Characterization of the Radiation Effect in A Binder by X-Ray Diffraction

Vjera Novosel – Radović, Nikol Radović, Milka Balen and Franjo Šafar

a Željezara Sisak, 44000 Sisak, Croatia
b Faculty of Geodesy, University of Zagreb, 10000 Zagreb, Croatia

* Corresponding author: E-mail: nradovic@geof.hr

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Dedicated to the memory of Professor Ljubo Golić

Abstract

The influence of x-ray radiation on samples of binder (Li₂CO₃, H₃BO₃, Na₂B₄O₇ · 10H₂O) was examined. The components were ground and placed as thin film on the Mylar foil and exposed to beam of primary x-ray on semi-automatic x-ray spectrometer (Au-anode, 20 mA/45 KV) successively for period 1 to 8 hours. Comparative results were observed for x-ray diffraction analysis, scanning electron microscope analysis and sieve analysis.

Keywords: Radiation effect, briquetting conditions, structural changes

1. Introduction

For analysis by X-ray emission spectrometry powder samples are prepared using the melting technique or the briquetting technique. In the case of briquetting a binder is added to the sample. The amount of binder will depend on the nature of the sample and its phase composition. For each type of powder sample the briquetting conditions are determined in advance. The briquetted samples should have a compact, smooth surface as well as good handling resistance. Only samples having positive handling resistance values are measured. Certain samples, however, may exhibit reduced handling resistance values during measurement. In this work handling resistance was measured with a VDM apparatus of own manufacture. Our examination of standard samples of iron ore, sinters, mixture for sinters, and high furnace slag pressed into briquettes with a binder and exposed to X-rays demonstrated diminished wear resistance as well as the appearance of surface cracking and edge sprinkling (Figure 1).

2. Experimental

The effect of exposure to X-rays in briquetted sinter samples was investigated on model samples. The model
samples were prepared with the binders Li$_2$CO$_3$ Merck, and H$_3$BO$_3$ and Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O Kemika. They were ground in a WC attachment of a Spex mixer mill for 30 minutes and placed, as a thin film, on a mylar foil in the sample holder PW 1427/40. Then they were irradiated in a Philips semi – automatic X-ray spectrometer PW 1410/10 (Au anode, 20 mA/ 45 KV) for the duration of one to eight hours.

The irradiated samples were examined by means of X-ray diffraction and scanning electron microscopy, and by sieve analysis. Diffraction patterns were collected at room temperature using a Philips counter diffractometer with monochromatized CoK$_\alpha$ radiation. From those patterns the maximum shift ($I_{\text{max}}$) and full width at half maximum intensity (FWHM) were assessed. The $I_{\text{max}}$ values were determined from the diffraction lines corresponding to dÅ interplanar spacing as follows: 1.39 Å for the Li$_2$CO$_3$ binder, 1.60 Å for H$_3$BO$_3$, and 1.56 Å for Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O. The respective FWHM values were 2.83 Å for Li$_2$CO$_3$, 3.17 Å for H$_3$BO$_3$ and 4.83 Å for Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O. Micrographs of the nonirradiated samples were taken with a scanning electron microscope and microanalyser, a Joel JXA – 50A. Both the irradiated and nonirradiated H$_3$BO$_3$ samples were examined by sieve analysis (DIN system). Samples of the fractions resulting from sieve analysis of the nonirradiated H$_3$BO$_3$ were subsequently irradiated for two hours. After irradiation each fraction was once again subjected to sieve analysis.

3. Results

Results of investigation are presented in figures and in tables. Figures 2 show characteristic sections of diffraction patterns of the Li$_2$CO$_3$, H$_3$BO$_3$, and Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O samples, before and after irradiation: H$_3$BO$_3$ was irradiated for two hours, Li$_2$CO$_3$ and Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O for eight hours.

The number, relative intensity, and shape of diffraction lines changed with the irradiation time. Concurrently, as a result of radiation exposure, changes in the $I_{\text{max}}$ (Figure 3) and FWHM (Figure 4) values were observed.

There was a shift in the $I_{\text{max}}$ values with respect to the initial values: to 0.017 for Li$_2$CO$_3$, to 0.036 for H$_3$BO$_3$, and to 0.137 $^\circ$2$\Theta$ for Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O. The FWHM value for Li$_2$CO$_3$ was 0.017, for H$_3$BO$_3$ 0.036, and for Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O 0.047 $^\circ$2$\Theta$. According to literature those changes were due to grain fragmentation or enlargement, and/or to microstrain. They produced a direct effect on the mechanical properties and microstructure of the material, which in our case was briquette with a binder. Table 1 shows changes in the grain size of the irradiated H$_3$BO$_3$ sample.

