Real Time Oil Corrosivity Measurement Using Radioactive Tracer Technology

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Southwest Research Institute

- 1,200 Acres
- 2M square feet of Laboratories and Offices
- 2,700 Employees
- $340M Revenue in FY02
- 11 Technical Divisions
- 1/3 Dedicated to Automotive R&D

Overview

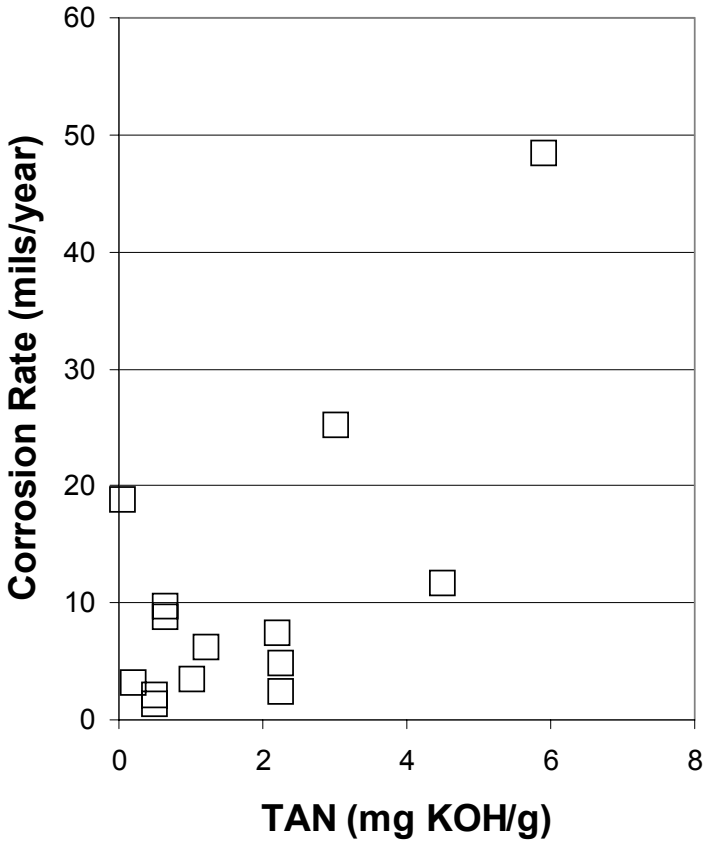
- SwRI Has Used Internal Funds to Develop a Unique Method to Measure Corrosivity Using Radioactive Tracer Technology
- Highly Sensitive Time Resolved Corrosivity Measurement Under Simulated Refinery Conditions to Measure the True Corrosivity of an Oil Sample

Background

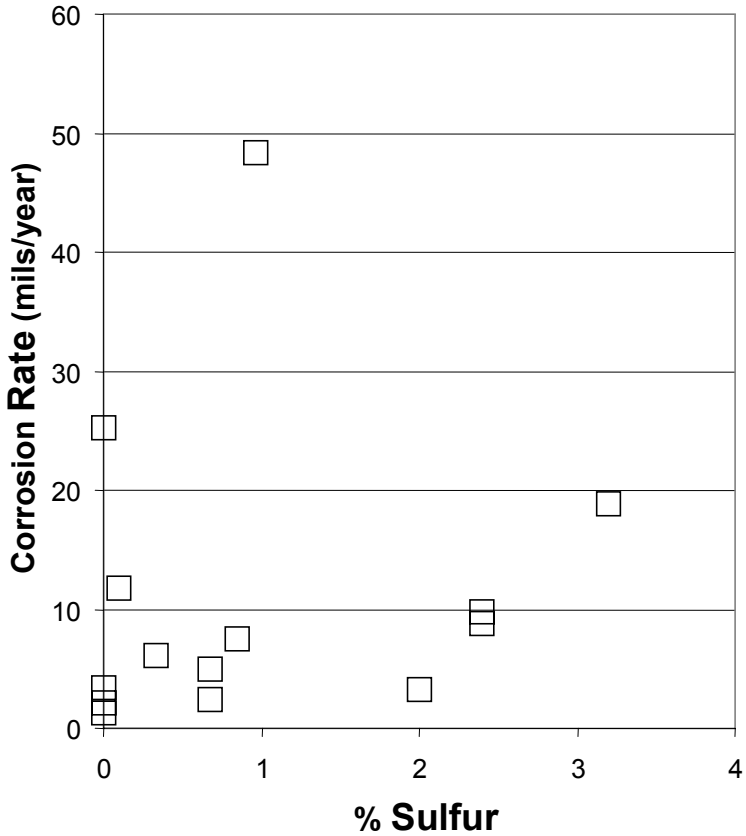
- Crude Oil Corrosivity Typically Predicted Through Proprietary Correlation Models Involving TAN, %S or Other Parameters
- Well Known That These Models Are Expensive to Develop, Are Not Reliable and Can Be Very Misleading

