CALUMITE SLAG — ITS BENEFITS TO THE GLASSMAKER† by W. Simpson*

Substantial improvements in the refining of glass are claimed by the use of Calumite brand slag. As a result of these and other improvements this relatively recent addition to the list of raw materials used by the glassmaker has become known throughout the world's glassmaking fraternity.

Until about sixty years ago each glass house kept its recipe for making glass a close secret but, eventually, as Universities established departments for the study of glass technology and National Research Institutes appeared, the glassmaker subsequently found there were only small differences in most cases between the various recipes which were in use.

These recipes changed very little until the appearance of the raw material Calumite slag which allowed changes to be made to the batch recipes and to the glass-melting technology with results which surprised these well established glassmakers.

The use of Calumite slag and its subsequent ability to improve the glassmaking economy has become so well known that it has become necessary to insist on the use of the full title of Calumite brand slag to ensure that it does not become used as a generic name for treated and possibly also untreated slag which may be supplied by other companies to the glass industry.

The word slag implies a rough waste material which should be made available at a very low price. This was the situation many years ago but, at the present time, in most countries, the demand for slag equates with its availability. The modern iron and steel producers have changed their blastfurnace practice in order to produce high-grade iron and, therefore, higher grades of steel. This has led to more sophisticated control over their own raw materials and, in turn, the day-to-day composition of the slag produced from any given blastfurnace has also become far more stable; in addition the quantities of slag available are only about 40% of that formerly available per tonne of iron produced.

Not all slag is suitable for use in glassmaking and even in those works where it is, close collaboration takes place between the Calumite slag producer and the iron works technical staff.

It has been known for centuries that blastfurnace slag with its composition somewhat similar to commercial glass could be used as a glassmaking ingredient. However, no one had acquired the ability to control and adapt its use in such a way that refining was dramatically improved with predictable and repeatable results.

It was not until approximately forty years ago that it was used in the United States of America on a regular basis in modern glass manufacture and then only in amber glasses.

The production of a sophisticated beneficiated material was put on a commercial basis by a glass technologist, R. W. Hopkins, who founded The Calumite Company; this again was in America. This company, and the more recently formed Calumite International Ltd, have a number of patents for the production of a beneficiated slag suitable for use in the manufacture of glass in most parts of the world where glassmaking exists in any volume. Some of the patents have been in existence for many years; one of the more recent is for the production of a superior type of Calumite but this is not being produced at present. In addition, patents are in existence to cover the method of use of Calumite slag to give good refining and also good amber colour control.

As a result of a long and wide connection with glassmakers in all five continents, The Calumite Company considers that it has the profound knowledge regarding the use of Calumite slag which is necessary in order to obtain the optimum benefits from its application to glass manufacture, these benefits including improved refining and faster melting, so allowing a higher furnace output to be obtained at a given temperature or the same or a higher output at a lower furnace temperature. A major result is improved fuel conservation, less refractory wear and, therefore, lower unit costs. Because of the easier melting, the glassmaker is able to eliminate the use of fluxes such as borates and fluorspar and with improved refining there is no need to use refining agents such as arsenic and sodium nitrate.

Details relating to the action of Calumite slag and typical batches containing this material can be found in Reference (1).

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

Batch composition	1	2	3
Sand	2000	2000	2000
Sodium carbonate	692	696	699
Limestone	555	500	463
Felspar	236	193	151
Calumite slag	—	50	100
Sodium sulphate	18.3	16	16
Theoretical glass composition (Wt %)			
SiO	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_3	0.20	0.20	0.20
TiO_2	—	0.01	0.02
Seed count ratio	160	4	1

One example of the use of Calumite slag to improve refining and extracted from the above mentioned paper is given in Table 1.

During the following decade the use of Calumite slag expanded throughout the United States of America and knowledge of its benefits spread, especially as it had been shown to be effective for the production of colourless as well as amber glass and in flat glass and glass-fibre also.

As a result, in 1968 Appleby Calumite Ltd was established in England followed a few years later by The Calumite Company Europe SA and the Calumite Deutschland GmbH. These companies were licensed to manufacture and market Calumite slag and have the use of the various patents available in their licence areas which stretched from Scandinavia to as far afield as Greece. In addition, by agreement with the American licensors, material from the UK plant can be shipped elsewhere and has, in fact, been delivered to glassworks in South East Asia, to East and West Africa, to Australasia and to South and Central America. A new company, Nippon Calumite Ltd, started production in 1980 in order to supply the Japanese glassmakers.

