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# Diffusion Coatings for Corrosion-Resistant Components in Coal Gasification Systems

Quarterly Technical Progress Report 11

Covering the period January 1, 2006 through March 31, 2006

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## DISCLAIMER

## ABSTRACT


Heat-exchangers, particle filters, turbines, and other components in integrated coal gasification combined cycle system must withstand the highly sulfiding conditions of the high-temperature coal gas over an extended period of time. The performance of components degrades significantly with time unless expensive high alloy materials are used. Deposition of a suitable coating on a low-cost alloy may improve its resistance to such sulfidation attack, and decrease capital and operating costs. The alloys used in the gasifier service include austenitic and ferritic stainless steels, nickel-chromium-iron alloys, and expensive nickel-cobalt alloys.

During this period, we conducted two 300-hour tests. In the first test, we exposed samples at 900°C under conditions simulating the high-temperature heat recovery unit (HTHRU). The second test was at 370°C, corresponding to the filter units following the HTHRU. The tests were showed the resilience of silicon nitride as a coating component, and the new coating procedures better penetrated the pores in sintered metal filter samples. Finally, we also received samples that were exposed in the Wabash River plant. Unfortunately, all these samples, that were prepared last year, were severely eroded and/or corroded.

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## EXECUTIVE SUMMARY

Advanced coal gasification systems such as integrated coal gasification combined cycle (IGCC) processes offer many advantages over conventional pulverized coal combustors. Heat-exchangers, filters, turbines, and other components in IGCC plants often must withstand the highly sulfiding conditions at high temperatures. In collaboration with U.S. Department of Energy and ConocoPhillips, we are developing corrosion-resistant coatings for high-temperature components in IGCC systems.

SG Solution's coal gasification power plant in Terre Haute, IN, uses ConocoPhillips' E-Gas technology. The need for corrosion-resistant coatings exists in two areas: (1) the tube sheet of a heat exchanger at ~1000°C that is immediately downstream of the gasifier, and (2) porous metal particulate filter at 370°C, which is downstream of the heat exchanger. These components operate at gas streams containing as much as 2% $H_2S$. A protective metal or ceramic coating that can resist sulfidation corrosion will extend the life-time of these components and reduce maintenance.

During this period, we conducted two 300-hour tests. In the first test, we exposed samples at 900°C under conditions simulating the high-temperature heat recovery unit (HTHRU). The second test was at 370°C, corresponding to the filter units following the HTHRU. The tests were showed the resilience of silicon nitride as a coating component, and the new coating procedures better penetrated the pores in sintered metal filter samples. Finally, we also received samples that were exposed in the Wabash River plant. Unfortunately, all these samples, that were prepared last year, were severely eroded and/or corroded.

# INTRODUCTION

Heat-exchangers, filters, turbines, and other components in coal-fired power plants must withstand demanding conditions of high temperatures and pressure differentials. Further, the components are exposed to corrosive gases and particulates that can erode the material and degrade their performance. In collaboration with U.S. Department of Energy and ConocoPhillips, SRI International recently embarked on a project to develop corrosion-resistant coatings for coal-fired power plant applications. Specifically, we are seeking to develop coatings that would prevent the corrosion in the tube-sheet of the high-temperature heat recovery unit of a coal gasification power plant of SG Solution's plant in Terre Haute, IN, which uses ConocoPhillips' E-Gas technology. This corrosion is the leading cause of the unscheduled downtime at the plant and hence success in this project will directly impact the plant availability and its operating costs. Coatings that are successfully developed for this application will find use in similar situation in other coal-fired power plants.

# WORK PERFORMED

In this quarterly report we describe the fate of samples of the following tests:

1. Exposure to simulated coal gas at 900°C: Test #10
2. Exposure to simulated coal gas at 370°C: Test #11
3. Exposure to coal gasification stream in the Wabash river plant.

## EXPOSURE TO SIMULATED COAL GAS AT 900°C: TEST #10

The top panel of Figure 1 shows the picture of the samples before they were exposed to simulated gasifier conditions at 900°C. The bottom panel is a photograph of the samples after exposure after 308 h. Table 1 lists the samples, the specific coatings, and some general observations.