Background (cont.)
Corrosivity vs. TAN and %S From SwRI Tests

Corrosion Rate vs. Total Acid Number (TAN)



Corrosion Rate vs % Sulfur



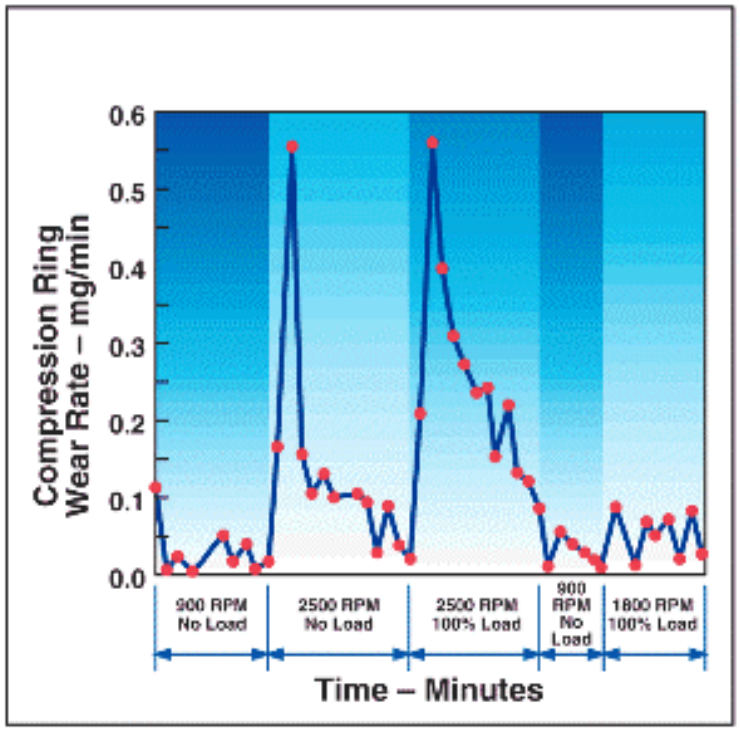
Background (cont.)

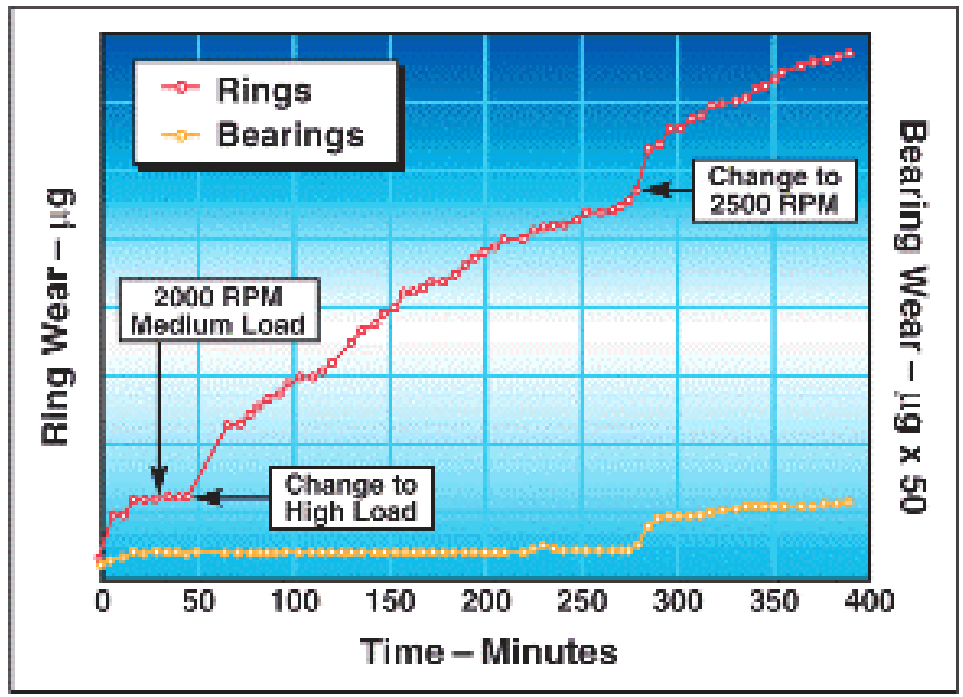
- Corrosivity Typically Measured Using Mass Loss Coupons in an Autoclave
- Mass Loss Measurement Proven to be Unreliable
  - Likely Significant Changes in Oil Corrosivity Over Lengthy Test (24 hrs or longer) due to Thermal Degradation of Naphthenic Acid
  - Requires Subtraction of Two Relatively Large Numbers (Before and After Coupon Mass) to Measure Relatively Small Mass, Resulting in Inaccuracies
  - Can Actually Show Weight Gain

