

TEST PROCEDURES FOR PLANT DEPOSITS, SCALES AND SLUDGES

UOP Method 933-94

SCOPE

This method describes an approach for determining the composition of materials such as deposits, scales and sludges of unknown composition that are created by chemical corrosion in pilot plants and refineries. Knowledge of the composition of such materials can determine the site or sites of the corrosion and possible remedies for the condition or conditions causing the corrosion. This method is an outline rather than an absolute procedure for determining the composition of such unknowns, and is intended as a guide, which may need to be modified by the investigator, in selecting testing regimes for unknowns of this type.

OUTLINE OF METHOD

Analysis schemes for a variety of unknowns are described, with decision points noted and analysis alternatives delineated. Explanations of a number of useful types of analyses are discussed in detail. Several sample pretreatment schemes are provided, and data interpretation including use of material balancing is discussed. No apparatus or reagents are specified in this method. Users are referred to the methods listed in *REFERENCES* for detailed apparatus and reagent listings.

DEFINITIONS

For purposes of this method, the following definitions are stipulated, with the understanding that materials of the type described herein are not always easy to categorize even within these broad definitions. For that reason, usage of the terms sample, deposit, scale, sludge and unknown as used in this procedure may overlap.

Deposits: Dry materials found loosely packed within reactors or related tubing and equipment. May contain dissimilar materials; for example, catalyst spheres in a coke matrix. May also contain some heavier hydrocarbons.

Scales: Dry materials more intimately bonded to surfaces within reactors or related tubing and equipment. May be multi-layered, indicating a number of different corrosion sites or chemistries.

Sludges: Materials wet with hydrocarbon or water or mixtures of the two. Usually found at cooler locations within the refinery process flow. May contain solids or suspended matter with compositions similar to deposits or scales.

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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SAMPLING

It is imperative that sampling for this procedure include documentation as to the source of the unknown. This can be accomplished by written notes describing the location where the sample was found and the sample itself in detail, by photographic or video imaging, or by sectioning the affected area and submitting the entire segment for analysis. A sufficient amount of unknown should be sampled so as to ensure representative sampling. The sampling and packaging for shipment should be done in such a way to avoid contamination and or changes in the sample between the time of sampling and analysis. All required regulatory guidelines are to be followed in shipping the samples. Appropriate paperwork, Material Safety Data Sheets (MSDS), etc., must accompany the sample or samples.

PROCEDURE

Few samples are true unknowns. Information such as type of process, location of the unknown within the process flow, plant metallurgy, nature of any upstream process upsets, etc., can provide considerable help in narrowing the field of possibilities as to sample composition. This information is also useful in deciding on the required analyses and hypothesizing as to sample composition. It is imperative that such information be passed on to the analysts, to save both analyst time and unnecessary cost to the customer. Interaction with the analysts is also recommended after the data have been collected and reported, as they are likely to have run many such samples, and are knowledgeable as to the metallurgy and chemistry related to the corrosion process.

When an unknown sample arrives in the laboratory, it should be handled in a hood or glove box using the appropriate protective equipment until it is determined that other handling procedures are safe and acceptable. The initial laboratory survey of the sample should note any physical attributes of the unknown, that include but are not limited to, color, granularity, homogeneity (or lack thereof), magnetic properties, degree and type of wetness (aqueous or hydrocarbon). A comparison of the physical attributes of the sample as received in the laboratory to the field sampling description indicates any changes that occurred in the interval between sampling and receipt in the laboratory. Here again, photographic or video imaging can be useful in documenting the sample as received. In most cases, only the corrosion products themselves are of interest, and the sample requires drying or filtering to remove any water or hydrocarbon present. In a few cases, the type of hydrocarbons present may be a clue to the origin of the corrosion, if that has not already been determined in the field.

The next step is to determine the tests to be run, and that depends to a great extent on the amount of sample available. Some tests are destructive, others non-destructive, some require large amounts of sample, others less. After the tests are specified, the sample must be homogenized and split-sampled correctly for those tests. The sample may need to be dried, or catalyst or metallic components sieved or separated by hand from the sample, before grinding and riffing. Any materials remaining on the sieves may then be analyzed separately, if desired. If there is hydrocarbon present, the hydrocarbon can be removed by extraction in a soxhlet apparatus, by oven drying or by filtration. Water may also be removed by oven drying. The residue remaining in the soxhlet thimble, after oven drying or after filtration, can then be homogenized and split-sampled for testing. If soxhlet extraction or filtration is used, the hydrocarbon removed from the sample can be concentrated and identified using Infrared (IR) Spectroscopy, Mass Spectroscopy (MS), Nuclear Magnetic Resonance (NMR) Spectroscopy or a variety of Gas Chromatography (GC) techniques (Table 1).