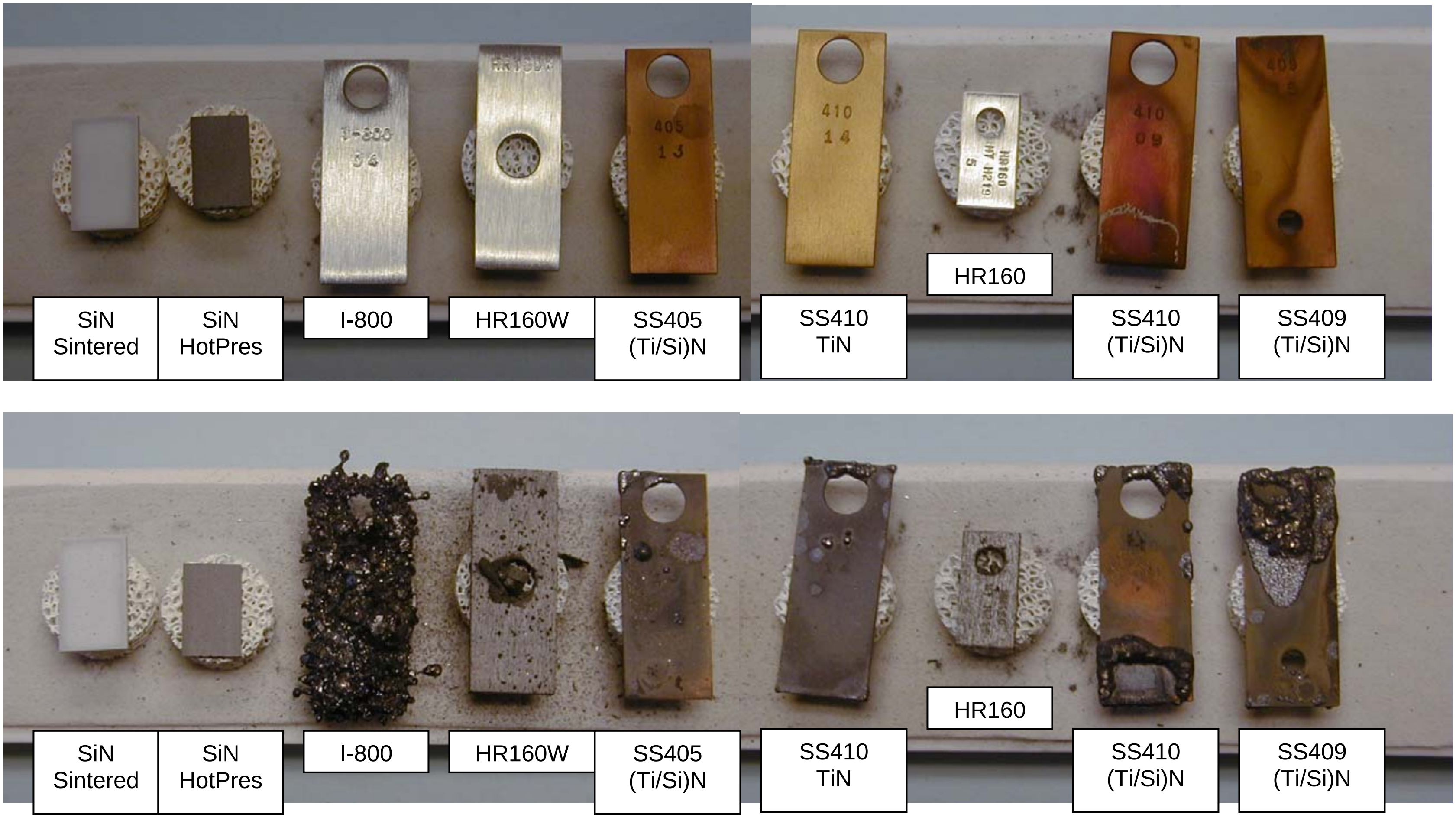


Figure 1.  Samples before and after exposure for 308 h at 900°C in simulated gasifier Test 10.