After two hours of irradiation the percentage of the 125–90 μm fraction rose from 2.32 to 19.54%, and of the 90–63 μm fraction from 0.56 to 7%. At the same time the 125 μm fraction percentage diminished from 94.95 to 71.97%, and the 63 μm fraction percentage from 2.12 to

![Figure 2](https://example.com/figure2.png)  ![Figure 3](https://example.com/figure3.png)  ![Figure 4](https://example.com/figure4.png)

**Figure 2.** Characteristic part of the X-ray diffraction patterns 1 – Li$_2$CO$_3$ recorded at 25 °C: A – before and B – after irradiation 8 hours, 2 – H$_3$BO$_3$ recorded at 25°C: A – before and B – after irradiation 2 hours, 3 – Na$_2$B$_4$O$_7$ $\cdot$ 10H$_2$O recorded at 25°C: A – before and B – after irradiation 8 hours.

**Figure 3.** Shift values $I_{\text{max}}$ for different binder samples

**Figure 4.** FWHM values for different binder samples
1.41%. Similar effects were observed in other fractions as well,\textsuperscript{10} Figure 5.

Sieve analysis of each of the sample fractions irradiated after separation from the total H\textsubscript{3}BO\textsubscript{3} sample, gives better information about the changes taking place inside the fractions. In addition to the grain sizes pertaining to the basic fraction, other sizes appear in each fraction after irradiation. Scanning electron micrographs of Li\textsubscript{2}CO\textsubscript{3} (Figure 6), H\textsubscript{3}BO\textsubscript{3} (Figure 7), and Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} · 10H\textsubscript{2}O (Figure 8) after two, four or eight hours of irradiation show grain fragmentation of different size and shape.

Increase in the number of smaller size fractions can be accounted for by breaking of the larger grain as a result of irradiation. Scanning electron micrographs of Li\textsubscript{2}CO\textsubscript{3} (Figure 6), H\textsubscript{3}BO\textsubscript{3} (Figure 7), and Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} · 10H\textsubscript{2}O (Figure 8) after two, four or eight hours of irradiation show grain fragmentation of different size and shape.

Table 1. Distribution of grain size fraction of boric acid irradiated by X-rays in function of exposure time

<table>
<thead>
<tr>
<th>Exposure time (h)</th>
<th>Percentage of fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&gt; 125</td>
</tr>
<tr>
<td>0</td>
<td>94.95</td>
</tr>
<tr>
<td>1</td>
<td>65.48</td>
</tr>
<tr>
<td>2</td>
<td>71.97</td>
</tr>
</tbody>
</table>

* mean values of no less than three measurements.

Figure 5. Distribution of grain size fractions determined in fractions separated from H\textsubscript{3}BO\textsubscript{3} sample and irradiated by X-rays after that for 2 h. Irradiation conditions: Au – anode, 20 mA/ 45 KV.

Figure 6. Scanning electron micrographs of Li\textsubscript{2}CO\textsubscript{3} recorded at 25 °C: before and after irradiation: 1 – 0, 2 – 1, 3 – 2 hours. Magnifications 1500 X.

Figure 7. Scanning electron micrographs of H\textsubscript{3}BO\textsubscript{3} recorded at 25 °C: before and after irradiation: 1 – 0, 2 – 1, 3 – 2 hours. Magnifications 15000 X.

Figure 8. Scanning electron micrographs of Na\textsubscript{2}B\textsubscript{4}O\textsubscript{7} · 10H\textsubscript{2}O recorded at 25 °C: before and after irradiation: 1 – 0, 2 – 1, 3 – 4 and 4 – 8 hours. Magnifications 15000 X.
4. Conclusions

Results show that standard samples preset into briquettes with Li₂CO₃, H₃BO₃, and Na₂B₄O₇ ⋅ 10H₂O binders exhibited diminished handling resistance following exposure to X-rays. Depending on duration of exposure X-ray diffraction patterns demonstrated changes in the number, relative intensity, and shape of diffraction lines, as well as a broadening and shift in position, Iₘₐₓ °2Θ. Examination of samples of the fraction resulting from sieve analysis of the nonirradiated H₃BO₃, which were first irradiated for one or two hours and then resubjected to sieve analysis, showed a different radiation effect. As a result of irradiation, in addition to the grain size pertaining to basic fraction, other grain sizes were also present. Grain fragmentation due to irradiation is visible on the micrographs. The amount of large grains increased as did the number of smaller grain sizes. Formation of sharply edged particles, interruption of initial lamellar structure, and appearance of cracks on the grain surface were observed. These radiolytic changes led to structural changes which, in turn, were responsible for diminished handling resistance of standard samples as regards their analytical use in X-ray emission spectrometry, as well as for the limited period of use.

5. References