For those tests requiring acid dissolution of the sample, note any chemical behavior, such as precipitate formation, color, gas evolution, etc; as this information also provides clues as to composition. The foregoing are examples of approaches, other testing regimes may also be used depending on sample composition.

Table 1 lists the types of techniques generally used in identifying unknown materials, and is not to be taken as being all inclusive. The UOP Alphabetical Method Listings¹ and ASTM Index², by subject, should be referred to for specific test procedures. IP, APHA, or other test types may be utilized if available.

A brief description of the techniques and their application to the identification of the unknown sample follows.

Test Descriptions

Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES): This test can simultaneously determine 30 or more elements (generally metallic) in a sample in a single determination after dissolution. Test results are usually reported as quantitative, although qualitative scans are sometimes used initially to narrow the field of elements for the quantitative scan. For samples of unknown composition, the range of determination is generally in the hundreds of mass-ppm to 50 mass-% range. The lower limit of determination is element and matrix specific. Interelement interferences can be a limiting factor when large amounts of elements (iron and tungsten are examples) that generate line-rich spectra are present. This is a destructive test.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS): Theoretically, this test can simultaneously determine all elements in the Periodic Table. It is an extremely sensitive instrumental technique, and its strength is in the determination of very low levels of specific elements in a relatively interference free environment. For example, the differences between many stainless steels is in the trace amounts of elements, such as niobium and tantalum, in their formulations. The levels at which these elements are present are at or below that which can generally be determined by ICP-AES, given the potential interferences. ICP-MS can determine niobium and tantalum at 1 to 10 mass-ppm levels in the steel or corrosion residues from the steels. Determination of the type of stainless steel that an unknown deposit originated from frequently pinpoints the location of the corrosion source. The test is destructive and generally requires dissolution of the sample prior to analysis, although some ICP-MS equipment can be fitted with laser samplers for sampling solids directly. Results from laser solid sampling are generally qualitative due to the unavailability of same-matrix standards. Results from liquid sampling are usually quantitative, although as with ICP-AES, the test can also be used in qualitative mode to prescreen the unknown before quantitative analysis. In solution, the sensitivity of this technique is in the low mass-ppb region for most elements, and as low as 0.1 mass-ppb for a number of other elements.

Atomic Absorption Spectrometry (AAS): This is a sequential, quantitative test that determines metallic elements. It is destructive, requiring sample dissolution prior to instrumental analysis. It is used where there is good reason to expect that iron (or some other single element) is the only corrosion product present in the unknown. The range of the determination is similar to that of ICP-AES. The test has time and cost savings over ICP-AES only when two or less element determinations are required.

Infrared Spectroscopy (IR): This analysis identifies functional groups (e.g., CO, CH, NH, OH, etc.) that are present in the sample. Positive identifications are made for pure compounds by comparison with standard spectra. For more complex mixtures, the functional group data generated are used to identify the source or sources of the sample within the process flow. Typically, low percent levels are required for detection in the IR spectrum. IR spectral information can be obtained on both solids and liquids.

Mass Spectroscopy (MS): Useful in determining molecular masses and chemical structure of organic materials. In conjunction with gas chromatography, it can be used to identify more complex mixtures of compounds.

X-Ray Fluorescence (XRF): This is a non-destructive test that can determine many elements in the bulk solid. The sample does need to be pulverized. Quantitation can be a problem due to unavailability of same-matrix standards in this application.

X-Ray Diffraction (XRD): This is a non-destructive test that can yield structural information (crystallinity or amorphous character), or speciation (SiO_2 as opposed to Si, $\text{Fe}_2\text{O}_3/\text{Fe}_3\text{O}_4$, etc.).

Nuclear Magnetic Resonance (NMR) Spectroscopy: High Resolution Liquid NMR is a non-destructive test that is useful in the determination of structural components of organic mixtures and identification of pure organic compounds. This technique can quantitate the mole-percent carbon, hydrogen, etc., of the structural components relative to each other, not the mass-percent of the structural components relative to the total sample. Solid State NMR is a non-destructive test that can yield structural and speciation information on non-magnetic materials. This technique quantitates in the same manner as does the liquids technique.

Loss On Ignition (LOI): This can be performed at a variety of temperatures, from drying at 105°C to remove water or light hydrocarbons, to calcination at 1000°C to render the sample to the metallic oxides (certain elements can be lost during the LOI step). For unknowns, determination of metals content generally requires dissolution of the residue remaining after an LOI at 538°C .

