

R & D on Analysis of Trace Metal Elements and Chemical Forms by Synchrotron Radiation

Background

XAFS (X-ray absorption fine structure) analysis^{*1} using the powerful synchrotron X-ray emitted by the SPring-8 (Super Photon ring-8GeV) is advanced analysis of a local crystal structure around an atom using the specific XAFS spectrum of a material and is expected to prove to be a useful technique to analyse trace metal elements and their chemical forms in wide-ranging research fields (Fig. 1). However, there is hardly any precedence of identifying chemical forms with XAFS analysis regarding such complicated material systems involving multiple compounds as coal and fly ash and the standard understanding is that the application of XAFS analysis to such complicated systems is extremely difficult.

Objectives

We apply XAFS analysis to such complicated material systems involving multiple compounds as coal and fly ash using the Spring-8 industrial consortium beamline, and clarify the potential of this analysis for trace metal elements and their chemical forms.

Principal Results

Application of XAFS analysis to a standard bituminous coal sample (NBS1632c) and standard fly ash sample (NBS1633b) of the US National Institute of Standards and Technology (NIST) produced the following results.

1. Development of Technique to Identify Chemical Forms with Transmission Mode XAFS Measurement

With transmission mode XAFS measurement^{*2}, a lower limit analytical concentration of $10^3 - 10^4$ mg/kg was achieved by stabilising the X-ray beam (Fig. 2-A)^{*3}. Identification of the chemical form and quantification of the mixing ratio of iron, etc. at this concentration level were proven to be feasible by comparing the XAFS spectrum of the sample with that of the standard material (Fig. 3).

2. Development of Technique to Identify Chemical Forms with X-Ray Fluorescence Mode XAFS Measurement

(1) Improvement of lower limit analytical concentration through optimisation of intake angle

With X-ray fluorescence mode XAFS measurement, improvement of the S/N ratio by more than one figure was achieved through optimisation of the intake angle of the XAFS spectrum to a solid state detector (SSD) which reduced the scattered X-ray noise. In this way, the feasibility of this mode of XAFS measurement for analysis of a concentration of some 10 mg/kg, a level difficult to achieve by the transmission mode, was established (Fig. 2-B).

(2) X-ray fluorescence mode XAFS measuring using high resolution detector

Using the fluorescence X-ray detector^{*4} jointly developed by the CRIEPI and companies participating in the industrial consortium beamline to the highest level in the world (Fig. 4), a lower limit analytical concentration of less than 1 mg/kg was achieved for elements ranging from titanium to cerium for which the excitation of the inner shell electrons is possible by X-ray fluorescence mode XAFS measurement using the industrial consortium beamline (Fig. 2-C). Moreover, the feasibility of identifying chemical forms at this concentration level through comparison with the standard material was established (Fig. 5).

Based on the above results, the ranges of the measurable concentration for complicated material systems involving multiple compounds by the above-mentioned two modes of XAFS measurement were established, making it possible to analyse the chemical forms of trace metal elements in compounds.

Future Developments

The next steps are verification of the applicability of XAFS analysis using a high energy X-ray to heavy elements and the detection limit of low concentration elements using the newly introduced high sensitivity X-ray detector and to expand the range of XAFS analysis by creating a database which includes data for standard materials.

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Reference

“Application of Synchrotron Radiation to X-Ray Analysis of Industrial Materials - Study on X-Ray Analysis and Technology Using Industrial Consortium Beamline at SPring-8”, CRIEPI Report (W01027 in Japanese)

“Analysis of Trace Metal Elements and Chemical Forms by Synchrotron Radiation Light - Application of X-Ray Absorption Fine Structure Analysis”, CRIEPI Report (W03034 in Japanese)

* 1 : XAFS analysis is an analytical technique made possible by the use of the SPring-8.

* 2 : Yamamoto, et. al, CRIEPI Report W01027. X-ray transmission mode XAFS measurement measures the strength of an X-ray transmitting through a sample. Meanwhile, X-ray fluorescence mode XAFS measurement measures a fluorescent X-ray generated on the sample surface and, therefore, can be applied to non-transmissive samples or extremely thin samples of which measurement by the transmission mode is difficult.

* 3 : The lower limit analytical concentration at each mode is set as equivalent to 10 - 30 times the actually measured S/N ratio.

* 4 : This fluorescent X-ray detector equipped with a high resolution X-ray spectral crystal offers the world's highest detection sensitivity ($10^8 - 10^{10}$ atoms/cm²) (Awaji and Yamamoto, etc. al., Jpn. J. Appl. Phys., 39, pp. L1252 - 1255 (2000)).

