FIBERGLASS-REINFORCED PLASTIC (FRP) PERFORMANCE UNDER THERMAL UPSET CONDITIONS

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ABSTRACT

Thermal upsets can occur in many processes where heat and chemical reactions are present. Some materials of construction perform well in spite of thermal upsets--even when these upsets are two or three times normal operating temperatures. The purpose of this paper is to examine the impact of thermal upsets in the range of 2.4 - 2.7 times the normal operating temperatures on FRP materials of construction. More specifically, the test environment was designed to simulate a chimney liner operating at 65ºC (150ºF) with thermal upsets of 182ºC (360ºF) and 204ºC (400ºF) respectively. The results will show the effect of the type of resin and veil on the performance of FRP when subjected to the test environment described above.

Keywords: Chimney Liner, Desulfurization, Fiberglass-Reinforced, Flue Gas, Nickel Alloy, Thermal Upset

INTRODUCTION

Due to significant nickel price increases in 2006 and 2007, FRP became the material of choice for chimney liners in wet flue gas desulfurization (FGD) environments. The only metal that has proved to be successful in wet chimney liners is N 10276 clad steel. Nickel price increases and decreases have significantly impacted the difference in cost between FRP and N 10276 clad steel.

However, the raw material cost of N 10276 clad steel continues to be higher than the installed cost of FRP as shown in Table 1. The price difference is not expected to erode further, but it is expected to increase as the economy recovers.

Since FRP chimney liners are currently used in many wet FGD processes, FGD engineers have been interested in the effect of thermal shock on FRP chimney liners. No data was available, so experiments were conducted to study the effect of thermal shock on wet FRP. These experiments and their results are described in the present paper.

TABLE 1
COST COMPARISON OF CONSTRUCTION MATERIALS

Construction Material	Installed Cost	Cost Ratio
Shop Fabricated FRP	$90 / Sq. Ft.	1.00
Field Fabricated FRP	$ 135 / Sq. Ft.	1.50
	Raw Material Cost Only	
N 10276 Clad Carbon Steel	$250 / Sq. Ft.	2.8

EXPERIMENTAL

Laminate Preparation

Laminates were made from two resin types. 1) brominated bisphenol-A epoxy vinyl ester resin (Br EVER) and 2) brominated novolac epoxy vinyl ester resin (Br NEVER). Laminates of each resin were hand laid-up with one of the following two laminate sequences: (1) V/M/M/M/M/M/M/WR/M/WR/M/WR/M/M/WR/M, where V= c-glass veil, M=450 g/m^2 chopped strand mat, and WR=7320 g/m^2 woven roving or (2) C/V/M/M/M/M/M/M/WR/M/WR/M/WR/M/M/WR/M, where C= carbon veil, V= c-glass veil, M=450 g/m^2 chopped strand mat, and WR=7320 g/m^2 woven roving. This resulted in a laminate that was approximately 12.7 mm thick. The laminates were made at room temperature using a methyl ethyl ketone peroxide (MEKP) cure system and were covered with a polyester film to prevent air inhibition. After curing at room temperature for one day, the laminates were post-cured for two hours at 100°C and cut into 15.25 x15.25 cm samples for testing.

Thermal Shock Testing

The laminate samples were placed on each end of an Atlas Test Cell, as shown in Figure 1. The cells were filled half full with a deionized water solution containing1500 ppm sulfuric acid, 250 ppm sulfurous acid, and 250 ppm hydrochloric acid. The cells were then placed in an oven, shown in Figure 2, at 65ºC for a given period of time. For the c-veil only laminates, the oven time was 3 weeks. For the carbon/c-veil laminates, the oven time was 12 weeks.

After 3 weeks and 12 weeks respectively, the samples were removed from the oven and the test cell. One sample was then placed on a muffle furnace, in lieu of the door, for 1 hour at 180ºC as shown in Figure 3. The other sample was placed in a plastic bag.