Radioactive Tracer Technology (RATT)

- SwRI Has Been Using Radioactive Tracer Technology (RATT) for Over 40 Years
- Principally Used at SwRI for Measuring Real Time Wear In Internal Combustion Engines
- Proven to be Highly Sensitive Time-Resolved Wear Measurement Technique

Sample Engine Wear Data

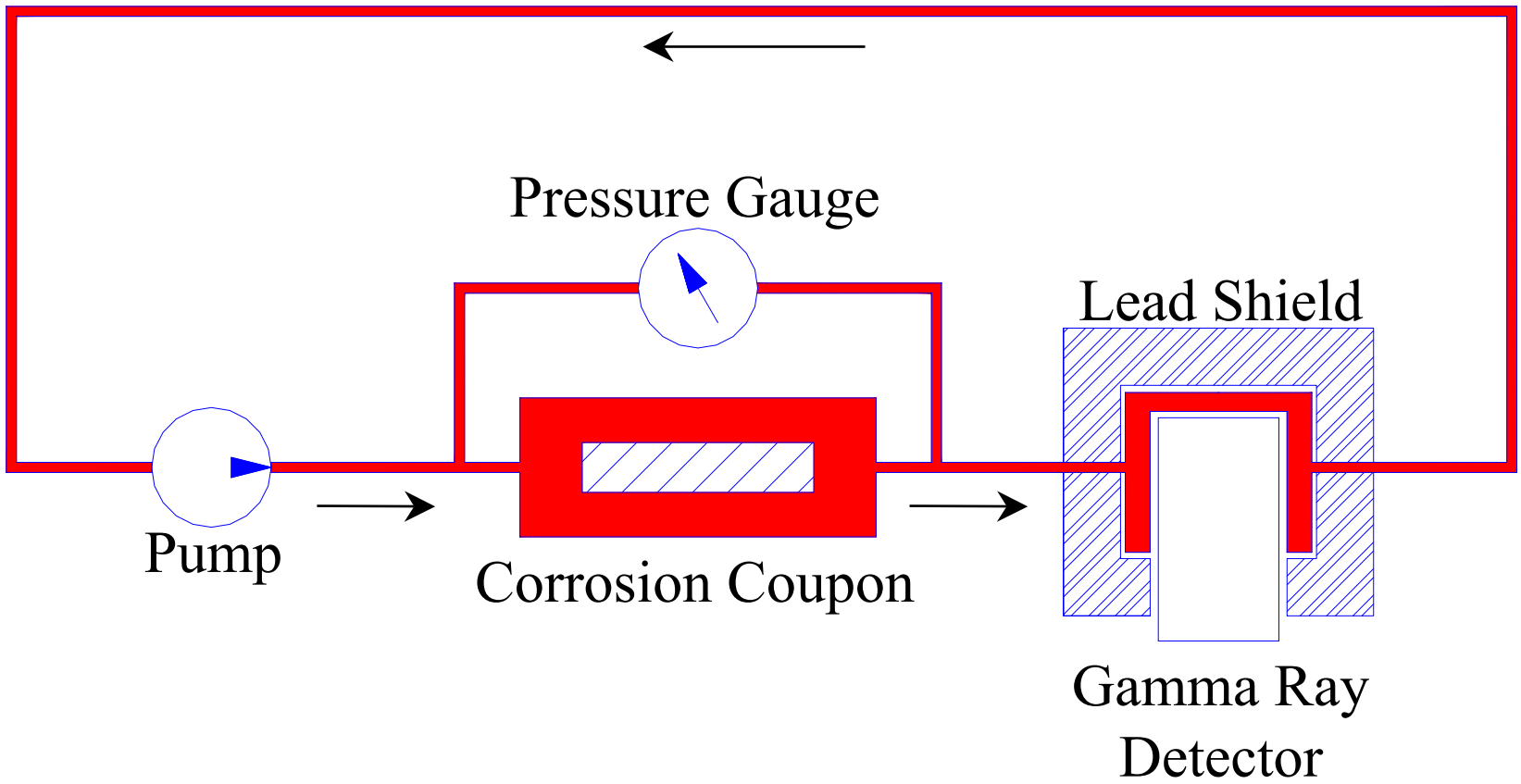




RATT Method-General Overview

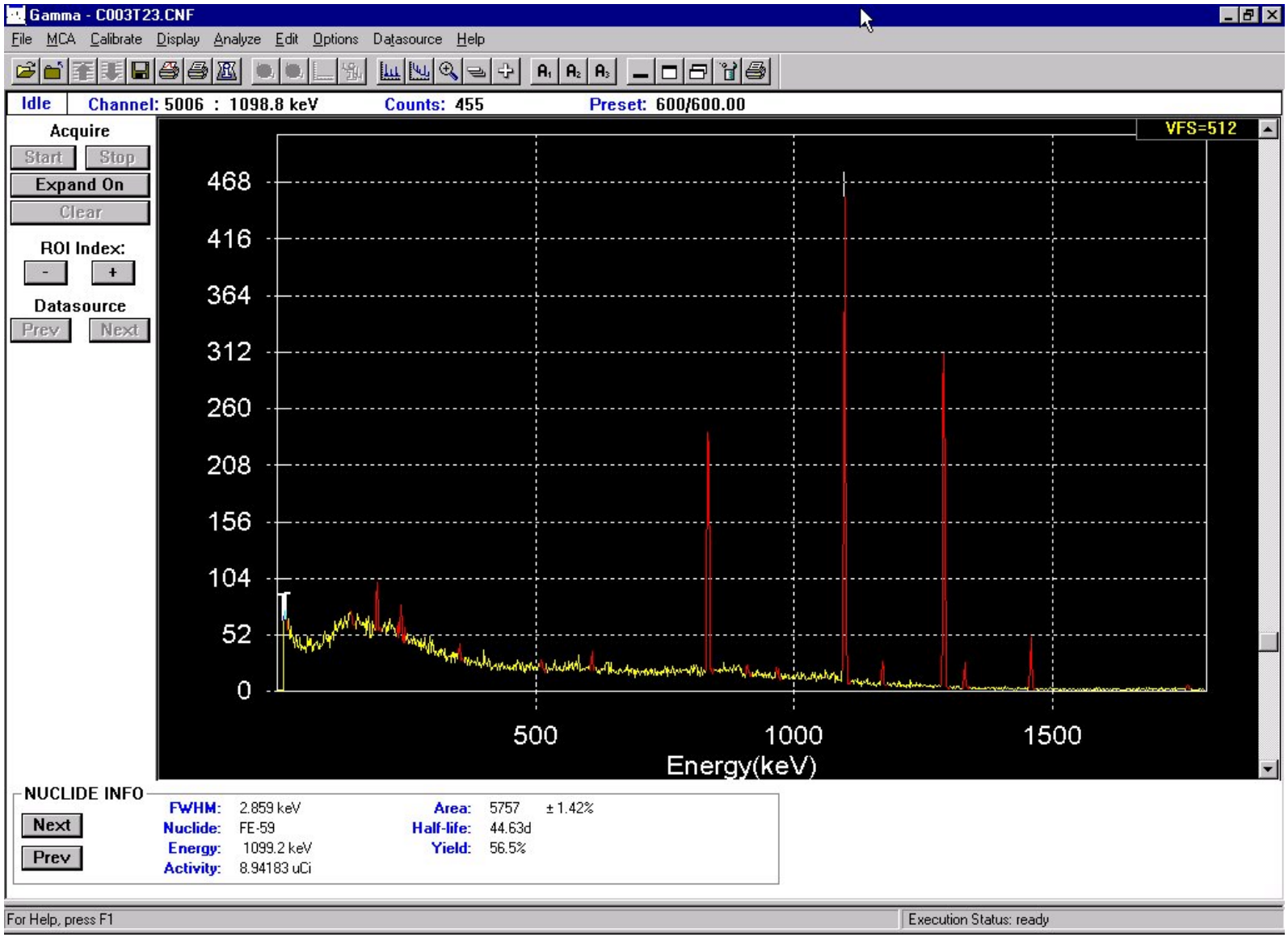
- Activate Corrosion Coupons In Nuclear Reactor (Thermal Neutron Activation)
  - Conversion of Stable Fe-58 Isotope to Radioactive Fe-59
  - Fe-59 Emits Detectable Gamma Rays at 1099 and 1292 keV
  - Half-life of 44.6 days
- Calibrate Coupon Activity to Correlate Measured Corrosion Product Activity in Oil to Coupon Mass Loss
- Install Corrosion Coupon in Flow Loop and Run at Simulated Refinery Conditions

