TRANSMISSION ELECTRON MICROSCOPY TECHNIQUES APPLIED TO THE SOLID PHASE CHARACTERIZATION OF ENVIRONMENTAL SAMPLES

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RESUMO
A caracterização de amostras ambientais é complexa devido à presença de inúmeras fases, cristalinas ou não, com variados tamanhos de partículas, e composição elementar em nível de traços. Dentre as técnicas disponíveis para análise e caracterização em fase sólida, a microscopia eletrônica de transmissão destaca-se na investigação da composição elementar e de fases em escala nanométricas e até mesmo atômica. Trata-se de uma técnica muito poderosa para caracterizar completamente as fases sólidas presentes nas amostras com elevada resolução analítica e espacial. Neste trabalho, imagens de transmissão de alta resolução, difração de elétrons, espectroscopia de dispersão de energia por raios X e espectroscopia de perda de energia de elétrons são brevemente descritas, com exemplos de aplicação, para demonstrar seu potencial para a caracterização de amostras ambientais.

PALAVRAS-CHAVE: Caracterização, amostras ambientais, MET, composição química, composição cristalográfica.

ABSTRACT
The characterization of environmental samples is not trivial due to the presence of many crystallographic phases, particles sizes and elemental composition in concentrations down to trace level. Amongst the available techniques for solid phase analyses and characterization, transmission electron microscopy (TEM) is unique on the investigation of both elemental and phase composition of samples down to nanometer and even atomic scale. However, TEM techniques are not to be used in exploratory studies of solid phases because just a very small part of the sample is investigated. It would be necessary previous bulk analyses of the sample. On the other hand, TEM is a very powerful technique to thoroughly characterize solid phases with high spatial and analytical resolutions. In this work high-resolution transmission imaging, electron diffraction, energy dispersive X-ray spectroscopy, and electron energy-loss spectroscopy are briefly described to show their potential on the characterization of environmental samples.

KEYWORDS: Characterization, environmental samples, TEM, chemical composition, crystallographic composition.
1. INTRODUCTION

The environmental samples quite often consist of several phases (e.g. phyllosilicates, sulfides, aluminum and iron (hydr)oxides, carbonates and not rarely organic matter), and particle sizes range from few nanometers to several micrometers. The smallest particles are very often tangled with each other or with larger particle and their complete separation are difficult and often unfeasible by physical or chemical methods (Elsass et al. 2008). Besides that, the structural characterization of phases with trace amounts of contaminants is not trivial due to particles’ heterogeneity, small grain size and low concentrations. This is often the case in soil or airborne particulates.

Synchrotron-based analytical techniques, such as X-ray absorption spectroscopy (XAS), may reach lateral resolution of about 30 nm (Egerton 2008), and are often combined with theoretical molecular modeling or with other spectroscopic techniques to investigate elemental speciation and bonding characteristics. Nevertheless, synchrotron-based techniques are difficult to access and to interpret the results. The electron energy-loss spectroscopy (EELS) analysis can be performed in analytical transmission electron microscopes, which are more accessible, and provide information similar to that given by XAS. The use of TEM techniques is very powerful to fully characterize a given sample in a very small scale, because it allows the combination of morphology by image analysis, chemical composition by energy dispersive X-ray spectroscopy (EDS), and further chemical information by EELS, phase characterization by electron diffraction, all in one machine and with better spatial resolution than any other scattering technique. Moreover, a spatial resolution down to few nanometers can be achieved by TEM. In modern (Scanning) TEMs the resolution can even go down to atomic scale. On the other hand, the TEM techniques should not be used in exploratory studies of solid phases, unless the nature of the sample being studied requires so, since a very minor part of a given sample is investigated. It could be time consuming, and, at the end, becomes an expensive technique once the average academic user fee around the world is about US$ 45.00/hour.

In the present work, some TEM techniques (high-resolution transmission imaging, electron diffraction, energy dispersive X-ray spectroscopy, and electron energy-loss spectroscopy) are briefly described. The aim is to show their potential on the characterization of solid phases, even for heterogeneous and complex materials such as environmental samples.

2. MATERIALS

The present work shows results from the investigation of Al- and Fe-rich Oxisol samples from an open-pit gold mine. The Oxisol liners samples were used in tailings disposal facilities containing sulfide minerals as a chemical barrier to prevent arsenic release to the environment (Ladeira and Ciminelli 2004). After 10 years of disposal, two of these tailings tanks were excavated to be reprocessed, and samples from both aged tailings and Oxisol liners recovered for analysis. The crystalline fraction of these samples was then investigated by TEM (Freitas et al., 2015), and some results are shown in this present work to illustrate the uses of TEM techniques. The samples were analyzed using a FEI-TEM LaB6 Tecnai G2-20 at 200kV. Some iron (hydr)oxides were also synthesized according to Schwertmann and
Cornell (2000) and used as reference materials. A sample of a gold mine tailings was also investigated to evaluate the association of antimony with other elements.