**Table 1. Samples Tested and Results Test 10**
**900°C for 308 h (Jan 10, 2006)**

| Sample No. | Material | Coating | Run | Appearance | % Wt. Gain |
|---|---|---|---|---|---|
| 1 | $Si_3N_4$ (sintered) | none | - | No attack | 0.00 |
| 2 | $Si_3N_4$ (hot pressed) | none | - | No attack | -0.03 |
| 3 | I 800 | none | - | Severe attack, friable sulfide deposits; could not weigh | |
| 4 | HR 160 W | none | - | Some flakes, and corrosion at the drill hole | -1.20 |
| 5 | SS405 | (Ti/Si)N | 89 | A few localized spots of sulfide | 3.22 |
| 6 | SS410 | TiN | 90 | Localized sulfide growth | 3.16 |
| 7 | HR 160 | none | - | Looks fine | -0.35 |
| 8 | SS410 | (Ti/Si)N | 91 | Sulfide deposits along certain lines | 10.58 |
| 9 | SS409 | (Ti/Si)N | 92 | Significant sulfide growth in one region | 12.92 |

This batch included two samples of silicon nitride. One of them was reaction-sintered material, the other was hot pressed and highly dense. Neither sample showed any sign of sulfidation attack or mass loss, indicating that the formation of SiO or SiO(OH)2 was negligibly small under the tested conditions.

The third sample was a coupon of an Inconel alloy. This sample was severely corroded. There was a friable deposit (mostly FeS, as determined by XRD deposit all over the sample, and it adhered to the disc of porous alumina on which it was resting. The test also included two samples (#4 and #7) of another specialty alloy, HR 160. One of these (#4) was of the welding grade, and it developed some flakes. Both these samples lost a mall amount of their weight, possibly from the loss of CoS, but they otherwise maintained their integrity. This result is in contrast to the fate of the HR160 coupon in the actual gasifier stream discussed below during which they underwent extensive corrosion/erosion.

The remaining four samples were various 400 grade steel coupons coated with TiN or (Ti/Si)N. There was varying amount of corrosion in these samples mostly evidenced as deposits of FeS, The corrosion was not uniform on the sample, but seemed to be localized in certain regions. In Samples 8 and 9 the corrosion occurred where the coatings were visibly defective.

## EXPOSURE TO SIMULATED COAL GAS AT 370°C: TEST #11

The purpose of this test was to see if the porous SS409 coupons that we had previously fabricated could be coated in their interior so that they would survive the conditions in the filter unit following the HTHRU. Along with the Cr/Al oxide and TiN coated porous samples, we also put in a batch of SS409 and SS410 coupons recently coated with various nitride coatings. Table 2 lists the samples, the specific coatings, and some general observations. The top panel of Figure 2 shows the picture of the samples before they were exposed to simulated gasifier conditions at 370°C. The bottom panel is a photograph of the samples after exposure after 300 h.

**Table 2. Samples Tested and Results Test 11**
**370°C for 300 h (Jan 10, 2006)**

| Sample No. | Material | Coating | Run | Appearance | % Wt. Gain |
|---|---|---|---|---|---|
| 1 | SS410 | (TiSi)N | 84 | Virtually unchanged | 1.43 |
| 2 | SS409 | (CrAl)Ox, porous | 88 | Virtually unchanged | 0.23 |
| 3 | SS409 | TiSiN/TiAlN | 92 | Some bands accentuated | 0.29 |
| 4 | SS409 | TiSiN/TiAlN, porous | 93 | Slightly lighter color | 10.25 |
| 5 | SS409 | TiSiN/TiAlN | 93 | Virtually unchanged | 0.02 |
| 6 | SS410 | TiSiN/TiAlN/TiAl | 94 | Virtually unchanged | 0.20 |
| 7 | SS409 | TiSiN/TiAlN/TiAl | 94 | Virtually unchanged | 0.03 |
| 8 | SS409 | TiSiN/W/TiAlN | 95 | Virtually unchanged | 0.10 |
| 9 | SS409 | TiAlN/WTiAlN/W/TiAlN | 96 | Virtually unchanged | 0.39 |
| 10 | SS409 | TiSiN/W/TiAlN | 98 | Virtually unchanged | -3.54 |
| 11 | SS409 | TiSiN/W/TiAlN | 99 | Virtually unchanged | 0.23 |

All the samples looked almost exactly as they went in. At this relatively lower temperature, we did not expect any of the nitride coatings to show any corrosion. The only sample to gain significant weight was the TiN coated porous SS409 coupon (Sample 4). This weight gain is surprising because there was hardly any visible change. Following the exposure, cross sections of both of the porous samples were prepared analyzed by SEM-EDX and XRF. Preliminary examination showed the presence of Ti on the interior surfaces, in the depths of the porous sample, a clear indication of the ability of our fluidized bed process to deposit metals in the pores that would not be covered in processes that operate by line-of-sight deposition methods.

