NOVEL CERAMIC COATINGS FOR THE PETROLEUM INDUSTRY

PAPER TO BE PRESENTED AT

COKING.COM SEMINAR, MARCH 11-13, 2008, GALVESTON, TEXAS

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(1) SYNOPYSIS

This paper presents results of testing zirconium coatings for mitigating coking of high fouling refinery petroleum streams on hot metal surfaces.

The zirconium coating comprises of synthesis of cubic zirconium coating on a metal substrate and infusion of the zirconium into the metal grain.

The fouling tests were performed using the Thermal Fouling Test Method, which utilizes a tube-in-shell heat exchanger to simulate refinery operations. The tests were performed at exchanger metal temperatures of 1010° F. Also the tests were made using carbon steel 1018 exchange heater metal for comparative purposes...

The fouling test results showed that the zirconium coated exchanger heater tubes resulted in a reduction of around 60% in fouling.

Scanning Electron Microscopy, Electron Dispersive Spectroscopy, Optical Microscopy, Metallography, Thermogravimetric analysis and Elemental analysis were used to characterize the zirconium coating material, exchanger coated heater tubes metal surfaces and the fouling coke deposits.

(2) FOULING OF HYDROCARBONS ON EQUIPMEMT METAL SURFACES

Fouling is the phenomena of deposition of undesired various organic and/or inorganic materials on hot metal surfaces of refinery processing equipment such as heat exchangers, furnace tubes, reactors, etc.

The fouling phenomenon leads to various costly operational problems:
Losses of energy due to poor heat transfer, loss of production due to reduced flow or frequent shut-down of operations and/or the use of costly chemical additives.

Fouling of processing equipment can be caused by a variety of mechanisms depending on feedstock, process and operating conditions. The various fouling mechanisms are summarized below:

(a) The deposition of organic materials such as macro-molecule asphaltenes, polymers and sludge's.

(b) Formation and deposition of coke material.

(c) Formation and deposition of inorganic materials such as sulfide and chloride salts, silica and alumina.

(d) Formation of by-products caused by chemical reactions such as oxidation, sulfidation and chlorination.

(3) MIST ZIRCONIUM METAL COATING PROCESS

The coated heat exchanger tubes used in this investigation were coated by the MIST process (Metal Infusion Surface Treatment). The MIST technology was started in the year 2000 and is covered by several patents.

The MIST technology is a low temperature application, whereby the process can combine any combination of 50 + elements into ~ 100 nanometer thick metal oxide coatings. The MIST process is commercially used in die casting, extrusion, metal forming, automotive, steel and catalytic cracking applications, and is under development for fuel cell application.

The MIST coatings comprises of forming the cubic zirconium at the metal surface, accompanied by an infusion into the treated metal grain at low temperature. Once the zirconium treatment is performed, the zirconium oxide stays in place, even though the treated metal parts are used at much higher temperatures of up to 1000°C or higher.

(4) THERMAL CHARACTERISTCIS OF MIST ZIRCONIUM COATING

The thermal stability of coatings used for high temperature applications such as furnace tube coatings, is of paramount importance. We determined the thermal stability of the MIST zirconium coating material used for coating the heater exchanger tubes used in this investigation, by thermal analysis from 20° C to 1000° C in air and nitrogen atmospheres. We found that the zirconium coating materials were thermally stable up to 1000°C in air and nitrogen. Actually, the thermal properties of the zirconium coatings were similar to the thermal properties of diamonds using the same analysis method and conditions (both lost ~ 3% of weight at 1000° C). The TGA thermograms of zirconium coating material and diamond in air and nitrogen are presented in Table 1.

(5) THERMAL FOULING TEST METHOD

The Thermal Fouling Test method is an accelerated test which is designed to reproduce in the laboratory the fouling and/or coking problems experienced in refinery or petrochemical processes.

The Thermal Fouling Test comprises of passing the hydrocarbon liquid through a resistance heated tube-in-shell heat exchanger, while monitoring inlet and outlet oil temperatures, oil flow and unit pressure. The test is performed at exchanger metal temperatures up to 1050 ° F and at 900 to 1000 psig for one to ten hours. The heat exchanger heater tubes are available in carbon steel, various stainless steel metallurgies (S/S 314, S/S 316 and S/S 445), aluminum, gold and various coated elements by the vacuum vaporization process (EFTA).

