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Final Report

Recycled CRT Panel Glass as an Energy Reducing Fluxing Body Additive in Heavy Clay Construction Products.

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R&D Final Report: Glass

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1. Introduction

The use of recycled glass as a heavy clay product fluxing body additive is not a new concept. CERAM Building Technology (CBT) have recently completed a major WRAP funded brick industry project (WRAP project GLA2-018) investigating the energy saving and emissions reducing benefits of using powdered recycled container glass for just such purposes. In addition CBT have undertaken smaller investigations, with both Electrical Recycling Company Ltd (Privately Funded Project) and ICER/Glass Technology Services Ltd (WRAP Project GLA15-006), in to the potential benefits of using Cathode Ray Tube (CRT) panel glass as fluxing body additive.

There is currently approximately 105,000 tonnes of CRT glass available annually, though this is likely to decline in future years as conventional CRT televisions and monitors are replaced by flat screen technology, therefore the CRT glass problem could be seen as a declining market, though the ICER 2003 indicated that by 2012 this is only likely to have declined to 100,000 tonnes due to the conversion of conventional television screens to widescreens. In order to counter the likely reduction in long-term availability with advancing television screen technology it is proposed to also undertake a small sub programme of testing to assess the blending potential for CRT panel glass with mixed colour container glass. This will give confidence to the end users with regards to longevity of supply.

The justification for this work is that from 16th July 2004 the number of landfill sites designated as Hazardous Waste Disposal Sites and registered in England and Wales has reduced significantly in line with the Landfill Regulations (England & Wales) 2002, and the European Hazardous Waste Directive 1991. The European Waste Catalogue identifies that CRT glass falls into this category of Hazardous Waste, therefore the cost of disposal and the requirement for pre treatment will have highly significant affects upon the cost of disposal. Use of CRT Panel glass as a fluxing body additive in heavy clay construction products would reduce the potential materials to landfill from CRT glass by c 70%.

It is proposed that this project will only investigate the potential use of panel glass, i.e. the lead free glass, from CRTs. The rational behind this is that the end users identified in this project will not be able to deal with lead containing glass due to the volatile lead release through the firing process. Release of lead would subsequently either be emitted to atmosphere via the stack or precipitate within the kiln's refractory, neither of which are desirable to the heavy clay industry.

The heavy clay construction products industry in the UK is made up of brick (including pavers), tile and pipe manufacturers. By far the largest consumer of raw material is the brick industry which accounts for approximately 8 million tonnes, whilst the tile and pipe industries accounts for approximately 150,000 tonnes and 250,000 tonnes respectively. On this basis the CRT panel glass available would constitute less than 1% of the raw material usage in these industries. If, as suspected, there are no technical, environmental or health and safety issues with the use of CRT panel glass in heavy clay construction products, this would be an obvious cost effective alternative to landfill disposal.

This project proposal is designed to build upon the findings of these previous investigations and to develop a more in-depth understanding of the critical factors affecting the potential use of recycled CRT panel glass as a heavy clay construction product fluxing body additive as an alternative to landfill disposal. This report forms the Final Report and specifically reports on the results of the laboratory testing. The project was originally designed to allow for trials of the three manufacturing processes to be proved in a "Works Trial" environment. Unfortunately due to energy pricing during the autumn and winter of 2005/6, manufacturers were unable to meet the time scales required for the project, and therefore WRAP took the decision to terminate the project before the trials could be completed. There is still therefore a significant need and opportunity to evaluate the benefits of the use of CRT glass as a fluxing additive in a full scale production environment.

2. Laboratory Trials

During the first half of 2005, extensive laboratory evaluations trails have been conducted in order to establish the potential benefits of using CRT panel glass, in the three body types, namely Brick, Roofing Tile and Pipe. The aim of these trials has been to establish a better understanding of how the glass addition levels affect the fluxing properties of the clay bodies to which the glass is being added. In addition using laboratory conditions it is possible to use the data collected to establish the optimum firing conditions for the work trials that were programmed for the autumn 2005 (but have not taken place).

2.1. Raw Materials

As with all ceramic materials, the raw materials are the primary source of the characteristics of the products in both the unfired (green) and fired state. Understanding the basic chemistry and mineralogy of these primary raw materials is therefore important. The following section of the report highlights the results of the initial analysis of the primary raw materials (clays) for the three products, brick, pipes and tiles, in addition to that of the CRT glass additive used throughout this investigation. It should be noted that as the CRT glass is already amorphous (no crystalline structure) it is pointless analysis the powder using XRD (X-ray diffraction) as this technique only works on materials that have a crystalline structure.

2.1.1. Chemistry

Determination of the chemistry of the raw materials and the CRT glass was undertaken using fusion bead analysis on an XRF spectrometer (X-ray fluorescence). There results are expressed as major element oxide percentages. The results from this project are presented in Table 1.

Oxide	Brick Bodies				Pipe Bodies				Tile Bodies				Glass
	B0	**B3**	**B5**	**B7**	**P0**	**P3**	**P5**	**P7**	**T0**	**T3**	**T5**	**T7**	**CRT**
SiO_2	56.54	56.20	56.67	56.62	60.43	60.67	60.48	60.67	57.50	57.52	57.64	57.46	60.33
TiO_2	0.98	1.00	0.94	0.96	0.95	0.93	0.92	0.91	1.06	1.04	1.02	1.00	0.38
Al_2O_3	19.26	19.29	18.26	18.43	20.67	20.19	19.82	19.47	20.42	19.82	19.53	19.16	2.16
Fe_2O_3	8.02	7.63	7.74	7.36	8.21	7.88	7.83	7.58	9.23	9.03	8.73	8.87	0.08
CaO	1.86	1.71	1.83	1.73	0.38	0.37	0.39	0.39	1.02	1.07	0.99	1.10	0.75
MgO	1.73	1.62	1.69	1.59	2.00	1.96	1.90	1.87	1.09	1.05	1.00	1.03	0.19
K_2O	3.90	4.18	4.06	4.29	3.81	3.96	4.02	4.09	1.83	1.94	2.06	2.16	7.62
Na_2O	0.51	0.75	0.83	1.03	0.87	1.07	1.18	1.37	0.10	0.30	0.45	0.58	7.93
P_2O_5	0.15	0.15	0.15	0.15	0.15	0.15	0.14	0.14	0.09	0.09	0.09	0.09	0.02
Mn_3O_4	0.14	0.13	0.13	0.13	0.14	0.13	0.13	0.13	0.09	0.09	0.08	0.09	0.01
ZrO_2	0.03	0.08	0.10	0.14	0.03	0.07	0.11	0.14	0.03	0.07	0.11	0.14	1.80
PbO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.04
BaO	0.08	0.32	0.45	0.70	0.06	0.33	0.52	0.69	0.09	0.33	0.54	0.72	9.18
SrO	0.04	0.28	0.40	0.61	0.01	0.27	0.44	0.60	0.03	0.27	0.46	0.60	8.58
LOI	6.88	6.59	6.66	6.39	2.39	2.35	2.37	2.26	7.53	7.47	7.29	7.26	0.23
Total	100.14	99.95	99.93	100.15	100.12	100.35	100.27	100.33	100.13	100.11	100.01	100.28	99.30

