R&D activities in Advanced Materials & Metallurgy

Specialized Technical Supports to Refineries & Pipelines for equipment reliability
- Material Failure Analysis
- Remaining Life Assessment
- Fitness for Service Assessment
- Corrosion Studies

Development of new technologies & state of the art tools/instruments for capability enhancement
- Non-Destructive Testing Techniques
- Mechanical Testing (MSTT, PABI, Creep etc.)
- Metallurgical Characterization
- Pilot plant study for Corrosion
- Collaborative Projects (BARC, NML, IITs, IIIT, CGCRI etc.)
Advanced NDT & Corrosion Studies at R&D

Advanced NDTs
- Miniature Sample Testing Technique (MSTT)
- TOFD & Phased Array
- Internal Rotary Inspection System (IRIS)
- Infrared scanning (Thermography)
- Portable Automated Ball Indentation (PABI)
- Gamma Ray scanning
- Radio Isotope Tracer

Corrosion Studies
- Evaluation of Corrosion Inhibitor for CDUs
- Microbial Influenced Corrosion (MIC) studies
- Corrosion Studies for processing of High TAN crude
- Corrosion Studies for Vegetable Oil co-processing
Mechanical Properties evaluation through NDT : MSTT (Miniature Sample Testing Technique)

- Pseudo NDT technique for RLA of high temp/ pressure thick walled component (Reactor etc)
- Development of correlation of mechanical properties of miniature vs. bulk samples
Miniature Sample Preparation and Testing

- A large samples / coupons from components required to be removed for quantification of damage / mechanical properties
- Post-sampling repair by welding – a difficult task
- An innovative idea – Develop a technique for removal of miniature surface samples from the component (Scooping)
- Does not introduce thermal or mechanical damage
- No post-sampling treatment / welding requirement
- Deemed to be non-destructive in nature
- So far mainly used in Nuclear industry for irradiated materials
- The studies on Cr-Mo steels used in Refining Industry will be beneficial for health assessment of components like reactor shell etc
Miniature sample preparation and testing

Scooped material can be used to evaluate the mechanical properties of the material using specialized technique

- General bulk mechanical properties
- Fracture toughness
- Embrittlement characteristics of material
- Creep strength

Objective

- Understand the sample specific parameters in miniature testing
- Establish correlations with standard sample testing

Status

- In-house designed miniature sample fixtures prepared
- Miniature samples fabricated for low alloy steel & tested
- Correlation of properties underway
Evaluation of mechanical properties of Materials
By PABI - A Non Destructive Approach for RLA

- Metallurgical and mechanical properties of service-exposed components vary with the cumulative time & temperature of exposure and environment.
- Quantitative damage assessment requires exact assessment of degradation in mechanical property of the components for reliable Remaining Life assessment.
- For determination of mechanical properties, large samples / coupons from components are required as per standard practice that calls a post-sampling repair by welding. This fact often limits RLA to a less reliable.
Evaluation of mechanical properties of Materials

By PABI - A Non Destructive Approach for RLA

- Effort to explore the possibility of utilizing automated ball indentation technique to assess the mechanical properties of the low alloy ferrite steel plates and pipes.
  - By generating co-relation constants to enable estimation of actual bulk material properties from PABI data for the experimental Cr-Mo alloys.

Significant features of the PABI

- In-situ applications for RLA of structures.
- Requires small test materials compared to conventional.
- No fabrication of std.test specimen required.
- Relatively rapid compared to conventional test
- PABI test is localized and can be used to characterize weld and HAZ.
Evaluation of mechanical properties of Materials
By PABI - A Non Destructive Approach for RLA

Materials Used Under Present Study:
1.25Cr-0.5Mo Service exposed steel plate-ASTM A387 Gr11Cl-2
1.25Cr-0.5Mo Virgin steel plate (ASTM A387 Grade 11 Class-2)
2.25Cr-1Mo Virgin steel plate (ASTM A387 Grade 22 Class-1)
1.25Cr-0.5Mo Virgin steel pipe (ASTM A335 Grade P-22)

