Diffraction Notes

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THE IDENTIFICATION OF CRYSTALLINE PHASES IN BOILER SCALE DEPOSITS BY X-RAY DIFFRACTION

INTRODUCTION

The analysis of boiler scale water deposits is an important tool both for maintenance of power generation systems and for failure analysis. Loss of heat transfer efficiency, increased fuel consumption, reduction in pipe carrying capacity, and the increased likelihood of pipe and boiler failures result from excessive boiler scale deposits. For example, a $CaCO_3$ deposit 0.1 in. thick on a heat transfer surface causes a reduction in the heat transfer coefficient of about 40% (Figure 1). Such heat transfer losses lead to increased operating temperatures to compensate for the reduction in efficiency, increasing the likelihood of temperature related failures.[1]

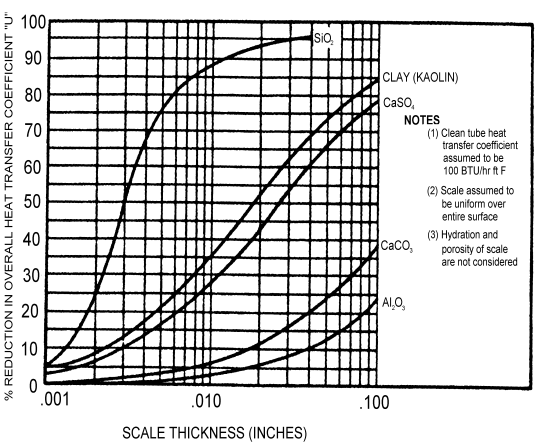

Fig. 1 - Heat Transfer Loss Due to Thickness
From McGraw-Hill Encyclopedia of Science and Technology, 1960, Vol. 9, pp. 606-607. Used with permission of McGraw-Hill.

Boiler scale deposits result from dissolved minerals in the water that have precipitated to the walls of the piping or other parts of the boiler. Some materials, such as iron oxides, are usually the result of dissolved oxygen in the water coming into contact with steel

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ANNOUNCEMENTS

On-Site Residual Stress Testing Available

Using an advanced computer controlled x-ray stress analyzer that utilizes solid state linear image sensors as position sensitive detectors, engineers from Lambda Research can evaluate samples at the client's site. Portable electropolishing apparatus allows complete subsurface analysis. The mechanical center-hole drilling and ring-core strain gage methods are now also available on-site. These capabilities are particularly valuable to clients who need residual stress measurements on parts that are impossible to ship due to size or location. Contact: Perry Mason

Stress Measurement in Coarse Grained Weldments by the Ring-Core Method

Lambda Research has developed a ring-core mechanical method of determining residual stresses as a function of depth to characterize the stress distributions in complex components. The technique can be used in coarse grained material such as weldments and castings. The principal stress distributions are obtained with depth resolution approaching that of x-ray diffraction techniques. The current technique is capable of determining the residual stresses to a depth on the order of 1.8 mm. Lambda is in the process of modifying the current technology to increase the depth range at which the residual stresses can be determined. Contact: Doug Hornbach

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boiler components. Others are present in the water when the water is initially injected into the system, such as calcites, and may form in the boiler during a change in pressure, temperature, water flow, etc.[2]

X-ray diffraction (XRD) qualitative phase analysis can be used to identify the crystalline compounds present in the boiler scale. A diffraction pattern is obtained from the sample for comparison with the phases listed in the Powder Diffraction File (PDF) published by the Joint Committee on Powder Diffraction Standards (JCPDS). X-ray fluorescence elemental chemistry assists in the comparison to the PDF.

The examination of boiler scale deposits by x-ray diffraction provides specific information concerning the crystalline phases present. X-ray fluorescence provides only the elemental composition of the deposit, and although a useful aid in the qualitative analysis of boiler scale deposits by x-ray diffraction, it should not be used alone. If a general conversion of elements to oxides is assumed, the results can be misleading. Multiple phases of iron oxide, such as hematite and magnetite, may be present. Mixtures of phases such as hydroxylapatite (containing calcium and phosphorous) and calcite, would not be readily identifiable using only x-ray fluorescence spectra.

APPLICATION

Selectively segregating phases by magnetism, density, and acid solubility aids in the identification of the boiler scale deposits. Lambda Research uses the methods of sample separation outlined in ASTM D934 to effect sample separation of complex boiler scale deposits.

Qualitative elemental analysis using energy dispersive x-ray fluorescence (EDXRF) on boiler scale deposits efficiently detects Na and higher Z elements in the composition of the deposit before phase analysis begins. A significant amount of a particular element without a corresponding crystalline phase may reveal the presence of amorphous material. Figure 2 shows a sample EDXRF pattern. Because the elements of interest tend to span a large range of atomic numbers (silicon to copper, for instance), no single excitation energy can optimally excite the elements in an average sample. Therefore, multiple EDXRF patterns are obtained using excitation energies designed to excite certain groups of elements.

