McCRONE ASSOCIATES, INC.

Environmental Monitoring During Decommissioning of a CNT Manufacturing Facility Using Polarized Light Microscopy and FE-SEM

E.F. Schumacher, S.F. Stoeffler, C.S. Schwandt, K.J. Diebold • McCrone Associates, Inc., Westmont, IL

Introduction

Commercial scale manufacturing of carbon nanotubes (CNTs) and their incorporation into a variety of materials are rapidly on the rise. Concerns about industrial hygiene, consumer safety and environmental impact accompany the proliferation of CNTs and other nanoscale materials in commonly used products and in construction materials. Methods for confirming, and ideally, quantifying presence of CNTs in the workplace and the larger environment are needed so that exposure can be measured and regulations put in place to protect workers and consumers who come into contact with these materials [1].

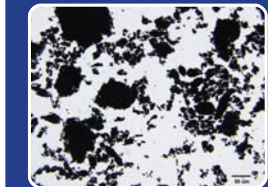
Due to their small size, CNTs are typically identified using a high resolution characterization technique such as transmission electron microscopy (TEM) or field emission scanning electron microscopy (FE-SEM). However, because of the time required to representatively analyze samples at the high magnifications required for CNT identification, such techniques are not well suited for rapid screening of large amounts of material, especially for samples consisting of mixtures of particulate typically found in industrial and environmental collections. Presence of background particulate can also preclude the use of fingerprint or bulk techniques such as Raman spectroscopy to identify CNTs, or elemental analysis for identification of CNT metal catalyst particles in a mixed particulate sample.

Four studies were carried out for an industrial hygiene consulting company whose client, a commercial CNT producer, was decommissioning a CNT manufacturing facility. Before the decommissioning process began, a baseline study was done to qualitatively map presence of CNTs throughout the building. Subsequent studies monitored cleanliness and worker exposure during removal of the CNT manufacturing equipment and final cleaning of the facility. Fast turnaround was required to ensure that the contract workers doing the cleaning would not be idle while waiting for results to determine whether a second round of cleaning was required for each room tested. Scheduling for mold remediation being done concurrently during the final cleanup also depended upon provision of results within a few days.

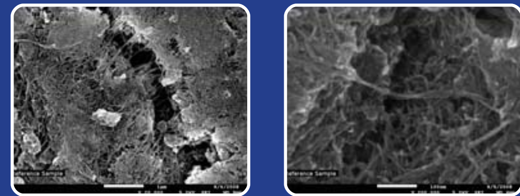
[1] A.D. Maynard et al., Journal of Nanoparticle Research. 9 (2007) 85-92

Characterization of CNT Reference Material

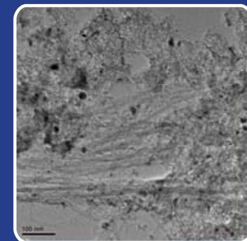
A reference sample of the producer's CNT material was characterized using polarized light microscopy (PLM), FE-SEM and TEM. PLM showed the CNT aggregates to have a characteristic, somewhat fuzzy appearance. Particulate collected on wipes and air filters during the studies was compared to the reference material.



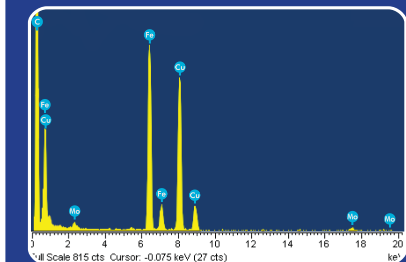
PLM image of CNT reference sample, 200X magnification



SEM secondary electron images of CNT reference sample (JEOL JSM-7500 FE-SEM)



TEM bright field image of CNT reference sample. (JEOL JEM-3010 300kV TEM)



TEM EDS spectrum of Fe/Mo catalyst particles in the CNT reference sample dispersed on a copper grid. Iron from a variety of sources is commonly found in particulate sampled from industrial environments; the composition of the catalyst particles did not provide a unique chemical fingerprint for the CNT reference material. This precluded use of a bulk technique such as ICP for trace elemental analysis to confirm presence of CNTs in mixed particulate samples.

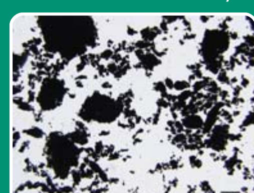
Summary of Methodology

PLM examination and isolation of fine black particulate with some degree of similarity to reference → Cleanroom isolation of particulate from slides or wipes for SEM/TEM → FE-SEM to confirm presence of CNT morphology → Possible follow-up with TEM

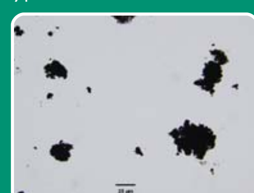
Samples collected from the manufacturing site were acquired in two ways. Wipe samples were collected by placing an everted plastic bag with a zip closure over the hand and wiping a surface. The bag was turned right-side-out as it was removed from the hand, after which it was sealed and labeled. Air filter samples consisted of 25mm diameter polycarbonate filters sealed in conductive cassettes.