After the first sample was removed from the muffle furnace, it was visually inspected for changes in appearance. If the appearance did not change, the second sample was placed over the muffle furnace opening at 204ºC for 1 hour. Both samples were photographed and placed back on the Atlas test cell and in the 65º oven for the prescribed time, for each type of veil, as described above. This procedure was repeated until both the samples showed significant changes in appearance such as delamination or blistering. The performance of the samples was rated by the type and severity of the changes in appearance

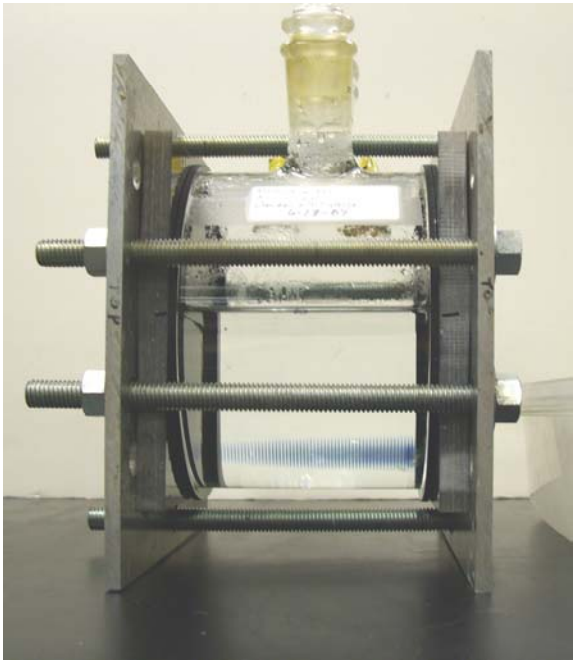

FIGURE 1 - FRP Laminates mounted on Atlas test cell prior to placement in oven.

FIGURE 2 - Atlas test cell placement in oven.

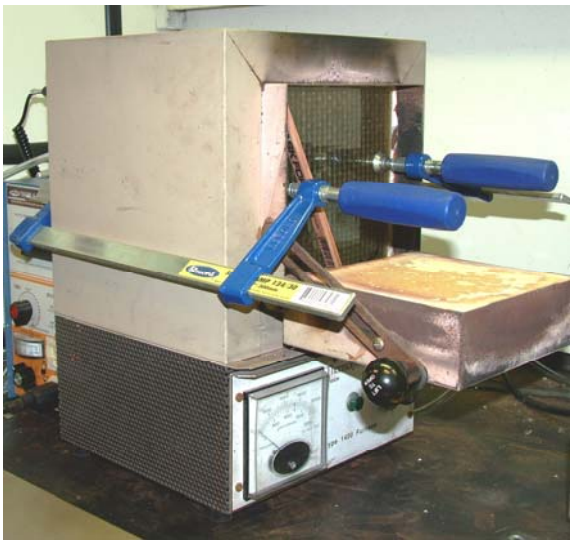

FIGURE 3 – Muffle Furnace Test Configuration

RESULTS

Figures 4 and 5 show the 9 week results of thermally shocking the brominated epoxy vinyl ester resin laminates with c-glass at 182ºC and 204ºC respectively.

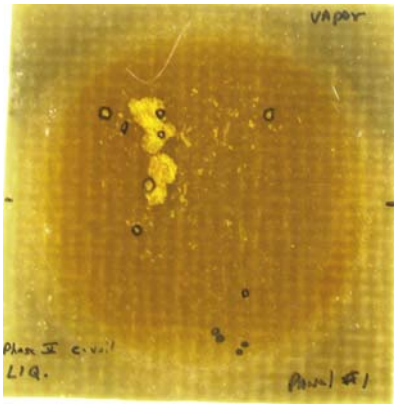

FIGURE 4 – Br EVER FRP laminate with a c-glass veil exposed to test solution for 9 weeks and 1 hour at 182ºC

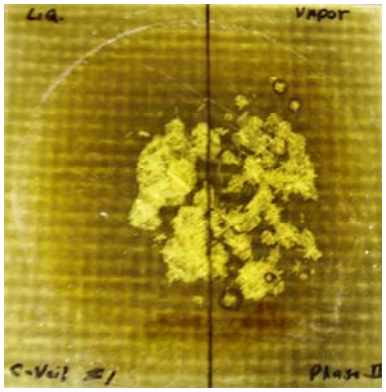

FIGURE 5 – Br EVER FRP laminate with a c-glass veil exposed to test solution for 9 weeks and 1 hour at 204ºC

