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CHARACTERIZING CINDER ROCK
WITH THE SCANNING ELECTRON MICROSCOPE

A. W. Casey

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CHARACTERIZING CINDER ROCK WITH THE SCANNING ELECTRON MICROSCOPE

ABSTRACT

We examined friable cinder rock by scanning electron microscopy and energy dispersive x-ray analysis (SEM/ED). Our technique consisted of impregnating the rock with epoxy resin and then locating porosity sites by the presence of epoxy. The resin was identified in the sample by correlating beam damage and elemental analysis by x-ray fluorescence (ED) with a characteristic phase in the SEM image.

Analyses of this type should be useful in interpreting experiments designed to simulate *in situ* retorting.

INTRODUCTION

This work was performed to determine the feasibility of using scanning electron microscopy (SEM) to identify porosity sites in cinder rock. In the particular case of *in situ* retorting,¹ this information can be combined with geological knowledge and knowledge of the history of the burn. A number of SEM operating modes and techniques lend themselves to this kind of analysis.^{2,3} These modes include: secondary electron imaging, energy dispersive x-ray fluorescence (ED) (elements Z >10), x-ray imaging (mapping), and backscatter electron imaging^{4,5} (atomic number contrasting).

EXPERIMENTAL

Approach

Our approach was to fill the pores of a sample of cinder rock with epoxy resin and identify the sites of porosity by locating these resin-filled pores. To do this, the sample was first impregnated and encapsulated with resin. Then the secondary-electron mode on the SEM was used to identify an interesting site. Energy dispersive x-ray fluorescence spectroscopy and beam-damage observations were used to pick out the resin phase.

Sample Preparation

A piece of cinder rock was selected for impregnating and encapsulating with plastic (similar to metallographic mounting). The plastic was Dow Chemical Co., XD7818 (similar to B15 Phenol (A)) cured with Jefferson Chemical Co., T-403 (polyoxy propylene amine).

The specimen and uncured plastic were placed in a vessel that could be evacuated. This vessel was evacuated until outgassing stopped. At this time the containment vessel was back-filled with air to 100 kPa (1 atm) pressure. Upon hardening, the encapsulated specimen was cut in half to expose the cinder rock. A section was selected for metallographic surface grinding and polishing. The flat, polished surface of the specimen was coated with a thin (<50 nm) conductive (carbon) layer to enhance SEM examination.

Apparatus

We used a model EBS-21 SEM made by Material Analysis Corp. This unit has many modifications including an x-ray fluorescence detection system. Also the unit has a large chamber equipped with a universal specimen stage with movements of 15 mm in both the x and y directions, 0- to 90-deg tilt, 360-deg rotation, and z movement from 0 to 50 mm. Other features include a high-resolution capability, a wide range of magnifications ($< 50 \times$ to $> 100\,000 \times$), and variable accelerating voltage from 50 V to plus 30 kV. There are also various operating modes: secondary electron imaging, backscattered electron imaging, stereo pairs, and x-ray fluorescence analysis including mapping.

DISCUSSION

The area selected for examination had to have a known epoxy-resin region so that the characteristics of the ED spectrum of the resin could be established. A large epoxy resin region was found by visual inspection and optical microscopy and indexed. This selection should be made before a conductive coating is applied to the specimen.

The first SEM/ED examination was by the secondary electron operational mode (typical imaging mode) and used to locate an interesting site. This site of the metallographic specimen has five contrasting grey (light to dark) regions. These five regions are identified by flag pointers in Fig. 1.

Fig. 1. SEM image (secondary electron) of the area studied. The flags denote the different regions. Note that regions 1-A and 1-B are similar shades of grey.

Region 1

The indexed epoxy-resin region (1A, bottom of Fig. 1) was subjected to x-ray fluorescence measurements by the spot mode (stationary electron beam) method at 20 kV and approximately 10 nA probe current. We were able to identify chlorine and silicon by intensity (Fig. 2). This suggested that it might be possible to do x-ray mapping (scanning mode of energy dispersive x-ray fluorescence) for chlorine and thereby identify epoxy-resin regions. The mapping was tried and abandoned because the chlorine signals were too weak.

