NO. 5 2004

SGT NEWS

Compiled and published by dmg world media (uk) ltd on behalf of the Society of Glass Technology

ANNUAL MEETING

The Society of Glass Technology's Annual meeting was held in Liverpool on 21-23 April 2004. The meeting was split into different sessions: scientific, New Researchers Forum on Glass, structure of amorphous materials, heritage and history, and industrial.

BATCH MATERIALS

A major part of the industrial session discussed batch materials, in particular calumite, nepheline syenite, feldspar and cullet. Stuart Jones of Calumite discussed the use of calumite as the "green alumina source". Calumite is based in Scunthorpe, UK and was established in 1969 as a joint venture between the Appleby Group and Calumite International (USA) to produce Calumite brand slag from granulated blast furnace slag. In 1999 the company expanded its activities into Central and Eastern Europe with the opening of a wholly owned subsidiary, Calumite sro, based in Ostrava in the Czech Republic.

Calumite from blast furnace slag provides a high quality alumina source for the glass maker which has many benefits. It can lead to lower emissions, reduced furnace temperatures, increased furnace pull, reduced seed counts and improved Redox control. The composition of Scunthorpe calumite is shown in ***Table I*** (overleaf).

The glassy nature of calumite allows $CaO–SiO_2$ reactions to occur at lower temperature, increased homogenisation of melt and wet sand grains encouraging the dissolution of sand grains. There is very little carbon in calumite so its addition will have a knock on effect of reducing CO_2 emissions compared to other calcia sources.

The introduction of calumite to an amber batch (replacing nephelene syenite) results in a claimed 42% reduction in the CO_2 emissions from the batch

BOSC D'ANTIC ON GLASS MAKING

Including essays on the manufacture of faience and the assaying of ores, published 1758–80.
Translated by Michael Cable

This is the second of three volumes illustrating progress in understanding glass making from the 17th century to the early part of the 19th. The first was Christopher Merrett's *Art of Glass* of 1662, an extensively annotated translation of Antonio Neri's *L'Arte Vetraria* first published in Florence in 1612. This volume from France covers the years 1758–80 and the third will describe glass technology in Austria and Germany in 1820–35. Each of these shows notable advances in understanding over the previous volume.

Paul Bosc D'Antic was a Protestant physician who became fascinated by glass making and gained influential friends who gave him the task of improving the manufacture of plate glass at Saint Gobain in 1755. He spent two years there before being dismissed but continued to make his career in glass making. At one stage he came to England hoping for a post at Ravenhead but was disappointed. After returning to France he eventually became physician to the King.

He wrote extensively and very readably on glass making and several other subjects, in papers published between 1758 and the appearance of his *Collected Works* in 1780. His most important essay is a long one on *Means of improving glass making in France* which in 1760 won him a prize offered by the Royal Academy of Sciences but also offended his erstwhile employers at Saint-Gobain. It was supplemented by extensive notes written for the 1780 publication.

This volume contains translations of the *Preliminary Discourse* that he wrote for the *Collected Works*, the prize essay with the notes inserted where appropriate, nine others concerned with various aspects of glass making, and two more on the assaying of ores and on the manufacture of faience.

The subjects of the nine papers include: bubbles in glass, smears in glass, crucibles from the Auvergne, manufacture of potash, use of unusual minerals as raw materials, and manufacture of sheet glass.

The volume is 250 pages long with six illustrations, A5 format (210 mm x 148 mm), ISBN 0-900682-44-2. Paperback. £25.00 (£20.00 SGT members).

Al_2O_3	MgO	CaO	SiO_2	Na_2O	K_2O	TiO_2	MnO	Fe_2O_3	C	S^{2-}	SO_3
14.00	8.50	38.50	36.00	0.30	0.30	0.60	0.50	0.23	0.02	0.70	0.02

Table I.

SiO_2	Na_2O	K_2O	CaO	Al_2O_3	Fe_2O_3
67.56	10.40	0.22	1.30	20	0.03

Table II. Feldspar composition (%).

material. A saving of 1800 t CO_2 per year on a 250 tpd furnace running at 50% cullet.

In his presentation "Turkish delight for the UK glass industry" Nihar Tapadar detailed the trial by Allied Glass of feldspar raw material from the Kaltun Mining Company of Turkey. Allied had been approached by Hilde Dahle, representing Kaltun, to use feldspar as a replacement for nepheline syenite.

The feldspar is low in iron, helping reduce pressure on colour, the composition is very consistent and the price is very competitive (see ***Table II***).