Table 1. Major element oxide geochemistry (%) of the primary raw materials and blends with the CRT glass powder. B = Brick, P = Pipe, T = Tile. The number relates to the % addition of CRT glass powder.

The B0, P0 and T0 analyses gives the true raw material composition based on chemistry. The CRT glass analysis represents the chemistry of the mixed source CRT panel glass used in this investigation.

The chemistry of the brick body raw material shows that silica and alumina dominate the composition, as would be expected. The moderate iron content (8.02%) confirms that this body would be expected to fire red in colour under oxidising conditions, which it does. The main alkaline fluxing element is potassium, indicating the presence of the illitic clay mineral in addition to kaolinite, feldspar, muscovite mica and quartz.

The chemistry of the pipe body again reflects the main source of the raw material, a carboniferous shale, dominated by quartz, feldspar, along with illite, kaolinite and chlorite clay minerals. The moderately high iron content (8.21%) again indicates that this body should fire red in colour under oxidising conditions, which it does. The main alkaline fluxing element is potassium, though both magnesium and sodium are higher than found in the brick body raw material. One aspect that should be noted is the very low LOI (Loss on Ignition) value. Measured at only 2.39% this indicates that the mineral water content of the body is very low. This is in fact an artificial value as this body is comprised of both primary clay and a calcined clay (from the same source). This blend gives a significantly more stable drying and firing characteristic to the pipe manufacturing process, and gives a much more reproducible fired characteristic. The low LOI value therefore reflects this mixture of both dry and pre-fired raw materials.

The tile raw material appears clay rich, compared to the other two raw materials, as indicated by the LOI value of 7.53%. The chemistry indicates that the main quartz and feldspar minerals are associated with all of the three clay minerals, illite, kaolinite and chlorite, this is typical for the Etruria Marl of which this is an example. The highest iron content of this material confirms the strong red fired body.

One of the major concerns with the use of a "waste" materials, recycled or not, under current legislation continue to be classed as "wastes" even when within the recycling loop. This has effects on this project, as currently CRT glass derived materials continue to be "waste" until transformed into bricks, based on current Environment Agency guidance.

In order to assess the potential environmental impact upon the recovery, transportation, storage and use of the CRT glass in heavy clay product manufacturing, the principle reason that CRT based products are currently classed as a Hazardous Waste is on the basis of the "toxic metal" content. Using current Waste Acceptance Criteria (WAC), the CRT glass powder has been accessed for the leachability of the heavy metal cations. The results are presented in Table 1a:

	CRT Glass Powder	WAC Threshold
	(ppm unless otherwise stated)	(ppm unless otherwise stated)
As	0.07	0.5
Cd	<0.02	0.04
Cu	<0.02	2
Cr	<0.02	0.5
Pb	<0.20	0.5
Zn	<0.20	4
Ni	<0.02	0.4
Hg	<0.20 ppb	0.01
Se	<0.20 ppb	0.1
Ba	2.10	20
Mo	0.02	0.5
Sb	1.26	0.06

Table 1a. Waste Acceptance Criteria (WAC) analysis (metal cation only) of the leachate derived from testing of the CRT glass powder. Values that are identified as "<" indicate that they are below the analytical level of detection specified for each cation.

The values of the leachable metal cations specified in the WAC is determined using the extraction method presented in BS EN 12457-3:2002. The results indicate that if this CRT glass powder was to be going to landfill it would meet all the requirements for "Inert Waste" with the exception of the antimony (Sb) leachate levels. At a measured level of 1.26 ppm, this would place the glass powder into the "Hazardous Waste" category, however pre-treatment is possible to reduce the availability of the antimony through leaching. Antimony as a metal is a common additive in glass compositions, especially those related to CRT glass and radiation absorption glass, such as that used by BNFL.

2.1.2. Mineralogy

Mineralogy	Brick Raw Material	Pipe Raw Material	Tile Raw Material
	B0 (%)	P0 (%)	T0 (%)
Quartz	36	26	26
Feldspar (Potassic)	5	0	0
Feldspar (Sodic)	5	7	0
Illite	17	25	9
Kaolinite	22	32	65
Chlorite	15	10	0
Cristobalite	0	<1	0

Table 2. Mineralogy of the primary raw materials (clays) as determined by XRD.

Table 2. shows the main mineral species as detected using XRD on powder samples. The mineralogy is as expected dominated by the normal silica and aluminosilicate minerals, Quartz, feldsapsr and the clay minerals (illite, kaolinite and chlorite).

The one notable difference is the mineral assemblage of the pipe body. Here, the mineral cristobalite was detected. Cristobalite is a high temperature polymorph of silicon dioxide, which confirms the presence of a high temperature component to the raw material. As previously stated, the pipe body contains a mixture of primary clay (in this case a carboniferous shale), and a calcined (by fluidised bed calcination) clay. The calcined portion of the body mix will have been converted to anhydrous phases, and the presence of cristobalite indicates a temperature of >900°C

2.2. Laboratory Trials

In order to evaluate the nature and level of reactivity of the CRT panel glass in the three different clay body types, a number of laboratory tests and firing trials have been undertaken. Initially, approximately 30kg of each clay body type was mixed dry and then tempered with an appropriate amount of water to achieve a mix with consistent plastic properties.

Following mixing and tempering, the clay was fed into a laboratory scale extruder, and a stiff column of clay extruded and cut into standard sized briquettes. This was undertaken for all three clay types, and in addition, ∅15mm x 100mm rods were extruded of the pipe clay bodies in order to undertake MOR measurements (used as control tests by Hepworths).