Sieving: Many samples arriving from the field contain catalyst spheres or extrudates, and some can contain metallic pieces. If the sample is a fluid powder, sieving can be used to separate the materials; however, more times than not, the catalyst and metallic pieces must be removed by hand. Catalyst material is generally not analyzed (composition is already known), but the metallic pieces and remaining material are analyzed.

Soxhlet Extraction: Used to remove hydrocarbon from the sample to allow proper grinding and riffing for sampling. Methylene chloride or isooctane are the most commonly used extraction solvents. The extract may also be analyzed for composition.

Optical Microscopy: Microscopy can show layering in certain types of deposits that indicate multiple corrosion sites and compositions. When the layers are separated and individually analyzed, specific corrosion sites can be identified and site specific remedies offered.

Thermal Gravimetric Analysis (TGA): This test is generally performed as a function of temperature (to approximately 700°C) in a variety of gases (air, nitrogen or helium) to determine the mass loss and reactivity of a sample. The results indicate whether the material contains carbon, and how much carbon versus how much metal. For unknowns, ramping in air to 700°C gives a good indication of composition. The burn profile, as a function of temperature, can be used to describe differences between samples.

Chemical Elemental Analysis: Carbon, hydrogen, nitrogen, sulfur, oxygen, chloride, bromide and fluoride determinations can be performed by a variety of available instrumental techniques. Multielement analyzers are available in some cases (CHN can be determined simultaneously by a single analyzer, for example).

Ion Chromatography (IC): Generally used to determine anions and some cations in aqueous matrices. This test gives useful information on those unknowns that arrive wet with water. It is not too useful on solids, because in dissolving for the analysis, species can be lost or changed.

Gas Chromatography (GC): Useful for separating organic mixtures for identification and quantitation. A wide variety of element-specific detectors are available to aid in identification of unknowns (see also Mass Spectroscopy).

Electron Microscopy: Scanning Electron Microscopy (SEM), with appropriate attachments, is used to identify specific entities (particles 0.01 mm^3 and larger) in a deposit or scale. For example, iron or chromium sulfide particles in a scale can be an indicator of sulfidation attack. Although in principle, carbon, nitrogen and oxygen can be detected, typically analyses are limited to atomic masses heavier than sodium. Metal-catalyzed coke can be differentiated from condensation-type coke based on morphology of the carbonaceous deposits. Transmission and Scanning Transmission Electron Microscopy (TEM and STEM, respectively) can be used to characterize sub-micron particles for morphology, structure and chemistry.

Surface Analysis: This is used to study elemental speciation and oxidation states of surface and subsurface features. With ESCA or XPS the outermost atomic layers are used to determine the oxidation state of the elements present. Auger Electron Spectroscopy determines the location of specific elements on a surface. Auger is more surface sensitive than the SEM, but can generally only be used on electrically conductive samples.

Table 1

**Properties Measured by Various Types of Techniques
Generally Used in the Identification of Unknown Materials
(All tests generate quantitative data, except those denoted with *)**

<u>Test Type</u>	<u>Description</u>
Spectroscopy	
Emission (ICP)	Individual Elements (many in one scan)
Atomic Absorption (AAS)	Individual Elements
Infrared (IR)	Component Identification on Functionality
Mass Spectroscopy (MS)	Organic Identification
X-Ray Fluorescence (XRF)	Individual Elements
X-Ray Diffraction (XRD)	Inorganic Structural Information
NMR Spectroscopy	Component Identification
Physical	
Loss On Ignition (LOI)	Volatile Content at Various Temperatures
Sieving	Separation by Particle Size
Soxhlet Extraction	Hydrocarbon Removal
Optical Microscopy*	Magnification
TGA	Volatile Content vs. Temperature
Chemical	
Carbon	Carbon Content
Hydrogen	Hydrogen Content
Nitrogen	Nitrogen Content
Sulfur	Sulfur Content
Oxygen	Oxygen Content (has some limitations)
Bromide	Bromide Content
Chloride	Chloride Content
Fluoride	Fluoride Content
Ion Chromatography (IC)	Most Anions and Some Cations
Gas Chromatography (GC)	
GC-FID	Specific Compound Identification
GC-NPD	Nitrogen Species Identification
GC-SCD	Sulfur Species Identification
GC-AED	Elemental Speciation
GC-MS	Specific Compound Identification
Electron Microscopy	
STEM*	High Magnification
TEM*	High Magnification
SEM*	High Magnification
Surface Analysis	
Auger*	Elemental Speciation
ESCA-XPS*	Elemental and Oxidation State

Data Interpretation

Material balancing is used to ensure that all the sample has been accounted for by the completed analyses. The test results need to be adjusted for oxide or other species, as in the following hypothetical example (Table2).