For the trial, the composition of the batch was calculated without altering the glass properties. One silo was emptied to receive enough material from Turkey to last two weeks and the production department was kept fully informed about events. Good communication was essential during the first supply of material from such a distant source. Allied Glass found that glass colour was initially slightly pink so the amount of selenium was reduced by 5-10%.

The conclusion of the trial was improved colour quality with the low iron raw material and the price was such that it has been adopted on a full time basis by Allied Glass.

THIRD SOURCE

The third source of alumina for the glass batch was detailed by Mike Lavender of MD Lavender & Associates. The Anyang nepheline syenite deposit in Shandong Province, China is one of five such sources available. It is not the best source with regard to purity and size but it is the best compromise on enough factors to make it the most economic. This is a rock type deposit, not a mineral or slag, with a minimum of 25 million tonnes and probably five times that amount available.

The site has a full extraction process in operation taking the drill and blasted material through primary and secondary jaw crushers, roll crushing then rod milling. The material is then screened and air classified before magnetic separation and storage in bags in the warehouse.

Two grades are available: NSG 020 with less than 0.20% Fe_2O_3 and NSG 015 with less than 0.15% Fe_2O_3 (see ***Table III***).

Table III.

	SiO_2	Al_2O_3	K_2O	Na_2O	CaO	MgO	TiO_2	Fe_2O_3
NSG 020	61.00	21.00	5.60	8.60	0.30	0.03	0.03	0.20
NSG 015	61.00	21.00	5.60	8.60	0.30	0.03	0.03	0.15

The glass recycling system operated by Berryman is the result of major investment.

Exploitation of the resource began only a year ago so domestic demand has yet to be fully taken up, some is going to South Korea and a Thailand based glass maker is investigating its feasibility. Worldwide deliveries of containerised shipments are available. The Chinese domestic ceramics industry is paying a premium on current production levels.

Cullet is the most influential batch component for the glass container manufacturer. Its guaranteed supply is a major problem for some companies and there are strategic alliances between manufacturers and collectors. John Marley of Berryman reviewed developments in cullet treatment.

The UK's consumption and production of glass reveals an imbalance, more green is available to recycle than is produced, nearly 1.5M tonnes doesn't get recycled (see ***Table IV***).

The gap between consumed and recycled in the UK is much larger than most other EU nations – The Netherlands achieves 91%. The glass is spread evenly throughout the country and new collection methods and public education have to be introduced if this proportion is to increase. Kerbside collection of mixed or separated glass is one initiative, collection from commercial premises such as pubs and clubs has not been fully exploited.

Berryman has changed its sorting from manual and magnetic operation in the 1980s to automatic ceramic and metal separation in the 1990s. Further investment in second generation sorting machinery has meant that smaller particles can be separated and colour separation is now feasible. The current rate of colour separation of a modern sorting machine is 7 tonnes/hour.

Ceramics in the cullet leads to inclusions and can cause breakage; metals lead to inclusions, bubbles and staining; and the wrong colour such as green in flint leads to reject ware and problems with the oxidation and reduction state of the glass. There are also problems with pyroceramics – cooker hobs and glass cookware – these can be sorted by x-ray technology on the sorting machinery.

Increased levels of collection will bring in more of the excess green glass, some of this might have to be exported, sold to glass fibre makers or as a last resort an alternative use found such as grit blasting or in aggregates. ■

Table IV. 2003 packaging statistics.

Glass consumed	**2,300,000 tonnes**	
Domestic	1,850,000	80%
Commercial	450,000	20%
Glass produced	**2,060,000 tonnes**	
Flint	1,350,000	66%
Green	380,000	18%
Amber	330,000	16%
Difference	**500k flint export**	
	750k green import	
Glass recycled	**865,000 tonnes**	
Flint	250,000	29%
Green	550,000	64%
Amber	65,000	7%

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SGT NEWS

LIVERPOOL 2004

A variety of technical and scientific papers covering the many uses of glass were presented at the Society of Glass Technology annual meeting in Liverpool.

WASTE IMMOBILISATION

There is plenty of interest in nuclear waste immobilisation and evidence is being gathered to determine safe disposal. Unstable isotopes oxidise and become part of the glass matrix locking them within the structure. The isotopes are still decaying, generating heat and new elements; can the glass remain stable over time when it might take a century for the waste to cool?

