Scientific paper

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

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Dedicated to the memory of Professor Ljubo Golič

Abstract

The influence of x – ray radiation on samples of binder (Li_2CO_3, H_3BO_3, $Na_2B_4O_7 \cdot 10H_2O$) 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.[1–4] 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 on its phase composition. For each type of powder sample the briquetting conditions are determined in advance[5]. The briquetted samples should have a compact, smooth surface as well as good handling resistance[6]. 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.[7,8] 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).

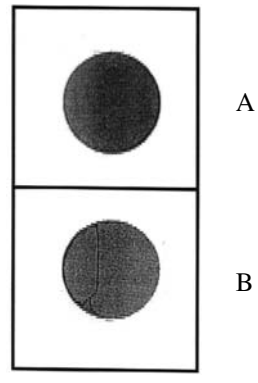

Figure 1. The sample of standard sinters A – before and B – after irradiation 4 hours in the Philips semiautomatic X-ray spectrometer (Au – anode, 20 mA/ 45 KV)

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_2CO_3 Merck, and H_3BO_3 and $Na_2B_4O_7 \cdot 10H_2O$ 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_α radiation. From those patterns the maximum shift (I_{max}) and full width at half maximum intensity (FWHM) were assessed. The I_{max} values were determined from the diffraction lines corresponding to *d*Å interplanar spacing as follows: 1.39 Å for the Li_2CO_3 binder, 1.60 Å for H_3BO_3, and 1.56 Å for $Na_2B_4O_7 \cdot 10H_2O$. The respective FWHM values were 2.83 Å for Li_2CO_3, 3.17 Å for H_3BO_3 and 4.83 Å for $Na_2B_4O_7 \cdot 10H_2O$. Micrographs of the nonirradiated samples were taken with a scanning electron microscope and microanalyser, a Joel JXA – 50A. Both the irradiated and nonirradiated H_3BO_3 samples were examined by sieve analysis (DIN system). Samples of the fractions resulting from sieve analysis of the nonirradiated H_3BO_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_2CO_3, H_3BO_3, and $Na_2B_4O_7 \cdot 10H_2O$ samples, before and after irradiation: H_3BO_3 was irradiated for two hours, Li_2CO_3 and $Na_2B_4O_7 \cdot 10H_2O$ 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_{max} (Figure 3) and FWHM (Figure 4) values were observed.

There was a shift in the I_{max} values with respect to the initial values: to 0.017 for Li_2CO_3, to 0.036 for H_3BO_3, and to 0.137 °2Θ for $Na_2B_4O_7 \cdot 10H_2O$. The FWHM value for Li_2CO_3 was 0.017, for H_3BO_3 0.036, and for $Na_2B_4O_7 \cdot 10H_2O$ 0.047 °2Θ. According to literature[9] 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_3BO_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

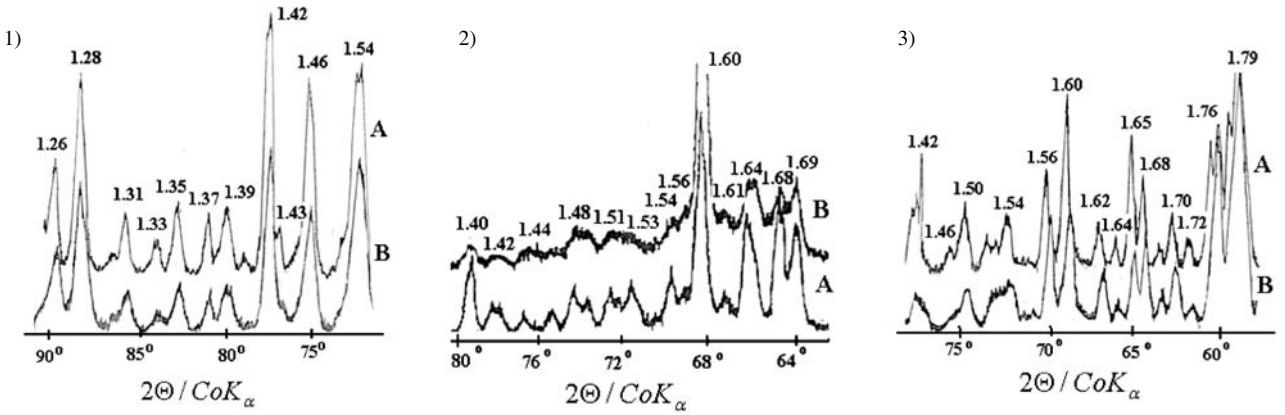

Figure 2. Characteristic part of the X-ray diffraction patterns **1** – Li_2CO_3 recorded at 25 °C: **A** – before and **B** – after irradiation 8 hours, **2** – H_3BO_3 recorded at 25°C: **A** – before and **B** – after irradiation 2 hours, **3** – $Na_2B_4O_7 \cdot 10H_2O$ recorded at 25°C: **A** – before and **B** – after irradiation 8 hours.