In a few countries, slag-processing companies have offered and supplied slag to glassworks, but generally this has resulted in the glass company becoming disenchanted with its use due to the variability in the material's chemical composition, its irregular physical sizing, contamination by either heavy minerals or refractory materials and also high and variable iron content.

Some sources of blended and treated slags have been made available but in most of these situations the supplier has no technical knowledge of glassmaking. Where a glass manufacturer has some knowledge of the use of slag in glassmaking, possibly from a third party, he generally does not have access to the knowledge and experience gained by the various technologists within the Calumite Group of Companies or access to the results of the various research projects initiated to increase that depth of knowledge. This is reflected in the low levels of slag known to be used by these companies.

Some glassworks have looked at Calumite slag solely as an economic source of alumina, but it is a mistake to do so; its real strength is its ability significantly to improve refining. This is illustrated in Table 2, which

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Table 2.

Glass composition by Wt %		
SiO_2	74	
CaO	10	
Na_2O	14.5	
Al_2O_3	1.5	
Alumina source		**Seed count ratio**
Hydrated alumina		10
Felspar		9
Nephelene syenite		7.2
1/3 Calumite slag/ 2/3 hydrated alumina		1

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illustrates the production of soda-lime-silica flint glass under identical melting conditions but using various alumina sources.

As can be seen from the table, as a result of the substitution by Calumite slag, of only one third of the alumina source producing the poorest refining, it was possible to improve the refining by a factor of ten. It is known that further substitution, that is by increased use of Calumite slag (if introduced correctly), in other words, mathematically, and following the correct technical approach, will result in further improvements to the refining rate.

An additional example of the improved refining achieved by the correct use of Calumite slag is given in *fig 1*. This shows the improved seed count as a percentage of the seed count obtained when Calumite slag was not incorporated in the batch for a soda-lime-silica flint glass against the actual Calumite slag level used.

It should be pointed out that the exact shape of the curve is defined not only by the quantity of Calumite slag in the batch but also by the reduction-oxidation state of the batch. This has been given a mathematical treatment by The Calumite Company such that a redox number or value can be assigned to any given batch. This concept has been shown to be of value to the glassmaker in many ways (2). Further information about this concept was given in a paper presented to the Society of Glass Technology at York in 1977.

Referring again to *fig 1,* it should be noted that for any given batch redox value, the refining rate increases in relationship to the higher quantities of Calumite slag incorporated into the batch.

Shown in *fig 2* is a summary of data supplied by an American glass manufacturer and shows very clearly the benefits obtained from the correct use of Calumite-brand slag. This manufacturer was operating his furnace at 1540°C (crown temperature) and experiencing high and variable seed counts.

Following the introduction of Calumite slag at a level of 75kg Calumite per 2000kg sand there was a dramatic reduction in both the seed count and its variability even after a 38°C reduction in crown temperature. The pull rate increased, as shown, with very little increase in the seed count or its variability. It is doubtful if such dramatic improvements could have been obtained consistently with untreated slag or without the correct advice for adjustments to other ingredients within the batch.

Calumite slag, when used correctly, can be incorporated into a batch in quite large quantities, this obviously being dependent on having a source of material which is reliable and under good technical supervision to ensure consistency.

For example, in glass-fibre it can be used such that it forms 25% of the batch weight. In flat glass, it can be used to supply all the alumina not supplied by the sand; similarly, very good emerald-green glass can be produced using Calumite slag as the sole source of alumina.

Amber glass is a special case whereby The Calumite Company and its licensees have a number of patents to ensure that they are able to control the correct use of the Calumite slag to produce not only a well-refined glass but also a very stable level of colour.

Among the patents for the production of amber glass are those which allow for the incorporation of another material sold under the brand name "Melite". By the correct use of Calumite slag together with Melite it is possible to remove all the sulphate and all but a little carbon (this latter ingredient being solely used to correct minor colour variations) and as a result the evolution of SO_3 into the atmosphere is reduced to a minimum. Again it must be emphasised that this can only be obtained by having the necessary technical background knowledge.

In Table 3, a progressive change from a conventional amber batch to a much simpler one is shown. The amber colour was stabilised, refining was improved and the SO_3, emission can be seen to have been reduced. A much higher reduction in SO_3 emission has been shown possible in amber batches belonging to other glassmakers.

The bulk of containers (other than those for wine and beer) are made from flint glass. Those companies with only a limited knowledge of the uses of slag in glass will tend to use relatively small quantities, probably 2% compared to the sand weight, whereas those companies with technology received from the suppliers of Calumite slag are using 4 to 6%.