3. RESULTS AND DISCUSSION

A conventional transmission electron microscope consists basically, from the top to the bottom, of an electron source (W filament or a LaB6 crystal), a set of electromagnetic lenses and apertures, and a projecting screen, as illustrated in the schematic shown in Fig. 1. The emitted electrons travel all the way down to the microscope screen, being deflected by the electromagnetic lenses depending on the operation mode – image mode (Fig. 1.a) or diffraction mode (Fig. 1.b).

![Figure 1: Schematics of lenses (double-head arrows) and apertures (black filled rectangles) in a conventional TEM showing the beam path (blue lines) from the filament tip all the way down to the TEM screen (or CCD camera) in bright field image mode (a) and diffraction mode (b). The red and green segments of lines represent the diffracted beam by the specimen (Freitas 2017).](image)

When the electron beam hits the specimen, it is scattered by the atoms and molecules as the electrons travel through the sample. The transmitted electrons and other signals generated by the sample-beam interaction carry various types of information that can be assessed if the microscope is coupled with the proper detectors. Because of that, the thickness of samples that allow electrons travelling through their structure is relevant. It does depend on the electron’s mean free path in each material, but generally speaking, the sample thickness should be <200 nm for TEM analysis. For high resolution TEM and EELS the
specimen should be as thinner as possible (<50 nm). The electron dose is also a point to be aware of since the high-energy electron beam (200 – 300 keV) may damage the sample if it is soft and non-conductive. If this is the case, low electron dose or even cryo-TEM is advisable.

3.1. Transmitted electron imaging

The images generated in a TEM are greyscale. The understanding of the mechanisms of contrast in transmitted electron imaging is very important, hence it allows the interpretation of the observed features in the specimen being imaged. Three mechanisms of contrast will affect the process of image formation: thickness, mass and diffraction contrast. In TEM, electrons travelling through thicker regions of the specimen will be less transmitted and that area will appear darker in the formed image on the screen (Fig. 2). Fig. 2.a shows particles of several phases present in the Oxisol sample dispersed on a thin holey carbon-coated TEM Cu-support grid. The sample is heterogeneous, and so several particles are superimposed and appear darker in the image. Thickness contrast is dominant for larger particles.

3.2. High resolution transmission imaging

Images of periodic dark and bright fringes may be formed at high magnifications by the contribution of diffracted electrons. The periodic fringes observed at the high resolution TEM (HRTEM) image may correspond to the lattice planes of the sample. In a conventional
(non-corrected) HRTEM, the brighter or darker points do not show the actual atomic positions, but atomic arrangement according the crystal structure (Fig. 3.a). Lattice defects or dislocations can also be assessed.

Figure 3: (a) HRTEM image showing an aggregate of As-bearing Al-hematite and Al-goethite nanoparticles found in Oxisol sample. (b) Fast Fourier Transform (FFT) from (a) shows spots corresponding to the lattice fringes seen in (a). The overlaid pairs of spots are lattice fringes of hematite (104) and goethite (600). (c-d) Inverse FFT (IFFT) images of hematite and goethite in the aggregate of nanoparticles. These IFFT images were performed from the overlaid spots shown in (b).

Fig. 3.a shows the HRTEM image of a nanoparticles’ aggregate of Fe-(hydr)oxide found in the Oxisol sample. Nanoparticles of both hematite and goethite were identified in this aggregate by image analysis using the Fast Fourier Transform (FFT) (Fig. 3.b). The FFT of a given image contains all its information but in a space of frequency. If there is any periodic pattern at the original image it will correspond to spots into the FFT. The inverse of the distance from the center of the FFT to a particular spot is the measure of the distance between the periodic lattice fringes observed at the HRTEM image, and so of the crystallographic planes. The lattice fringes’ distances 0.164 nm and 0.277 nm, respectively, correspond to the distances between the planes (104) for hematite, and (600) for goethite. These spots at the FFT were then selected to perform the inverse FFT (IFFT) images shown in Figures 3.c-d, where hematite and goethite nanoparticles in the aggregate were shown.
3.3. Electron diffraction

Diffraction analysis at the TEM can be performed in different ways, which depend on the beam illumination arrangement. The selected area electron diffraction (SAD) measurements are done by illuminating the sample with a parallel beam, and allow diffraction analysis of sample areas > 200 nm of diameter. To assess structural information of smaller areas of the sample, it is necessary to perform convergent-beam electron diffraction (CBED) or nano-beam electron diffraction (NBD), which can be done in few nanometers areas. The basic difference of SAD, CBED and NBD is therefore how narrow is the focused beam used to illuminate the desirable area of the sample. These diffraction techniques may be applied to assess fundamental crystallographic information such as crystal system, Bravais lattice, point and space groups, to study dislocations and defects, to do thickness measurement, and lattice parameters refinement (Morniroli and Steeds 1992; Morniroli and Jacob 2012; Saitoh et al. 2013).

