UPDATE - ANODIC PROTECTION OF CONTINUOUS DIGESTERS TO PREVENT CAUSTIC CRACKING AND GENERAL CORROSION

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ABSTRACT

Anodic protection systems have been installed in eight hydraulic continuous digesters and one impregnation vessel. Results indicate that corrosion and caustic cracking have been mitigated by the application of anodic protection. Operating characteristics, hardware improvements and digester inspection results are discussed. Potential and coupon monitoring systems using existing nozzles in digesters has proven to be an economical way to determine the susceptibility to corrosion and/or caustic cracking.

INTRODUCTION

Since the sudden de-pressurization of continuous digesters during 1980, the pulp and paper industry has strived to understand the mechanism and determine the most cost effective solution to the serious problem of caustic cracking (embrittlement) of continuous digesters. Instrumental to the search for solutions was the formation of the Technical Association of the Pulp and Paper Industry (TAPPI) digester cracking committee. They broke new ground within TAPPI by collecting funds from digester operators and the vessel designer to contract research projects in order to evaluate several mitigation techniques.

Digester owners would like to identify a cost effective technique requiring little maintenance and inspection that has a long history of success. Unfortunately, at this point in time none of the possible solutions totally meet the required conditions. Digesters should be routinely inspected regardless of repair techniques.

As is the case with other corrosion solutions, combination of several techniques may turn out to be the optimum method of crack prevention.

Anodic Protection

Unlike the other possible mitigation methods such as weld overlay, plasma spray or shot peening, anodic protection does not cover nor physically modify the weld (included heat affected zone).

Anodic protection stablizes the thin passive layer on the carbon steel in caustic sulphide digester environments by changing the electrochemistry at the solution-metal interface. Singbeil and Tromans(1) as well as Singbeil and Garner(2) have shown that cracking of welds will only occur if the electrochemcial potential of the metal is restricted to a narrow range. Anodic protection forces the digester potential from this dangerous zone into an area of complete passivity thus eliminating both general corrosion and caustic cracking. A full description of the theory has previously been published.(3) The purpose of this paper is to provide an update on the use of anodic protection.

ANODIC PROTECTION RESULTS

Tables 1 and 2 list the history and inspection results of the digesters equipped with anodic protection.

Minimization of corrosion in kraft digesters (batch) by the use of anodic protection was verified over 25 years ago by Watson.(4) The experience in protecting continuous digesters has confirmed this work. All general corrosion of anodically passivated vessels has been reduced to the expected magnitude of 0.25 to 0.05 mm per year (1-2 mpy) as measured by weight loss coupons. Actual wall thickness loss has been significantly higher in several vessels due to acid cleaning. In-situ coupon testing during hydrochloric acid cleaning has indicated a weight loss translated into effective wall thinning of 0.762 mm per year (30 mpy) during a single 8 hour clean.

This corrosion was somewhat unexpected as it was confirmed that all recommended procedures were carefully undertaken. The acid was properly inhibited showing no hydrogen evolution on fresh coupons and the temperature never exceed 150° F.

Caustic Cracking

The majority of continuous digester operators are concerned about the insidious nature of caustic cracking as opposed to general corrosion. The detection and weld repair of cracking is time consuming and expensive. As such, the results of anodic protection of cracked digesters is extremely important.

Protection of digester A was deemed necessary due to general corrosion in the cooking zone. Subsequent inspections (1981) indicated significant cracking of the upper welds. Several areas were totally cleaned of cracks while the depths of remaining cracks on the same welds were measured using a four pin resistivity meter. Until 1984 all cracking (both initiation and propagation) was arrested. During the 1984 inspection new cracks were detected and existing cracks had increased in severity. By the time a representative of our company had arrived on site the cracks were removed. As all cracks were considered to be due to causic embrittlement no samples were removed from the vessel.

It was verified that except for a short period of time after the 1983 shutdown, the anodic protection system was energized and operating correctly. It was concluded that the cracking must have occurred during the brief period of time the system was not energized.

Subsequent work by Bennett(5) has shown that construction or repair welds can be cracked by hydrogen at time of welding. Results from digester D can provide an insight into another possible reason cracks were found in digester A.

Digester D was severely cracked at all circumferential welds prior to installation of anodic protection. Significant repair work was performed to remove cracks and build up the weldments with carbon steel.