A photograph and schematic diagram of our fouling test unit, and photographs of a new and fouled exchanger heater tubes are presented in Table 2.

When and if fouling occurs, fouling deposits build up on the exchanger heater tube, which results in reducing the heat transfer to the oil. Fouling is measured by the change in the liquid outlet temperature (Δ temperature fouling). For fouling measurements of lighter hydrocarbon streams, an exchanger equipped with a micro-filter is used, and fouling is measured by the change in the pressure across the heat exchanger (Δ pressure fouling). Typical fouling graphs of Δ temperature fouling of low and high fouling petroleum streams are presented in Table 3.

(6) EFFECT OF TUBE METALLURGY AND TREATMENT ON COKING

Furnace tube metallurgy and metal surface treatment play an important role in coke formation, deposition and mitigation as illustrated in the following examples.

In the steam cracking furnace tubes operating at 1800°F to 2000°F, catalytic coke formation is continuously occurring which may lead to tube metal carburization (carbon diffusion in the metal grain). Metal carburization is mitigated by a coating of nickel and chromium sulfide which is produced by the addition of sulfur additives (up to 100 ppm) to the feedstock to form the coating, which act as barriers for carbon infusion into the metal grain. Photographs of a cokified furnace tube and a carburized furnace tube are in Table 4.

A second example involved a change of furnace tube metallurgy from carbon steel to 9-chrome resulted in mitigating furnace fouling in a HDS process. Laboratory fouling tests using our Thermal Fouling Test Unit showed that high sulfur naphtha fouling could be reduced by using exchanger heater tubes of stainless steel 316 in comparison to carbon steel. Fouling test results of naphtha at 1000°F metal temperature are presented in Table 5. The use of 9-chrome furnace tubes performed satisfactorily for a several years.

In a third example, Thermal Fouling Testing of heat exchanger tubes coated by high temperature vapor deposition with aluminum and silicon, showed reduced fouling in comparison with fouling using carbon steel heat exchanger tubes. Thermal fouling test results are shown in Table 6

(7) THERMAL FOULING TESTING OF ZIRCONIUM COATED HEAT EXCHANGER TUBES

Heat exchanger tubes coated with zirconium coating (about 1 micron thickness) were tested using the Thermal Fouling Test method described in item 4.

A high fouling crude oil / resid blend with low viscosity was selected for this investigation, as low viscosity fluids have better test repeatability than high viscosity petroleum resids in the Thermal Fouling Test method.

Initially the crude oil / resid blend was tested using carbon steel 1018 exchanger metal at 800°F, 900°F and 1010°F, to select a reasonably high fouling operating conditions. Fouling test results are presented in Table 7. Exchanger metal temperature of 1010°F was selected for testing the coated exchanger test tubes as this temperature is within the coker furnace metal operation.

Three exchanger heater tubes with varying zirconium based coatings were tested at 1010°F using the same test operating conditions that were used for testing the carbon steel exchanger tubes. Fouling test results of the zirconium coated exchanger tubes are presented in Table 8. Photographs of a fouled carbon steel exchanger tube and a fouled zirconium tube are presented in Table 9.
A comparison of the fouling graphs (exchanger LOT vs. time) when using carbon steel exchanger and zirconium coated exchanger tubes are presented in Table 10.

In summary, the zirconium coated tubes showed efficacy varying from 52% to 62% in comparison to carbon steel exchanger tubes. Considering that the laboratory fouling tests are accelerated tests, these results are promising.

(8) CHARACTERIZATION OF FOULED ZIRCONIUM COATED TUBES

The fouled zirconium exchanger tubes and their fouling deposits were investigated by Scanning Electron Microscopy, Elemental Analysis, Thermogravimetric Analysis and Electron Dispersive Spectroscopy.

Scanning Electron Microscopy (SEM)

The SEM Micrographs of the deposits from the zirconium coated exchangers were different from the fouling deposit from the carbon steel heat exchanger and coke deposits from delayed coker furnace tubes. The deposits from the zirconium coated exchanger appear to have different morphology showing a smoother surface and more agglomerated than the other two deposits. Comparisons of the Electron Micrographs of the three deposits are presented in Table 11.

Elemental Analysis of Deposits

Polycondensed aromatic as defined by carbon / hydrogen atomic ratio is a good indicator of the chemical composition of coke deposits, which is dependent on the temperature used in the process.