The briquettes for each clay type, and glass addition level were then stamped with identification codes, and selected samples marked and measured for drying and firing shrinkage values. The remaining briquettes were dried and archived ready for the firing trials. Each clay type was fired initially at the typical works firing temperature, and then based on the underload firing curves, 2 reduced firing temperatures were selected. At each firing temperature samples of all the body compositions were fired, typically 30 briquettes per body composition, resulting in approximately 120 briquettes per firing.

Following the firings physical property measurements were undertaken to assess the benefits to the different bodies, including water absorption measurements (24hr cold water and 5hr boiling water) and the suite of drying and firing shrinkage measurements.

2.2.1. Underload Firing Curves

Underload firing curves are determined by laboratory firings under highly controlled conditions, and are designed to simulate the level of deformation resulting from the densification (through vitrification) of a clay body with an applied load. The 34kN/m^2 load used in the tests undertaken at CERAM, replicate the typical load the brick at the bottom of a 16 brick high setting pattern would be expected to experience through the firing process. This load is typical for the setting patterns used in UK brick works which use high setting height kilns, typically seen on the larger works producing +2 million bricks per week. The methodology and information obtained from underload firing curves is also applicable for both roofing tiles and pipe bodies, as these are material based reactions.

The test is conducted on 6 briquettes cut from the production-made bricks, in order to maintain the manufactured compaction and structure of the dried bricks. Each briquette is nominally 75x35x25 mm (lxwxh) and set in a 2x2x2 crossed setting pattern, and fired at a constant rate of 60°C/hr, up to a predetermined set point, or degree of linear shrinkage, which ever occurs first.

2.2.1.1. Brick Body

Figure 3 shows the underload firing curve for the brick bodies. The brick clay samples all show a very similar underload deformation curve. Even with the highest addition level of 7% glass addition into the brick body has resulted in little deviation in the curves. This indicates that, although, additional glass flux is present in the matrix, the other minerals present are reacting to the elevated temperatures in a controlled manner.

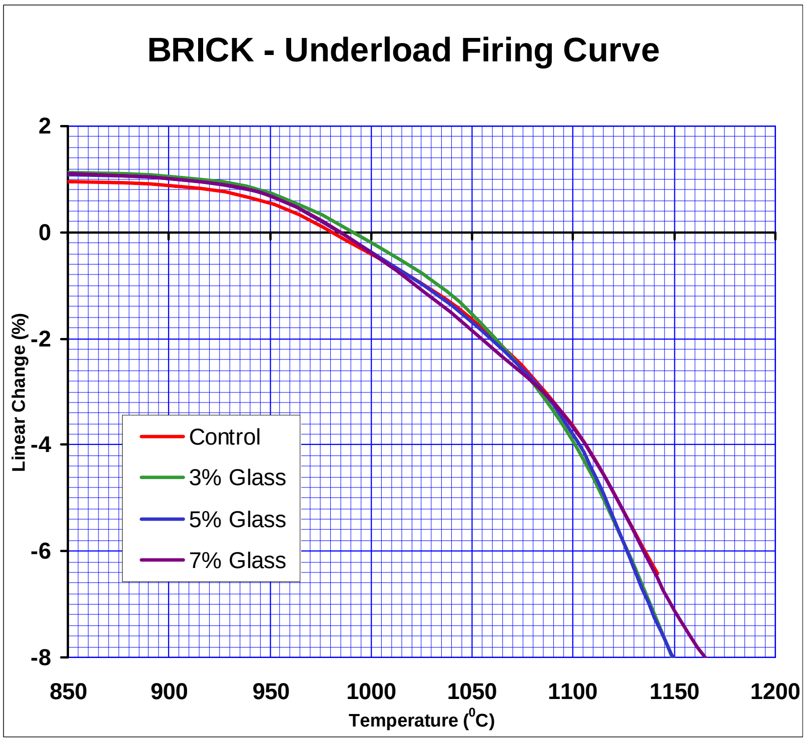

Figure 3. Underload Firing Curve – Devonian Shale Brick Clay, Wienerberger Steer Point Brick Works

The brick body curves can clearly be seen to be composed of two main sections of differing steepness. From 950°C-1075°C the curves for all the bodies have a similar angle, which after 1075°C steepen to differing degrees. The importance of the underload curve is that it shows manufacturers the stability of the body through the firing regime. The steeper the curve, the more sensitive the clay body is to temperature, and therefore the more critical it is that a manufacturer knows to what temperature a body can be fired without excessive vitrification, and thus the potential for complete meltdown.

2.2.1.2. Roofing Tile Body

The underload firing curve for the Etruria Marl tile body, Figure 4, does show some benefit from the addition of the CRT panel glass. From approximately 970°C the deformation curves deviate, resulting in the control and 3% glass curves maintaining a steady shallower curve, and the 5% and 7% glass curves steepening. All 4 curves steepen at approximately 1050°C but maintain the separation until all the curves converge at approximately 1150°C, at which temperature bloating in all samples is evident.

The curves indicate that whilst glass additions do have a beneficial effect on the firing curve deformation (vitrification) there appears to be little or no benefit in adding 7% glass over that of 5%, as the 2 curves appear to follow a very similar underload curve. Eternit's Cannock works typically fires at 1105°C, and on the basis of the underload curves it would be possible to achieve the same degree of linear shrinkage at 1095°C (3% glass), 1085°C (5% and 7% glass).

