing agents, introducing economies in raw materials, fuel savings, reduced temperatures, increased furnace life, increased throughput, better glass homogeneity, lower seed counts, and reduced stack emissions.

generity which manifests itself in cord gradings also has a marked effect on increasing production.

Amber glass

Table 3 shows a typical amber formula both with and without Calumite. With this particular formula major ingredients have been reduced and the sulphate input has been lowered by approximately 50%. The sulphur bearing materials, in this case pyrites, has been eliminated and the carbon almost completely removed. It is important to note that the oxide content and thereby glass properties are almost identical; it is also important to note that the theoretical SO₂ emissions decrease significantly. In addition, Calumite properly employed in amber glass, can provide multiple benefits similar to those mentioned previously.

Figure 3 shows actual furnace data obtained during a recent trial using Calumite in amber glass. Looking at points A and B which represent comparable tonnages it can be seen that temperature as

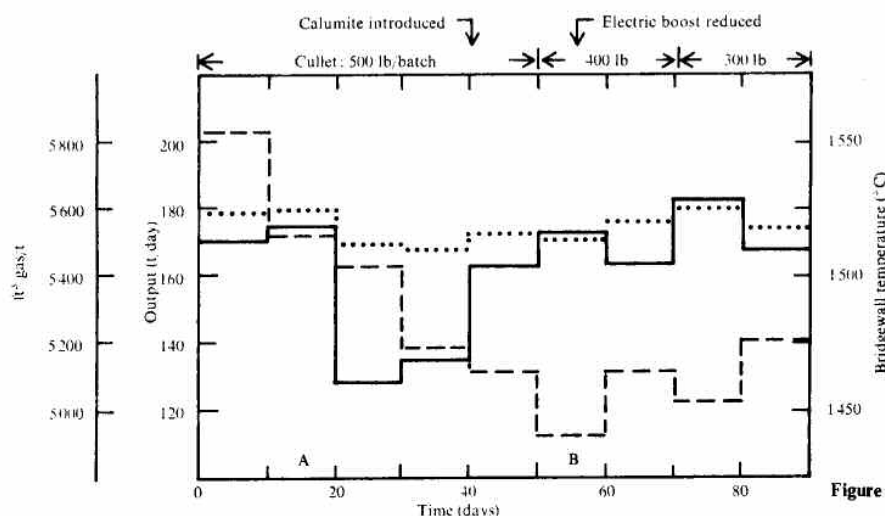


Figure 3. Furnace data for amber tank

— output
 - - - gas consumption
 bridgewall temperature

Figure 2 shows furnace data which were obtained during a recent trial using Calumite in the melting of flint glass. Looking at points A (without Calumite) and B (with Calumite) it is easily seen that temperature reductions as well as fuel savings were realised. In this particular case temperature reductions of 16–22 deg C and fuel reductions of 10–15% were obtained. Other very similar trials have shown temperature reductions as much as 38–100 deg C. An important thing to note from these data is that the booster melt was also reduced by approximately 200 kW and seed counts were eliminated.

With reduced temperatures and energy input comes increased furnace life or increased capacity and reduced stack emissions. The improved glass homo-

well as fuel reductions are realised. A very important fact to note is that the booster melt was also progressively reduced by approximately 200 kW. This indicates that expensive electric energy would not be necessary at lower tonnages. As in the flint glass trial (Figure 1) the quantity of cullet was also reduced substantially without using extra fuel.

An amber tank which, without Calumite, suffered quality problems when pulling more than 60 t/day had 2½% Calumite added and thereafter was making good glass at 90 t/day.

By properly balancing the sulphide and sulphate input, contributions to lower stack emissions have been made. However, far more important than this are the fuel and temperature reductions. A reduction in

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Table 3. Typical amber container formulae

	A	B
<i>Batch composition (lb)</i>		
Sand	2000	2000
Soda ash	715	727
Burned lime	338	215
Felspar	200	—
Calumite	—	239
Gypsum	18	10
Pyrites	4.27	—
Iron oxide	3.96	6.10
Carbon	3.50	1.00
<i>Theoretical glass compositions (wt %)</i>		
SiO ₂	71.95	71.91
Al ₂ O ₃	1.38	1.37
Fe ₂ O ₃	0.251	0.251
CaO	6.93	7.10
MgO	4.66	4.50
Alkali	14.74	14.73
S ²⁻	0.069	0.074
TiO ₂	0.02	0.06
MnO	—	0.01
<i>Theoretical SO₂ emissions (lb/t)</i>		
	6.41	4.78

the fuel means fewer pollutants emitted. Stack studies to verify this are planned.