The fouling deposits from the zirconium coated exchanger showed a carbon / hydrogen atomic ratio of 1.21, 1.30 and 1.27, which are very similar to the carbon / hydrogen atomic ratio of deposits of the carbon steel exchanger. These deposits showed lower carbon / hydrogen atomic ratio than coke deposits from a delayed coker furnace tube (average 2.50). This is understandable as the zirconium and carbon steel exchanger deposits were produced at lower temperatures (1010° F) than the metal temperature of the coker furnace tube. The elemental analysis of the deposits from the zirconium coated exchanger, carbon steel exchanger and ten delayed coker furnace coke deposits are presented in Table 12.

Thermogravimetric Analysis

The Thermogravimetric Analysis (TGA, 20° C to 1000° C in air) showed that the zirconium coated deposits contained similar coke content as the carbon steel deposit (99wt.%,) with one noticeable difference, that the zirconium exchanger deposit showed higher decomposition temperature (545° C to 675° C.)

The zirconium coated deposits showed higher coke content than the coker furnace deposit (~ 94 wt.%). This is due to the presence of iron sulfide in the coker furnace deposit. The decomposition temperature of the furnace coker deposit (628° C - 597° C) which was in the same range as the zirconium coated tube. The TGA analysis data and Thermograms are presented in Tables 13 and 14.

Electron Dispersive Spectroscopy (EDX)

The EDX analysis of the zirconium coated exchanger deposits showed mainly carbon (~90wt.%) and small quantities of sulfur and oxygen. No zirconium atoms were found in the fouling deposits, indicating that the zirconium coating remained intact at the high exchanger temperature used in the test (1010°F).
The EDX analysis of the zirconium coated exchanger, before and after the fouling tests are presented in Table 15.

The EDX analysis of the coated exchanger metal surface after the fouling test showed no hydrogen sulfide deposit formation, indicating that the zirconium coating protected the metal surface from sulfidation reactions. Deposits from delayed coker furnace tubes always show a thick layer of iron sulfide in the deposit adjacent to the tube metal, which is commonly followed by coke deposition (as shown in Table 16).

In summary, the fouling deposits produced from thermal testing the MIST zirconium coated exchanger heater tubes showed chemical, thermal and morphological properties in the same range as deposits produced from the delayed coker furnace tubes.

Acknowledgement:
The heat exchanger tubes used in this investigation were coated by:

Coker Coaters, LLC,
Part of C3 International Group of Companies

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Presented at
Coking.com seminar
March 11-13, 2008
Galveston, Texas
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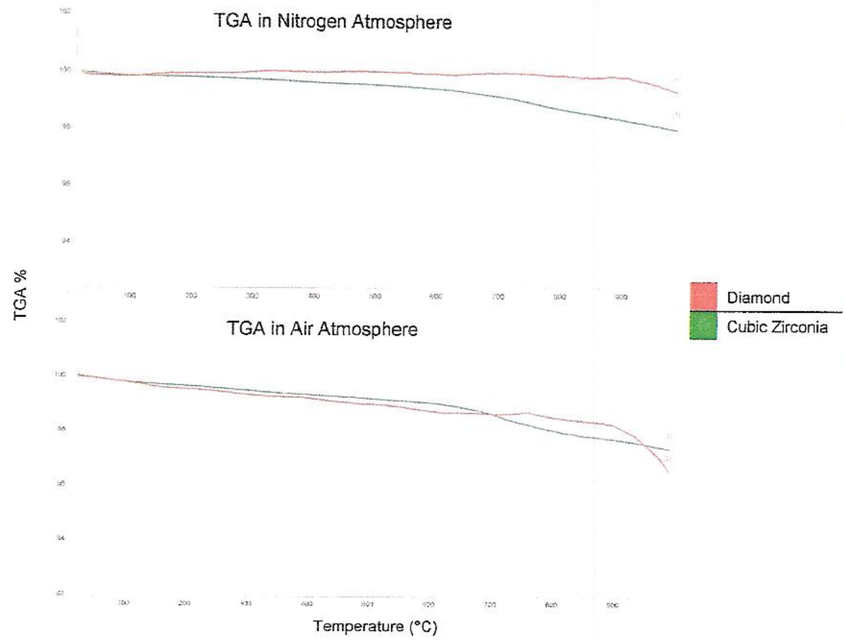
Requirements of Coatings for High Temperature Applications