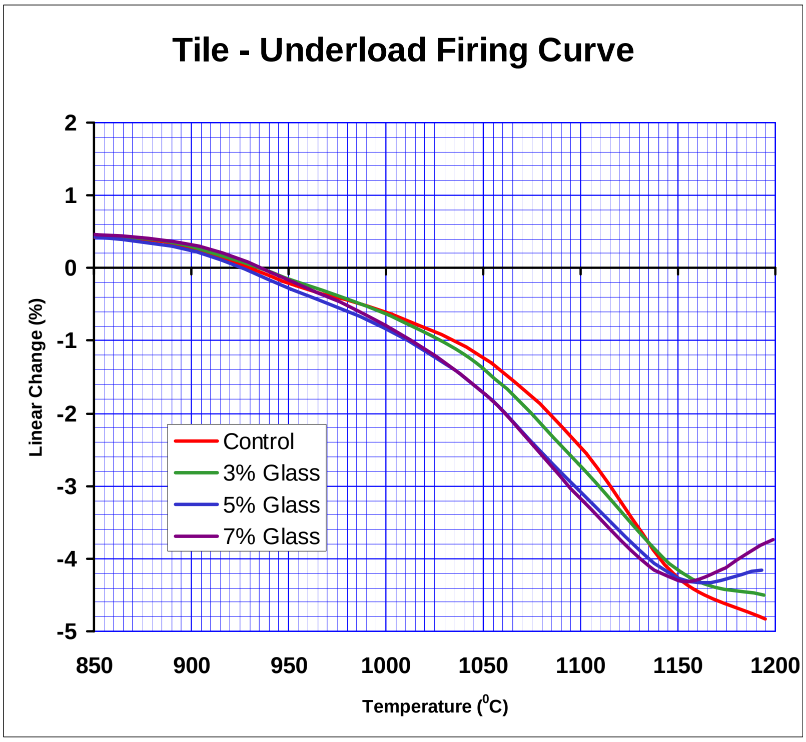

Figure 4. Underload Firing Curve – Etruria Marl Tile Clay – Eternit Cannock Works

2.2.1.3. Pipe Body

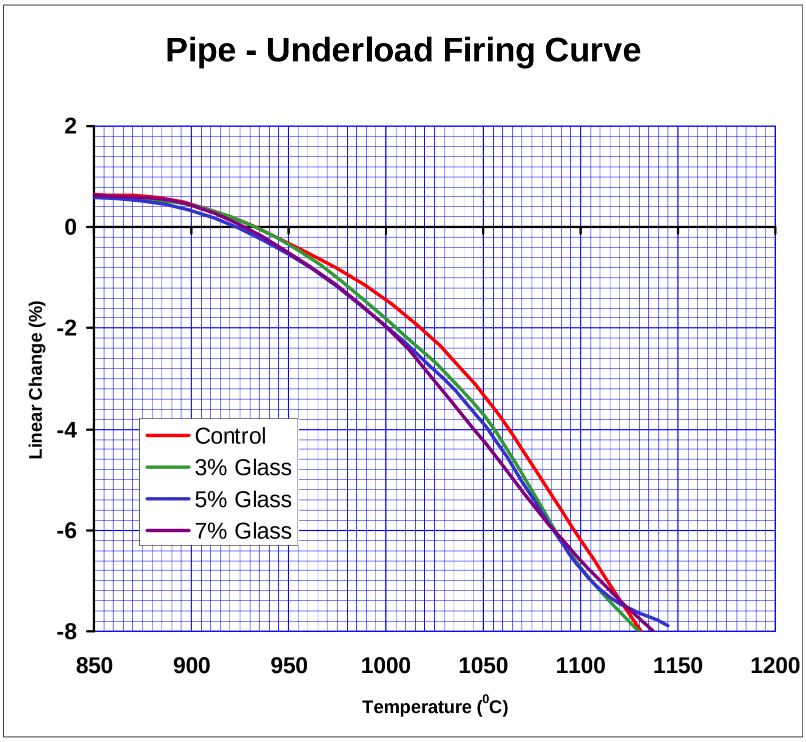

Figure 5. Underload Firing Curve – Carboniferous Shale Pipe Clay – Hepworth Hazelhead Works

The underload deformation firing curve shown in Figure 5. shows that above 950°C the four firing curves separate, the curves progressively getting steeper based on the increasing glass content of the body. At the works firing temperature of 1100°C there is still a differential linear shrinkage between the control body and those containing glass. From approximately 1070°C the three curves of the glass containing bodies start to converge. All three curves for the glass bodies converge at approximately 1090°C, giving a linear shrinkage equivalent to that of the control body at the works firing temperature of 1100°C.

2.3. Physical Properties

2.3.1. Brick Body

The brick body under investigation is a Devonian Shale from Wienerbergers Steer Point Works in Devon. The clays are unusual in the sense that only Steer Point and Pinhoe (Ibstock) use this geological strata. The products produced that Steer Point are a standard 10 hole extruded bricks, typically fired on edge and 15 brick high units.

Based on the underload firing curves, firings were undertaken at the works soak temperature, 1090°C, and then at two reduced temperatures of 1070°C and 1050°C. As expected there is little difference between the Wet-Dry shrinkages for all the body types, but with the fired shrinkages, the lower the firing temperature the lower the level of fired shrinkages. The Dry-Fired shrinkages indicates that the bodies are all reasonably stable and therefore should not lead to concerns over pack instability during firing.

Brick Drying and Firing Shrinkages (%)

	1050°C			1070°C			1090°C		
	Wet-Dry	Dry-Fired	Wet-Fired	Wet-Dry	Dry-Fired	Wet-Fired	Wet-Dry	Dry-Fired	Wet-Fired
Control	2.3	1.6	3.9	2.5	2.1	4.5	2.3	3.4	5.6
3% Glass	2.1	2.1	4.1	2.3	2.7	5.0	2.1	3.8	5.8
5% Glass	1.9	1.7	3.6	2.0	2.3	4.3	2.0	3.1	5.1
7% Glass	2.1	2.2	4.2	2.4	2.5	4.8	2.2	3.3	5.5

Table 6. Drying and firing shrinkages for the brick bodies, at the three different firing temperatures.

The water absorption measurements undertaken on the fired briquettes are presented in Figures 7 and 8. Figure 7 show the 24hr cold water absorption values which indicates that whilst the general trend is the lower the firing temperature the higher the water absorption value, there is a superimposed trend that shows that the lower the firing temperature the greater the effect between the control body and the 7% glass body. With increased soak temperature the effect of the glass content in terms of the reduction of the water absorption value diminishes.

Figure 8 shows the 5hr boiling water absorption values, and as is seen with the 24hr cold water values, the lower the firing temperature the higher the measured values, and again superimposed upon this trend is the greater the effect of the glass content upon the difference between the control value and that of the 7% glass addition body values.

No brick body containing glass at a reduced temperature achieves the same value as the control at the works firing temperature, for either the 24hr cold water or 5hr boiling water absorption values, therefore it can be concluded that the glass is not able to compensate the 20°C reduction in firing temperature.

