Bastion Technologies, Inc.

SUGGESTIONS FOR THE REPAIR

OF

CRACK TO A REGEN 2 PREHEATER

Advanced Design & Analysis

NOVEMBER, 2009

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BASTION TECHNOLOGIES

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0	22/09/2009	Initial Release
1	10/16/2009	2nd Release
2	11/02/2009	3rd Release

1.0 References

1.1 Governing Codes

1. *2007 ASME Boiler & Pressure Vessel Code Division II Part D*

1.2 Reference Codes

2. *Standards of the Tubular Exchanger Manufacturers Association, 8th Edition* (*8th Edition*, TEMA)
3. *Corrosion Engineering, Mars G. Fontana, ISBN-13 978-0071003605 (6/1986)*

4. *Structural Welding Code, AWS D1.1-D1.1M, 2006, American Welding Society*

1.3 Contract Documents

5. Regen 2 Preheater Exchanger
   Regen 2 Preheater Expansion Joint Clamshell
   Drawing Number S4042-13169-1, Mitternight Boiler Works, Inc. for Rhodia, Inc.
   Drawing Number S4042-13169-2, Mitternight Boiler Works, Inc. for Rhodia, Inc.
   Drawing Number S4042-13169-3, Mitternight Boiler Works, Inc. for Rhodia, Inc.
   Drawing Number S4042-13169-4, Mitternight Boiler Works, Inc. for Rhodia, Inc.

1.4 Technical References

6.	*Photo of Regen 2 Preheater*	*07/07/2009*
1).	*Photo 1 Crack of Regen 2 Preheater*	*08/20/2009*
2).	*Photo 2 Crack of Regen 2 Preheater*	*08/20/2009*
3).	*Photo 3 Crack of Regen 2 Preheater*	*08/20/2009*
4).	*Photo 4 Crack of Regen 2 Preheater*	*08/20/2009*
5).	*Photo 5 Crack of Regen 2 Preheater*	*08/20/2009*
6).	*Photo of Regen 2 Preheater*	*07/07/2009*
7.	*Photos (Internal Damage of Bottom of Rogen 2 Preheater Exchanger:*	*10/26/2009*
a.	*Photo 1 Internal Crack of Regen 2 Preheater*	*10/26/2009*
b.	*Photo 2 Internal Crack of Regen 2 Preheater*	*10/26/2009*
c.	*Photo 3 Internal Crack of Regen 2 Preheater*	*10/26/2009*

1.5 Other References

8. Drawing Fig 1 *Structure of Original Regen 2 Preheater Repair*
By Jim X. Wei, Bastion Technologies, Inc.
Houston, TX 77058, USA

9. Drawing Fig 2 *New Structure of Enamel Lining of New Regen 2 Preheater*
By Jim X. Wei, Bastion Technologies, Inc.
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Advanced Design & Analysis
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Evaluation

On Sept., 9th, 2009, Structural engineering and analysis staff of Bastion Technologies, Inc. had a meeting with fixed equipment specialists of Rhodia Inc. at the Rhodia Inc. conference room.

On Oct. 26, 2009 at the Rhodia facility, John Willis, the fixed equipment specialist of Rhodia Inc., and engineering and analysis staff of Bastion Technologies, Inc had an appointment and discussion about the photos of the interior damages of Regen 2 Preheater.

Design data:

Please refer to Drawings of Vessel Arrangement & Data from Mitternight Boiler Works, Inc. for the design data.
(Customer Contract No. 34-244920) and photos provided by Mr. John Willis.

Design Pressure (psig):

Shell Side	**External**	**Tube Side**
14.5	**atm**	**14.5**

Design Temperature (^oF):

Shell Side	**Tube Side**
1050/800	**1450/800**

Working Temperature (^oF):

Preheat Air from Peabody Furnace Max. Temp: 1250 ^{o}F
Preheat Air Outlet to Stack: 800 ^{o}F
Process Gas Inlet: 576 ^{o}F
Process Gas Outlet: 1000 ^{o}F

