

X-RAY CHARACTERIZATION OF TIRE DERIVED PARTICLES RESULTING FROM DIFFERENT SOLVENTS

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INTRODUCTION

Currently, 200 million scrap tires are being annually stockpiled, landfilled, or illegally dumped, with ca. 50 million scrap tires being recycled in a variety of ways. The current disposal methods are causing numerous short-term environmental problems. Whole tires occupy large amounts of space and may "float" or rise to the top of landfills, causing puncturing of the landfill cover. In an attempt to prevent floating, many landfills require that the scrap tires be shredded, a process which is energy intensive and wasteful. Scrap tire stock piles produce large health risks by providing a place for rodents and mosquitos to breed -- aiding in the spread of diseases.¹ Large stockpile fires have also broken out in major cities in Florida, Texas, Virginia, and Washington. These fires are long lasting and produce unwanted smoke into the environment.² For many reasons, the recycling of scrap tires is desirable.

Current attempts to upgrade the hydrocarbons in the scrap tires to produce oils and carbon materials have met with limited success.³

Scrap tires represent a "renewable" source for feedstock for chemicals and for energy, containing $3 \cdot 10^5$ BTU's per tire and high abundances of carbon and hydrogen.

Scrap tires also contain several inorganics which are impregnated into the rubbery portion and iron (with a brass surface) from their steel belts. These inorganics are likely to hinder the recycling of the rubbery portion of the tires.⁴ Their removal is necessary because when combusted in a conventional boiler, the inorganic will cause air pollution and/or boiler scale build up as well as interfering with various catalytic processes.

Removal of the inorganics is the subject of this research.

EXPERIMENTAL

Whole tires were cut into 1 inch by 1 inch squares. These tire chunks were then treated with different liquids (n-methyl pyrrolidinone, nitric acid, 50% hydrogen peroxide, and sulfuric acid) by placing the tire chunks in the liquids and stirring at ambient conditions. A tire derived particle (TDP) was then recovered by filtration. After drying, the particles were placed in plastic cups, covered with a thin mylar film, and placed in the sample chamber of our x-ray spectrometer for analysis.

Our x-ray protocol involved collecting intensity at increments of $\Delta 2\theta = 0.025^\circ$ over the range from $2\theta = 10.00^\circ$ to $2\theta = 110.00^\circ$ using a sample spinner.

X-ray fluorescence spectroscopy (XRF) has been an established research tool for at least seventy-five years in the area of elemental analysis.⁵ Wavelength dispersive XRF has been used in this project to monitor the removal of the inorganic species noted above by the several processes we have developed. For each WDXRF spectrum, the choice of the monochromator used to disperse the secondary X rays emitted by the analyte element(s) in the sample and the detector used to measure the secondary X rays are important. For the

WDXRF spectra reported herein, a graphite crystal monochromator ($d = 3.38 \text{ \AA}$) was used to disperse the secondary X rays emitted by the various analytes in the samples. Both a gas proportional counter (gpc) and a scintillation counter (sc) were used to detect and collect the secondary X rays. The former has a high efficiency for collecting "softer" X rays ($\lambda > 1.25 \text{ \AA}$), while the latter has a high efficiency for collecting hard X rays ($\lambda < 1.25 \text{ \AA}$).

Wavelength dispersive x-ray fluorescence spectroscopy was used to measure the abundances of the inorganic species in the tire before processing and to analyze the removal efficiency of the different liquids for these inorganics.

RESULTS AND DISCUSSION

The resulting TDP's had surface areas in 0.1-2.0 mm^2 range.

ANALYSIS OF THE TIRE CHUNKS. The wavelength dispersive XRF spectrum (using Cr radiation and the gas proportional counter) of an untreated tire chunk is shown in Figure 1. The spectrum contains peaks due to zinc ($\lambda K_{\alpha} = 1.436 \text{ \AA}$), calcium ($\lambda K_{\alpha} = 3.359 \text{ \AA}$), and sulfur ($\lambda K_{\alpha} = 5.373 \text{ \AA}$). The chromium peak ($\lambda = 2.290 \text{ \AA}$) in the WDXRF spectrum is due to the use of chromium as the exciting radiation (tube) for the experiments. Chromium produces "soft" X rays which do not penetrate deeply into the rubbery portion of the scrap tire. Consequently, the x-ray peak due to iron ($\lambda K_{\alpha} = 1.937 \text{ \AA}$) is barely discernible in the spectrum.