Melite 40. Most recent studies plus the development of a dilute iron silicate product, hereafter called Melite 40 have permitted the extension of these theories to the point where sulphates can be completely eliminated from amber glass batches. Table 4

Table 4. Typical composition of Melite 40 (US source)

Component	Content (wt %)
SiO ₂	39.22
Al ₂ O ₃	24.30
Fe ₂ O ₃	26.30
CaO	2.39
MgO	5.49
Alkali	2.08
SO ₃	0.13
C	0.09

shows a typical analysis of Melite 40, which is currently being employed very successfully in America, and Table 5 shows Melite 40 being introduced into amber batches.

As can be seen the addition of iron oxide is completely eliminated and the sulphate source is again reduced. Again, it is important to note the theoretical SO₂ emissions.

It also shows the subsequent complete elimination of sulphate and the ultimate batch as far as a simple amber glass with increased stability, ease in meltability, and decreased stack emissions.

Table 6 shows typical formulae for emerald green glasses with and without Calumite, and the potential benefits of using it are comparable to those obtained with flint and amber. Theoretically the limiting factors controlling the use of Calumite in standard

Table 5. Typical amber container formulae

	A	B	C	D
<i>Batch composition (lb)</i>				
Sand	2000	2000	2000	2000
Soda ash	715	727	726	726
Burned lime	338	215	229	232
Felspar	200	—	—	—
Calumite	—	239	207	207
Gypsum	18	10	8	—
Pyrites	4.27	—	—	—
Iron oxide	3.96	6.10	—	—
Melite 40	—	—	22	22
Carbon	3.50	1.00	1.00	0.50
<i>Theoretical glass compositions (wt %)</i>				
SiO ₂	71.95	71.91	71.92	71.92
Al ₂ O ₃	1.38	1.37	1.38	1.38
Fe ₂ O ₃	0.251	0.251	0.249	0.249
CaO	6.93	7.10	7.03	7.03
MgO	4.66	4.50	4.55	4.55
Alkali	14.74	14.73	14.74	14.74
S	0.069	0.074	0.065	0.065
TiO ₂	0.02	0.06	0.06	0.06
MnO	—	0.01	0.01	0.01
<i>Theoretical SO₂ emissions (lb/t)</i>				
	6.41	4.78	3.80	1.70

Table 6. Typical emerald green formulae

	A	B
<i>Batch composition (lb)</i>		
Sand	2000	2000
Soda ash	689	713
Burned lime	149	107
Limestone	337	325
Felspar	204	122
Calumite	—	100
Saltcake	16	16
Iron chromite	12	12
Cobalt oxide	0.2	0.2
Carbon	1.0	—
<i>Theoretical glass compositions (wt %)</i>		
SiO ₂	71.83	71.82
Al ₂ O ₃	1.65	1.65
Fe ₂ O ₃	0.154	0.158
CaO	9.20	9.19
MgO	2.17	2.17
Alkali	14.60	14.60
SO ₃	0.20	0.15
Cr ₂ O ₃	0.19	0.19
TiO ₂	—	0.02
MnO	—	0.01

and Georgia greens would be the total supply of oxide in the glass composition or the economics involved. The residual sulphate and the evolution of sulphur dioxide gases can be controlled as desired. Although a typical Georgia green formula has not been shown here, Calumite is also used in varying amounts in this type of green.

Conclusion

The foregoing brief description of the preparation and use of Calumite indicates the advantages that are being obtained, or may be obtained, by the correct use of a beneficiated slag, but it must be incorporated into the batch correctly to realise its advantages to the full. Calumite has been shown to produce signifi-

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cant improvements in refining, melting, and fuel utilisation, due not only to its sulphide content but to its chemical and physical composition. Because of the improvements obtained, glass makers have been able to dispense with the use of other melting aids such as fluorspar, nitrates, arsenic, borates, etc. and, following this change, have used less decoloriser. The use of Calumite together with Melite 40 has significantly influenced the level of SO₂ evolved from amber glass furnaces. Its use has had a positive effect on the economies of glass melting during the past few years.

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