- PABI inferred as a suitable tool to Non-destructively measure the yield strength and ultimate tensile strength properties.
- PABI is found to be a good technique to measure the mechanical properties (yield strength, tensile strength and Fracture Toughness) within 5% variation compared to standard properties of virgin materials.
UT based TOFD – Technique

- Time of flight of diffracted signals is monitored
- System comprises of two small crystal angle probes (30-70 Deg.), probe assembly unit with special holders for D Scan & A Scan, dedicated computer with software
- Special probes to emit short wider pulses for improved accuracy in Time of flight measurement
- Imaging technique with hyperbola fringes at defect tips
- Defect depth and size from the inspection surface are reported
UT based TOFD – Technique

- Periodic inspection of pressure vessels, where man entry not permitted due to presence of catalyst, internal lining etc.
- Applicable to pipes, Tubes, Plates or components of any complex shapes such as nozzles etc.
- Integrity assessment of weldment of thick walled components (> 12mm) after Heat treatment, Hydro testing or service exposure
- Verify the cracks not detectable by Radiography
- Online monitoring of welds during service up to 250 Deg.C
- Shear wave TOFD is currently an area of research worldwide (for <12mm thickness)
UT based TOFD – Technique

- Commercial equipments available that have software to aid signal interpretation, provide D-scan & B-scan images
  - Size of defects with respect to depth, width & length
- Application of Phased array for
  - Use of many miniaturized crystals in one probe system
  - Detect defects
  - Defect sizing by embedded signal identification technique,
Internal Rotary Inspection System (IRIS)

- Heat Exchanger Tubes of Air Fin Coolers, Boilers, relatively thin walled tube of ferrous & non-ferrous materials used in corrosive service conditions often result in very fast thickness loss in unpredictable manner.

- Usually these tubes are inspected & tested during shutdowns or at the time of failures conventionally at both ends only which limits to part assessment only. Full length tube inspection internally has always been challenge.

- To enhance the reliability of these equipments and to optimize the operation & maintenance cost, the need for reliable inspection of these equipments have been felt over the period

- Internal Rotary Inspection Systems, (IRIS) – a solution, which is a computer aided fast inspection system for the internal inspection of tubes and pipes for detection of thickness loss for assessment of integrity & reliability.
Internal Rotary Inspection System (IRIS)

- IRIS is an ultrasonic based pulse/echo water immersion technique, where each tube is flooded with water and scanning is done at circumference of the wall by a rotating probe pushed through the entire length.

- The screen displays a real time “B” scan (cross-section thickness map) data image of the tube wall as the probe travels inside the tubes along with C-scan: surface area thickness map

- Each scan shows ID & OD wall profile including pitting, corrosion, bulging, dents, thinning. Wall thickness is measured directly on screen.

- The technique allows for inspection of both ferrous & non ferrous materials in tube sizes from 15 mm to 75 mm ID. Lengths up to 12 meter can be inspected at one stretch.

- Proper internal cleaning (scale removal) of the tubes is utmost requirement as the leftover hydrocarbons/scale deposits at the tubes internal will adversely affect quality of data grabbing & scan interpretation.
Internal Rotary Inspection System (IRIS)

- Mostly used for assessment of High Pressure Reactor Effluent Air Fin Coolers (REAC)
- REAC’s handle effluent stream of H₂, HC, NH₃ & H₂S at a pressure of 160 Kg/cm² & Temp. of 210 Deg.C
- Aluminium finned Carbon steel tube of Plug type construction. Typically SA 192 tubes (25.4mm x 4.5mm x 10.5M length)
- Usually a bank of REAC’s with an average of 1500 nos. of tubes exist in each unit
- Ammonium bisulphide formation within the tubes causes choking, erosion-corrosion at tube ends & under deposit pitting
NON CONVENTIONAL DIAGNOSTICS