Shown in Figure 2 is the WDXRF spectrum of the same tire chunk using a scintillation counter rather than a gas proportional counter for x-ray detection and a molybdenum ($\lambda K_{\alpha} = 0.711 \text{ \AA}$) radiation source. A small peak due to bromine ($\lambda K_{\alpha} = 1.041 \text{ \AA}$) is clearly discernible, along with the Mo peak. There is, of course, no chromium peak in this spectrum.

When the steel belts were removed from the rubbery section of the tire, ground to a powder, and then submitted to our XRF analysis, the peaks due to iron, copper and zinc are clearly discernible.

TREATMENT WITH THE PROCESS LIQUIDS. The four liquids had different effects on the tire chunks. The n-methyl pyrrolidinone is absorbed into the tire chunk, causing the rubbery portion of the tire to swell. NMP cleaves the adhesion between the rubbery portion of the tire and the steel belts, while the tire chunk becomes very brittle and easily grindable. It proved difficult to recover the NMP from the tire chunks.

Concentrated nitric acid degrades the tire chunk into particles and dissolves the steel belts. The WDXRF spectrum of the resulting TDP is shown in Figure 3. Comparison of the WDXRF spectra of the untreated tire to that of the TDP indicates that the zinc, calcium, and sulfur abundances have been drastically reduced in the TDP by the nitric acid treatment at ambient conditions. Lengthening the time of treatment results in complete removal of the unwanted inorganics.

Figure 4 shows the WDXRF spectrum of the residue produced by evaporating the nitric acid filtrate to dryness. The characteristic peaks due to the metal species are provided in this spectrum, verifying the absence of the unwanted inorganics in the TDP. The large iron peak is due to the fact that the nitric acid dissolves the steel belts.

Comparison of the intensities of the zinc peaks in Figures 1, 3, and 4 indicates that the mass balance for zinc in these three samples is not well established and/or that the enhancement/absorption effects for the Zn peaks cannot be ignored in these samples.

Treatment with 50% hydrogen peroxide at ambient conditions does not degrade the tire chunks nearly as rapidly as does the nitric acid treatment. This treatment also extracts the inorganics, which are subsequently found in the residue evaporated from the filtrate. This method also attacks the steel belts, as evidenced by the large iron peaks in the WDXRF of the residue from the evaporate.

Concentrated sulfuric acid degrades the tire chunks almost as well as the nitric acid at ambient conditions but does not dissolve the steel belts. The steel belts may then be removed easily (and essentially in tact) from the rubbery portion of the tire and collected on the stir bar. Comparison of the WDXRF intensities indicates that the sulfuric acid did not remove the zinc, calcium, or sulfur at ambient conditions.

A summary of current results is presented in Table I. Additional results will be discussed.

CONCLUSIONS

Tires chunks may be treated at ambient conditions with different liquids, producing different effects. The unwanted inorganics can be extracted from the tire chunks, leaving a TDP with a high carbon and hydrogen content and a greatly reduced surface area. Wavelength dispersive x-ray fluorescence spectroscopy may be used to monitor the reduction in abundances of each of the unwanted inorganics. Altering the conditions of the WDXRF experiment provides different information about the distribution of inorganics in the tire chunk and the TDP's.

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TABLE I. EFFECTS OF LIQUIDS OF SCRAP TIRE PARAMETERS.

LIQUID USED	INORGANIC REMOVAL			FATE OF STEEL BELT ADHESIONS	CONDITION OF LIQUID
	Zn	Ca	S		
NMP	no effect			cleaved	absorbed into rubber
nitric acid	E	E	E	dissolved	recyclable
sulfuric acid	no effect			cleaved	recyclable
hydrogen peroxide	E	E	E	dissolved	recyclable

E Extracted by the liquid.