- Thermal Stability at the Operating Metal Temperature
- Adhesion to metal surface, preferably infusion into the metal groin
- Resistance to attack by chemical reactions (sulfidation, oxidation)

Table 1: Thermogravimetric Analysis of Diamond and Cubic Zirconia



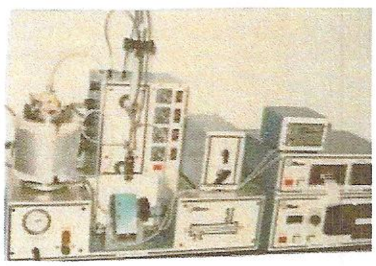


Table 2
Thermal Fouling Test Unit
&
New and Fouled Heat Exchanger Tube

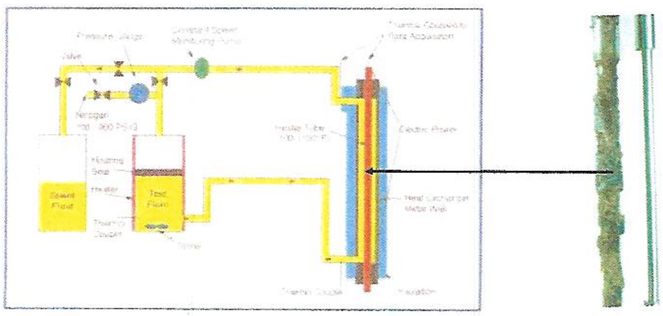


Table 3
Thermal Fouling Graphs of Low and High Petroleum Stream

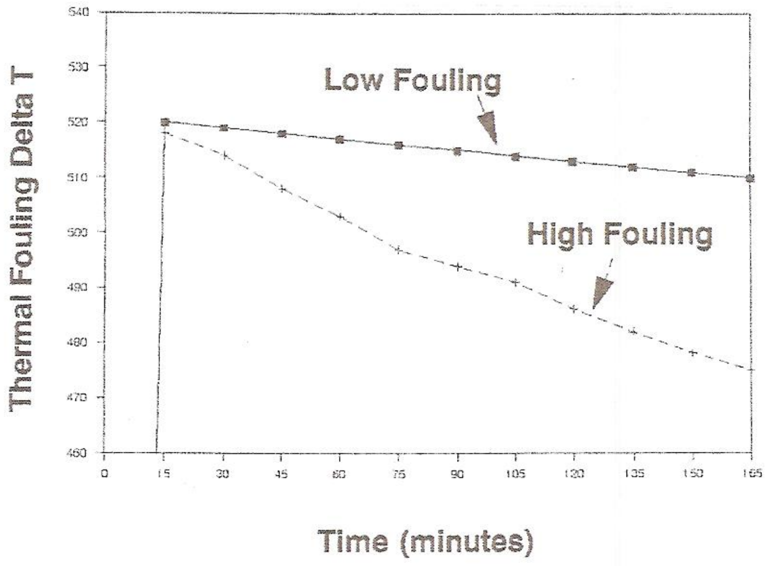
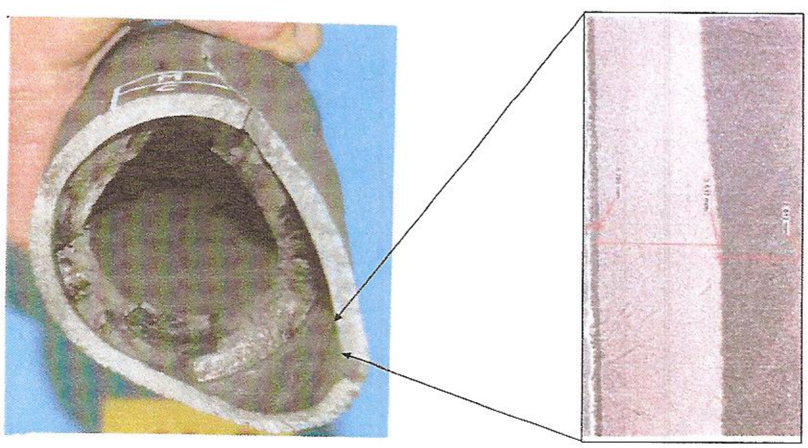