Anodic protection had protected the vessel for approximately 1-1/2 years. Extremely small indications were detected on previously cleaned surfaces. These indications appeared to be fine cracking and/or minor weld defects. Light grinding to a depth of 0.025 mm (1 mil) removed the damage. Protected precracked D.C.B. (double cantilever beams) specimens showed no caustic cracking.

The vessel was then ready for service. In order to perform subsequent inspections on the effectiveness of protection, the corrosion engineer decided to grind flush several weld caps. To his astonishment he found severe cracking below the top weld pass. Metallurgical examination of "boat" samples indicated that the damage was due to hydrogen cracking which occurred during original construction and/or repair.

It has become painfully obvious that at least two types of cracking (caustic and hydrogen induced) has occurred in digesters. Any surface hydrogen induced cracks can serve as initiation sites for caustic embrittlement.

Although the author is not a welding expert, it would appear that weld repairs of this relatively high carbon containing digester steel must be carefully performed. Factors such as the amount and time of preheat and storage of weld rods must be carefully controlled to prevent welding defects.

Digester B had a history of impregnation zone weld cracks. The anodic protection of this vessel also had problems for several years. However, once operational caustic cracking was totally eliminated.

Problems with Anodic Protection Systems

Considering the complexity of anodic protection systems installed in pressure vessels most of the problems have been minor.

The first several systems used commercially available three pin retractable reference probes. Proper sealing of the reference electrode was difficult to ensure. The reference end of these probes have subsequently been changed to a single more robust design with double pressure seals.

The protection scheme for digester B had significant problems. Supervision of installation was performed by mill personnel. The cathode entry bussbars were inadvertently changed from carbon to sensitized stainless steel.

These bussbars failed due to the higher power dissipation resulting from an increase of 8 times the electrical resistivity of stainless as compared to low carbon steel. This was the first kraft digester protected. In order to ensure adequate current output, the maximum rectifier output voltage was significantly increased.

Combination of this higher than required voltage and breakage of the bussbars immediately adjacent to the digester wall resulted in extraordinary high current densities discharging from the vessel. The small area was forced trans-passive and/or the current density resulted in a drop of pH to a level where passivity could no longer be maintained.

Subsequent work indicated this condition cannot occur if the maximum rectifier output voltage was limited to a value of twice the normal voltage at full output current.

Additional in-situ protection of vessels has shown that although 300 series austenitic stainless steels should not embrittle this material cannot be used as a cathode in kraft digesters. The exact mechanism of damage is being investigated however hydrogen embrittlement, caustic cracking and/or acid cleaning of the cathodically reduced passive film is suspected. All cathodes and associated hardware are fabricated from low carbon steel to prevent this problem. To date no corrosion nor cracking has been identified.

COMPATIBILITY OF ANODIC PROTECTION WITH OTHER REPAIR TECHNIQUES

Although anodic protection has proven to stop general corrosion and caustic cracking some digester operators have chosen other repair techniques.

Hopefully, use of these single mitigation methods will result in complete arrest of caustic cracking. If on the otherhand cracking continues, anodic protection can provide supplement protection.

Stainless Steel or High Nickel Weld Overlay

One of the initial solutions attempted was weld overlay utilizing stainless steel and/or high nickel alloys. Conceptually a properly applied overlay will physically cover the highly stressed metallurgical altered carbon steel weld. Needless to say the overlay must be carefully applied by trained personnel. Pre and post heating of the welding zone may be a necessity.

It is difficult to refute the success of weld overlays in batch digesters. However, unlike continuous vessels, batch digesters are usually completely overlaid, resulting in no stainless-carbon steel interfaces exposed to liquor.

Dependent upon the digester corrosion potential application of a weld overlay can galvanically move the carbon-stainless steel interface potential into a region of higher general corrosion, caustic cracking or complete passivity.

Figures 1 through 3 illustrate the three electrochemical conditions that can effect cracking and/or corrosion at the heat affected interface zone. All three of these conditions have been reported by Wensley(6) with coupon tests in white liquor clarifiers. In actual digesters previously corroded but not cracked welds are not routinely overlayed. As such, the weld potential was previously in the cracking zone and it is probable that overlays will galvanically passivate the heat affected zone or simply transfer the previous cracking to the interface assuming sufficient tensile stresses are present. (Figures 4 and 5)

Properly applied anodic protection will ensure that the new heat affected zone potential is forced into the passive region.