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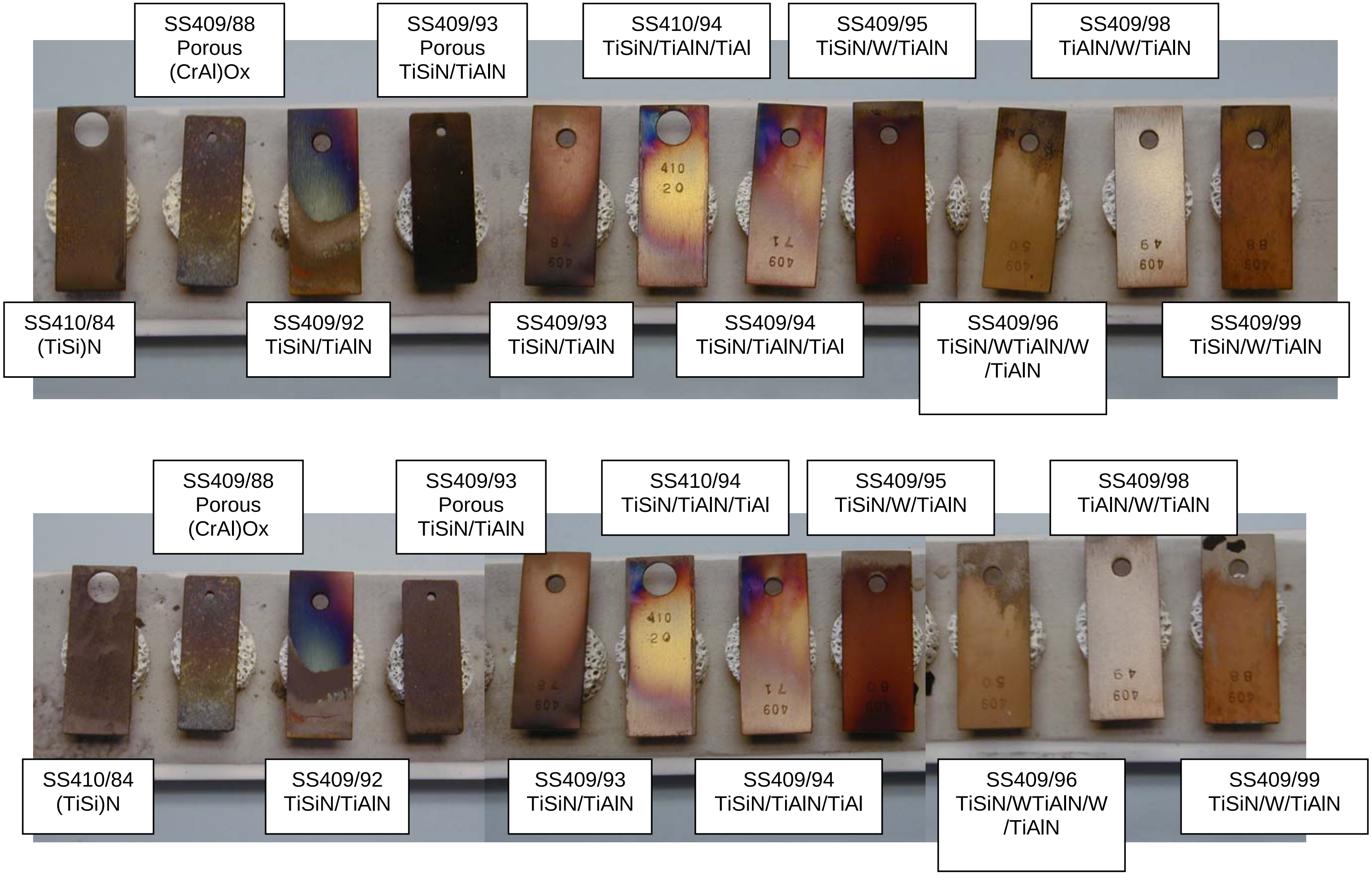


Figure 2. Samples before and after exposure for 300 h at 937°C in simulated gasifier Test 12.