Table 2
Example
Deposit from a Pilot Plant

<u>Elements</u>	<u>Results, mass-% AR</u>	<u>Assumed Species</u>	<u>Results Adjusted for Species, mass-% AR</u>
Iron	35.0	Fe₂O₃	55.3
Nickel	3.75	NiO	6.0
Chromium	6.35	Cr₂O₃	9.5
Niobium	0.04	Nb₂O₃	0.1
Carbon	25.8		25.8
Hydrogen	0.1		0.1
Nitrogen	0.1		0.1
Sulfur	0.3		0.3
			Total:97.2

In the example, the test results indicate coking in the plant, and some type of stainless steel corrosion. Identifying the type of stainless steel is not straightforward since the rate of corrosion of the individual elements is generally not directly proportional to the concentrations of the elements in the alloy. However, the niobium results are consistent with type 347 stainless steel, which may indicate the probable site of the corrosion to a process engineer. This knowledge could then be utilized in arriving at a solution to the problem. The adjusted total, 97.2 mass-%, indicates good sample recovery, within the allowable difference calculated from the sum of the variances of the individual test results. Totals below 95 or above 105 mass-% could mean, at the low end, that not all the sample has been accounted for, and at the high end, that the assumed species may be in error.

Scales are particularly interesting samples. Many times they consist of distinct layers of material from different corrosion sites, resulting from different chemistries. When the layers can be separated, it is useful to analyze the layers as separate samples. When this is done, the corrosion sites that produced the specific layers can usually be identified and separate remedies, if necessary, designed.

Sludges are generally composed of corrosion residues and process products and byproducts, and may be wet with hydrocarbon or water or mixtures thereof. After Soxhlet Extraction, the two phases can be separately identified.

A comprehensive discussion of failure analysis, including a number of additional examples from a variety of corrosion sources within petrochemical refineries, is the subject of the article attached to this method (see *APPENDIX*). It provides a more detailed discussion of the principles presented herein. It also gives an indication as to the complexity of the process involved in identifying unknowns, and the need for having resources available with extensive backgrounds in metallurgy when more complex scenarios are encountered.

REFERENCES

1. *Alphabetical Index of Active Methods* (for the most current year), UOP, Process Performance Systems and Equipment, 25 E. Algonquin Rd., Des Plaines, IL 60017-5017 (708-391-2529)
2. *Annual Book of ASTM Standards* (for the most current year), **00.01**, Subject Index, Alphanumeric List, www.astm.org

APPENDIX

AN INTEGRATIVE APPROACH TO CORROSION FAILURE ANALYSIS*

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ABSTRACT

When environmental factors are a major contributor to a corrosion-related failure, an integrated, multidisciplinary approach for determining the cause of the problem is required. Typically, the techniques employed are limited to metallography, scanning electron microscopy, and elemental analysis by either an energy-dispersive or wavelength-dispersive x-ray spectrometer attachment. However, just knowing the elements present in a deposit may not be sufficient to ascertain the cause of a corrosion-related failure. A preestablished strategy of carefully examining the component, obtaining a service history, and documenting the observations prior to sectioning is critical. Prior to sectioning, a decision must also be made as to the analysis of deposits because such deposits can easily be contaminated, be lost, have spatial position destroyed, or be present in limited quantity.

This paper presents the analytical limitations, detectability limit, and expected type of information from various techniques. The utility of these nontraditional techniques is discussed and demonstrated by several examples.

WHEN A COMPONENT FAILS during service, determining the cause of the failure often becomes paramount prior to instituting a plan of action. The methodology for a general failure analysis is well documented.^{1,2} However, when corrosion products or deposits are involved, an integrative strategy that focuses on the deposits is required, or the conclusions can be incorrect. The objective of this paper is to take the analyst beyond the traditional approach that uses scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) and demonstrate how other analytical techniques can be integrated into a failure analysis.

When a failure analysis is initiated, the strategy or methodology must be rooted in common sense. Thus, even before examining the failed component, a detailed service history must be established. This extra time for documenting, observing, and studying can help in developing potential hypotheses and determining the analytical techniques that can directly prove or disprove the possible hypothesis. For example, if the component is encrusted with a deposit, then analytical technique that includes identifying the composition of the deposit and establishing the corrosive agent is necessary. Furthermore, once a component is sectioned, such as for metallographic preparation, deposits can be ruined, contaminated, or lost. Premature sectioning can also compromise the documentation. Finally, a limited quantity of the deposit is available, and only the definitive analyses can be performed.

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ASM International, Materials Park, OH 44073-0002, 1992, pp. 93-98,
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Once the observations have been documented and related to the service history, the strategy for the failure analysis can then be formulated. When corrosion products are present, a systematic analytical procedure must be incorporated into the game plan. The strategy should include examination of deposits on the metal surface, the cleaned surface, the microstructure near the deposits, and the bulk properties.