- Infrared scanning (Thermography)
- Gamma ray scanning
- Radio isotope tracer

Advantages

- Wide applications for trouble shooting and debottlenecking
- Predictive maintenance / optimization
- Non-invasive
Infrared Scanning

- Hot spot detection in a equipment or pipeline operating at high temperature (500 deg C or higher)

Radioactive Tracer

- Residence time studies
- Gas (vapour) flow patterns / distribution
- Catalyst particles (solid / liquid) distribution
INFRARED SCANNING

- Troubleshooting of FCC Reactor Riser to identify coke formation above the feed nozzles
- Identification of hot spot in Stripper inlet

TRACER STUDIES

- Efficiency study of cyclone in catalyst and hydrocarbon disengagement
- Measurement of catalyst loss from Cyclone
- Measurement of catalyst distribution in Stripper
Study of air and spent catalyst distribution in Regenerator

Distribution of air flow in Regenerator air grid

GAMMA SCANS

Condition monitoring of internals of Distillation Columns, Absorption columns, Reactor, Vessels etc.

Cat / vapour flow in Riser, Stripper etc.
GAMMA RAY SCANNING HARDWARE

- A suitable Radioactive Source
- A Detector
- Mechanical Arrangements for
  - Pulleys / wire ropes for lifting and lowering of source and detector
  - Motors and control systems

GAMMA-RAY SCANNING TECHNIQUE

- Radioisotope selection
- Detector Selection
- Mechanical arrangement
- Data acquisition System
- Scan interpretation
  - Mechanical Problem
  - Process Problem
RADIOISOTOPE SELECTION

- $^{192}\text{Ir}$, $^{60}\text{Co}$, $^{241}\text{Am}$ & $^{137}\text{Cs}$ Radioactive Sources are commonly used.
- Selection of source depends upon Diameter ($d$) & Thickness ($w$) of the column
  - For $d < 30\text{cm}$: $^{241}\text{Am}$
  - $30\text{cm} < d < 3.0\text{M}$: $^{192}\text{Ir}$
  - $d > 3.0\text{M}$: $^{60}\text{Co}$
- Source activity calculation
  \[
  \text{Activity} = \frac{(D \cdot d^2 \cdot 2^w \cdot h \cdot v \cdot t)}{T}
  \]
- Adequate collimation of the radioactive source for good sensitivity and to reduce background noise.
- Generally collimation should be of order of minimum thickness to be detected.
DETECTOR SELECTION

- Commonly used radiation detectors are Ionization chamber, Proportional & Geiger-Muller counter, Scintillation counter and Semiconductor detector
- Scintillation detector; Sodium Iodide thallium activated NaI(Tl), has high absorption power for Y-ray

SCANNING PROCEDURE

- Source & Detector are lowered simultaneously in small increments
- The signal is monitored for proper count rate at the detector
- Scan profile in terms of cps vs. Travel is obtained
- Single/double pass array or grid scan are followed as per the requirement
Advances in NDT and Corrosion Monitoring

Figure 1: Single-pass trays

Figure 2: Double-pass trays

Figure 3: Orientation of grid scan lines
Evaluation of corrosion inhibitor for crude column and other strippers through on line corrosion skid

- **Performance evaluation of column O/H inhibitors and optimization of dosage rate for various commercially available corrosion inhibitors**

- **Skid Mount Facility having**
  - Tapping stream from column O/H top
  - Electrical furnace for heating, Flash column
  - Metallic Coupons, Corrosion probe, thermocouple, pH meter, data logger
  - Inhibitor injection and other metering pumps to accelerate the test condition
  - Provisions for forced condensation on coupons

- **Performance evaluation is measured in mpy by weight loss method over a test duration of 500 hours**

- **Corrosion probe result will indicate for instant variations in corrosion rate**
Microbial Influenced Corrosion (MIC) study in Pipeline in presence of corrosion inhibitor