The analysis of the deposits is guided by prior experience with samples of similar origin. As boiler

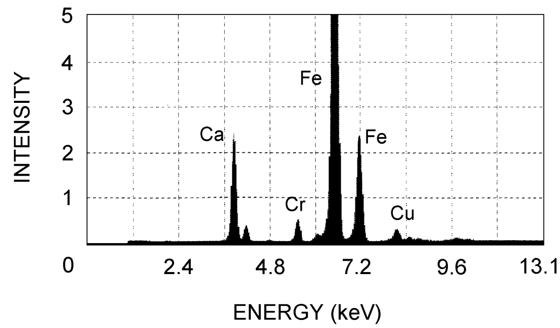

Fig. 2 - EDXRF Pattern from Boiler Scale Sample

scale deposits tend to contain a limited number of possible compounds, the analysis is initially focused on finding the commonly occurring phases. The temperatures at which the deposits have been formed provide additional clues concerning the phases present in the deposit.[3] Any diffraction peaks that are not identified by a search for the commonly found phases are included in a full search of the JCPDS files beginning with the mineral files.

Boiler scale deposits are often provided as powders ready for mounting on a diffractometer or the Debye-Scherrer camera to be tested in general accordance with ASTM D934.[4] Occasionally, deposit samples may need to remain attached to the substrate material throughout the analysis, or the deposit forms in stratified layers that are of varying composition. Diffraction patterns may be obtained on samples both in bulk form and on layered deposits. In all of these cases, another diffraction pattern is obtained for the substrate material, so that crystalline phases from the substrate may be identified and eliminated from the analysis of the deposit.

An example of the elemental fluorescence analysis and the diffraction pattern from a boiler scale sample are shown in Figures 2 and 3. The identifiable crystalline phases from the boiler scale deposit are given on Table I. Note the presence of two different iron oxides and calcium carbonates as well as hydroxylapatite, a calcium phosphate. Other common compounds found in boiler scale deposits include calcium sulfates and crystalline silica.[5] Organic, oil, and other amorphous phases cannot be identified by the technique.

Table I - X-ray Diffraction Qualitative Phase Analysis of Boiler Scale

Phase	Formula	PDF#	Crystalline Structure	Relative Abundance
Calcite	$CaCO_3$	5-586	Rhombohedral	Major Phase
Magnetite	Fe_3O_4	19-629	Cubic	Secondary Phase
Hematite	Fe_2O_3	33-664	Rhombohedral	Minor Phase
Hydroxylapatite	$Ca_5(PO_4)_3(OH)$	9-432	Hexagonal	Trace
Aragonite	$CaCO_3$	41-1475	Orthorhombic	Trace

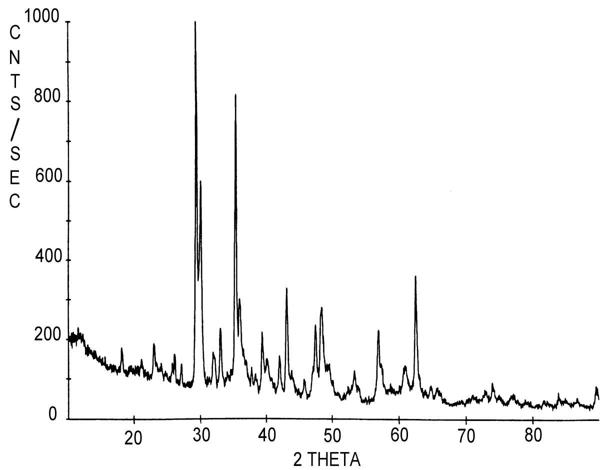

Fig. 3 - Diffraction Pattern from Boiler Scale Sample

Crystalline phase determination of boiler scale deposits can be a useful tool for correcting problems with excessive deposits, which significantly increase the downtime and insurance costs of a boiler operation. With a highly crystalline sample containing few phases, identification of an individual phase can be achieved with as little as 1 to 2 percent of the phase present in the sample.[(6)] The phases found in a deposit allow the engineer to both understand more fully the sources of the deposits and to take corrective steps by monitoring proper water chemistry, appropriate material selection, and other factors. Lambda Research offers full qualitative XRD and EDXRF capabilities for the analysis of boiler scale, other water formed deposits, and crystalline substances, in general.

1 Cowan, Jack C. and Donald J. Weintritt, Water- Formed Scale Deposits (Houston: Gulf Publishing Co., 1976) 10.
2 Cowan 204.
3 Cowan 4, 74, 120.
4 American Society for Testing and Materials, "Standard Practices for Identification of Crystalline Compounds in Water-Formed Deposits by X-Ray Diffraction," ASTM Designation: D934 - 80 (Reapproved 1985) (Philadelphia: ASTM, 1985).
5 Cowan 4, 69, 113, 168-169.
6 ASTM Designation: D934 - 80 1.

A2LA Extends Accreditation to Canada

Accreditation by the Standards Council of Canada (SCC) opens new doors for Lambda Research in Canada. The Mutual Recognition Agreement, recently signed by the American Association for Laboratory Accreditation (A2LA) and the Standards Council of Canada, mutually recognizes laboratory accreditation in Canada and the United States. Under this agreement, the stringent A2LA accreditation achieved by Lambda Research to ISO Guide 25 is recognized throughout North America and beyond. This agreement strengthens our working relationship with our Canadian clients. New programs are available for quality control testing at reduced cost tailored to our client's testing requirements.

Sectioning Capability for Large Nickel Base and Titanium Components

Lambda Research has developed sectioning procedures using an abrasive carbide blade band saw technique which allows full size components such as turbine disks to be sectioned for residual stress studies in inaccessible locations. The technique cuts without inducing significant heat, and although slow, operates automatically and is ideally suited for sample preparation and monitoring of stress relaxation. Contact: Perry Mason

References