Ben Parkinson of Warwick University is investigating caesium borate volatility in high level waste vitrification. Alkali borosilicate glasses are the traditional choice for waste immobilisation because they have a lower melting temperature than silicate glasses. Phosphate glasses have also been investigated but they have problems associated with their low glass transition temperature and cannot be loaded with as much waste.

Caesium is volatile at the vitrification temperatures typically used (1000°C), this can lead to the significant problem of ^{137}Cs species evaporating from the melt and condensing around vents and outlets.

The research looked at stable caesium isotopes in borate and mixed alkali borosilicate glasses these were made by melting and quenching, and then analysed by x-ray diffraction to see if they were fully amorphous.

Caesium borate glasses – density, glass transition temperature, ^{11}B N_4 and ^{133}Cs MAS-NMR chemical shift all closely matching previous caesium borate glass results.

Mixed alkali borosilicate glasses – lowering of glass transition temperature from 500 to 455°C with increasing Cs_2O content – minimum at ~9% Cs_2O mole %. There were linear increases in both density and molar volume.

Future work will look at high temperature nuclear magnetic resonance, thermogravimetric analysis to see what sort of mass loss occurs with temperature and leaching tests.

WORKING WITH VENETIAN STYLE GLASS

Ian Hankey is the glassworks manager at Teign Valley Glass in Bovey Tracey, Devon. The company uses traditional manufacturing methods, working molten glass pretty much as it has been made over hundreds of years.

It was while he was working at the Royal College of Art that he was first approached by Reino Liefkes of the Victoria & Albert Museum and Dr Sarah Fearn of Imperial College in the summer of 2002. Dr Fearn is working in conjunction with the V&A researching glass conservation using advanced surface analysis techniques in order to find methods of arresting glass disease – the breaking down or corrosion of unstable glass.

The glass worked at Teign Valley Glass is Glasma, which is supplied by MRJ Furnaces. This glass is used because of the clarity and quality of the finished piece. Like all leadless glasses, it is not as long working as a high lead crystal, and so the window of workability is significantly smaller.

From a composition determined from analysis of a 17th century façon de Venise goblet a 20 kg glass batch was made up to make some plate sized samples. The first attempt badly corroded the pot, a second attempt involved charging in one go and melting for 16 hours. It was seedy at this point so it was held for a further 4 hours. After 20 hours it was still seedy suggesting a melting temperature of +1300°C or a soak time of days rather than hours.

As there was only a few days to melt the glass and work it, it was decided to try a cane test to determine the softening point and therefore the safe annealing temperature of the glass. The surprise was that the glass was easy to handle at 1200°C, which suggests a working temp of 1180°C. Because of this, an annealing temp of 520°C was estimated. But the cane slumped at 500°C. More testing gave a softening temp of 480°C. This in turn gives us a safe annealing temp of 450°C – remarkably close to that of lead crystal.

This was quite a shock. It seemed that the window of workability could be as great as that of lead crystal.

When making the blown plates that Dr Fearn needed for her research the glassmaker finally got the opportunity to feel how the glass worked. Ian Hankey reported that, "It was absolutely brilliant!" It was impossible to blow off centre. Skill levels increased dramatically just from the experience of working with this glass.

The 17th century façon de Venise goblet on which replica glass composition was based:

	Weight (%)
SiO_2	70.60
Na_2O	20.25
CaO	2.61
MgO	1.07
K_2O	3.68
Al_2O_3	1.10
Fe_2O_3	0.31
MnO	0.37

THE APPLICATION OF FABRIC FILTERS TO GLASS MANUFACTURING PROCESSES

Rüdiger Margraf of Lühr Filter gave a lecture on the experiences his company has had in

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For details of forthcoming local section events in your area, contact the following. All SGT members and non-members welcome.

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installing more than 100 bag filters downstream of glass tanks.

Modern glass plants are characterised among other things by the need for reliable observance of the required emission levels in the clean gas of particulates, heavy metals (Pb, Se, …), carcinogens (As, Cd, …), and gaseous, inorganic substances (HF, HCl, SO_x). They need sufficient extraction capacity in continuous operation without pressure fluctuations in the tank, low operating costs, long service lives of the filter material, a good ability to extract additive powder, high availability, and low maintenance costs.

Consideration has to be made of the specific process engineering requirements for each plant.

Fabric filters are working at crude gas temperatures up to a maximum of 240°C. It is often necessary to install a cooling stage upstream of the fabric filter. Powder injection for the separation of HF, HCl and SOx needs to be considered and for the corrosion protection of the plant hardware. The Lühr Filter installations use either recuperator or evaporative cooling.