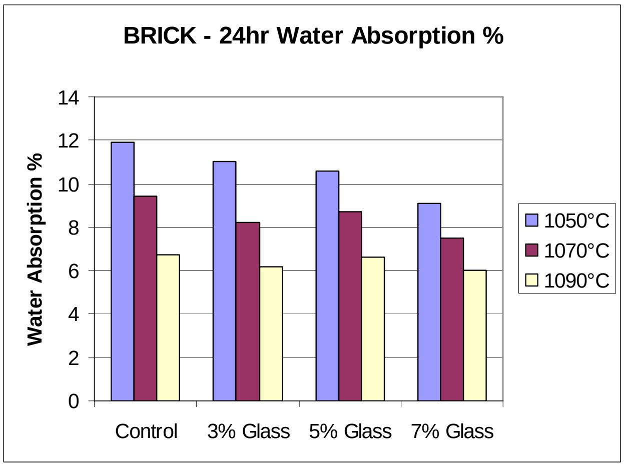

Figure 7. 24hr Water Absorption values for the brick body.

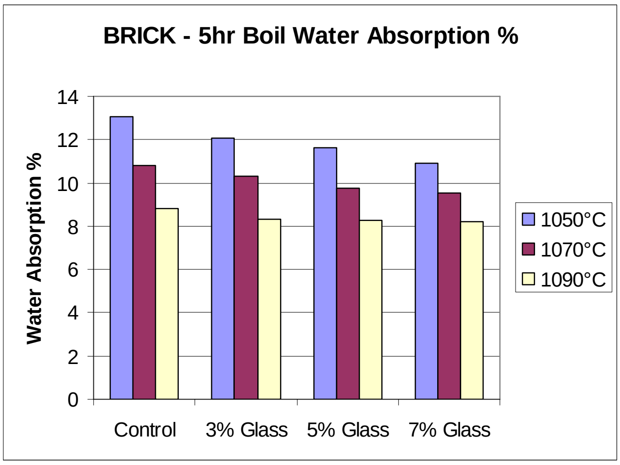

Figure 8. 5hr Boiling Water Absorption values for the brick body.

2.3.2. Roofing Tile Body

Roofing Tile Drying and Firing Shrinkages (%)									
	1070°C			1085°C			1110°C		
	Wet-Dry	Dry-Fired	Wet-Fired	Wet-Dry	Dry-Fired	Wet-Fired	Wet-Dry	Dry-Fired	Wet-Fired
Control	6.6	3.2	9.6	6.5	3.8	10.1	6.7	4.5	10.9
3% Glass	6.1	3.7	9.6	6.0	4.4	10.2	6.0	5.0	10.7
5% Glass	6.0	4.1	9.8	5.9	4.7	10.3	6.0	5.1	10.9
7% Glass	5.8	4.7	10.3	5.9	5.0	10.7	5.9	5.8	11.3

Table 9. Drying and firing shrinkages for the roofing tile bodies, at the three different firing temperatures.

As seen with the brick body the Wet-Dry shrinkages are consistent, and change little between the 4 body types. The fired shrinkages also follow an expected trend, resulting in the greater the Dry-Fired shrinkage corresponding to the higher firing temperatures. Unlike the brick body results, the tile body shows shrinkage sensitivity to the glass content. At each of the firing temperatures used in the trials, greater Dry-Fired shrinkages occur with increasing glass content of the body.

The trends seen in the firing shrinkages indicates that not only temperature but also glass content has an effect upon the overall performance of the modified body.

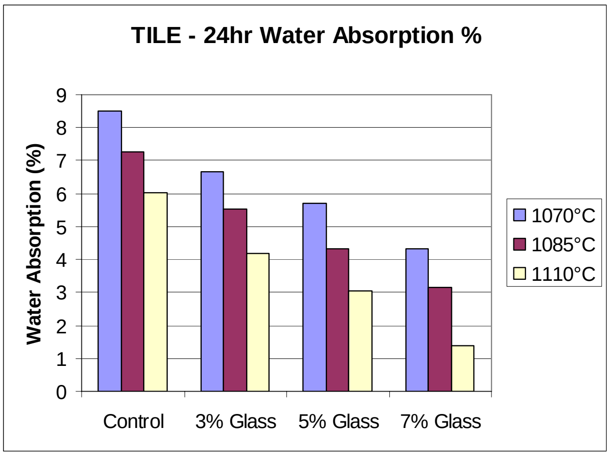

Figure 10. 24hr Water Absorption values for the roofing tile body.

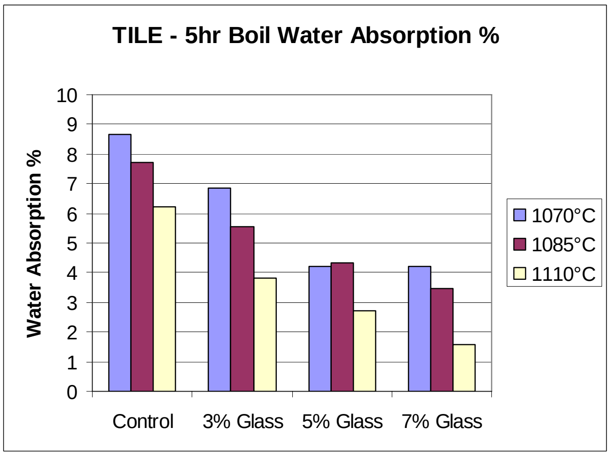

Figure 11. 5hr Boiling Water Absorption values for the roofing tile body.

The water absorption measurements undertaken on the fired briquettes are presented in Figures 10 and 11. Figure 10 show the 24hr cold water absorption values which indicates that whilst the general trend is the lower the firing temperature the higher the water absorption value, but unlike the brick body results, both temperature and glass content trends follow a similar pattern, resulting in regular incremental reductions in values with increasing glass content and temperature.

Figure 11 shows the 5hr boiling water absorption values. Whilst in general the values decrease with increasing glass content, at the lowest temperature, 1070°C, there is little or no improvement in value between the 5% glass and 7% glass body. For the 1085°C firing, the reduction in value between the 5% and 7% bodies is approximately half that of the reduction between the 3% and the 5% bodies. The reduction for the highest of the firing temperature, at 1110°C, is fairly even between 3%-5% and 5% -7%.

These results show that the effect, and therefore the benefit of glass content, diminishes with decreasing soak temperature, such that there is no benefit in adding in excess of 5% glass into the body at a firing temperature of 1070°C, but there is at 1110°C. The results also show that for this property, it is possible to achieve lower 5hr boiling water absorption values by the addition of 3% glass, and firing the tiles at 25°C below the current works temperature.