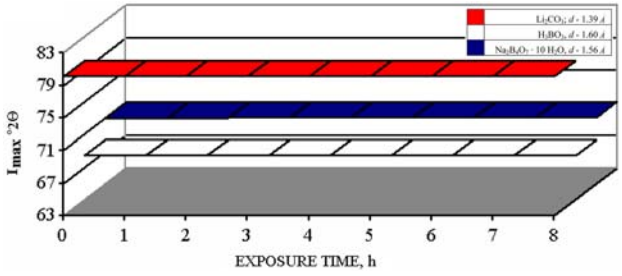

Figure 3. Shift values I_{max} for different binder samples

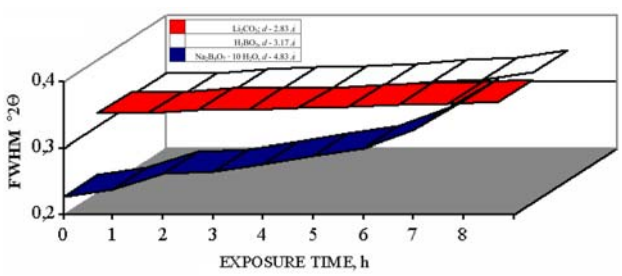

Figure 4. FWHM values for different binder samples

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

Exposure time (h)	Percentage of fractions grain size ranges of fractions (μm)*			
	> 125	125–90	90–63	< 63
0	94.95	2.32	0.56	2.12
1	65.48	29.43	1.57	3.46
2	71.97	19.54	7.00	1.41

* mean values of no less than three measurements.

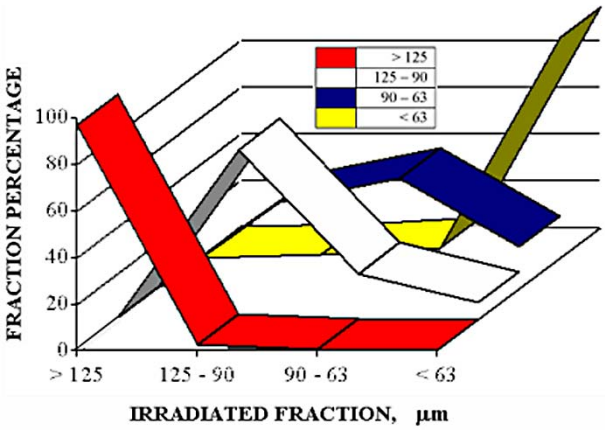

Figure 5. Distribution of grain size fractions determined in fractions separated from H_3BO_3 sample and irradiated by X-rays after that for 2 h. Irradiation condiations: Au – anode, 20 mA/ 45 KV.

1.41%. Similar effects were observed in other fractions as well,[10] Figure 5.

Sieve analysis of each of the sample fractions irradiated after separation from the total H_3BO_3 sample, gives better information about the changes taking place inside the fractions. In addition to the grain sizes apperataining to the basic fraction, other sizes appear in each fraction after irradiation. Scanning electron micrographs of Li_2CO_3 (Figure 6), H_3BO_3 (Figure 7), and $Na_2B_4O_7 \cdot 10H_2O$ (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. Formation of sharply edged particles can be seen in Figure 6, interruption of the initially regular lamellar structure in Figure 7, and appearance of cracks on the grain surface in Figure 8. These radiolytic changes led to structural changes which, in turn, were responsible for diminished handling resistance of standard samples[11] as regards their analytical use in X-ray emission spectrometry, as well as for the limited period of use.

