dsf refractories

DSF CTB
The Optimum Tin Bath Block Solution

Summary

Tin bath block composition has been finely honed over several decades to combat deleterious bath-block interactions. Issues such as “tadpoles”, 7” splitting and H_2 open bubble have been resolved, however nepheline flakes have remained a significant issue with the potential of major production losses.

The perceived solution has been to abandon alumino-silicate chemistry and assessment of available oxides has led to calcium aluminate materials. Calcium aluminate is not however the panacea to tin bath ills; whilst the flaking phenomenon is minimised, it has inherent hydration characteristics which leads to bubbling in both the short and potentially long term. The step change to purely calcium-aluminate technology can be perceived as excessive, particularly as tin bath block development is predicated on an evolutionary basis in which the past basic tenets are preserved alongside the new desired capability.

DSF CTB represents the evolutionary change to combat flaking; based on “traditional” alumino-silicate chemistry, it incorporates calcium aluminate where it counts. With 70 hot end bath applications there have been no reports of flaking problems.

This report outlines why DSF CTB is different from other more generic compositions and with the aid of detailed electron microscopy the underlying processes to its success have been validated using an actual ex-campaign tin bath block sample.

Background

From a thermo-dynamic viewpoint, the hypothetical equilibrium reaction between alumino-silicate and alkali, specifically soda (Na_2O) at tin bath temperatures is nepheline.
As this new compound forms the differential between the density/volume of the reagents, and products, creates a plane of instability and subsequent shear of the surface.

These sheared surface “fragments” known as flakes can become attached to the underside of the glass ribbon and if not detected can result in ribbon fracture with all the associated cost to the re-establishment of a continuous ribbon.

Acknowledging the nepheline hypothesis in conjunction with respecting previously defined criteria, DSF developed CTB which has been used in tin bath applications since 1995.

The manufacture of the material utilised a non-traditional casting technique and was fired to an optimum temperature, such that the heat-work applied to the material created a structure of low permeability and low diffusivity.

Permeability, the ease of which vapour phases can move through a structure is the root cause for “deep” alkali reaction, hence the potential for a major volume of the refractory surface to convert to nepheline; therefore, minimise permeability and minimise nepheline formation.

Permeability however has an inverse relationship with H_2 diffusivity and for pressed and slip cast tin bath materials this has created a non-optimal compromise.

DSF CTB is not subject to this compromise; combining a low permeability with a structure that impedes the flow of H_2 affording a low desirable H_2 diffusivity.

Product Selection

The selection of a tin bath material is based on the product meeting the chemical and performance criteria and a strong reference list to give the glassmaker confidence in the performance and longevity of the material. DSF CTB encompasses both.

The critical material characteristics have been established over many years of tin bath operation and block evaluation; an explanation of the founding of these criteria is given below:-

i) Chemistry

In the 1960's baths blocked with 25% Al_2O_3 compositions were the source of "tadpole" defects, a long glassy attachment on the underside of the ribbon originating from Na_2O fluxing of the block surface; the resultant albite phase was molten at 1000 to 1100°C.

This was solved by increasing the Al_2O_3 content of the block, however more recently it has been discovered that high Al_2O_3 is a catalyst to nepheline formation (flaking), hence the chemistry must be held within prescribed limits:-

$\%Al_2O_3/(\%Al_2O_3+\%SiO_2)$	>0.40, DSF CTB:- 0.43
Al_2O_3	38-42%, DSF CTB:- 40.9

ii) H_2 Diffusivity

As the commercialisation of the float process continued from the 1960s into the 1970s, it became evident that certain blocks were the root cause of H_2 open bubble defects in the ribbon.

The phenomenon governing the problem was attributed to thermal transpiration; the flow of gas through a porous medium (bath block) against a temperature gradient when the porous medium contains passages comparable with or smaller than the mean free path of the relevant gas.

Pore size distribution analyses determined that baths suffering bubble problems contained blocks which had 75% of their pores in the range 0.1-0.6µm (mean free path of H_2 0.17µm).

The diffusivity test was developed as a prediction tool for thermal transpiration potential without the requirement for complex and time consuming pore size distribution analyses.

This isothermal (ambient) test incorporates a fixed volume of hydrogen below a test sample and air (N_2) above, noting that the tin bath environment is 95% N_2, 5% H_2.

Initially there is an upward flow of H_2 (comparatively small molecular weight) creating a pressure differential. This drives a balancing flow of air eventually achieving an equilibrium state at a pressure corresponding to zero total volume flow.

This peak value can be used directly to predict the pressure that will develop in the tin bath.

Many years of experience has shown that blocks exhibiting a diffusivity value <150mm of water do not give H_2 bubble issues.

Whilst an upper limit is fundamental, a lower limit must also be considered as diffusivity and permeability have an inverse relationship. Consequently, a low diffusivity infers a high permeability, material which is prone to soda penetration the catalyst to nepheline formation and flaking.