Simplified System Schematic



Corrosivity Test Setup

Sample Gamma Spectrum



RATT Method (cont.)

- Monitor Oil in Real-time (at 10-minute Increments) for Accumulation of Radioactive Corrosion Products
- Relate Measured Radioactivity to Cumulative Corrosion Product Mass
- Differentiate Cumulative Corrosion Mass to Obtain Corrosion Rate

Features and Benefits

- **Time Resolved Corrosivity Data**
  - Typically 10-minute Resolution
  - Shows Features Unable To Obtain With Weight Loss
  - Ability to Capture Initial and Longer Term Corrosion Rates
- **Short Term Test**
  - Total Test Time Typically 5 hours
  - Oil Properties Less Likely to Change Significantly in Shorter Term

Features and Benefits
(cont.)

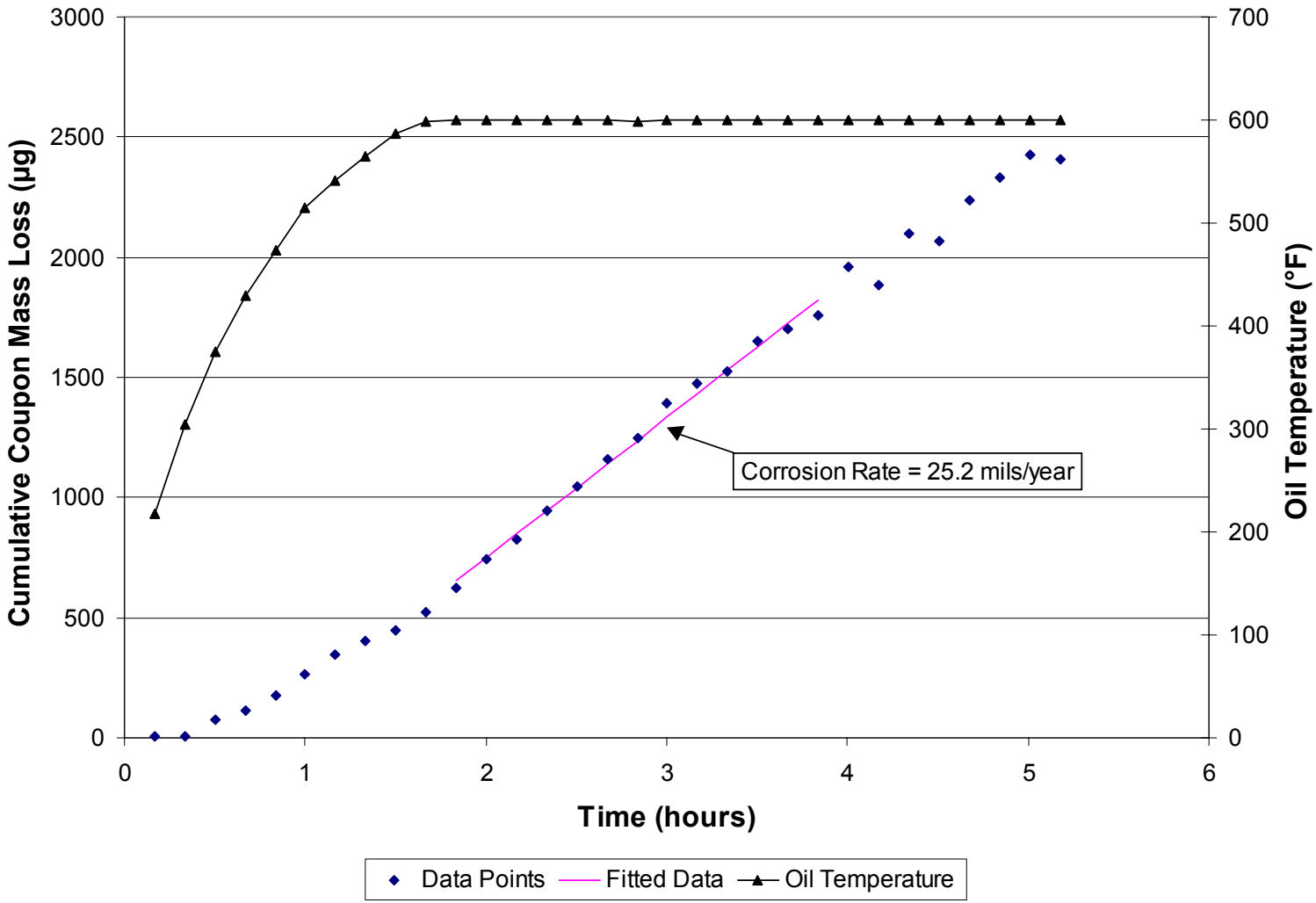
- Recirculating Flow Loop
  - Ability to Tailor Tests for Specific Conditions
- Accurate
- Repeatable
- Highly Sensitive

