



## AN ABSTRACT OF THE THESIS OF

Mohammed Yousef Alrashed for the Master of Science degree in Chemistry presented on Friday January 22, 2016 5:00 PM SH 217.

Title: The Use of Coal Fly Ash as a Catalyst Support in the Fabrication of Carbon Nanotubes.  
Thesis Chair: Dr. Eric Trump. Abstract: Carbon nanotubes (CNTs) can be used for many different purposes. An effective process of manufacturing CNTs is through fabrication in a chemical vapor deposition (CVD) apparatus from ethylene through the use of a metal catalyst and an expensive porous silica support. The goal of this project is to substitute a much less expensive material. Fly ash is described as the unburned particulate material that is derived from the combustion of fossil fuels. It is a useful material that can be used to manufacture CNTs because it is a waste product and, therefore, it is not expensive. Oil fly ash is a waste product in Saudi Arabia and has been investigated as a very inexpensive catalyst support for growing CNTs. In the United States, the petroleum refining process does not generate fly ash. Therefore, fly ash from coal combustion was investigated. Class C fly ash, which has not previously been investigated, was collected from Jeffrey Energy Center near St. Mary, Kansas, and was prepared at different weight percents of iron and at different calcination temperatures. Raman spectroscopy showed that coal fly ash is mainly composed of silica and alumina. The neutron activation analysis showed that there were other elements present in the Class C fly ash. The process used produced small nanotube growth as indicated by scanning electron microscopy. Proposed future research to examine the pore sizes of the fly ash through the use of electron microscopy could determine the best size to successfully manufacture CNTs. Research could be conducted to see whether Class F fly ash could be successfully used in the manufacturing process.

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(Thesis Advisor Signature)

Keywords: Carbon Nanotubes - Fly Ash- Catalyst

THE USE OF COAL FLY ASH AS A CATALYST SUPPORT IN THE FABRICATION OF  
CARBON NANOTUBES

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A Thesis

Presented to

The Department of Physical Sciences

EMPORIA STATE UNIVERSITY

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In Partial Fulfillment

of the Requirements for the Degree

Master of Physical Science – Chemistry Concentration

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by

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May 2016

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## **Acknowledgments**

Thanks are due to the Emporia State University Department of Physical Sciences; Eric L. Trump, Ph.D., Associate Professor at Emporia State University; Placidus B. Amama, Ph.D., Assistant Professor, Department of Chemical Engineering, and graduate student Haider Al Khelaifi at Kansas State University; Jeffrey A. Geuther, Ph.D., Nuclear Reactor Facilities Manager at Kansas State University; and Prem S.Thapa, Ph.D., at the University of Kansas, Microscopy and Analytical Imaging Lab, KU Research. I would like to thank my family and friends. Thank you, my father and mother, I can always count on you not to over think something. Finally, I want to say thank you to my wife, Fatima, and my fraternity who all supported me.

## TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS.....	iii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	vi
LIST OF FIGURES .....	vii
<u>Chapter 1</u>	
INTRODUCTION.....	1
A- Historical Background.....	2
B- Making Use of Coal Waste.....	6
C- Class C and Class F Fly Ash.....	8
D- The CVD Process.....	11
<u>Chapter 2</u>	
MATERIALS AND METHODS .....	14
A- Materials.....	14
B- Instruments.....	14
C- Experimental Section.....	18
1- Sample Preparation .....	18
2- Heating the Sample.....	19
D- The CVD Process Sampling.....	23
<u>Chapter 3</u>	
RESULTS AND DISCUSSION .....	26

A- Neutron Activation Analysis (NAA).....	26
B- Scanning Electron Microscopy (SEM).....	29
C- Raman Spectroscopy.....	32
<u>Chapter 4</u>	
CONCLUSION.....	35
<u>Chapter 5</u>	
REFERENCES .....	36

## List of Tables

<b>TABLE 1.</b>	Page
Chemical Analysis of Fly Ash From Three Different Power Plants in Russia.....	10
<b>TABLE 2.</b>	
Elements Identified by Neutron Activation Analysis.....	27
<b>TABLE 3.</b>	
Elements detected by NAA. Note the significant amounts of cerium and zirconium.....	28