During this analysis we discovered that the spot mode caused electron beam damage to the epoxy resin (Fig. 3). Beam damage subsequently proved to be a good indication of the presence of epoxy resin.

We chose to examine area 1B because it had the same dark grey color as area 1A. This area was carefully examined using a backscattered electron (atomic number contrasting) mode⁵ to get more surface and phase information (metallographically prepared sample). Figure 4 shows the surface of the specimen prior to any x-ray analysis. An ED scan of area 1B showed the same ratio of chlorine to silicon as found in the indexed epoxy-resin region, 1A (Fig. 5).

Also, close examination again revealed electron beam damage to the epoxy resin region (Fig. 6).

The area shown in Fig. 6 was examined by ED using a scan mode at 200×. The elements identified by intensity were Si, Ca, Al, Mg, K, S, Cl, Ti and Fe (see Fig. 7). The elements with higher intensities (Si, Ca, Al, and Mg) were selected for x-ray imaging or mapping (Fig. 8). This was used for comparison to the backscattered image at 200× (Fig. 6). The darker grey regions of Fig. 6 very closely correlate with the dark (absence of rock composition) areas in Fig. 8. From this correlation one could conclude that all of the darker areas of Fig. 6 are epoxy resin.

Other Regions

Region 2 is a crystalline formation with multidirectional filamentous orientation and consists basically of the elements (by intensity) Si, Ca, and Al. We think this material came from the sheathing of a thermocouple (Fig. 9).

Region 3 is another solid-type structure that is basically Si, Al, Ca, K, Mg, and Fe (see Fig. 10).

Fig. 2. X-ray fluorescence spectrum (energy dispersive) of region 1A showing a strong chlorine peak and a weak silicon peak.

Fig. 3. Beam-damaged epoxy resin. Damage was caused by x-ray analysis in the spot mode.

Fig. 4. Electron backscattering images of region 1B prior to x-ray analysis.

Fig. 5. X-ray fluorescence spectrum (ED) of area 1B. The ratio of chlorine to silicon peak intensities is the same as that found in the indexed region (see Fig. 2).

Fig. 6. Electron-beam damaged epoxy resin. This area shown before x-ray analysis in Fig. 4.

Fig. 7. X-ray fluorescence spectrum (ED) of the area shown in Fig. 6.

Fig. 8. X-ray mapping of Mg, Al, Si, and Ca. If we compare the light images with the image in Fig. 6, we can conclude that the dark areas in Fig. 6 are epoxy resin.

Fig. 9. SEM image of region 2. The structure indicates this material came from thermocouple sheathing.

Fig. 10. SEM image of region 3 in backscatter mode. The area at right shows solid rock, while at the left a more porous rock is seen.

Region 4 is a porous-type formation with many identifiable darker areas that correlate with the surface morphology of epoxy resin (Fig. 11). Here again the backscattered electron mode was used to enhance compositional differences.

Region 5 is the lighter grey phase and according to atomic number contrasting techniques should be a higher atomic number. X-ray fluorescence indicated a high concentration of iron in this area (Fig. 12).

CONCLUSIONS

The combination of SEM and ED operating modes clearly identifies surface porosity sites by detecting regions of epoxy resin larger than 20 μm . The choice of SEM/ED operational modes depends on the size and depth of the epoxy region.

Finally, we have the following suggestions for future work:

1. Increase the pressure (up to 68 MPa) during impregnation of the cinder rock. This will improve the technique by filling more inner connecting pores. (By knowing the density of the filler material and the volume used, we can calculate the rock density.)
2. Add labelling compounds to the epoxy resin. Labels could be high Z materials to aid in the microscopy work, radioactive material for autoradiography analysis, or fluorescent compounds for black lamp identification methods.

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Fig. 11. Backscattered-electron image of region 4. This is a porous region with epoxy resin grey tones and surface morphology.

Fig. 12. X-ray mapping of region 5. The light area at the top is rich in iron.

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