Table 4: Cokified Steam Cracker Furnace Tube and Caburization



Cokified Furnace Tube

Carburized Furnace Tube

Table 5
Fouling of Naptha Using Varying Exchanger Metallurgies

Heater Metal Type	C/S 1018	S/S 304	S/S 316
Heater metal temp (°F)	1000	1000	1000
Unit pressure (psig)	750	750	750
Fluid flow rate (cc/min)	3.0	3.0	3.0
Test time (minutes)	90	90	90
Thermal Fouling (ΔT, °F)	46	11	10

Table 6
Fouling of Crude Oil Using Varying EFTA Coated Exchanger Tubes

Metal Coating Type	C/S 1018	Aluminum	Silicon
Heater metal temp (°F)	1000	1000	1000
Unit pressure (psig)	750	750	750
Fluid flow rate (cc/min)	3.0	3.0	3.0
Test time (minutes)	90	90	90
Thermal Fouling (ΔT, °F)	46	21	19

Table 7
Thermal Fouling Testing of Carbon/Steel 1018 Exchanger Tubes

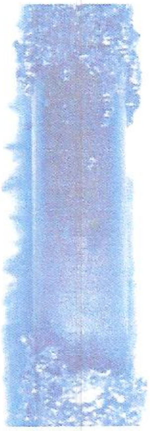
Test Operating Conditions			
Exchanger Heater	C/S 1018	C/S 1018	C/S 1018
Exchanger temp (°F)	800	900	1010
Unit pressure (psig)	950	950	950
Unit Atmosphere	Nitrogen	Nitrogen	Nitrogen
Oil flow rate (cc/min)	3.0	3.0	3.0
Test time (minutes)	90	90	90
Thermal Fouling Measurements			
15 minutes	0	0	4
30 minutes	0	4	8
45 minutes	6	11	21
60 minutes	10	16	67
75 minutes	14	21	74
90 minutes	18	28	90

Table 8
Thermal Fouling Testing of Zirconium Coated Heat Exchanger Tubes

Test Operating Conditions			
Exchanger Heater	1	2	3
Exchanger temp (°F)	1010	1010	1010
Unit pressure (psig)	950	950	950
Unit Atmosphere	Nitrogen	Nitrogen	Nitrogen
Oil flow rate (cc/min)	3.0	3.0	3.0
Test time (minutes)	90	90	90
Thermal Fouling Measurements			
15 minutes	5	3	12
30 minutes	22	21	30
45 minutes	33	32	36
60 minutes	41	45	36
75 minutes	45	45	36
90 minutes	47	45	36
Effectiveness (%)	52.0	53.0	62.0