Fracture surfaces from a petrochemical or refinery failure are often covered with deposits. When possible, the deposits of the fracture surface should usually be analyzed prior to cleaning. However, if thick deposits have formed after the failure, then their removal becomes critical. To prevent damage to the underlying surface, the most gentle removal process should be used initially.³ Application of a polymer dissolved or softened with a solvent (for example, cellulose acetate softened by acetone), that can be peeled away after drying and resetting, is an excellent technique for gently removing a deposit for further analysis. Subsequent analyses can include SEM-EDX spectroscopy or x-ray diffraction (XRD).

One common analytical technique utilized for analyzing corrosion deposits is the SEM-EDX. Two basic types of EDX detectors are commonly used. With a beryllium window, elements heavier than sodium can be simultaneously detected; with an ultrathin window or windowless detector, boron and possibly beryllium are detectable. Alternatively, a wavelength energy-dispersive spectrometer attached to an electron optic column can only monitor one element at a time but has greater sensitivity, particularly for elements with low atomic numbers. Furthermore, peak overlap problems such as for the oxygen K-line and transition metal L-lines as shown in Figure 1 are nonexistent. To provide a common basis for discussion, Table 1 lists many different techniques that are often incorporated into an integrated failure analysis and describes typical sample size required, detectability limits, depth of analysis, and type of information obtainable.

One of the most powerful analytical combinations emphasized in this paper is combining SEM-EDX with XRD. With XRD, the crystalline species are identified. Being able to differentiate between various iron oxide species can help determine whether the deposit is from aqueous corrosion or is just mill scale produced during fabrication.

EXPERIMENTAL APPROACH

In all of the failure analyses described in this paper, a detailed service history was initially outlined, a thorough macroexamination was performed, and macrophotographs were taken for documentation purposes. Having examined the failed component and all of the pertinent documentation, a chronological strategy of the work to be performed and samples to be obtained was made. This course of action, as previously noted, helped to eliminate the possibility of sectioning a sample prematurely, contaminating or losing a deposit, or destroying a deposit that would subsequently need to be analyzed.

Removal of deposits was accomplished in a variety of ways, including acetone-softened replicating tape, double-sided tape, gentle scraping, or chemical solvent reprecipitation. For electron-optic instruments such as the SEM or Auger electron spectroscopy (AES), obtaining suitable electrical conductivity may be necessary. When carbon coating was not feasible, as with the AES, the accelerating voltage was reduced to minimize the effect of electrical charging. For SEM-EDX, the lowered voltage must be sufficiently high to excite x-rays of interest. In other instances, the deposit was pressed into indium foil or spread thinly onto the mounting stub by spin drying.⁴ For deposits analyzed by XRD, samples were ground to 200 mesh.

The examination of the fracture surface of some corrosion failures was often complicated by thick, adherent deposits. After completing all of the analyses of the deposits, the most mild cleaning operation was performed first so that the fracture surface was not destroyed or disrupted. The mildest initial technique

utilized was soap or solvent cleaning followed by replica stripping or brushing with soft bristles. Chemical etching in an inhibited alkaline or acid solution was used as a last resort. Prior to and after each cleaning operation, particularly with the inhibited acid or alkaline steps, a micrograph was taken of an easily identifiable, noncorroded region. A comparison of these micrographs helped identify whether damage from the cleaning operation had occurred. At all times, the alloy was verified, and where appropriate, microstructural analyses, including microhardness, grain size, and identification of inclusions, were performed. To demonstrate a number of different types of examples and to emphasize the integrative analytical approach, only brief documentation summaries are given. Although not emphasized in this paper, the other aspects of a failure analysis, including macroexamination, metallography, SEM fractography, mechanical property evaluation, and nondestructive testing, should not be ignored or minimized.

EXAMPLES OF INTEGRATIVE APPROACH

SEM-XRD ANALYSIS - A combination of SEM-EDX and XRD analyses can be used to identify the corrosion products and the cause of corrosion. For example, after two years of service, a thin-walled copper tube, which had been used occasionally to carry liquid propane to a grain dryer, leaked. During visual inspection, several pits that penetrated through the wall and a black adherent deposit on the inside of the tubes were noted. Metallographic analysis revealed that the tube was highly pitted underneath the deposit. Alloy, temper, and grain size were as expected. The corrosion deposit was removed with acetone-softened replicating tape and first examined with the SEM-EDX for elemental analysis and then with XRD for crystalline compound identification. The main elements detected by SEM-EDX were copper, oxygen, and sulfur, and by XRD the compound $\text{Cu}_{1.97}\text{S}$ was identified. These results suggested that a sulfide in the propane was the corrodent. However, dry sulfides should not attack copper, but moist sulfides will corrode copper alloys.⁵ The pitting attack caused by the combination of discontinuous oxide film; occasional dryer usage; and sulfide, water, and oxygen seems to be the probable corrodent combination.