The wipes and filters were examined visually and with a stereomicroscope to determine particle loadings. Sections supporting black particulate were removed and mounted on glass slides for PLM examination. Larger aggregates of black particulate were directly transferred to slides using a fine tungsten needle. Particulate was temporarily mounted in nonane for PLM examination and then allowed to dry to facilitate removal and transfer to SEM substrates. PLM images were acquired when black particulate appeared similar to the CNT reference material, as shown below. Black particulate was classed as showing low or possible similarity to the reference, and general characteristics such as the sample loading or the presence of other particulate types were noted.

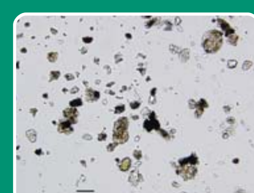
Low similarity to reference



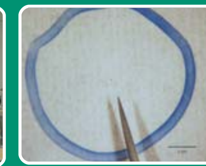
CNT reference material



Possible similarity to reference



Typical industrial particulate



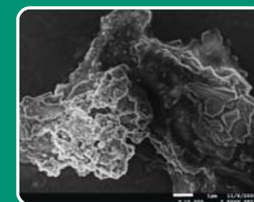
Area containing particulate circled on glass slide

Particulate viewed at higher magnification

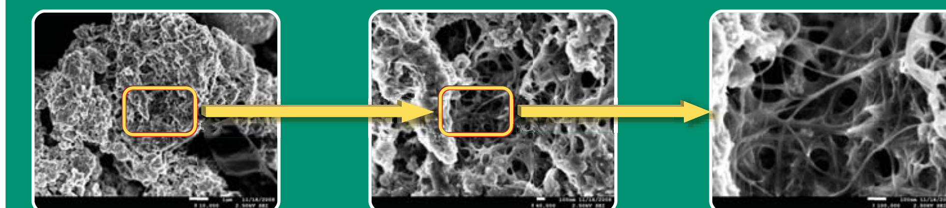
Transfer to SEM substrate

A light microscopist working in an ISO CL5 cleanroom examined the black particulate previously isolated on glass slides, and representatively transferred material to precise locations on scribed substrates for FE-SEM examination. Material was also sampled directly from heavily loaded wipes and filters. When TEM analysis was required, a small amount of particulate was dispersed in 2-propanol, a drop of which was allowed to dry on a holey carbon-coated copper grid.

FE-SEM secondary electron image of particulate from sample in which CNTs were not found (right), and image of an aggregate in which presence of CNTs was indicated (below, left).



Higher magnification images (below, center and right) confirm presence of CNTs. The carbon nanotubes were typically found in compacted aggregates of mixed particulate. They were quickly identified in some samples, but more extensive examination was required to find them in others, giving a qualitative comparison of CNT loadings between samples.



Results were summarized in tables appended to full reports of methodology and findings.

Date Requested	Filter ID	PLM Observations	Image	SEM ID of Nanotubes	Images
16 October	A	Moderately heavy load, abundant black/dark particulate, some possibly similar to reference.	Yes	No	3
	B	Light/moderate load, some black/dark specks, possibly similar to reference	Yes	Yes	6
3 November	C	Light/moderate load, mostly light in color. Limited amount of black/dark particulate, no similarity to reference.	No		
	D	Moderate load, abundant black/dark particulate, possibly similar to reference	Yes	Yes	9
	E	Light load, mostly light in color. Limited amount of black/dark particulate, no similarity to reference	No		
	F	Moderate/heavy load, abundant black/dark particulate, possibly similar to reference	Yes	Yes	9

Conclusion

Though not typically considered as a method for identification of nanomaterials, PLM proved valuable to rapidly screen for presence of CNTs in a large number of samples consisting of mixed particulate. In the course of four studies carried out for an industrial hygiene consulting company, 83 wipes and 30 air filters were examined. PLM indicated possible presence of CNTs in 60 out of 113 samples. Using FE-SEM and TEM, presence of CNTs was confirmed in 34 out of the 60 samples. Repeat sampling and SEM analysis of several wipes gave consistent results, heightening confidence in the screening methodology. Monitoring allowed for assessment of facility decontamination and levels of possible worker exposure to CNTs during the cleanup process.

Acknowledgements

We would like to thank ICU Environmental, Health and Safety – a Total Safety Company, and Unidym, Inc. for granting their permission to present these results. We would also like to thank members of the McCrone Associates staff for their assistance in preparing this presentation. This work was first presented at Microscopy & Microanalysis 2011, proceedings published by Cambridge University Press.