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Regen 2 Preheater Exchanger	*See Attachment*
Regen 2 Preheater Expansion Joint Clamshell	*See Attachment*
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S4042-13169-3	*See Attachment*
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Photo 4 of Crack of Regen 2 Preheater	*08/20/2009*	*See Attachment*
Photo 5 of Crack of Regen 2 Preheater	*08/20/2009*	*See Attachment*
Photo 1 Interior Damage of Bottom of Rogen 2 Preheater Exchanger	*10/26/2009*	*See Attachment*
Photo 2 Interior Damage of Bottom of Rogen 2 Preheater Exchanger	*10/26/2009*	*See Attachment*
Photo 3 Interior Damage of Bottom of Rogen 2 Preheater Exchanger	*10/26/2009*	*See Attachment*
Photo 4 Interior Damage of Bottom of Rogen 2 Preheater Exchanger	*10/26/2009*	*See Attachment*
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Photo 15	*Interior Damage (of Top) of Rogen 2 Preheater Exchanger*	*10/26/2009*	*See Attachment*
Photo 16	*Interior Damage of (Top) of Rogen 2 Preheater Exchanger*	*10/26/2009*	*See Attachment*

The metal wall cracking of *Rogen 2 Preheater Exchanger* caused by STRESS CORROSION and HYDROGEN EMBRITTLED METAL DAMAGE.

The bottom portion of the preheater is fabricated with the material of carbon steel. The tube sheets are made of thickness t = 2”, 304SS stainless steel. The carbon steel vessel base (bottom) and the tube sheet of the preheater were welded together. Ordinary carbon steel is widely used for sulfuric

acid in concentrations over 70 %. The surface of the carbon steel will form a thin passive surface film layer, while contacted to the sulfuric acid in concentrations over 70 %.
Storage tanks, pipelines, tank cars, and shipping drums made of steel commonly handle 78 %, 93%, 98% acids and oleum.

1. For the diluted sulfur fluid (liquid or gas), the hydrogen in the sulfur fluid causes the damage of carbon steel structure. It is a phenomena associated with the methane formation. The reaction may occur at the surface of the carbon steel, as well as may occur at the carbon steel material internally.

Some of the hydrogen atoms in the sulfur fluid absorbed on the metal surface, diffuse into the metal. Carbides in the grain interior dissolve and, the carbon migrates to the grain boundaries where it reacts with hydrogen to form hydrocarbon intermediates and ultimately methane molecules which start to form and can not diffuse through the lattice. The reaction and nucleation sites are at grain boundaries. The chemical reaction is as follow:

$$C + 2H2 \quad \text{------}\rightarrow CH_4$$

Methane molecules in principal can precipitate at the grain boundaries, voids and interfaces within the metal lattice causing very high pressures from inside of the cavity they are in. In particular, prolonged exposures to a hydrogen producing environment at temperatures in excess 392 ^{o}F (200 ^{o}C) can result not only in severe decarburization, but also in the formation of methane gas. The equilibrium methane pressure increases as the temperature increases. Under certain conditions these voids line up, usually at grain boundaries (nucleation sites) leading to fissures (pressure vessel wall metal material cracks). These fissures will be developing quickly. Finally the hydrogen embrittlement causes the pressure vessel failure. (Please refer to the photos of the Interior Damage of Bottom of Rogen 2 Preheater.). Hydrogen diffusion largely depends on the characteristics and integrity of the oxide film, and the size and density of defects in the protective film. Whether or not steel deteriorates by surface decarburization, or methane fissuring and internal decarburization, depends on the temperature and the barrier properties of the oxides and hydrogen fugacity (effective pressure) at the surface. At relatively high temperatures and low fugacity, surface decarburization proceeds faster than internal fissuring. Both types of attack will occur if both fugacity and temperature are sufficiently high.

2. Due to the corrosion of the tube bundle in the Preheater, the condensed sulfur acid fluid leaked out from the tube bundles. Since the leakage of sulfur fluid to the space between the stainless steel tube sheet and the interior of the bottom of the Preheater, and external of the tube bundle, the sulfur fluid caused the corrosion of the fluid penetrations. Although the refractory bricks are installed at the interior of the Preheater, it is only for heat insulation purpose. It would not reduce the speed of the hydrogen embrittlement of the carbon steel, because of the hydrogen penetration.

3. During welding, solidification cracking is a form of hot cracking that could occur in weldments. If the vessel is not postweld heat treated (PWHT), the thermal stress cracking is likely to occur.
4. Based on the photos, the previous weld repair was made using the stainless steel welding rods. The joint with stainless steel and carbon steel will set up a galvanic cell which will generate electrochemical corrosion.
5. Postweld heat treatment (PWHT) of the vessel shall be pre-qualified provided that it shall be approved by the Engineer and the following five conditions shall be met.