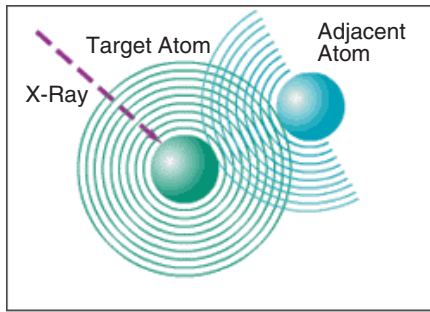


Fig.1 Principle of XAFS Analysis

The interference between the wave released from the atom which has absorbed the X-ray and the reflected wave from the adjacent atom makes it possible to observe the oscillation structure in the XAFS spectrum. Analysis of the XAFS spectrum produces information on the state of the electrons of the target atom and the type, distance and coordination number of the adjacent atom.

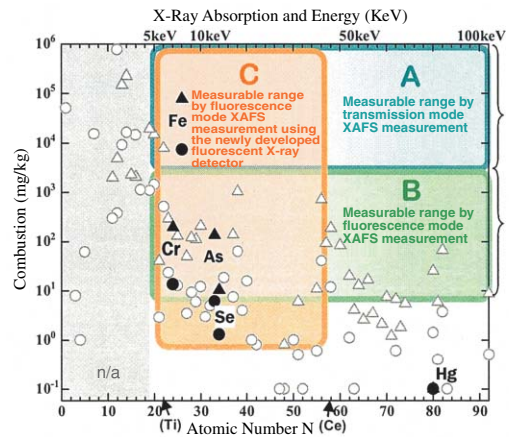


Fig.2 Identifiable Range of Chemical Forms by XAFS Analysis Achieved by the Present Research

The measurable concentration ranges of transmission mode XAFS measurement (A), fluorescence mode XAFS measurement (B) and fluorescence mode XAFS measurement using the newly developed high resolution detector (C) are shown. Also shown are the quantitative analysis results of NBS1632c (○) and NBS1633b (△) by the NIST and the elements with which XAFS analysis was conducted in the present research (●, ▲).

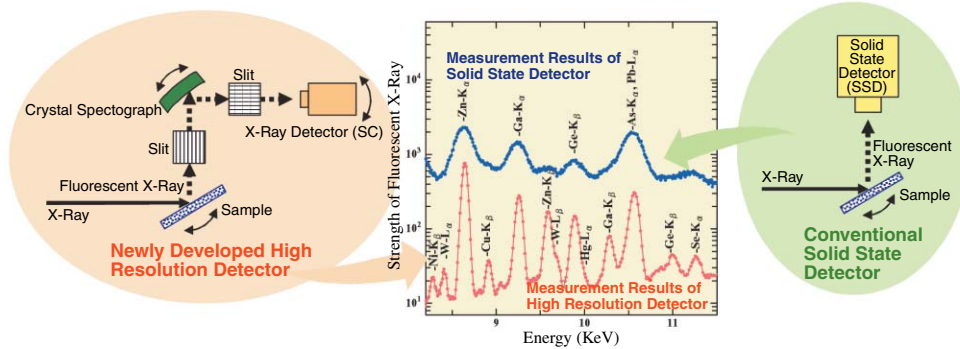


Fig.4 Comparison between Newly Developed High Resolution Detector and Conventional Solid State Detector

The development of a high resolution detector equipped with a crystal spectrograph and slits has significantly improved the energy resolution and S/N ratio, both of which are essential for the XAFS analysis of the trace metal elements of a compound.

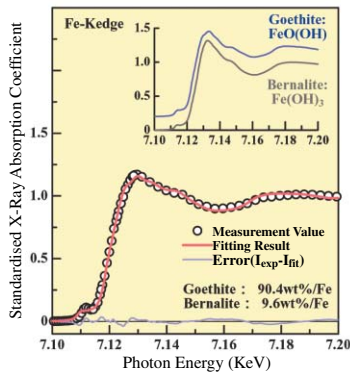


Fig.3 XAFS Measurement Results for Fe in NBS1633b

The iron contained in NBS1633b is identified as a compound of which the main constituents are FeO(OH) and Fe(OH)₃ as shown in the inserted figure.

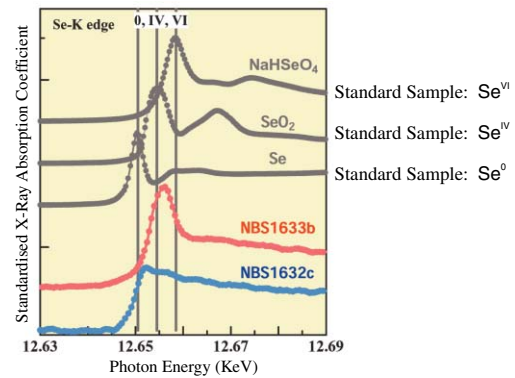


Fig.5 XAFS Measurement Results for Selenium (Se) Using High Resolution Detector

Using the XAFS spectrum, it is established that the state of selenium oxidation is low oxidised compounds, such as FeSe₂, in the case of NBS1632c or a mixed compound of Se^{IV} and Se^{VI} in the case of NBS1633b.