Sampling of Test Results from IR Project

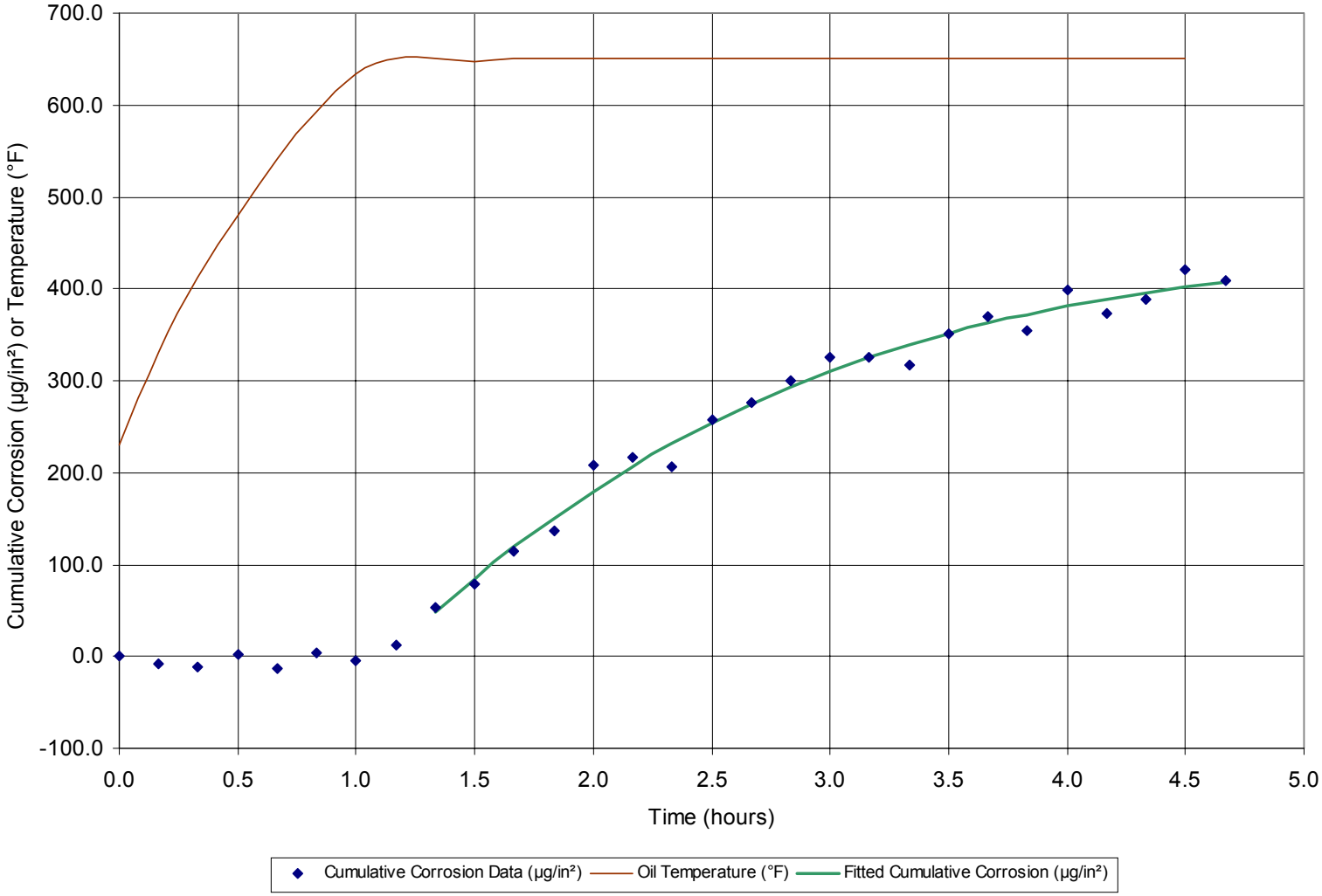
Test Oil	TAN (mg KOH/g)	Sulfur (%)	Measured Corrosion Rate (mils/yr)
CPA Spiked Mineral Oil	0.5	0	2.1
CPA Spiked Mineral Oil	1.0	0	3.5
CPA Spiked Mineral Oil	3.0	0	25.2
Whole Crude	0.06	3.2	18.8
Whole Crude	4-5	0.1	11.8
650+	1.2	.33	6.2
VGO	5.9	0.96	48.4