Per AWS D1.1/D1.1M 2006 Section 3:

(1) The specified minimum yield strength of the base metal shall not exceed 50 ksi (345 MPa).
(2) The base metal shall not be manufactured by quenching and tempering (Q&T), quenching and self - tempering (Q&ST), thermo - mechanical controlled processing (TMCP) or where cold working is used to achieve higher mechanical properties.
(3) There shall be no requirements for notch toughness testing of the base metal, HAZ, or weld metal.
(4) There shall be data available demonstrating that the weld metal shall have adequate strength and ductility in the PWHT condition.
(5) PWHT shall be conducted in conformance with 5.8 of AWS vD1-D1.1M, 2006.

Suggestions

A. Based on the information, photos and drawings of the Regen 2 Preheater provided by Rhodia Inc., after careful review of the drawings and the photos of the existing 7 to 9 feet long crack running along the boundary of the previous weld repair(07/07/2009, 08/20/2009), as well as the photos of Interior Damage of Bottom of Rogen 2 Preheater Exchanger (10/26/2009), we have the following suggestions:

1 In accordance with 2007 ASME Boiler & Pressure Vessel Code, Division II, Part D "Mandatory Appendices" A-330 Stress Corrosion Cracking:

Most ferrous and non ferrous materials are susceptible to some form of stress corrosion cracking. For ferrous materials, susceptibility includes carbon and low alloys steels, austenitic stainless steels, ferritic stainless steels (to a lesser extent), and the higher-strength martensitic and precipitation-hardened stainless steels.
Methods of reducing susceptibility to stress corrosion cracking include the selection of an alloy that is more resistant to cracking. For some materials, the susceptibility is reduced by controlling welding heat input and the heat treating processes.

2 In accordance with 2007 ASME Boiler & Pressure Vessel Code, Division II Part D "Mandatory Appendices" A-452 Stress Corrosion Cracking:

Material which has been sulfur embrittled cannot be salvaged. It must be scrapped.

Although it is not suggested, a temporary repair could be made, if the embrittled portion of the existing weld is scrapped. The embrittled portion is to be replaced with the new carbon steel vessel material which matches the original vessel steel material and a stiffening ring (shown in Fig. 1). The external of the vessel should be welded on with a pair of flanges or the two angle rings as a pair of new flanges of the vessel. Between the two flanges or the angle rings, install the G44 3M NEXTEL 2500 ^{o}F/1370 ^{o}C gasket (or other equivalent material gasket). *The purpose of installing the gasket is to block the contact of the stainless steel tube sheet to the carbon steel vessel base portion, in order to eliminate the corrosion caused by the corrosion electrochemical reactions, due to the galvanic cell.* The detail in figure 1 is shown. The internal wall surfaces of the Preheater needs to be sandblasted after repair. Then sprayed and covered with the corrosion resistant and thermal resistant layer. After the above processing, the interior refractory brick materials need to be re-installed.

B. In the future, if the vessel is replaced with a new vessel, the enamel lining should be applied on the inner wall of the new vessel. The enamel lining material will protect the vessel from the attack of the sulfur acid, such as SO_2, $SO_{3,}$ or the diluted sulfur acid (H_2SO_4), etc. of high temperature fluid or acid vapor penetration. Please refer to figure 2.

CONCLUSION

1. The vessel crack in the affected weldments is due to the thermal solidification cracking.
2. The Preheater vessel crack is caused by the Hydrogen diffusion from the sulfur acid fluid.
3. The postweld heat treatment (PWHT) of the new vessel is required.
4. The enamel lining should be applied on the inner wall of the new vessel for better corrosion protection (Fig. 2).