Carbon steel reboiler tubes of a sour-water stripper leaked and caused a premature shutdown. The external surfaces were deeply pitted and covered with reddish-brown corrosion products. Similar corrosion products were present in the interior, but the through pitting had initiated from the outside. The main component of the deposit as detected by SEM-EDX was iron with a minor amount of sulfur; oxygen could not be detected with the analyzer, which was present on the SEM. Magnetite (Fe_3O_4) was identified by XRD as the primary species. Lesser amounts of lepidocrocite and goethite, both different forms of $\text{FeO}(\text{OH})$, and α -sulfur were also noted. The presence of magnetite, lepidocrocite, and goethite suggested corrosion by dissolved oxygen in the water as opposed to a sulfide-type attack.

Determination of low levels of fluorine when oxygen and transition metals are present in high concentrations is most difficult with an SEM-EDX. An XRD analysis was required to identify the cause of failure of two Hofer fittings from an HF alkylation pilot plant. After a period of continuous use in the pilot plant, hydrofluoric acid (HF) and hydrocarbons were left in the plant under a nitrogen blanket during a prolonged shutdown. The lines were flushed so that some plant modifications could be made. During the modification, some lines were exposed to air. Prior to start-up, no leaks were observed; however, after HF and hydrocarbons were introduced, a leak was detected in the weld of the fitting. Metallographic examination revealed both transgranular and intergranular cracking of the Monel 400 fitting. The SEM-EDX analysis of the deposit from the inside of the fitting identified nickel and copper as the major components with lesser amounts of potassium, chromium, iron, and manganese. The XRD identification of K_2NiF_6 was the key in determining that the failure was from stress corrosion cracking in moist aerated HF vapor⁶ rather than from a caustic environment.⁷ During the pilot plant modification, some neutralizing solution (potassium hydroxide) must have been drawn back into this section of the plant and

became entrapped. The potassium hydroxide then reacted with HF to produce the appropriate hydrous HF conditions for stress corrosion cracking.

Occasionally the fracture morphology and the species identified by SEM-EDX on the fracture surface are inconsistent with the proposed failure mechanism. The XRD can help confirm the existence of a constituent and provide the missing clue. Such a multidisciplinary strategy was necessary during the analysis of a cracked Type 304 stainless steel four-way fitting from a pilot plant. Metallographic examination revealed severe intergranular attack and sensitization of the stainless steel. Numerous small pits were also observed on the grain facets of the fracture surface. Elemental analysis of the deposits showed iron, chlorine, chromium, copper, and a trace amount of sulfur. Given the large amount of chlorine present, a typical conclusion of the cause of the failure would have probably been stress corrosion cracking by chlorides. However, chloride stress corrosion cracking of stainless steel can propagate by either a transgranular or intergranular mechanism. The XRD was able to assist, as sodium chloride was identified in the deposit along with evidence for cuprous chloride, ferric chloride and ferrous chloride. The probable agent causing the intergranular cracking of this four-way fitting was the ferric and ferrous chlorides,⁸ which were produced because of extensive chloride attack of the stainless steel.

The XRD can be used to determine the temperature of a metal exposure. In the examination of a deposit found in the flue gas line expansion bellows of a fluidized catalytic cracking (FCC) unit, the SEM-EDX analysis of this material showed elements typical of an FCC catalyst. However, XRD identified α -Al₂O₃, mullite (3Al₂O₃ · 2SiO₂), and the high temperature form of tridymite (Si₂O); no zeolite was found. The observed components are consistent with the thermal degradation of an FCC catalyst and indicate a thermal exposure of at least 1100°C.

SURFACE SCIENCE ANALYSIS - Surface science techniques such as x-ray photoelectron spectroscopy (XPS) and AES can provide useful information as to the chemistry of the surface layers. Because most deposits have rough surfaces, sputter profiling can become compromised. Although these approaches have been used extensively in the study of corrosion⁹ and stress corrosion cracking¹⁰ under controlled environments, the results obtained under complex, industrial conditions can be misleading because of the deposition of subsequent products. As an example of the successful use of XPS, an outer surface coating on the inside of a 90/10 cupro-nickel tube had to be identified. Examination showed cuprous oxidation state, probably in the form of cuprous oxide; a small amount of cupric oxidation state, probably cupric oxide or the corresponding hydroxide; and graphitic carbon. The identification of the graphitic carbon indicated that residual carbon remained after annealing and had not been adequately removed. In another instance, AES was employed to identify a sulfur contaminant on a test coupon during a coking study.¹¹ Hydrogen sulfide can be used to reduce the formation of carbonaceous deposits by forming a sulfide scale that restricts carbon ingress.¹² The presence of the sulfur scale was the reason for the unexpected lack of carbonaceous deposits under conditions that should have produced them.