The test results show that the brominated epoxy vinyl ester resin laminate had significant blistering and delamination upon exposure to 204ºC air for 1 hour. The laminate exposed at 182ºC had slight blistering

Figures 6 and 7 show the 12 week results of thermally shocking the brominated epoxy vinyl ester resin laminates with both carbon veil and c-glass veil at 182ºC and 204ºC respectively.

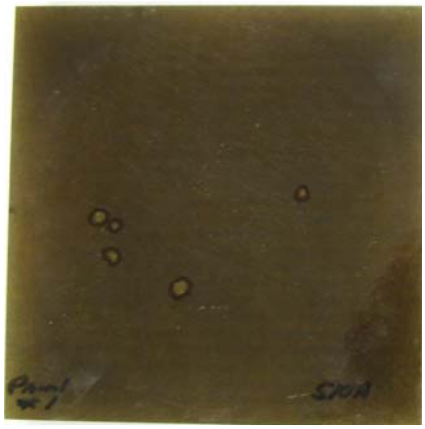

FIGURE 6 – Br EVER FRP laminate with a carbon and c-glass veil exposed to test solution for 12 weeks and 1 hour at 182ºC

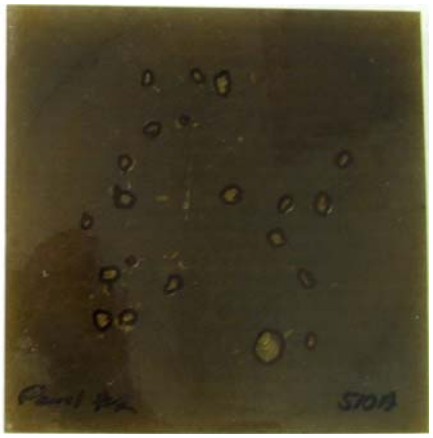

FIGURE 7 – Br EVER FRP laminate with a carbon and c-glass veil exposed to test solution for 12 weeks and 1 hour at 204ºC

The brominated epoxy vinyl ester resin laminate had moderate blistering upon exposure to 204ºC air for 1 hour. The laminate exposed at182ºC had slight blistering.

Figures 8 and 9 show the 24 week results of thermally shocking the brominated novolac epoxy vinyl ester resin laminates with carbon and c-glass veil at 182ºC and 204ºC respectively.

FIGURE 8 – Br NEVER FRP laminate with carbon and c-glass veil exposed to test solution for 24 weeks and 1 hour at 182ºC

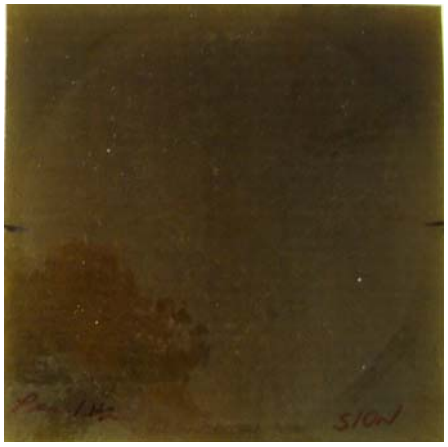

FIGURE 9 – Br NEVER FRP laminate with carbon and c-glass veil exposed to test solution for 24 weeks and 1 hour at 204ºC

After 24 weeks in the 65ºC test cell, the brominated novolac epoxy vinyl ester resin laminate did not blister upon exposure for 1 hour at either 182ºC or 204º.

Figures 10 shows the results of thermally shocking the brominated epoxy vinyl ester resin ester lamiante at 182ºC after 36 weeks in the test cell.