Range diffusivity:- 50-150mm H_2O	DSF CTB:- 50-150 mm water, 75 mm H_2O mean

iii) 7” Splitting

The phenomenon of blocks splitting in a horizontal (lamination) plane at around 6 to 7” from the tin contact surface can probably be consigned to the history of bath block development.

At the outbreak of block splitting in the 1970s, baths were traditionally blocked with expansion gaps designed to prevent tin ingress of the joints.

This meant that due to the temperature gradient the blocks were in contact compression stress to a depth of ~6 to 7”, at which point a compensating tension stress was created acting at 90^o to the compression field.

The blocks were therefore under considerable internal stress and if the blocks were not elastic a crack would form at the lowest point of compression contact.

Under normal operating conditions this apparently did not create a problem, however if the bath temperature changed, tin could access the joint and penetrate the lamination causing large pieces of refractory to float up through the tin.

Two tests were developed to assess the elastic nature of blocks:-

a.) Proof test:- 1/8th scale model of a bath block is bolted to a metal frame and crushed on its width and thickness faces (as in service), the deformation to failure is measured by a transducer. “Inelastic” blocks deform only 0.2 to 0.4% of their original length, “elastic blocks” 0.5 to 1.0%.
b.) Compressive Young’s modulus, a sample is loaded and deformation measured by transducers. From the resultant plot of stress vs strain defines the Young’s modulus as the gradient of the straight part of the graph.

Proof Test:- 0.5% minimum	DSF CTB:- 0.5 – 0.7%
Young’s Modulus:- 5-14 GPa	DSF CTB:- 6.51 GPa (@1000^{o}C)

Whilst a material may meet the aforementioned criteria it has been proposed that the portion beyond the straight line (plastic deformation) is also very important, this was based on observation of block integrity post campaign in correlation with the known Modulus of Elasticity (E) and the Modulus of Rupture, M.O.R; a dimensionless ratio was developed:-

M.O.R/E; ideally the material has a high value for M.O.R (tensile strength) and a low value for Young's Modulus. The higher the ratio the more resilient the material will be to induced stresses in the bath.

M.O.R/E:- DSF CTB, appraised as low risk (G.Evans Glassref Consulting)

7" splitting is hopefully a phenomenon of the past, however an inherent elasticity of the bath block is still relevant; there are considerable stresses encountered by the blocks during heat-up, planned and unplanned cooling the latter specifically related to power outages. The material has to compensate compression and tension in conjunction with altering stress fields around the securing holes.

Ignoring this criterion could result in costly downtime at some stage in the campaign.

iv Nepheline Flaking/Peels

The most dominant float bath block current issue is flaking; the formation of a layer 3-4mm thick which peels off the top surface of the block. The process is initiated by Na+ ions from the glass ribbon diffusing through the tin and subsequently penetrating the block surface.

The ions reduce oxides (primary Fe_2O_3) in the refractory to form Na_2O, this flux is absorbed by the glass phase initially, hence the glass phase constituent criterion for bath blocks and then the crystalline phase Nepheline starts to form.

The emergence of this phase is accompanied by a volume increase of approximately 20% and a shear stress between converted and unconverted areas forms.

Eventually the surface volume expands to such an extent that it cannot be held by the bulk of the block and exacerbated by temperature changes, the surface peels from the block and eventually attaches to the underside of the ribbon.

When this occurs the bath monitoring team must quickly remove the attached flake before the ribbon reaches the Lehr where the presence of a foreign object with associated inhomogeneous annealing of the glass can result in ribbon loss.

Flaking is therefore a considerable problem and this has spawned the adoption of bath block materials based on calcium aluminate, however this step overlooks the step development approach which has endured for decades for tin bath block materials.

DSF CTB has never suffered a flaking issue; why?

It is alumino-silicate, however the first kinetic barrier to Nepheline formation is DSF CTB's low permeability; 0.2 nPerm versus a 2.5 nPerm maximum specification. Fundamentally Na_2O cannot penetrate the material. The second kinetic barrier is a glassy phase, but most importantly the glassy phase contains CaO and this takes the Na_2O/block reaction from Nepheline dominant to Plagioclase dominant.

Plagioclase is still a feldspar, but the inherent low permeability of DSF CTB limits the volume of reaction hence reduces the shear stress available for flake formation and importantly the reagent Na_2O and reactants (Al_2O_3 & SiO_2) form products which result in only moderate volume change hence surface and bulk coexist without a fracture plane.

To illustrate this, please see the table below and the associated volumetric change:-

Phase	DSF CTB As manufactured	DSF CTB Reaction layer ex Tin Bath
Mullite	46.9	44.7
Glass Phase	14.5	0
Plagioclase	0	28.9
Nepheline	0	11.4
Quartz	4.6	4.6
Cristobalite	26.6	7.6
Anorthite	6.4	0

The reagent (Na_2O) has interacted with the amorphous part of the glass phase and the interspersed anorthite and cristobalite crystals within the glass phase.