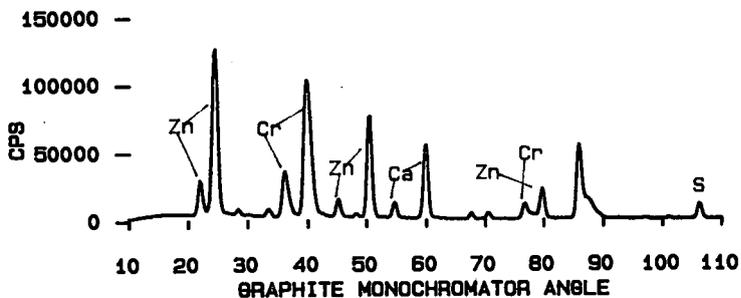


FIGURE 1. WDXRF SPECTRUM OF UNTREATED TIRE CHUNKS; Cr/GPC.

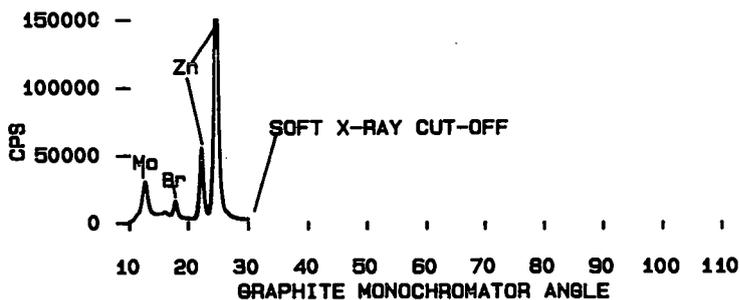


FIGURE 2. WDXRF SPECTRUM OF UNTREATED TIRE CHUNK; Mo/SC.

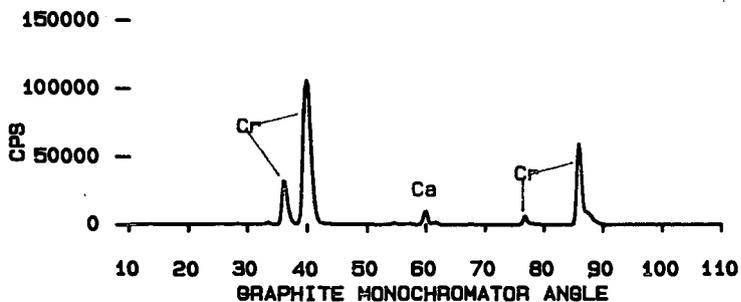


FIGURE 3. WDXRF SPECTRUM OF TDP FROM THE NITRIC ACID TREATMENT; Cr/GPC.

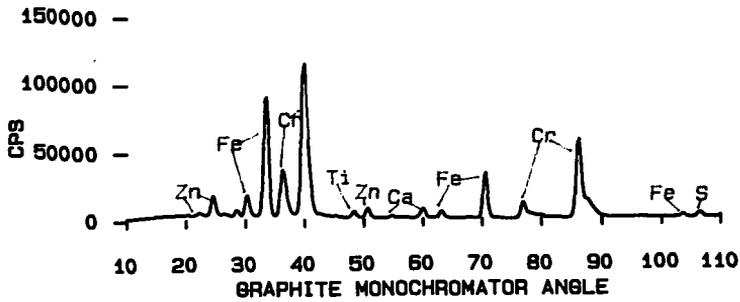


FIGURE 4. WDXRF SPECTRUM OF RESIDUE FROM NITRIC ACID TREATMENT; Cr/GPC.

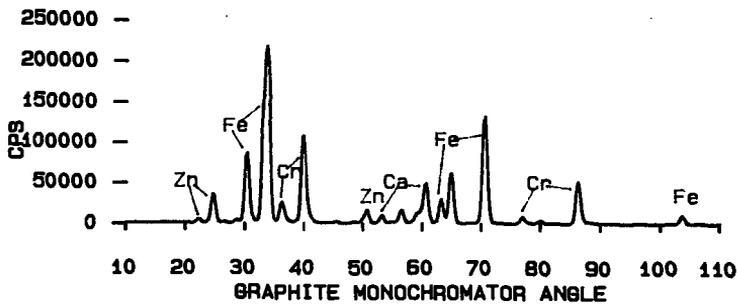


FIGURE 5. WDXRF SPECTRUM OF THE FILTRATE RESIDUE FROM THE 50% HYDROGEN PEROXIDE TREATMENT; Cr/GPC.