The basic design of a fabric filter is shown, this represents a flat-bag filter with horizontally installed filter elements. The filter casing is divided into a crude gas and a clean gas chamber by means of perforated (cell) plates.

The flat-bag filter elements are mounted on support cages and are horizontally orientated. They filter elements are inserted into the filter casing from the clean gas side. The sealed ends of the elements are located into fixings on the rear wall of the filter casing, at the open end of the element they are sealed onto the cell plate with a dust tight seal, this seal is achieved without the use of bolts. The gas flow passes through the textile filter material from the outside to the inside, with particles being collected on the outer surface of the filter elements.

Various methods of on – and off – line cleaning systems utilising compressed air are used in order to remove the particles from the filter elements.

The agglomerates, built up by recirculated particles, are deposited on the filter material. Adhesive primary particles are separated at this mobile pre-filter layer. Due to the fact that the adhesive forces of the agglomerates of the older particles are lower, they can be removed very easily from the filter material by means of the filter cleaning device.

AN UPDATE OF FICTIVE TEMPERATURE THEORY

David Gelder of Mathematics for Manufacturers discussed the fictive temperature for the Structure of Amorphous Materials one day meeting. Is it a useful representation of glass properties but is there a more suitable model for modern manufacturing demands?

Viscosity, specific heat, diffusion coefficients, and density are defined in terms of a “fictive temperature” which indicates the structural state.

As generally used, it works well enough to manage processing from 50°C below to 100°C above the annealing temperature, but perhaps not from 100°C below to 200°C above? Glass starts liquid and stress free. It becomes solid - still stress free, with cold surfaces and hot centre. On cooling to uniform temperature the surfaces go into compression, and the centre into tension.

Thermal stress develops, and at high temperatures relaxes. Relaxation rates depend on temperature and fictive temperature – the structure also relaxes towards equilibrium.

From the glass processors’ viewpoint: what material model fits these facts?

Whereas the glass scientists’ viewpoint: what facts fit my material model?

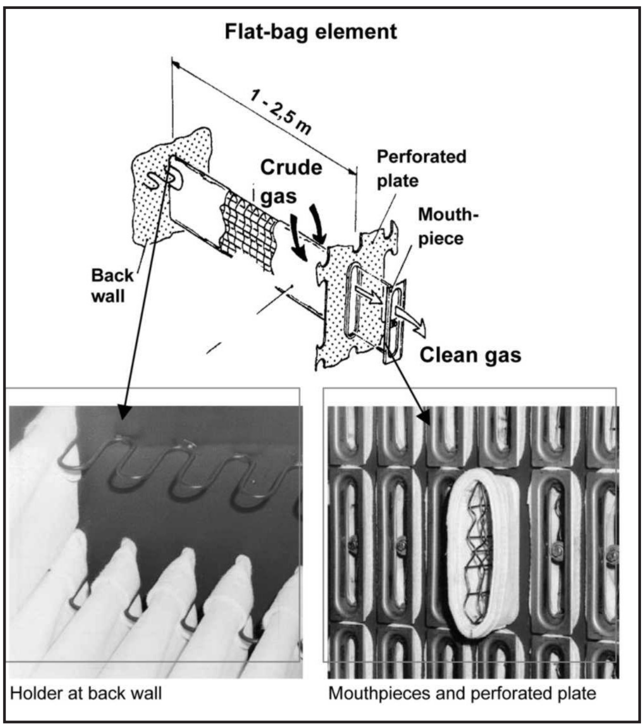
Conventionally, ‘equilibrium temperature’ is taken and called ‘Fictive temperature.’ Material properties are presumed to depend on a combination of actual and fictive temperatures.

Material data suggests glass properties do not vary smoothly. Structural changes can arise from ‘changes in preferred bond orientation.’ Changing temperature stresses the bonds - which break as in mechanical stress relaxation.

‘Something happens’ in many glass compositions about 150°C above the annealing temperature. We don’t know just what; but if we did, could we take advantage of it to link material properties and improve compositions?

Which way to move? The problem is not with using one ‘structural parameter.’ The problem is calling it ‘fictive temperature’ and then assuming it is the ‘equilibrium temperature.’ A first move is to take a measure of phase separation and use it like fictive temperature.

There are still more steps to take for a better understanding of structure–property relations but these may feed through to improved glass compositions for forming. ■



The Lühr filter installation.

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