Batch composition	A	B	C	D
Sand	2000	2000	2000	2000
Soda ash	715	727	726	726
Burned lime	338	215	229	232
Felspar	200	—	—	—
Calumite slag	—	239	207	207
Gypsum	18	10	8	—
Pyrites	4.27	—	—	—
Iron oxide	3.96	6.10	—	—
Melite	—	—	22	22
Carbon	3.50	1.00	1.00	0.50
Theoretical glass composition (Wt %)				
SiO_2	71.95	71.91	71.92	71.92
Al_2O_3	1.38	1.37	1.38	1.38
Fe_2O_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
Theoretical SO_3 emissions (lb/tonne glass)				
	6.41	4.78	3.80	1.70

Table 3. Amber glass batch changes

Recent research has led the companies within the Calumite Group to appreciate that, in a flint glass, it is possible to use 10% or more Calumite slag compared to the sand weight. In general, the limitation imposed on the quality of Calumite slag has been the final colour of the glass, 'is it of an acceptable commercial quality?'. The recent work mentioned has shown that by the correct use of an appropriate oxidising agent it is possible that 5 to 6% of Calumite slag can be used with either low-iron or relatively-higher-iron flint sands and still produce commercially acceptable colour. However, by the use of suitable levels of cerium concentrate, it is possible to eliminate cobalt oxide and all or most of the selenium used and also to get good colour with high levels of Calumite slag even when the higher-iron sands are used.

It is not possible to give full details of this recent work but a brief summary is as follows:

- By producing a reduced flint glass, following the introduction of Calumite slag, good colour is obtained together with good refining using low-iron sands (the batch is much less oxidised than conventionally).
- By obtaining the correct level of oxidation and the correct incorporation of Calumite slag, good refining and commercially satisfactory colour can be obtained even with higher iron flint sands.
- By the correct use of Cerium concentrate these 'higher-iron-sand' glasses can be satisfactorily decolorised with a less-oxidised (reduced flint) batch resulting in an acceptable colour, good refining and, by the use of less sulphate, the SO_3 evolution will satisfy the environmentalists.

The production of Calumite slag is described in Reference[3]. As mentioned earlier, there is a necessity for close collaboration with the ironmaking company in

Fig 1. Graph to show improved refining of a solda-lime-silica flint glass with increased usage of Calumite brand slag when compared to a glass with no Calumite slag (a conventional glass).

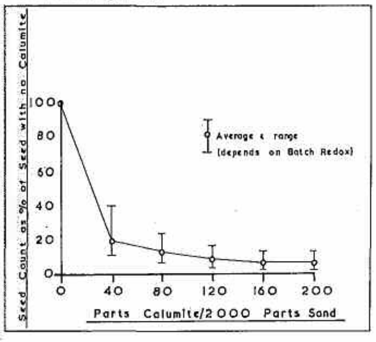
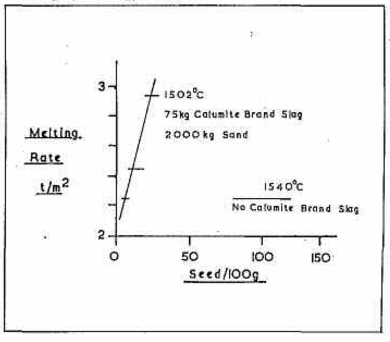


Fig 2. Graph showing the benefits from the introduction of Calumite brand slag to a flint glass furnace. (Better refining and lower furnace temperatures even when furnace throughput is greatly increased.)



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order to monitor their liquid slag analyses, to examine and select the correct type and quality of slag and then to subject it to processing which is closely monitored to produce the desired final quality of product. It is estimated that to install a plant of this sophistication with its necessary storage, bulk loading and dust-control systems and its bagging facilities, the present cost would be in the order of one million pounds sterling.

It is for this reason that other companies, when they try to produce a cheap product from a low-cost plant, ultimately cease their operation, especially when the glassmaker is not prepared to risk the quality of his glass by using inferior and variable products.

It is hoped that as a result of this brief history of the development of Calumite slag and the examples of the improvements possible, especially after reference to previous papers, glassmakers who have had doubts about the use of the material may feel more confident in the knowledge of the consistency of the product, in the expertise available to guide the glassmaker in its use and to do the necessary batch calculations and also in the fact that many companies are already obtaining the benefits so claimed.