## List of Figures

<b>Figure 1.</b>	Page
SEM images of CNTs grown, at 650 °C.....	3
<b>Figure 2a.</b>	
SEM images of different magnifications for the first sample of fly ash after heating at 750 °C.....	3
<b>Figure 2b.</b>	
SEM images of different magnifications for the second sample of fly ash after heating at 750 °C.....	4
<b>Figure 3.</b>	
SEM images of different magnifications, well-defined CNFs, apparently formed by tip growth, were clearly visible as seen by the red-colored circles, at 700 °C .....	4
<b>Figure 4.</b>	
SEM images of carbon nanotubes grown (a) with methane at 1170 K and (b) with ethanol at 1070 K .....	5
<b>Figure 5.</b>	
SEM images of MWNTs and CNFs covering the surface of 5 wt % Fe loaded fly ash.....	6
<b>Figure 6.</b>	
Showing differences of fly ash and colors in the sample.....	8

**Figure 7.**  
Class F and Class C fly ash, showing components of fly ash and other elements present  
.....9

**Figure 8.**  
Class F and Class C fly ash, showing chemical classification .....9

**Figure 9.**  
Class F and Class C fly ash, showing differences in density .....10

**Figure 10.**  
The Triga Mark II Uranium Fission Reactor at Kansas State University.....14

**Figure 11.**  
Scheme of Triga Mark II Uranium Fission Reactor at Kansas State University.....15

**Figure 12.**  
Neutron activation analysis (NAA) was performed to identify elements present in the sample.  
This is the reactor core.....15

**Figure 13.**  
Schematic diagram of Raman spectroscopy, which was used to study CNTs.....16

**Figure 14.**  
SEM at the University of Kansas, Microscopy and Analytical Imaging Lab, KU Research.  
Photo by Eric L. Trump, Ph.D., Emporia State University.....17

<b>Figure 15.</b>	
First sample 2.5 (wt %) Fe loaded fly ash, sandy to yellow color.....	19
<b>Figure 16.</b>	
The second sample 20 (wt %) Fe loaded fly ash. Note the darker brown color.....	19
<b>Figure 17.</b>	
2.5 (wt %) Fe loaded fly ash, after heated for 12 hours at 800 °C.....	20
<b>Figure 18.</b>	
Tablets of 2.5 (wt %) Fe loaded fly ash.....	20
<b>Figure 19.</b>	
20 (wt %) Fe loaded fly ash, after heating for 15 hours at 40 °C.....	21
<b>Figure 20.</b>	
20 (wt %) Fe loaded fly ash; the color of the sample changed from light brown solution to dark brown solid.....	22
<b>Figure 21.</b>	
20 (wt %) Fe loaded fly ash. After heating the sample, powder was obtained .....	22
<b>Figure 22.</b>	
2.5 (wt %) Fe loaded fly ash. After heating the sample a solid pellet was obtained .....	23
<b>Figure 23.</b>	
Sample tablet being introduced into the CVD apparatus at Kansas State University. Photo by Eric L. Trump, Ph.D., Emporia State University.....	24

**Figure 24.**  
A comparison of samples before and after CVD. Note the black color, indicating that carbon was deposited. Photos by Eric L. Trump, Ph.D., Emporia State University.....25

**Figure 25.**  
During neutron activation analysis, neutron capture transforms certain stable isotopes of elements into radioactive isotopes .....26

**Figure 26.**  
SEM images of 2.5 wt % Fe loaded fly ash (a) at 500x magnification. The arrow shows small CNTs. Image (b) is at 6500x magnifications.....29

**Figure 27.**  
SEM images 2.5 of wt % Fe loaded fly ash (c) at 1000x magnification. The arrow in the left of the image shows CNTs growth. Image (d) shows CNTs at 50000x magnification .....30

**Figure 28.**  
SEM images 2.5 wt % Fe loaded fly ash (a) at 500x magnification. The arrow shows small CNTs. In image (b) 20 wt % Fe loaded fly ash at 500x magnification shows that there were no CNT produced.....31