2.3.3. Pipe Body

Pipe Drying and Firing Shrinkages (%)									
	1070°C			1085°C			1100°C		
	Wet-Dry	Dry-Fired	Wet-Fired	Wet-Dry	Dry-Fired	Wet-Fired	Wet-Dry	Dry-Fired	Wet-Fired
Control	3.0	6.3	9.1	3.1	7.5	10.4	2.9	8.7	11.4
3% Glass	2.9	7.1	9.8	3.0	7.6	10.3	2.7	8.7	11.1
5% Glass	3.4	6.9	10.1	3.3	7.7	10.7	3.2	8.6	11.5
7% Glass	3.1	6.7	9.6	3.1	7.9	10.7	2.7	8.7	11.2

Table 12. Drying and firing shrinkages for the roofing tile bodies, at the three different firing temperatures

The Wet-Dry shrinkage values, as seen previously, are consistent, and reflect the variability in the making moisture content of the bodies. The Dry-Fired shrinkage values are all relatively similar, which would tend to indicate that the glass additions are having less of an effect than the actual firing temperature.

Overall the differences, at any given temperature, between the control and the different glass addition levels is minimal, therefore stability of the body during firing appear not to be dramatically effected by the addition of the glass.

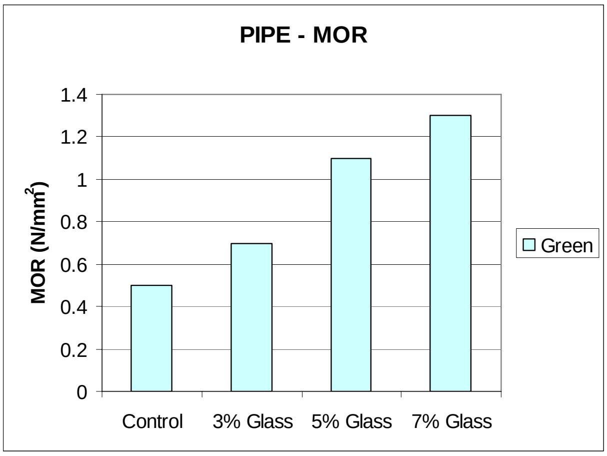

Figure 13. Modulus of Rupture (MOR) values for the green (dry) pipe body.

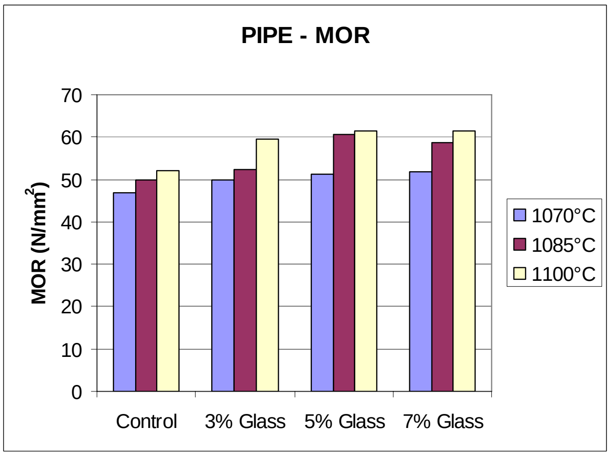

Figure 14. Modulus of Rupture (MOR) values for the fired pipe body.

Modulus of Rupture (MOR) values for both the 'green' and fired extruded clay bars are presented in Figures 13 and 14. MOR values indicate the flexural strength of a given body, and is used by Hepworths as a pre production quality control on the clay feed. This allows for any deviation from the norm to be identified prior to committing the raw materials into the manufacturing process.

The 'green' MOR values are significantly lower than would typically be expected by Hepworths. Subsequent investigation shows that the clay body, specifically the clay portion of the mix was not at the same particle size as would be tested by Hepworths. The trends shown therefore are not regarded as being significant as they do not reflect common manufacturing practice at Hepworths.

The fired MOR values however do reflect strengths typically measured by Hepworths on their pipe body raw materials. With the exception of one value, 5% glass fired at 1085°C, all the bodies show increasing MOR strengths which correspond to both increasing glass content and firing temperature.

Figures 15 and 16 show the water absorption values for both 24hr cold water and 5hr boiling water methods. For the 24hr water absorptions the general trends are that with increasing temperature and increasing glass content, the values decrease. The only exception to this is the 1070°C - 7% glass body which has a slightly higher value than the 5% glass body at the same temperature.

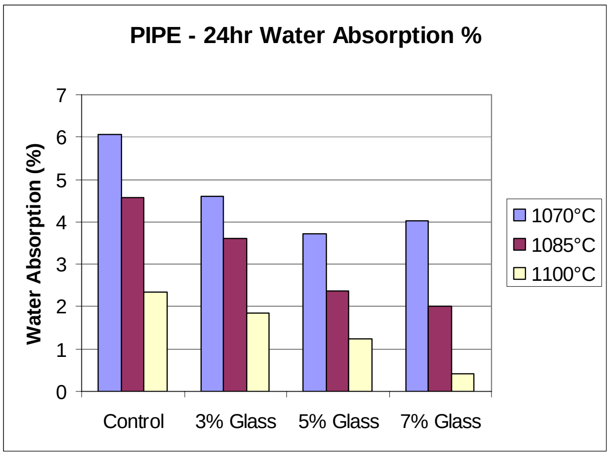

Figure 15. 24hr Water Absorption values for the pipe body.

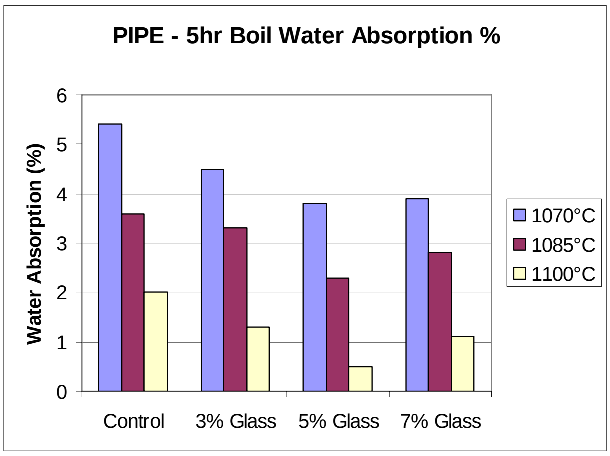

Figure 16. 5hr Boiling Water Absorption values for the pipe body.