## EXPOSURE OF COUPONS TO COAL GAS IN THE WABASH RIVER PLANT

A batch of coated and uncoated samples were sent to ConocoPhillips for testing in their Wabash River plant gasifier. These included specialty alloys such as Haynes alloy HR160 and Inconel 800 as well as steel samples—both uncoated and coated with either Cr/Al oxide or TiN. Table 3 lists these samples and their composition.

**Table 3. Samples for Gasifier Exposure Tests**
**April 29, 2005**

| Coupon | Alloy | Marking | Coating | Run No. | Size (mm) |
|---|---|---|---|---|---|
| 1 | HR160 | 05 | None | - | 41.7x19.6x3.2 |
| 2 | I 800 | 08 | None | - | 51.2x19.4x3.7 |
| 3 | SS 410 | 05 | None | - | 51.2x19.6x3.0 |
| 4 | SS 304 L | 02 | None | - | 51.2x19.5x3.0 |
| 5 | SS 409 | 12 | Cr-Al/Al/Ox | 59 | 51.5x19.5x3.9 |
| 6 | SS 409 | 16 | Cr-Al/Al/Ox | 70 | 51.3x19.5x3.8 |
| 7 | SS 409 | 17 | Cr-Al/Al/Ox | 70 | 51.4x19.5x3.8 |
| 8 | SS 405 | 15 | TiN | 66 | 51.2x19.6x3.6 |
| 9 | SS 405 | 16 | TiN | 66 | 51.2x19.5x3.4 |
| 10 | SS 409 | 18 | TiN | 68 | 51.5x19.5x3.8 |
| 11 | SS 409 | 20 | TiN | 68 | 51.4x19.5x3.9 |

Figure 3 shows a picture of the samples before and after exposure. The unlabeled samples were those that ConocoPhillips had put in for their own work. The samples were subjected to 1,100 h of the high-temperature synthesis gas environment. All the samples were severely damaged, with many of them even falling off the coupon tree and getting lost in the gasifier. One of the samples (#5) SS409 coated with Cr/Al oxide had already survived over 500 hours in simulated coal gas stream with no apparent degradation. Only the Haynes alloy (#1) remained on the sample holder, but even this sample showed extensive sulfidation attack. Other samples that seemed to have survived to some extent were Inconel 800 (#2), austenitic stainless steel SS304 (#4), and two SS409 samples coated with TiN (#10 and #11). Note that the Inconel 800 coupon was severely sulfided even in the laboratory test. The severity of damage in all these samples suggests that the environment in the gasifier is much harsher than that provided in the laboratory test. To a large extent this may be due to the erosion by particles that is not provided in the lab set up. However, the specific problem of tube sheet corrosion is not exacerbated by erosion due to ash particles, and so the coupon tree set up may represent a vastly more severe a test.