What is the estimated volume change:-
100g of Glass Phase + Cristobalite + Anorthite occupy 41.1 cc
100g of Plagioclase + Nepheline + Cristobalite occupy 38.4 cc

So theoretically there is a small reduction in volume or at least parity, certainly not the 20% hypothetically proposed. Therefore, there is no driving force for delamination with the resultant flakes. This is validated by SEM examination of DSF CTB tin bath block surface layers.

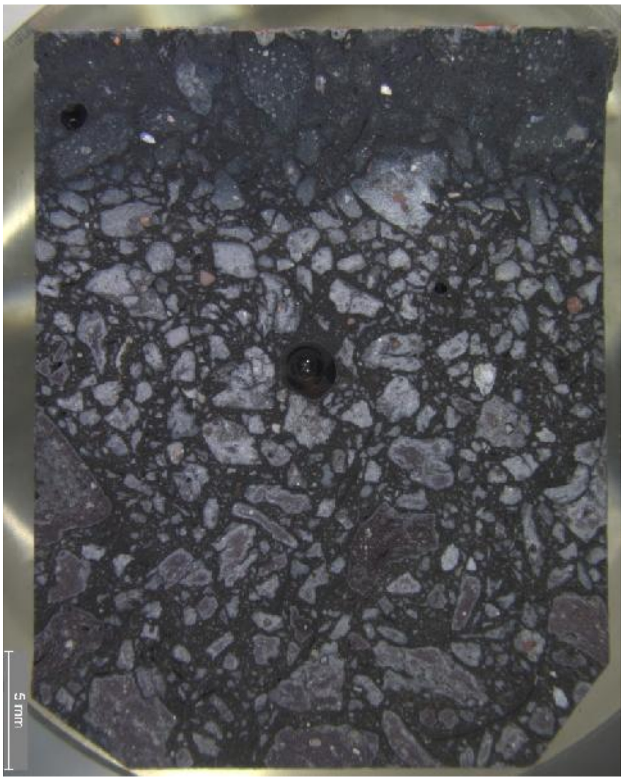

Fig.1 DSF CTB Core Section, no visible delamination plane between dark and light layers. Core sample taken from block ~9 years into campaign; block was available due to power outage and bath loss.

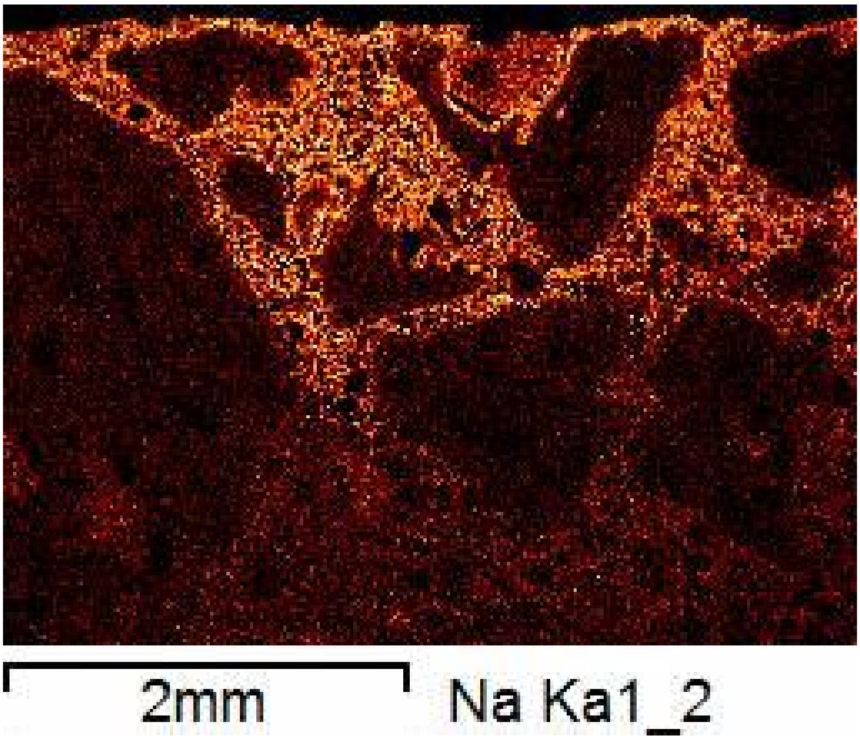

Fig.2 Elemental Mapping of Na_2O shows a 2mm penetration depth after ~9 years operation

Conclusion

DSF CTB has been engineered under the auspices of decades of experience of tin bath specialists. It combines all the defined criteria with a CaO containing glass phase which affords excellent Nepheline flaking resistance.

DSF CTB is a step change material, evolutionary rather than revolutionary and in contrast to calcium aluminate compositions, DSF CTB poses no hydration and subsequent de-hydration bubble risk.

It has been verified that the principle properties of the material which result in non-flaking are physically, low permeability, and chemically, reagents which combine with Na_2O to create no substantial volume change.