Whilst in general the values decrease with increasing glass content, at the lowest temperature, 1070°C, there is no improvement in value between the 5% glass and 7% glass body, and only minimal difference between 5% and 7% for the 1085°C bodies. For the 1085°C firing, the reduction in value between the 5% and 7% bodies is approximately a quarter of that of the reduction between the 3% and the 5% bodies. The reduction for the highest of the firing temperature, at 1100°C, is fairly even between 3%-5% and 5% -7%.

The trends shown for the 5hr boiling water values are all similar shaped, showing an upturn for all the firing temperatures between the 5% and 7% glass additions. It also shows that the difference between the 5%-7% values increases with increasing temperature, which indicates that the glass is reacting to the temperature but at this level at the detriment of the porosity.

2.4. Fired Product Chemistry and Mineralogy

The process of transforming the mineral assemblage of the “unfired” products to that of the “fired” products results in the formation of a ceramic glass, which fundamentally is the ceramic binder that provides the physical properties to the finished products.

The addition of a powdered glass, in this case CRT panel glass provides not only additional fluxes, but also the potential to act as a catalyst for the formation of new glass compounds or mineral phases.

2.4.1. Fired Chemistry

The fired chemistries of the lowest temperature fired products are presented in Table 17. As would be expected the chemistry is very similar to that of the unfired bodies, but minus the volatiles (CO_2, H_2O and OH typically).

In addition to the chemistry of the fired products, the levels of Fluorine retained in the bodies were also measured by ISE (Ion Selective Electrode). Of interest is the fact that all samples irrespective of raw material type, or firing temperature, or glass addition all recorded the same Fluorine content of 0.02%, against a lower level of detection of 0.01% for this technique. This indicates that as well as having low Fluorine levels overall, no additional losses or absorptions can be quantified in the samples due to the sensitivity of the technique. Unfortunately the “proof of the pudding” which would have been the measurements of the stack emissions from the production trials are not now going to be undertaken to prove the potential benefits of Fluorine capture by the glass fluxes.

Oxide	**Fired Brick Bodies**				**Fired Pipe Bodies**				**Fired Tile Bodies**			
	B0	**B3**	**B5**	**B7**	**P0**	**P3**	**P5**	**P7**	**T0**	**T3**	**T5**	**T7**
SiO_2	59.95	59.63	59.15	59.41	61.68	61.76	61.70	61.40	61.74	61.78	61.97	61.60
TiO_2	1.06	1.06	1.06	1.04	0.98	0.95	0.93	0.93	1.14	1.12	1.10	1.07
Al_2O_3	20.88	20.81	20.47	19.98	21.15	20.67	20.25	19.74	21.93	21.29	21.00	20.54
Fe_2O_3	8.56	8.30	8.07	7.81	8.42	8.01	8.04	7.70	9.91	9.70	9.39	9.51
CaO	1.92	1.88	1.82	1.76	0.38	0.37	0.39	0.38	1.10	1.15	1.06	1.18
MgO	1.83	1.77	1.74	1.68	2.06	2.00	1.97	1.90	1.17	1.13	1.08	1.10
K_2O	4.26	4.50	4.59	4.62	3.94	4.03	4.10	4.15	1.96	2.08	2.21	2.32
Na_2O	0.51	0.74	0.90	1.06	0.84	1.03	1.16	1.29	0.11	0.32	0.48	0.62
P_2O_5	0.16	0.16	0.17	0.16	0.15	0.15	0.15	0.14	0.10	0.10	0.10	0.10
Mn_3O_4	0.14	0.14	0.13	0.13	0.14	0.13	0.13	0.13	0.10	0.10	0.09	0.10
ZrO_2	0.03	0.08	0.12	0.16	0.03	0.08	0.11	0.14	0.03	0.08	0.12	0.15
PbO	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
BaO	0.07	0.35	0.55	0.75	0.06	0.34	0.52	0.69	0.10	0.35	0.58	0.77
SrO	0.04	0.29	0.47	0.65	0.01	0.27	0.44	0.60	0.03	0.29	0.49	0.64
LOI	0.43	0.36	0.37	0.31	0.20	0.19	0.16	0.12	0.53	0.47	0.29	0.26
Total	99.86	100.09	99.63	99.54	100.06	100.00	100.07	99.33	99.97	99.98	99.98	99.98

Table 17. Chemistry of the fired products determined by XRF

	Fired Brick Bodies				Fired Pipe Bodies				Fired Tile Bodies			
	All values are in ppm unless otherwise stated				All values are in ppm unless otherwise stated				All values are in ppm unless otherwise stated			
	B0	B3	B5	B7	P0	P3	P5	P7	T0	T3	T5	T7
As	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Cd	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cu	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Cr	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Pb	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Zn	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
Ni	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Hg	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb
Se	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb	<0.20 ppb
Ba	<0.02	0.06	0.11	0.14	<0.02	0.06	0.11	0.14	<0.02	0.06	0.11	0.14
Mo	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Sb	<0.02	0.04	0.05	0.06	<0.02	0.03	0.05	0.06	<0.02	0.02	0.05	0.06

Table 18. Leachable metal cations as measured with reference to the specified test method n the WAC. All values indicate that the products would be classed as inert wastes if disposed of in land filled.

Table 18. shows the WAC (Waste Acceptance Criteria) values for the metal cations measured from the leachate derived from the low temperature fired products in each product type. Although in the “raw” state the CRT glass powder would have been classed as “Hazardous Waste” due to the levels of Antimony (Sb), the addition into all the clay bodies, even at a 7% addition level, fall below the maxima threshold for Inert Waste classification. In practice this means that even in an aggressive environment, the leachate from clay bodies containing CRT glass powder do not leach toxic metal compounds and therefore this would indicate that in “normal” service conditions they would be perfectly safe and none polluting to either soil or ground water.