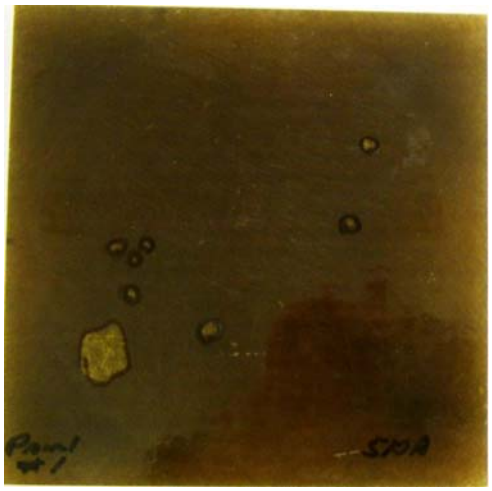

FIGURE 10 – Br EVER FRP laminate with carbon and c-glass veil exposed to test solution for 36 weeks and 1 hour at 182ºC

The brominated epoxy vinyl ester resin laminate that was exposed for 1 hour at 182ºC after 36 weeks had even more blistering than the laminate that was exposed after 24 weeks under the same conditions.

Figures 11 and 12 show the results of the respective exposure of the brominated novolac epoxy vinyl ester resin laminates that were exposed to182ºC and 204ºC after 36 weeks in the test cell.

FIGURE 11 – Br NEVER FRP laminate with carbon and c-glass veil exposed to test solution for 36 weeks and 1 hour at 182ºC

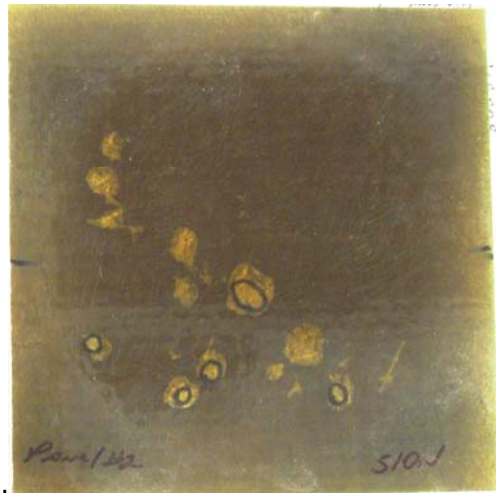

FIGURE 12 – Br NEVER FRP laminate with carbon and c-glass veil exposed to test solution for 36 weeks and 1 hour at 204ºC

In this case, the laminate exposed to 204ºC air for 1 hour blistered, but the laminate exposed to 182ºC air did not blister.

The results clearly show that the brominated novolac epoxy vinyl ester resin out-performed the brominated epoxy vinyl ester resin under thermal shock conditions. Also the carbon and c-glass veil combination out-performed the c-glass veil alone. The blistering appears to have resulted from a combination of time of exposure to the chemical solution, the number of shock cycles, the number and type of veils, and the thermal shock temperature conditions.

The migration of chemicals into the corrosion barrier of a laminate has long been known to be part of the cause of blistering. However, chemical resistance testing has shown that temperature and the composition of chemicals play a key role in the occurrence and severity of blistering. Chemicals such as hydrochloric acid and water are often associated with blistering at elevated temperature. In the

case of water, the more pure the water, the more likely the laminate is to blister, and the more pure the water, the lower the temperature at which blistering occurs.

Novolac resins have more polymer cross-linking than bisphenol A resins. Cross-linking slows the migration of chemicals into the laminate and thus reduces the amount of chemical that is available for rapid expansion during thermal shock. A double veil is also know to slow down the migration of chemicals into the laminate and thus reduces blistering due to chemical migration.

CONCLUSIONS

FRP based on brominated novolac epoxy vinyl ester resin (Br NEVER) appears to have better resistance to thermal shock than FRP based on brominated epoxy vinyl ester resin. Also, a combination of carbon and c-glass veil appeared to perform better than a single c-glass veil alone. To minimize blistering, it appears that a combination of brominated novolac epoxy vinyl ester resin and carbon and c-glass veil have better blister resistance than the resin and c-glass veil alone.

AKNOWLEDGEMENTS

The author would like to thank Don Daniel for his excellent work on the laminate preparation, chemical exposure, and thermal shock testing.

NOTICE

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