REFERENCE

1. 2007 ASME Boiler & Pressure Vessel Code Division II Part D
2. Corrosion Engineering, Mars G. Fontana, ISBN-13 978-0071003605 (6/1986)
3. Standards of the Tubular Exchanger Manufacturers Association, 8th Edition - 1999 (TEMA, 8th Edition - 1999)
4. *Structural Welding Code*, AWS D1.1-D1.1M, 2006, American Welding Society

ATTACHMENT

Fig 1 Structure of original Regen 2 Preheater repair

Fig 2 Structure of Enamel Lining of New Regen 2 Preheater

Documented Photo List:
Photos of Regen Preheater External Damages (Cracks)

Documented Drawing list

Documented Photo List:
Photo of Regen Preheater Internal Wall Damages (Cracks)

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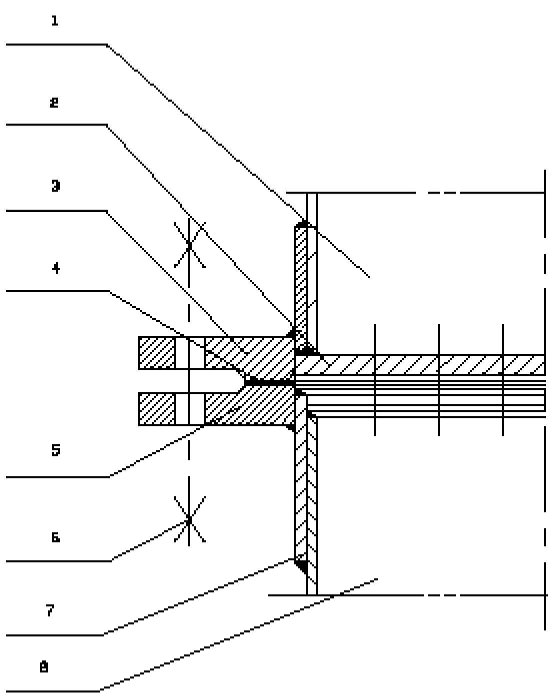

ITEM	NAME	MATERIAL
8	VESSEL BASE PORTION	CARBON STEEL
7	NEW STIFFENING RING	CARBON STEEL
6	STUDS & NUTS	CARBON STEEL
5	FLANGE OF VESSEL BASE	CARBON STEEL
4	GASKET	G44 3M NEXTEL 2500 °F/1370 °C
3	UPPER FLANGE	CARBON STEEL
2	TUBE SHEET	304SS
1	UPPER PORTION OF VESSEL	CARBON STEEL

FIG 1 STRUCTURE OF ORIGINAL REGEN 2 PREHEATER REPAIR

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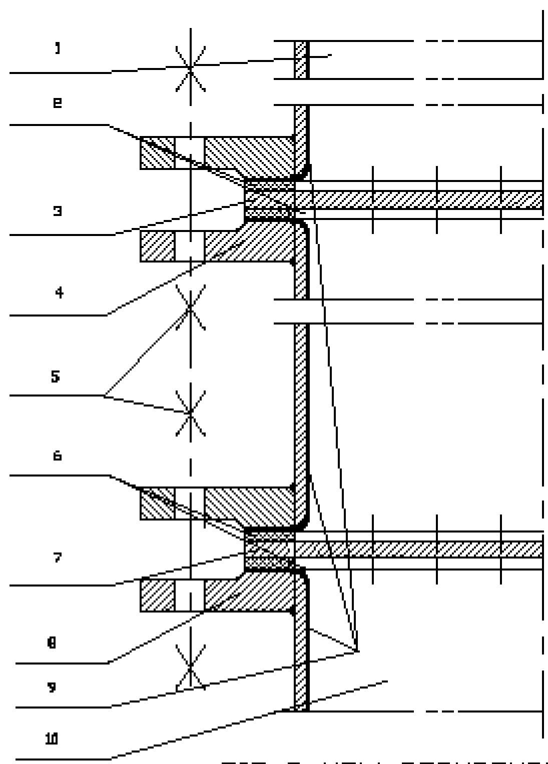

ITEM	NAME	MATERIAL
10	VESSEL BASE PORTION	CARBON STEEL
9	ENAMEL LINING	ENAMEL OR OTHER HIGH THERMAL LINING MATERIAL
8	FLANGES OF VESSEL BASE PORTION	CARBON STEEL
7	LOWER TUBESHEET	904SS
6	GASKETS	G44 3M NEXTEL 2500 °F/1370 °C
5	STUDS & NUTS	CARBON STEEL
4	UPPER FLANGES	CARBON STEEL
3	UPPER TUBESHEET	904SS
2	GASKETS	RUBBER OR OTHER GASKET MATERIAL
1	UPPER PORTION OF VESSEL EXPANSION JOINT	304SS

FIG 2 NEW STRUCTURE OF ENAMEL LINING OF NEW REGEN 2 PREHEATER