2.4.2. Fired Mineralogy

	Brick Bodies 1090°C				Brick Bodies 1050°C			
	B0	B3	B5	B7	B0	B3	B5	B7
Quartz	27	21	19	20	26	26	22	24
Cristobalite	0.5	1.6	2.3	3.0	0.0	1.1	1.8	2.1
Mullite	9.0	6.3	2.2	4.9	5.9	2.0	4.3	0.2
Other	63.5	71.1	76.5	72.1	68.1	70.9	71.9	73.7

	Pipe Bodies 1100°C				Pipe Bodies 1070°C			
	P0	P3	P5	P7	P0	P3	P5	P7
Quartz	20	20	18	18	24	19	21	21
Cristobalite	0.3	1.2	2.3	2.5	0.0	1.0	1.9	2.3
Mullite	3.0	3.5	5.8	3.1	6.4	4.2	3.1	2.3
Other	76.7	75.3	73.9	76.4	69.6	75.8	74.0	74.4

	Tile Bodies 1110°C				Tile Bodies 1070°C			
	T0	T3	T5	T7	T0	T3	T5	T7
Quartz	24	25	23	21	26	26	25	24
Cristobalite	1.8	2.9	2.8	3.4	2.0	2.6	2.4	3.3
Mullite	12.0	11.0	4.3	11.0	0.2	1.4	7.0	4.8
Other	62.2	61.1	69.9	64.6	71.8	70.0	65.6	67.9

Table 19. Selected mineralogy of the fired products measured at the highest and lowest firing temperatures. The minerals identified are key high temperature minerals which indicate the formation of conversion of phases into crystalline mineral species or into the ceramic glass.

Table 19. shows the results of the investigation of the mineralogy of the fired products, at the highest and lowest firing temperatures. The results in general terms indicate that increasing additions of the CRT glass powder results in the formation of a key silica polymorph, Cristobalite, whilst in contrast, one of the other high temperature mineral phases commonly found in clay products, the alumino silicate, Mullite, decreases in some cases, and remains static or slightly increased in others. The significance of this is uncertain, but corresponds to a reduction in the "free" quartz content with increasing glass content. Conversion of quartz to cristobalite indicates a higher heat work index, possibly indicating that the glass is acting as a catalyst in the formation of this mineral phase at the soak temperature in the kiln.

The reduction of the Mullite may indicate that the alumino silicate phase is being bound into the glassy matrix due to the elevated levels of fluxing elements. Unfortunately quantification of the glass content of the bodies is very difficult to calculate using XRD as glass has no crystalline structure to be detected. However, the visual appearance of the bodies with higher glass content, look more "glassy", which is also borne out by the physical property measurements, specifically compressive strength and water absorption values presented in section 2.3 of this report.

3. Waste Management Legislation

3.1. UK Hazardous Waste Regulations

One of the principle issues as yet unresolved, and potentially an issue that could inhibit the use of CRT panel glass as a fluxing body additive, it the legislative and waste regulations requirements for transporting, receiving, storing and using the recycled CRT glass on the works and in the manufacturing process.

Current Environment Agency (EA) guidance, and in accordance with the new Hazardous Waste Regulations, indicates that CRT panel glass is classed as a hazardous waste, due to its chemical composition, and therefore remains a hazardous waste classification throughout the recycling and reprocessing process. The EA's current view is that up to the point at which the fired product containing the CRT glass comes out of the kiln, the glass would be classed as hazardous and therefore would retain all the waste handling/management requirements up to this point.

There is strong feeling within the heavy clay manufacturing sector that they do not wish to designate the works as sites that would require a waste management license. This is due to a number of reasons not least the impression that rather than accepting processed mineral materials, as the glass technically would be, on to the works, the perception of the waste management license to neighbours would be that general waste would be being stored on site. The current situation of the glass being classed as a hazardous waste material would therefore be likely to cause even more concern, as to the hazardous nature of the material. Brickworks, especially ones located in urban areas, already suffer from the NIMBY effect. This industrial sector is already heavily regulated through legislation pertaining to the quarrying, health and safety, and environmental impact, and thus another package of enforced administration would not be welcomed.

Following discussion of these issues, WRAP is working with the Environment Agency and DEFRA to resolve this situation. Critical is the interpretation of when, during a reprocessing process, a waste is no longer a waste. It is felt that until this area of uncertainty is fully addressed it is highly unlikely that the heavy clay sector would pursue CRT glass applications beyond the life of this project.

As currently the WEEE Directive implementation has again been deferred by the UK Government, probably until the middle or end of 2006, there is now a real need to confirm the potential recycling options available for recovered CRT panel glass. Due to the premature curtailment of this project that actual benefits have not been proven in a production environment, as has been published for the container glass projects. This still leaves some uncertainties, but the laboratory work is very encouraging.

4. Conclusions and Further Work

Originally the results of these laboratory trials were to be used to develop the final works production trials to be undertaken in 2005/ early 2006. Unfortunately this has not happened due to the project being terminated by WRAP prior to completion. It is hoped that funding from alternative sources will be found in order to allow for the completion of this research.

In general terms the technical potential for the use of CRT panel glass is as applicable as that already established for recycled container glass. It is likely that as with container glass, CRT glass will not generate the same benefits across the spectrum of UK clays and manufacturing processes. It is probable that specific manufacturers will benefit, and others may not for incorporation of glass into the body prior to firing.

However, there continues to be a number of issues that will require resolving if CRT panel glass is to stand any chance of being used in a ceramic flux application in the future. These issues are essentially linked to the legislative framework that governs the collection, storage, transportation and final distribution of the CRT glass. Unfortunately the current view from the Environment Agency is that this type of glass will continue to be a “waste” throughout the collection and supply chain. This puts undue burden upon the recycling process, and ultimately requires the end user to hold a waste management licence.

Interested parties are actively lobbying to have this overall “bureaucratic” and heavily regulated system simplified. Fundamentally a waste is only a waste if the intention is to dispose of the material (in the majority of cases to landfill). This is clearly not the case in the recycling supply chain, and therefore one possible debate that requires airing is the whole classification of recovered recycled materials as “waste” in the first place.

Finally, as with any consumable, the use of CRT panel glass will be price sensitive. If the cost to the end user it too high, even if the benefits are significant, it is unlikely that there will be large take up of this material. Currently market pressures, specifically in energy pricing, especially the gas price, is closing the gap between what the end users will pay verses the value of the saving in energy. As the projected cost of energy is projected to rise, CRT glass still has the potential to offer selected end users viable benefits.

CRT glass therefore remains as an unproven heavy clay fluxing body additive, and take up by UK manufacturers is unlikely until the production scale results confirm the laboratory findings. There is therefore a real need that this work be continued, and works trials undertaken, if CRT glass is to be accepted as a “viable” option in the future.