QUANTIFICATION OF FERRITE SPINEL AND HEMATITE IN FLY ASH MAGNETICALLY ENRICHED FRACTIONS

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ABSTRACT

Iron oxide phases, including ferrimagnetic spinel structure phases, are found in all fly ashes and other coal combustion by-products. Magnetically enriched fractions of several fly ashes were used to investigate Rietveld quantitative X-ray diffraction (RQXRD) of the iron oxide phases in fly ash. A comparison between “magnetite” (ferrite spinel) to hematite ratios obtained by RQXRD with those obtained by isothermal remnant magnetization was made.

INTRODUCTION

Coal combustion by-products (CCBs) are the wide variety of solids resulting from burning coal and scrubbing flue gases to lower sulfur oxides emissions. All CCBs contain one or more iron oxide phases [1,2]. One of the challenges in analyzing these materials is knowing and modeling the composition of the phase usually identified as magnetite. Some ashes contain almost pure spinel structure magnetite, FeFe2O4 or Fe3O4, while others show substantial levels of substitution by Mg2+, Al3+, Ti4+, Ni2+, and Cr3+ on the Fe2+ and Fe3+ sites [3]. Because of these substitutions, the phase is often called by a more general name, ferrite spinel, as suggested by McCarthy et al. [3]. Quantitative X-ray diffraction (QXRD) analysis of fly ash, including magnetite or ferrite spinel phases, by the Reference Intensity Ratio method was described by McCarthy et al. [2,4]. This paper deals with QXRD of the magnetic oxides in two fly ashes by the Rietveld method [5], and with application of the results to compare “magnetite” to hematite ratios determined by XRD with ratios determined by magnetic measurements.

The fly ashes used in this study were collected at a coal-burning power plant in Kentucky by the United States Geological Survey (USGS) [6]. The ashes were separated into magnetically enriched and depleted samples.

The ferrite spinel phase is only a minor component of fly ashes, typically only 1-3 wt% and only rarely exceeding 5 wt% [2,4], so the availability of the magnetically enriched fractions enabled RQXRD on samples with abundant ferrite spinel. The insights gained from modeling the ferrite spinels in these ashes will be useful in future studies of fly ashes and other CCBs.

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EXPERIMENTAL

The magnetically enriched fly ash fractions [6] were obtained by passing 5-10g of size-fractionated fly ash suspended in distilled water through a plastic vessel containing a magnet. The water containing the fly ash was circulated through the vessel for 30 minutes using a peristaltic pump. The water and remaining fly ash were removed and the magnetically enriched fraction was washed from the vessel with distilled water, followed by two additional hand separations. The resulting material was washed with acetone and dried to give the magnetically enriched fraction. The enrichment method did not permit monitoring the masses of fractions, so the amount of iron oxides in the original bulk sample could not be determined.

Data were collected using a Philips X'Pert Multi-purpose Diffractometer (MPD) employing a long line focus Cu X-ray tube, divergence and anti-scatter slits fixed at 1°, a receiving slit (0.2mm), diffracted and incident beam Soller slits (0.04rad), a curved graphite diffracted beam monochromator, and a sealed proportional counter. Generator settings used were 45kV and 30mA.

XRD specimens were slurry mounts on zero-background quartz slides. To explore the potential accuracy of the method, standard mixtures with known weight percentages of the target phases were prepared for quantitative analysis by side drifting into an aluminum well mount.

The structure data required for the Rietveld method were obtained from the CCB Analysis Web site [7] as described previously [8,9]. The Rietveld code used was the publicly available DOE package, GSAS [10]. The general RQXRD analysis protocol has been described previously [9].

RESULTS AND DISCUSSION

Modeling of the Iron Oxide Phases

The peak profiles for the iron oxide phases hematite (Fe₂O₃) and magnetite in the magnetically enriched fractions of fly ash were examined (Figs. 1 and 2). The profile of hematite is indicative of a single phase. The high angle "shoulder" on the ferrite spinel peak profile (Fig. 2), however, indicates that either: (a) multiple spinel phases are present, or (b) one or more zoned solid solutions are present. Although the latter cannot be ruled out, the former was considered to be more likely. Thus, the magnetite/ferrite spinel was modeled with two spinel structure phases: pure magnetite, which has a larger unit cell parameter consistent with the dominant portion of the profile, and a hercynite (FeAl₂O₄)-substituted magnetite which would have a smaller cell parameter (the ionic radius of Al³⁺ is smaller than that of Fe³⁺) consistent with the higher angle portion of the profile. An approximately 50:50 magnetite-hercynite solid solution was suggested from a simple Vegard’s law relationship between the end member phases. Harrison et al. [11] reported that the aluminum substitution in magnetite would be predominately on the octahedral site, and thus this site was chosen for the 0.50 Fe:0.50 Al fixed site occupancy. For a first attempt, the magnetically enriched fractions were quantitated with a model including only pure hematite and magnetite. This yielded an unsatisfactory result with significant residual intensity in the difference plot, as shown on the bottom of Fig. 3. The top of Fig. 3 shows the improved fit obtained from refining both magnetite and the magnetite-hercynite ferrite spinel phase.
Figure 1. Overlay of the (012) 24.2º peak of hematite from several magnetically enriched fractions of a Class F fly ash.