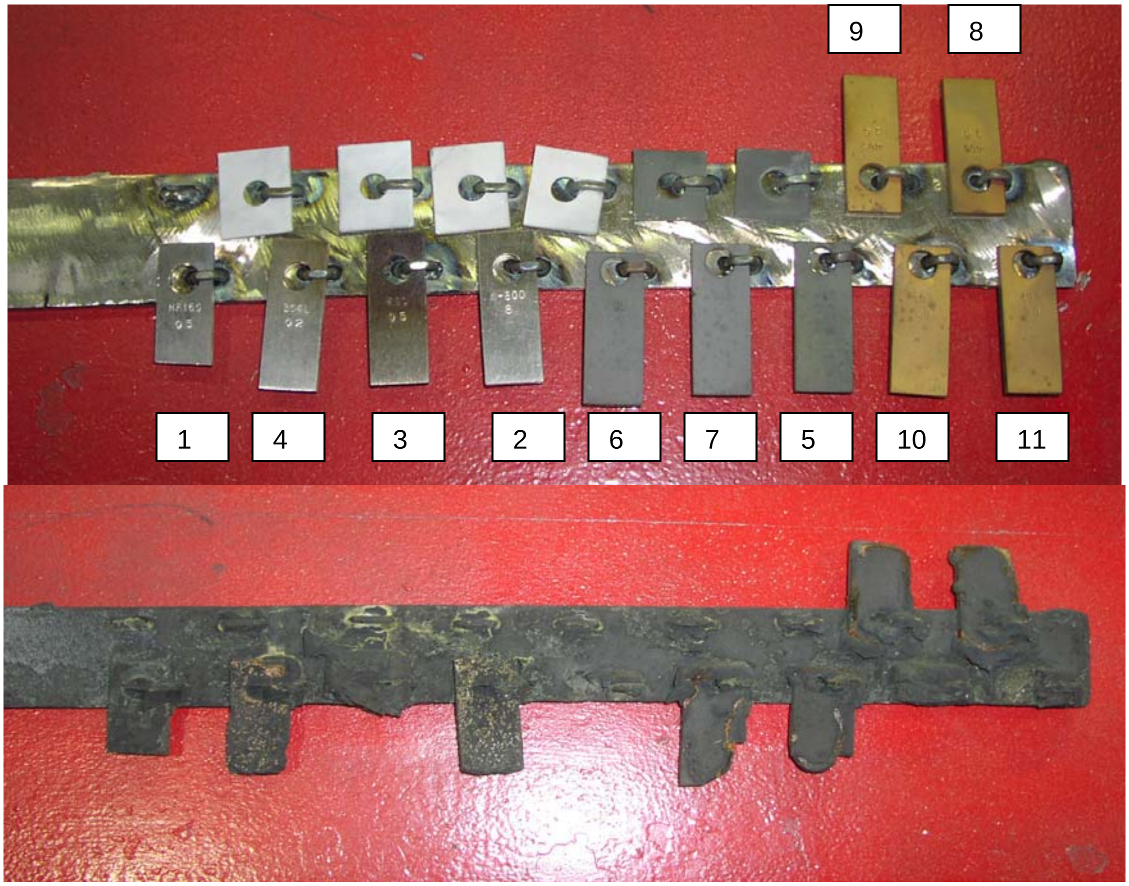


Figure 3: Samples before and after exposure to the hot gas stream in the Wabash River Plant during May-Sep, 2005 (1,100 hours, petcoke syngas)

A second batch of samples was submitted to ConocoPhillips for testing in their gasifier in October 2005. They are listed in Table 4, and Figure 4 shows their photographs of the tree with the samples before and after exposure in the high temperature, abrasive synthetic gas stream for 3,814 hours. During removal of the coupon tree, the coupon designated as 410-01 was inadvertently broken off. This was the only coupon to have remained intact. A second detached coupon that can be seen in the photo was recovered during an earlier vessel inspection, as it had already broken off.

**Table 4. Samples for Gasifier Exposure Tests**
**October 17, 2005**

| Coupon | Alloy | Coating | Run No. | Weight (g) | Size (mm) |
|---|---|---|---|---|---|
| 1 | SS 409 | Cr/Al/Al-Ox | 76 | 11.4886 | 51.1X19.3X1.74 |
| 2 | SS 410 | Cr/Al/Al-Ox | 73 | 9.9638 | 51.2X19.4X1.5 |
| 3 | SS 409 | Ti/Al Nitride | 77 | 11.3632 | 51.1X19.5X1.7 |
| 4 | SS 409 | Ti/Al Nitride | 77 | 11.1244 | 51.2X19.4X1.7 |
| 5 | SS 410 | Ti/Al Nitride | 79 | 9.9997 | 51.2X19.4X1.5 |
| 6 | SS 405 | Ti/Al Nitride | 80 | 7.8017 | 51.0X19.4X1.3 |
| 7 | SS 409 | Ti/Ta Nitride | 81 | 11.3005 | 51.0X19.3X1.7 |
| 8 | SS 409 | Ti/Ta/Al Nitride | 82 | 11.3563 | 51.1X19.4X1.7 |
| 9 | SS 409 | Ti/Al Nitride | 85 | 11.5160 | 51.1X19.4X1.7 |
| 10 | SS 410 | Ti/Si Nitride | 86 | 9.9388 | 51.1X19.4X1.5 |
| 11 | SS 405 | Ti/Si Nitride | 87 | 7.7653 | 51.0X19.4X1.3 |
| 12 | SS 409 | Ti/Si Nitride | 87 | 11.4653 | 51.1X19.3X1.7 |
| 13 | SS 410 | Ti/Si Nitride | 87 | 9.8130 | 51.1X19.5X1.5 |

## CONCLUSIONS AND FUTURE WORK

- Titanium nitride and chromium-aluminum oxide coatings appear to offer best protection, as long as there are no defects.
- The recent modifications in the coatings procedure have led to improved coatings, although we still encounter certain pinhole and line defects where corrosion is evidenced.
- Further analysis of exposed samples by XRF.
- Testing of recently prepared multi-layered TiN coatings at 900°C.
- The conditions at the test coupon tree in the gasifier are very abrasive and may not represent the conditions best suited for evaluating tube sheet coatings.