**Figure 29.**  
The Raman spectra for the 2.5 wt % Fe catalysts fly ash.....32

**Figure 30.**

The Raman spectra for the two fly ash supported catalysts (a) 2.5 wt % Fe fly ash, and (b) 20 wt % Fe fly ash catalyst. The G peak ( $1518\text{ cm}^{-1}$ ) to D peak ( $1334\text{ cm}^{-1}$ ) intensity ratio indicates the extent of graphitization. The presence of the D and G bands indicates the presence of carbon nanotubes. The Raman Spectrum of 20 wt % Fe (shown in red) is superimposed on the other spectrum to emphasize the lack of CNTs produced. The 10 wt % (not shown) also had no CNT growth.....33

## 1. Introduction

Carbon nanotubes (CNTs) are tubular cylinders made of carbon atoms and have extraordinary mechanical, electrical, thermal, optical and chemical properties. When studied at an individual tube level, their unique structures exhibit properties such as 200 times the strength and 5 times the elasticity of steel <sup>[1] [2]</sup>. In addition, according to Nanocomp (Merrimack, New Hampshire), a commercial manufacturer of nanotubes, they have 5 times the electrical conductivity, 15 times the thermal conductivity, and 1,000 times the current capacity of copper. Their densities are almost half that of aluminum. As they are carbon-based products, carbon nanotubes have almost no environmental or physical degradation issues that are common in metals, such as thermal expansion and contraction, being sensitive to radiation, and being corrosive. Environmental and physical degradation issues normally result in greater system failure of the performance-sensitive applications in different sectors such as in aerospace, automotive, energy and consumer products <sup>[3]</sup>.

Typical CNT diameters range from less than one nanometer to fifty nanometers. The typical carbon nanotube length is several microns. CNTs shorter than this are typically not useful. There are different techniques that have been used to produce nanotubes in sizable quantities <sup>[4]</sup>. These techniques include laser ablation, arc discharge, high-pressure carbon monoxide disproportionation, and chemical vapor deposition (CVD). In most of these processes, the most suitable environments for them to take place are in a vacuum or using process gases. The CVD growth of the CNTs can occur in a vacuum environment or in an atmospheric pressure environment. Large quantities of nanotubes can be synthesized by these methods, advance the catalyst process, and ensure there is continuous growth for the CNTs, therefore making them commercially viable <sup>[5]</sup>.

Coal is mined from a quarry and transported to power stations where it is placed in different grades. It is then milled into a fine powder and then placed in pre-heaters to burn at 1400 degrees Celsius. After this burning process, the left over material is usually discarded at the bottom of the furnace, thus the name bottom ash. The fine, burnt coal particles that were captured in the filtration equipment are then deposited into holding

bins, whereby it is accessed as hard ash. Separators are used to separate the hard ash into the finer and coarse materials, and this process will continue until the product is fine, and this is classified as fly ash [6].

## **A- Historical Background**

In Saudi Arabia, Habib, et al., [20] used oil fly ash without added metals to produce CNTs (see Figure 1.). These tubes were synthesized by CVD. They relied on metals, such as iron, which were naturally present. Salah, et al., [19] used a new method by a low-pressure chemical vapor deposition system (LPCVD) to develop a large-scale production of CNTs using fly ash for different applications (see Figure 2a, 2b). In South Africa, Hintsho, et al., [32] have produced CNTs by the catalytic chemical vapor deposition method (CCVD) at a temperature from 400-700 °C. Moreover, they used acetylene gas, and received a donated fly ash sample from the Electricity Supply Commission (ESCOM) and Innovation Center. Therefore, a recycled waste material was used as a catalyst. However, the CNTs and carbon nano fibers (CNFs) were produced in very low yields (see Figure 3). In Japan, Yasui, et al., [33] added iron as a catalyst for the production of carbon nanotubes. In this method, they obtained multi-walled carbon nanotubes (MWCNTs) productions, which were of very low yield (see Figure 4). In Australia, Dunens, et al., [22] used Class F fly ash with added iron as a catalyst. Class F is produced by the combustion of older anthracite coal. Their process used CVD to produce CNTs from ethylene, hydrogen and nitrogen [1:1:2] at 650°C. However, the CNFs were impregnated into the substrate (see Figure 5). In this study, Class C fly ash, from the combustion of younger lignite coal with added iron and using preparation and synthesis methods similar to those of Dunens, et al., was used. The use of Class C has not been previously reported in the literature as a catalyst or catalyst support.