Table 9: Fouled Carbon Steel and Zirconium Exchanger Metal Heater Tubes

Carbon Steel Exchanger



Mist Coated Exchanger

Table 10
Fouling Graphs of Carbon Steel and Zirconium Exchanger Heater Metal

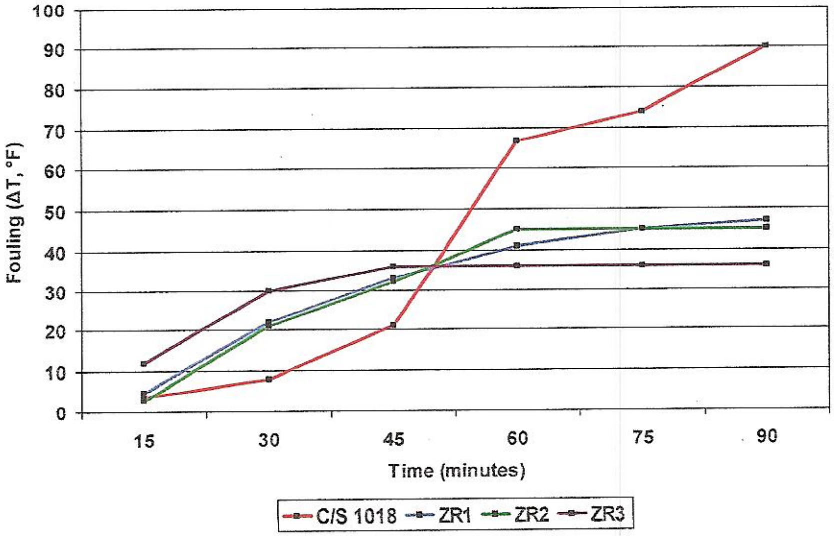


Table 11: Scanning Electron Micrograph of Fouling Deposits

Carbon Steel Fouling Deposits

Zirconium Fouling Deposits

Delayed Coker Furnace Tube Deposits

Table 12: Aromaticity (C/H) Atomic ratio of Fouling Deposits

	Carbon Steel Deposit	ZR1 Deposit	ZR2 Deposit	ZR3 Deposit	Delayed Coker Deposit
Carbon (wt. %)	88.94	89.14	89.10	89.04	
Hydrogen (wt. %)	5.77	6.12	5.59	5.84	
Oxygen (wt. %)	1.49	1.04	1.16	1.20	
Carbon/hydrogen atomic ratio	**1.28**	**1.21**	**1.30**	**1.27**	**2.24, 2.53, 2.37, 2.66, 2.61, 2.64, 2.40, 2.48, 2.41**

Table 13: Summary of Thermal Analysis of Deposits
(TGA, 20 - 1000°C/air)

	Carbon Steel Deposit	Zirconium Coating Deposit		Delayed Coker Furnace Deposit	
		A	B	A	B
Coke (wt. %)	99.2	99.2	99.7	93.4	94.1
Coke. decomposition temp (°C)	521	545 - 630	546 - 675	628	597

Table 14: Thermal Gravimetric Analysis of Exchanger Deposit and Delayed Coker Furnace Deposit

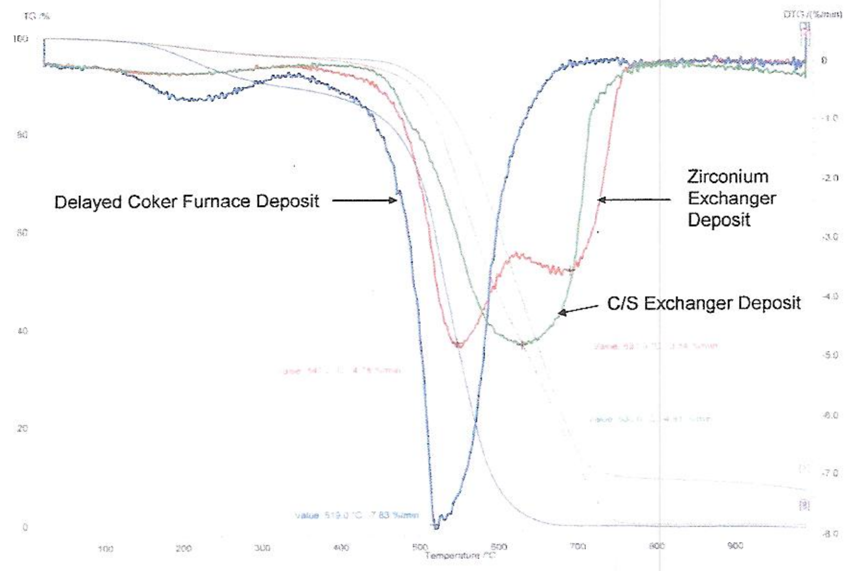
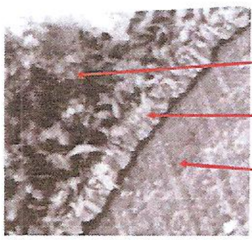
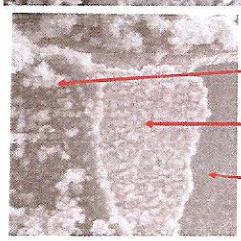


Table 15
EDS Analysis of Zirconium Exchanger Tube
Before and After Fouling Test

	Before Fouling Test		After Fouling Test	
Carbon (wt. %)	0.00	0.00	90.09	89.46
Aluminum (wt. %)	8.82	0.34		
Zirconium (wt. %)	62.18	37.7		
Silicon (wt. %)	0.00	3.49		
Iron (wt. %)	27.54	53.35		
Sulfur (wt. %)	-	-	4.66	6.36
Oxygen (wt. %)	0.00	0.00	4.65	4.18





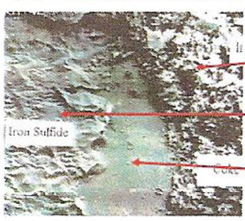


Table 16
Delayed Coker
Furnace Tube
Deposit