WET CHEMICAL ANALYSIS - Because of the heavy reliance on SEM-EDX systems by fractographers for deposit analysis, wet chemical methods¹³ are often neglected or ignored. Analysis for nitrate, cyanide, or sulfate and total carbon, sulfur, nitrogen, or hydrogen can often provide insightful information as to the type and source of the deposit. Furthermore, wet chemical techniques often have greater detectability limits and can be more accurate and reproducible because larger, more representative samples can be used. Several examples illustrate the utility of such methods. Cupro-nickel condenser tubes that had been severely perforated were suspected to have been attacked by ammonia and/or acid in the presence of a powerful oxidizing agent. The SEM-EDX analysis using a beryllium window detector revealed the presence of copper, sulfur, chlorine, manganese, iron, nickel, sodium, and potassium. Quantification was difficult because of the inhomogeneity of the deposit, and nitrogen could not be detected. Chemical analysis of the deposits by emission spectroscopy, atomic absorption spectroscopy,

silver nitrate titration for chlorine, peroxide fusion for sulfur, and chemiluminescence for nitrogen were combined with XRD. The high concentration of sulfur and the identification of various nickel sulfides indicated that the corrosion was the result of hydrogen sulfide and oxygen with no evidence of ammonia attack by NH_3 or nitric acid.

In another example, several sections of carbon steel condenser tubes from a gas condenser unit fouled shortly after installation. The tubes operated under gas-phase and water conditions. Several through perforations found in the gas-phase half of the tubes were initiated from the inside. A greater deposit buildup was noted on the water-phase layer. Deposits were removed for SEM-EDX analysis, Leco-sulfur, gravimetric chloride, and total cyanide. The sulfur, chloride, and cyanide levels were found to be quite low. By XRD the gas-phase layers were identified as Fe_3O_4 . These condenser tubes appeared to fail by pitting initiating in the gas phase as a result of the combination of oxygen and a moist environment.

ORGANIC ANALYSIS - Organic analysis of a carbonaceous deposit cannot be performed with SEM-EDX. Techniques such as infrared spectroscopy, mass spectroscopy, gas chromatography, Raman spectroscopy, nuclear magnetic resonance, and their various combinations must be used to determine how the deposit formed. Dissolution of the deposit and subsequent analysis by one of the mass-spectroscopy-type instruments can identify the molecular weight of the various species that are present. Nuclear magnetic resonance can differentiate aromatic from aliphatic hydrocarbons. As a specific example, laser Raman spectroscopy was utilized to characterize and identify the source of deposits on the inside of cupro-nickel condenser tubes. A graphitic carbon was noted. A virtually identical spectrum was obtained when plastic end caps were used during fabrication. An amorphous carbon film was observed when no end caps were utilized, and no amorphous or graphitic carbon film could be detected when metal end caps were included. The effects of various cleaning processes can be monitored to develop a method for removing the deleterious film.

CONCLUSIONS

As demonstrated by the examples presented in this paper, characterizing a deposit is not an easy assignment. An integrative approach is often necessary to solve some of the more complex corrosion-type failures. Care must be exercised in selecting the appropriate analytical tools. The inclusion of XRD, wet chemistry, XPS, AES, and organic spectroscopic techniques with SEM-EDX should be considered when formulating the failure analysis strategy. Sometimes the implementation of the best strategy does not provide conclusive evidence and only helps eliminate various possibilities. When the corrodent, or cause of the deposit, cannot be identified conclusively, examination of Pourbaix diagrams,¹⁴ potentiodynamic data, or simulated corrosion testing can prove particularly helpful.