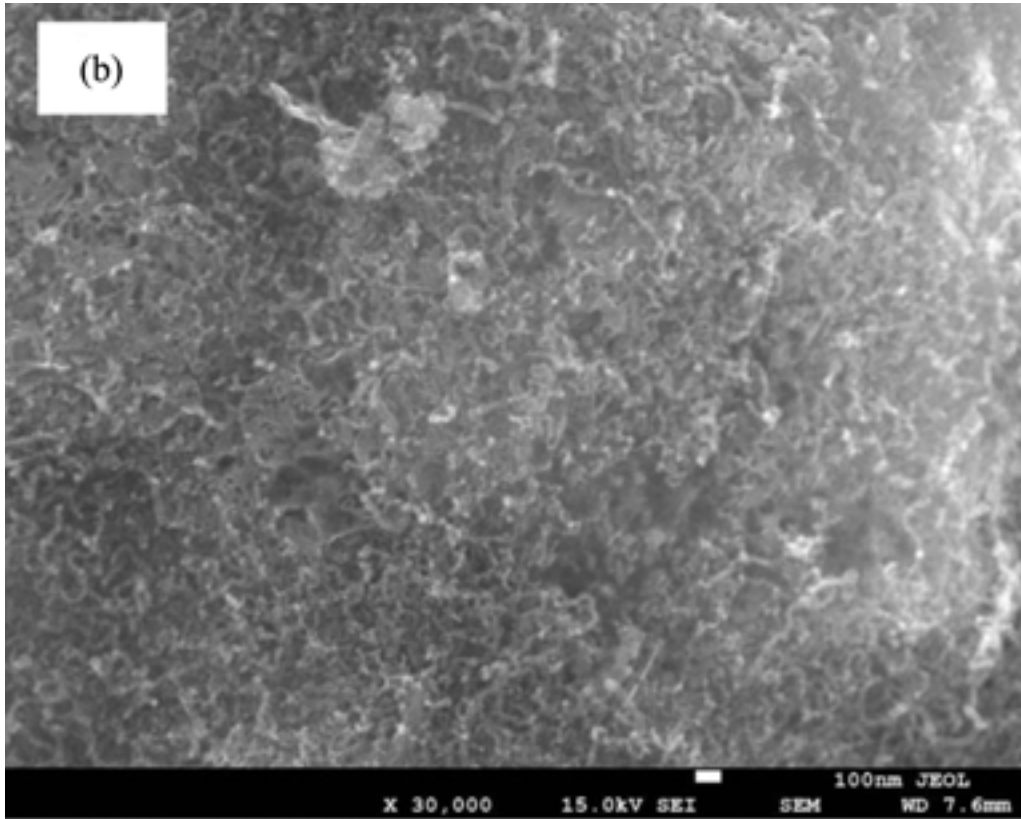


Figure 1. SEM images of CNTs grown, at 650 °C [20].