Figure 2. Overlay of the (220) 30.2º peak of ferrite spinel in the magnetically enriched fractions.

### Determination of the Ratio of Ferrite Spinel to Hematite

The ratio of magnetite/ferrite spinel to hematite for the magnetically enriched fractions was of interest to the USGS. Prior to the determination of these ratios in the USGS fly ash samples, the refinement procedure and the potential accuracy of the RQXRD analyses were investigated using a set of standard mixtures of the target phases. The experiments included RQXRD of just magnetite and hematite, and of magnetite, hematite, quartz, and maghemite ($\gamma$-Fe$_2$O$_3$). A detailed report of all experiments has been given by Winburn [12].

Identification of maghemite along with magnetite in fly ash is a common computer search/match result. Maghemite, a tetragonal phase based on a spinel superlattice structure, has a powder
pattern almost identical to that of magnetite. Whether maghemite is actually present, or its identification is just a result of peak coincidences with magnetite, is not known. In a fly ash, all of the strong peaks of maghemite overlap with magnetite, and when quartz and hematite are also present (as is the case with most CCB materials), even the weak superlattice peaks are masked by other phases. Because maghemite is also ferrimagnetic (it is the “iron oxide” of magnetic tapes and disks) several experiments included this phase among the reference mixtures.

Results for a representative standard mixture are shown in Table 1. For determination of the ratio of ferrite spinel to hematite, a refinement of just the cubic magnetite and hematite, in the presence of impurity quartz, yielded ratios with an accuracy (relative error) within ±10% of the known values. The inclusion of maghemite as a minor phase (5% or less) in several mixtures led to satisfactory refinements, but when mixtures having more maghemite and less magnetite were studied, the Rietveld refinements were either inaccurate (more than 100% relative error) or the refinement did not converge. Thus, maghemite has not been included in the RQXRD model for fly ash ferrite spinel phases. The question of whether maghemite is actually present in fly ash was not able to be answered by these experiments.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Reference</th>
<th>RQXRD</th>
<th>Reference Ratio</th>
<th>RQXRD Ratio</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>51.7</td>
<td>51.8</td>
<td>1.00</td>
<td>1.00</td>
<td>0%</td>
</tr>
<tr>
<td>Hematite</td>
<td>20.1</td>
<td>21.7</td>
<td>2.6</td>
<td>2.4</td>
<td>7%</td>
</tr>
<tr>
<td>Quartz</td>
<td>10.1</td>
<td>10.8</td>
<td>1.00</td>
<td>1.00</td>
<td>0%</td>
</tr>
</tbody>
</table>

RQXRD, with “magnetite” reported as the sum of magnetite + 50:50 magnetite-hercynite, was applied to the magnetically enriched fractions of the Class F fly ashes provided by the USGS. The ratios obtained were compared against the S values reported by Cathcart et al. [6]. The S value is the ratio of the isothermal remnant magnetization (IRM) of the sample obtained by applying a backfield induction of 0.3T and a forward induction of 1.2T. The magnetite saturates below 0.3T, so this is a direct indication of the amount of magnetite. The difference in the IRM between 0.3T and 1.2T is a measure of the amount of hematite present although, due to the large differences in magnetization of the two species, a direct measure of the amount of hematite is not possible. Also, due to the fact of the large difference in the magnetizations of hematite and magnetite, a high proportion of hematite will only affect the S value slightly. An S value of 1.0 indicates that only magnetite is present, while a value of 0.9 indicates that a significant amount of hematite is present [6].

A plot of the calculated ratios of ferrite spinel to hematite vs. the S value obtained at the USGS is shown in Figure 4. The data indicate some trend in the relationship between the calculated ratios and the experimental S values, showing a sharp decrease in the ratio as the S value drops below 0.9. It should be noted that the Al for Fe substitution in the ferrite spinel (magnetite-hercynite) phase will produce a smaller magnetic moment compared to pure magnetite, and may account for why the two methods give somewhat different results.
Figure 3. RQXRD plot of a magnetically enriched fraction of fly ash using magnetite and a magnetite-hercynite solid solution phase to model the spinel peaks (top), and using only magnetite to model the spinel peaks (bottom).

Figure 4. Comparison of calculated ferrite spinel to hematite ratios for magnetically enriched fractions of fly ash to the S value.
CONCLUSIONS

Magnetically enriched fly ash fractions containing abundant ferrite spinel have been used to develop improved Rietveld quantitative analysis models. For the fly ashes studied here, it was shown that the phase commonly identified in CCB materials as “magnetite” could be modeled as a mixture of spinel structure phases, at least one of which had significant Al for Fe substitution.

Rietveld quantitative X-ray diffraction analysis of standard mixtures was used to establish that an accuracy well within ±10% of the known amounts of magnetite, hematite and quartz was possible. When significant amounts of maghemite were added to the mixtures, accurate RQXRD analyses were not possible, or the Rietveld refinements would not converge.

In magnetically-enriched fly ash fractions, comparison of “magnetite” to hematite ratios obtained by RQXRD and by isothermal remnant magnetization showed a moderately good correlation.

REFERENCES

[7] The CCB Analysis Web Site can be found at http://qxrd.chem.ndsu.nodak.edu/ccbs/.