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Table 1
Chemical Analysis Techniques

Technique	Minimum Sample Size Required	Approximate Detectability	Depth of Analysis	Type of Information Obtainable
EDX: Be Window Thin Window	0.01 mm ³ 0.01 mm ³	0.5% 0.5%	5-20µm 3-20 µm	Elemental: Na-U Elemental: Be-U
WDX	0.01 mm ³	0.1%	5-20 µm	Elemental: Be-U
XRD	1 mm ³	2%	—	Crystalline Compounds
Cl Titration (silver nitrate titration)	5g	100 ppm	—	—
Emission Spectroscopy (Inductively Coupled Plasma)	500 mg	10-100 ppm	—	Elemental
Atomic Absorption (Graphite Furnace)	500 mg	0.05 ppm	—	Elemental
N-Analysis (Chemiluminescence)	500 mg	50-100 ppm	—	—
Auger Electron Spectroscopy	0.1 mm ³	1%	1 µm	Elemental: Be-U
X-Ray Photoelectron Spectroscopy	100 mg	0.5%	3-10 µm	Oxidation State of Element: Li-U
C Analysis (Infrared Detection)	500 mg	100 ppm	—	—
O Analysis (Neutron Activation)	1000 mg	0.1-0.01%	—	—
S Analysis	100 mg	100 ppm	—	—
X-Ray Fluorescence	500 mg	1 ppm	—	—

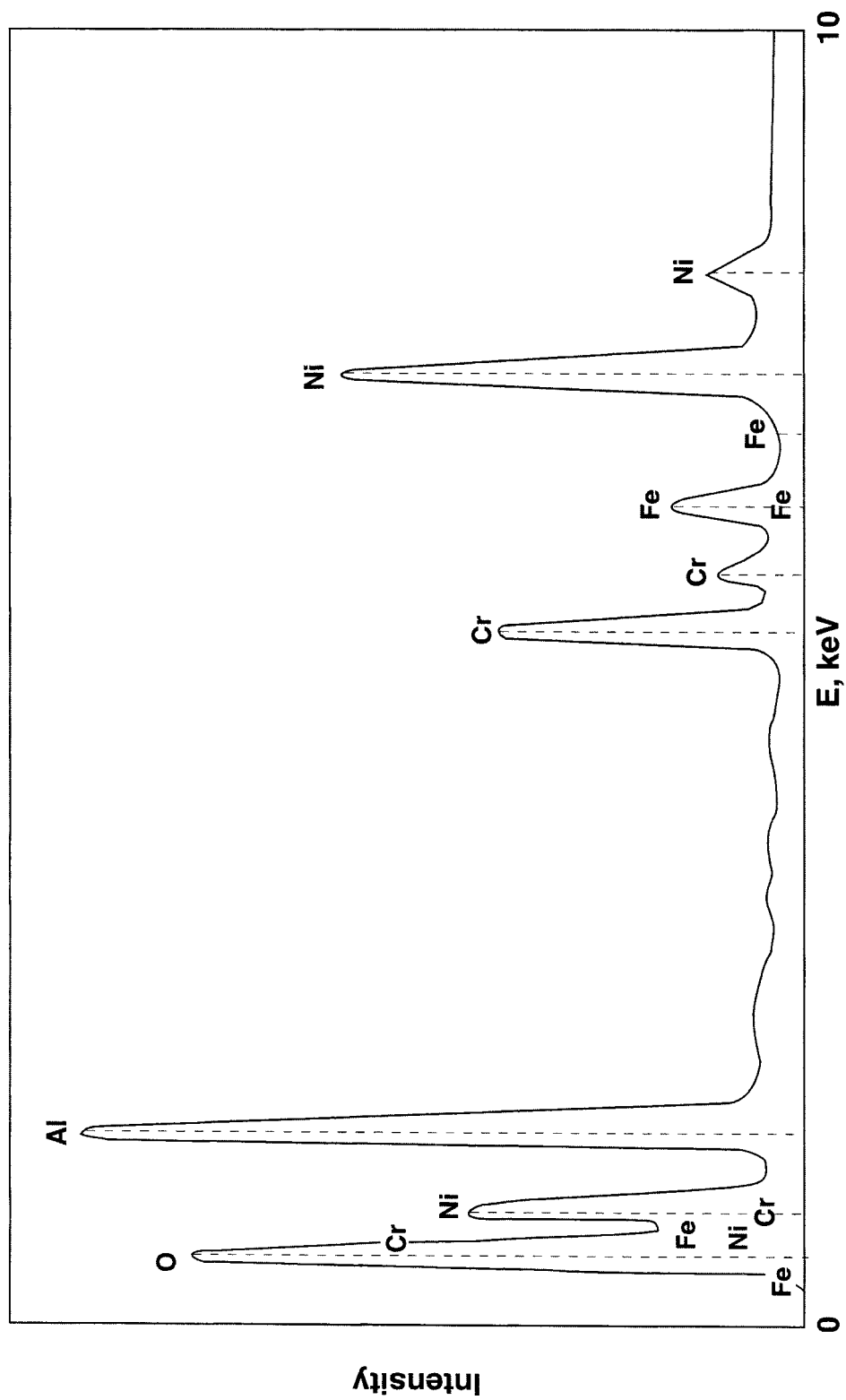


Figure 1

Peak overlap for O k-line and transition metal L-lines