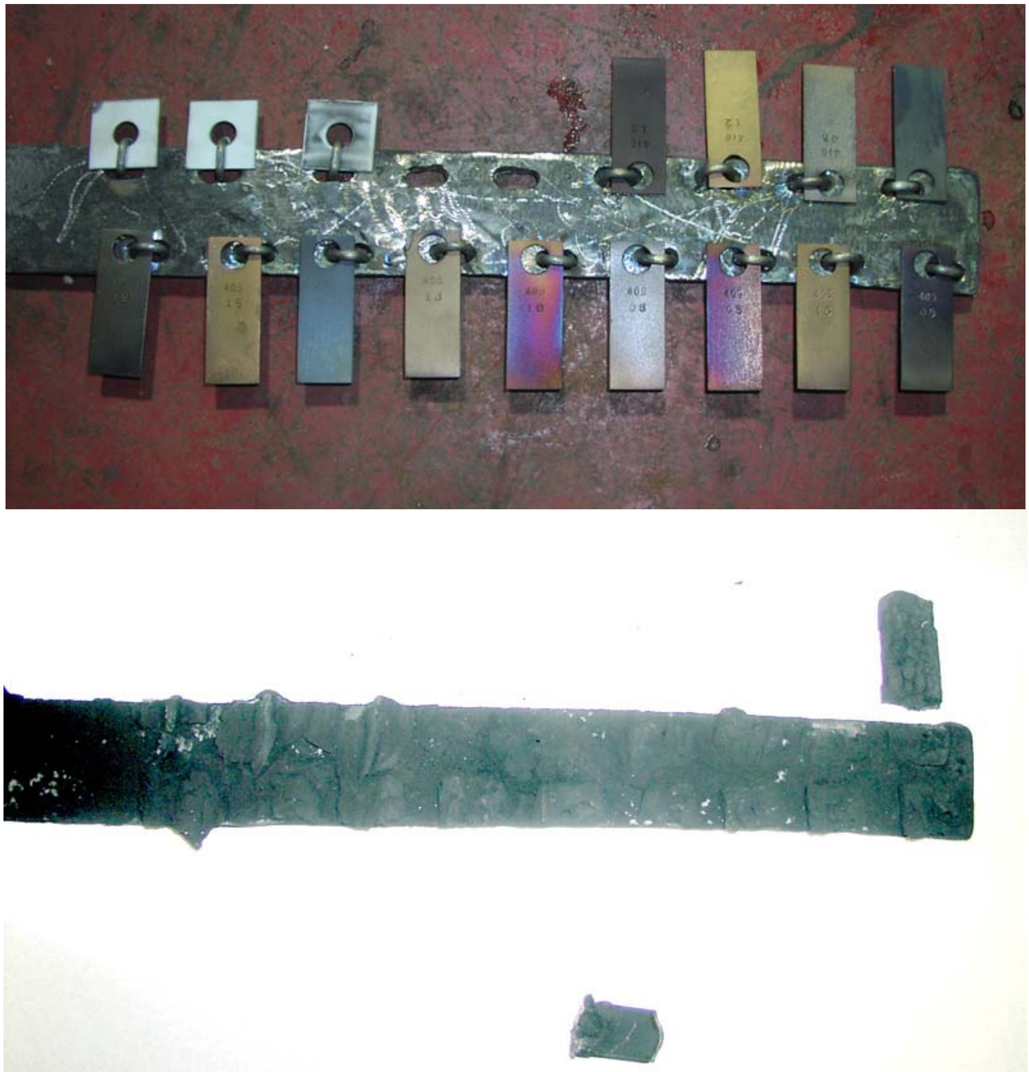

Figure 4. Samples before and after exposure to the hot gas stream in the Wabash River Plant during May-Sep, 2005 (3,814 h)