Plasma Spray

Unsealed plasma spray coatings applied to transition welds, have shown signs of spalling. Guzzi(7) has postulated that kraft liquor penetrates the porous plasma spray causing general corrosion of the underlying carbon steel. It is possible that accelerated corrosion of the carbon steel results from galvanic potential differences between the digester and high nickel plasma spray. Assuming the above mechanism, anodic protection will prevent corrosion of the carbon steel and hence minimize deterioration of the plasma spray bond.

Sealed plasma spray has performed very well without the use of anodic protection.

Shot Peening

Peening of the weld converts residual surface tensile into compressive stresses. Minimization of tensile stresses will prevent caustic cracking. Unfortunately, corrosion of the weldment can minimize the effectiveness of shot peening. In fact, corrosion will expose a layer higher in tensile stress than prior to peening.

Once again minimization of corrosion by the use of anodic protection will significantly increase the longevity of the beneficial effects due to shot peening.

DIGESTER POTENTIAL AND COUPON MONITORING PROGRAMME

Table 3 lists the conditions necessary for caustic cracking. Slight differences in liquor chemistry (organics) can affect the severity of cracking(8) and perhaps initiation. Digester to reference potentials vary considerably during startup and upset pulping conditions. Several mills have requested a method to continuously monitor digester potentials as well as detect caustic cracking.

Figure 6 outlines the electrical block diagram of a typical monitoring scheme.

If anodic protection is installed at a later date, no additional instrumentation is required.

Coupon evaluation is performed by Pulp and Paper Research.* Cold worked coupons are installed on the retractable reference probe. Both general corrosion and caustic cracking is detected with this type of coupon monitoring service.

Installation of new 2" nozzles in a continuous digester can be expensive. Recently, several mills have installed the monitoring hardware through existing 3" sky climber nozzles (Figure 7). The probe is positioned flush with the digester separator cone to prevent mechanical damage yet expose the coupons and reference electrode to impregnation zone liquor.

*Patent Pending

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LIST OF TABLES

LIST OF FIGURES

Table 1 Summary of Vessels Anodically Protected

Digester Code	Digester Type	Process	Year of Startup	Design Capacity (ADT/DAY)	Date of Anodic Protection Energization
A	Single Vessel	Soda	1970	730	March 1979
B	Single Vessel	Kraft	1967	250	April 1982
C	Single Vessel	Kraft	1965	425	Jan. 1983
D	Single Vessel	Kraft	1966	820	Sept. 1983
E	Single Vessel	Kraft	1965	700	Aug. 1984
F	Single Vessel	Kraft	1972	425	Aug. 1985
G	Impregnation Vessel	Kraft	1981	750	June 1985
H	Single Vessel	Kraft	1981	965	July 1985?
I	Single Vessel	Kraft	1968	925	Sept. 1985?

Table 2 Summary of Inspection Results

Digester Code	Condition Prior to Anodic Protection Installation	Inspection Results
A	Corrosion of cooking zone. Cracking of Impregnation welds (Unknown at time of installation)	Sept. 1979 - Corrosion mitigated July 1980 - " " July 1981 - " " First crack inspection showed cracking of transition welds July 1982 - Corrosion and cracking mitigated July 1983 - Corrosion and cracking mitigated July 1984 - Corrosion mitigated cracks found in impregnation zone
B	Corrosion of wash zone. Cracking of impregnation welds.	Sept. 1982 - Cracking and corrosion continued as system de-energized Sept. 1983 - Bussbars replaced Sept. 1984 - No corrosion nor cracking
C	Corrosion of welds	Sept. 1983 - No cracking - mitigation of weld corrosion Sept. 1984 - No cracking - mitigation of weld corrosion
D	Caustic cracking of all circumferential welds	April 1985 - Caustic cracking mitigated - hydrogen induced subsurface cracking detected
E	Erosion corrosion of "vessel" above top separator	Jan. 1984 - Corrosion mitigated April 1985 - Corrosion mitigated
F	Caustic cracking of transition welds. Top of digester replaced.	
G	Caustic cracking of transition welds behind blank plates	
H	Caustic cracking of transition welds	
I	Top digester replaced. Caustic cracking of carbon steel adjacent to stainless steel weld overlay	