- To control internal corrosion <1.0mpy, corrosion inhibitor (CI) is doped at 4 to 6ppm
- Literature search revealed in presence of some of microbes the CI becomes ineffective
- Extensive static (250nos.) and dynamic laboratory tests (160 nos.) carried out simulating the pipeline environment condition
- Test results revealed 5 to 20mpy corrosion on these samples
- Field tests requires to assess the effect of MIC in running product pipelines
Evaluation of Naphthenic Acid corrosion in Laboratory

- Processing of High TAN crude can improve Refinery margin significantly

- Naphthenic acid corrosion
  - Temperature 250-370degC
  - High Velocity (WSS about 100Pa)
  - Sulfur / Naphthenic content (TAN / NAN)
  - Metallurgy

- Nap acid corrosion plays a vital role in unit safety and equipment reliability

- High Tan crude processing within the existing metallurgy is a challenge for old refineries
Evaluation of Naphthenic Acid corrosion in Laboratory

Naphthenic Acid Corrosion Control Strategies

- Assessment of Feedstock / Process Stream characterization and System evaluation / Define high risk circuits
- Options: Crude blending, Mitigation w.r.t. Crude blending, Metallurgy upgradation, Chemical inhibition
- Establish monitoring protocol for corrosion rate, Laboratory test with simulated process conditions, Comparative corrosivity study, etc
- Finalize and implement comprehensive monitoring program to ensure effective corrosion control
Evaluation of Naphthenic Acid corrosion in Laboratory

Development of Predict Crude Model Software thru JIP

- Joined a renowned JIP on prediction of corrosion in Refinery due to Naphthenic acid & High sulfur
  
  ✓ The JIP designed to evaluate corrosion rate of various steels by varying Temperature, TAN/NAN, Wall shear stress
  
  ✓ Corrosion studies carried out at Honeywell Process Solution Division
  
  ✓ Dr. Russell Kane (guide of the programme) : A renowned corrosion specialist

- JIP joined by 18 major oil world companies
Evaluation of Naphthenic Acid corrosion in Laboratory Studies carried out under JIP

- Tests in special type autoclave with synthetic crude oil with doped S & Nap. Acid in presence of metallic coupon
  - Synthetic Crude Oil – ultra low sulfur
  - To have better control of parameters contributing to corrosion
  - Large nos of short term & long term autoclave tests
  - Covered all Refinery alloys being used in CDU / VDUs

- Testing variants used were commonly encountered in Refinery
Evaluation of Naphthenic Acid corrosion in Laboratory

Studies carried out under JIP

- Target sulfur concentrations were achieved through addition of $\text{H}_2\text{S} / \text{N}_2$ gas mixtures

- Target TAN achieved using neat Naphthenic acids values up to 5.5

- The results of the experimental findings - Development of a software “Predict-Crude” to predict corrosion rates in Naphthenic Acid bearing process system having various metallurgies.
PREDICT CRUDE MODEL

- Predict-Crude software determines corrosion rates for refinery materials
  - Carbon steel, 5Cr, 9Cr, 12Cr, 304L, 317L, and 904L
  - Covers all refinery metallurgy

- The input parameters and their ranges for the model are given below
  - Temperature: 230 – 370°C
  - Type of Naphthenic acid type: high or low molecular weight
  - Acid content: TAN 0 to 4.6 mg KOH / g
  - Active sulfur level: low (<0.5%), med (>0.5%), high (1.5-4.0%) or very high (>4.0%)
  - Pipe dimensions & flow parameters to calculate wall shear values: 1-135 Pa
PREDICT CRUDE MODEL- BENIFITS

- The data generated and model is capable for decision for selection of opportunity crude to process in our refinery
- The model is capable for better feedstock blending strategies of crudes
- Selection and performance evaluation of Naphthenic acid corrosion inhibitor to avoid major refinery changes in refinery infrastructure
- The model is capable of trouble shooting for high TAN hydrocarbon streams
- We have enriched experience for planning & execution of corrosion test matrix for corrosion testing
Thanks