3.4. Spectroscopy

The beam-sample interaction in an electron microscope generates several signals such as Auger, secondary and backscattered electrons, X-rays, and cathodoluminescence. The collection of X-ray, for example, enables to identify the elemental composition. When the electron beam hits the sample, an inner-shell electron of an atom can be knocked out, and an outer-shell electron will fill the vacancy in the inner-shell. In this process, X-ray with characteristic energies are emitted. This is the principle of the EDX spectroscopy (or simply EDS) in a TEM (Fig. 4).

Figure 4: High-angle annular dark field (HAADF) STEM image of an oriented aggregate of Al-hematite nanoparticles. (b-d) EDS maps showing the distribution of Fe, Al and As in the Al-hematite.
The Fig. 4 shows the STEM-EDS maps for Fe, Al and As performed in the hematite nanoparticles’ aggregate. There is no segregation of either Al or As. In this case, the homogenous distribution of As and Al along with Fe suggests they are not present as isolate impurities or forming clusters. Nevertheless, semi-quantification analysis should not be done for light elements (Z < 11), as low fluorescence produce absorption within the sample (Williams and Carter 2009). For light elements, it is better to perform EELS analysis. This technique is based on the energies losses of transmitted electron beam due to the inelastic scattering by the electrons of the specimen. The energy-losses for the ionization edges are characteristic of each element, and can be used for elemental identification, oxidation state measurement, and phase identification (Egerton 2008). Chemical information and elemental distribution across the sample can be obtained by both EDS and EELS analyses as they are complementary techniques. The STEM-EDS and EELS analysis may identify a wide range of elements with spatial resolution that is nearly the probe size (around 2nm for the microscope used in this work). In general, the EDS detection limit is around 1 wt% for thermionic electron sources (W or LaB6), and about 0.1 wt% for field emission gun (FEG) microscopes. The EELS detection limit for heavier elements (10 < Z < 25) is lower than for EDS. However, its sensitivity for light elements may be ten times higher than EDS (Leapman and Hunt 1991). Elemental mapping can also be carried out by STEM-EELS. This technique has been successfully applied in a wide range of studies both in materials and life sciences (Colliex 2017; Leapman 2017). Fig. 5 shows the results of the EELS-SI analysis for a sample on which the interest was to investigate the association of antimony (Sb) with Fe and Al in a tailing from a gold mine.

![Figure 5](image)

Figure 5: (a) Bright field TEM image showing of Fe-(hydr)oxides precipitates (darker particles) on Al-silicates. (b-d) EELS maps for Fe, Sb and Al taken from STEM-EELS-S analysis of the area inside the white rectangle in (a). (e, f) EELS spectra taken from the precipitate indicated by the arrow in (a). The spectrum in (e) shows the Sb N- and Fe M- edges at 31 eV and 54 eV, respectively. The spectrum in (f) shows the O K-edge at 532 eV. (g) EDS taken from the precipitate pointed in (a). The Cu signal arises from the support TEM Cu-grid.

The bright field TEM image (Fig. 5.a) shows Fe-(hydr)oxides precipitates (darker particles) and Al-silicates. The EDS pointed in (a) shows the presence of As, S, Al, Si, Fe and O (Fig. 5.g). The EELS (Fig. 5.f) indicate the presence of Fe-(hydr)oxides by the O K-edge. Combining the results with the elemental mapping for Fe, Al and Sb (Fig. 5.b-d) it was possible to infer that Sb is associated to the Fe-(hydr)oxides and not with the Al-rich ones.
4. FINAL CONSIDERATIONS

The TEM techniques have been successfully applied in a wide range of studies in many fields. In the environmental context, the techniques briefly described here, allowed to identify chemical and mineralogical composition of complex samples. It enabled the fully solid phase characterization with high spatial resolution by combining transmitted electrons image analysis, electron diffraction, EDX and EELS spectrosopies.

5. ACKNOWLEDGMENTS

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6. REFERENCES


Ladeira ACQ, Ciminelli VST. Adsorption and desorption of arsenic on an Oxisol and its constituents. Water Res.2004; 38 (8); 2087-8


Morniroli JP, Ji G, Jacob D. A Systematic Method to Identify the Space Group from PED and CBED Patterns Part I - Theory. Ultramicroscopy 2012; 121; 42–19

Morniroli JP, Steeds JW. Microdiffraction as a Tool for Crystal Structure Identification and Determination. Ultramicroscopy 1992; 45 (2); 219–21