The Calumite Group of Companies is currently selling over 6,000 tonnes/week and due to additional plants coming on-stream expect this to increase to approximately 8,000 tonnes/week. With an ever-increasing number of customers, the company is willing to enter into discussion with any glass company in order to help them improve the economy of their glass manufacture.

Following the presentation of this paper the author added the following comments:

"You will appreciate that the paper just presented was allocated to Section Six of this excellent and topical Congress. Section Six covers the raw-material market and its effects on glass technology. I trust that you have found the paper of interest and relevant to the effect of one raw material with subsequent changes in glass technology as a result of its introduction. However, it will have been seen from the expressed comments that these effects have some relevance to all of the preceeding sections of the Conference.

Section One relates to the 'Supply and Sources of Raw Materials'. It can be seen that we have taken another industry's by-product, upgraded it and over the years expanded the number of reliable sources: in addition from our continuing researches we have made positive improvements to glass-making technology.

Section Two relates to 'Benefaction of Raw Materials'. We have made every effort to produce a beneficiated technically-consistent product now used on a world-wide basis.

'Formulation of the Batch Mixture' was the topic of Section Three and we can show that this is most important when using Calumite brand slag to optimise fully the benefits from its use and to allow the removal of unnecessary and often expensive ingredients.

Section Four considered 'Batch Composition and Pollution Problems' and from the text it is seen that atmospheric pollution can be improved by the use of Calumite-brand slag together, in some cases, with Melite. This is achieved by following our patented principles to remove or greatly reduce the use of sulphates in amber-glass batch formulations.

Referring to the use of Cerium concentrate as a decoloriser, we can offer advice to allow the removal of toxic selenium from a flint glass and also in its use as a refining agent as a replacement for arsenic or antimony oxide in lead glass.

'Energy Saving' was the subject of Section Five; the text of the paper has made obvious that this is one of the most important achievements obtained by the use of Calumite brand slag.

In conclusion I trust that it will be realised that although Calumite slag is not a magic material it is an extremely versatile and valuable one." □

References

(1) Simpson, W. *Glass Technology*, 1976, 17, (1) 35-40.
(2) Simpson, W. & Myers, D. D. *Glass Technology*, 1978, 19, (4) 82-85.
(3) Myers, Simpson & Weiss, *Glastechn Ber*, 1977, 50 (5) 81-87.

25% reduction in soda ash manufacturing costs

FMC Corporation has announced that the Wyoming Department of Environmental Quality has granted necessary environmental permits for the company to proceed immediately with construction and operation of its test solution mine at Green River, Wyoming. The new mining process will be used to extract trona, the basic component of refined soda ash.

According to FMC Vice-President William A. McMinn, general manager of the Industrial Chemical Group, the demonstration mine will be in operation by this summer. He said that the company plans to use the solution mining process being tested ultimately to expand the capacity for refined soda ash at its Green River mine and plant site by one million tons by the mid-1980's, raising its rated annual capacity to 3.85 million tons.

According to Mr McMinn, soda ash manufacturing costs are eventually expected to be reduced by an estimated 25% compared to the company's current methods. He emphasised, however, that FMC would continue to operate its existing dry trona mine at full capacity in order to

The test mine site is located about 15 miles south of FMC's present soda ash refining plant at Green River where mineral rights to proven trona reserves have recently been acquired by the company.

The demonstration mile will be much larger than the typical pilot plant operation, Mr McMinn stated, at approximately 20% of the full-scale operation. The company official explained that this scale is critical in order to confirm the technological design and environmental data required for the commercial plant of one million tons of solution-mined soda ash.

According to Mr McMinn, contracts for a dual underground pipeline that will connect the demonstration mine site with the existing processing plant have been awarded

construction is now underway of a solvent plant that will feed the solution mining process. Both projects will be completed by mid-year.

The drilling of entry and exit wells will begin in March, with completion scheduled by this summer. The wells will be connected by fracturing, and then solvent will be pumped from the plant site and injected under pressure into the entry wells. The dissolved trona will be extracted and pumped back to the processing facilities.

FMC Corporation has committed more than $30 million to the test solution mining project, following extensive research, test drilling and small scale experiments in the existing mine. This work has led to applications for new patents to augment the company's existing solution mining patents.

FMC expects the commercialisation of solution mining to benefit domestic customers by providing increased supplies and to assist it to further penetrate overseas markets with its natural soda ash. According to Mr McMinn, mounting energy costs on synthetic ash producers have already made conventional mining of natural soda ash competitive in many world markets despite traditional transportation and duty barriers. Reduced costs from solution mining