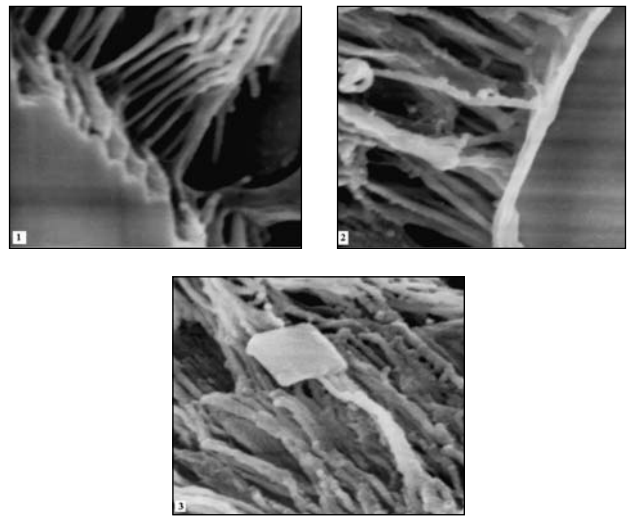

Figure 7. Scanning electron micrographs of H_3BO_3 recorded at 25 °C: before and after irradiation: **1** – 0, **2** – 1, **3** – 2 hours. Magnifications 15000 X.

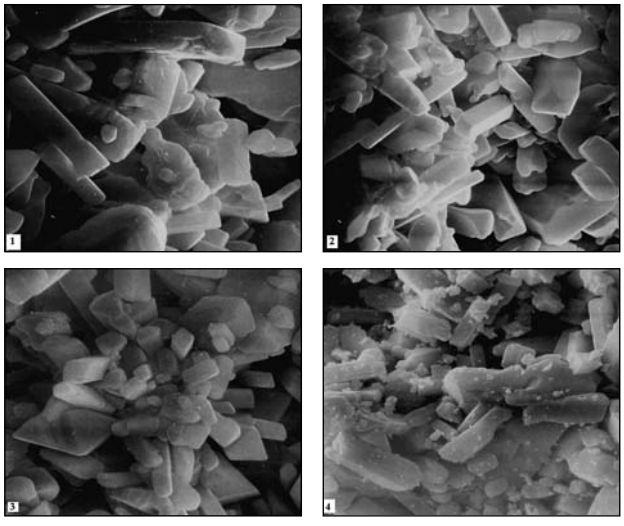

Figure 6. Scanning electron micrographs of Li_2CO_3 recorded at 25 °C: before and after irradiation: **1** – 0, **2** – 1, **3** – 4 and **4** – 8 hours. Magnifications 1500 X.

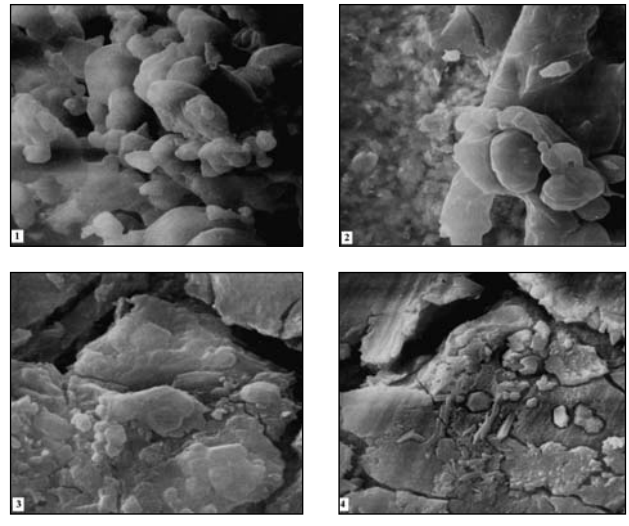

Figure 8. Scanning electron micrographs of $Na_2B_4O_7 \cdot 10H_2O$ recorded at 25 °C: before and after irradiation: **1** – 0, **2** – 1, **3** – 4 and **4** – 8 hours. Magnifications 15000 X.

4. Conclusions

Results show that standard samples preset into briquettes with Li_2CO_3, H_3BO_3, and $Na_2B_4O_7 \cdot 10H_2O$ 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, I_{max} °2Θ. Examination of samples of the fraction resulting from sieve analysis of the nonirradiated H_3BO_3, 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

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Povzetek

Briketi narejeni z Li_2CO_3, H_3BO_3 in $Na_2B_4O_7 \cdot 10H_2O$ kot vezivom so po obsevanju z rentgenskimi žarki izkazovali zmanjšano zmožnost splošne uporabe. Rentgenski posnetki izkazujejo spremembe v številu, relativni intenziteti in obliki difrakcijskih maksimumov. Te radiološke spremembe so predvidoma vplivale na strukturne spremembe in tako posredno vplivale na uporabnost briketov v rentgenski emisijski spektrometriji.