Corrosivity vs. Time

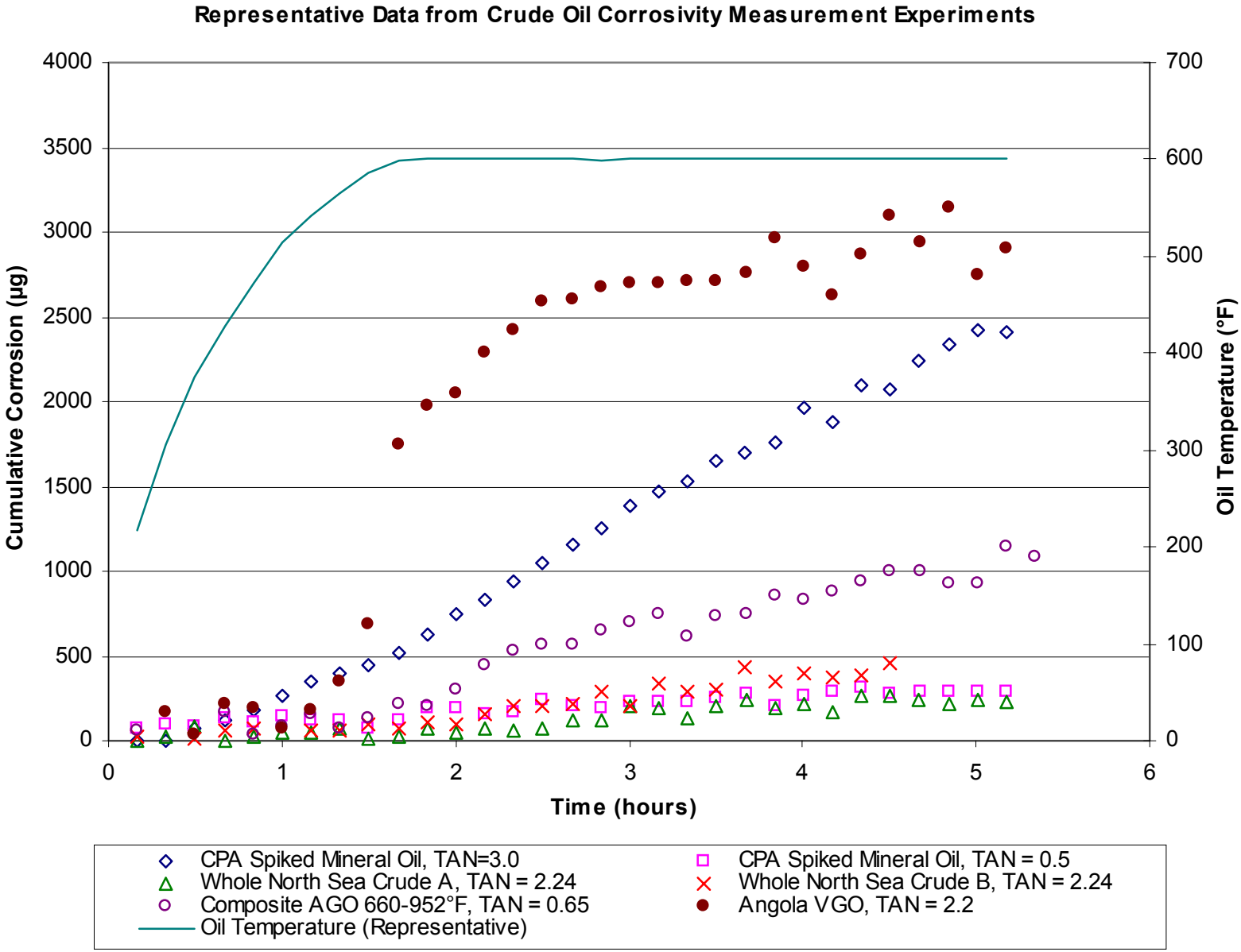
CPA (TAN=3.0) Spiked Oil Test



Corrosivity vs. Time
VGO Test



Sampling of Crude Oil Tests



Applications

- **Versatile Oil Corrosivity Measurement**
  - Whole Crudes, Fractions, AGO's, VGO's
- **Database Development**
- **Model Development**
  - Time Resolved Corrosivity Data Can be Used as Input to Proprietary Models
- **Crude Oil Blend Optimization**
  - Measure Corrosivity as Function of Blend Ratio
- **Inhibitor Research**
  - Determine Inhibitor Effectiveness
  - Determine Optimum Concentration

Applications
(cont.)

- In-Plant On-line Corrosion Monitoring
- Materials Selection
  - Can Measure Corrosion Resistance of Various Materials
- Operating Conditions Research
  - Temperature, Shear Stress, Pressure
- Research and Development
  - Corrosivity Models
  - Corrosion Inhibitor Optimization

Specifications

- Sample Volume 1500 ml
- Current Stand Limitations
  - Maximum Oil Temperature 650°F
  - Maximum Shear Stress 500 Pa
  - Maximum Oil Pressure 100 psi
- Possibility of Upgrading to Higher Operating Conditions If Needed

Conclusions

- SwRI has developed a unique, versatile and highly sensitive method to accurately determine the corrosion rate of oils.
- This method is designed as a tool to allow the buyer or seller of opportunity crudes to make informed decisions on crude values and for the refiner to assess crude corrosivity before it is refined.

Conclusion (cont.)

- Interested in forming a Joint Industry Project (JIP) to further develop this technology.
  - Investigation of
    - Shear Stress Effects
    - Temperature Effects
    - Other Refinery Conditions
  - Standardization of Corrosivity Measurement Procedure
  - Development of an Oil Corrosivity Index