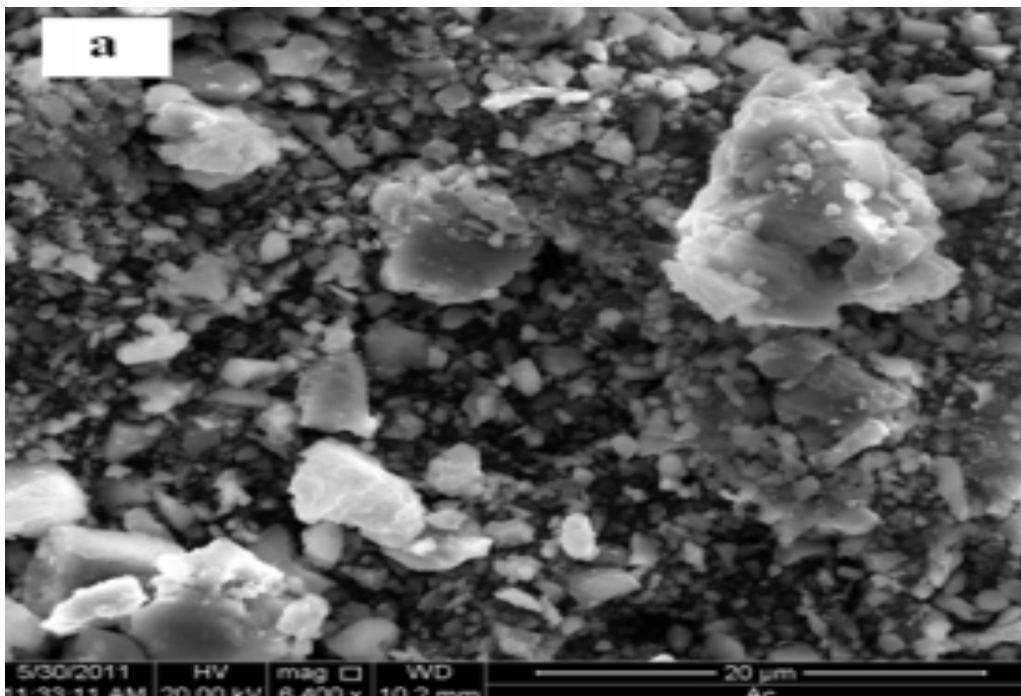


Figure 2a. SEM images of different magnifications for the first sample of fly ash after heating at 750 °C [19].



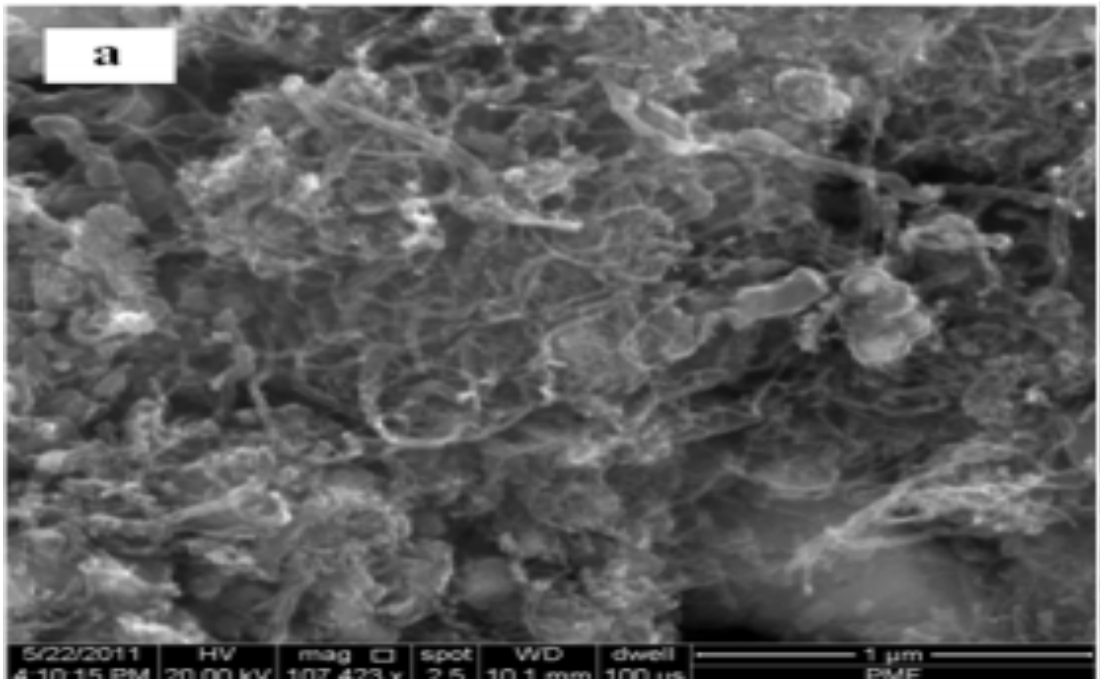


Figure 2b. SEM images of different magnifications for the second sample of fly ash after heating at 750 °C [19].

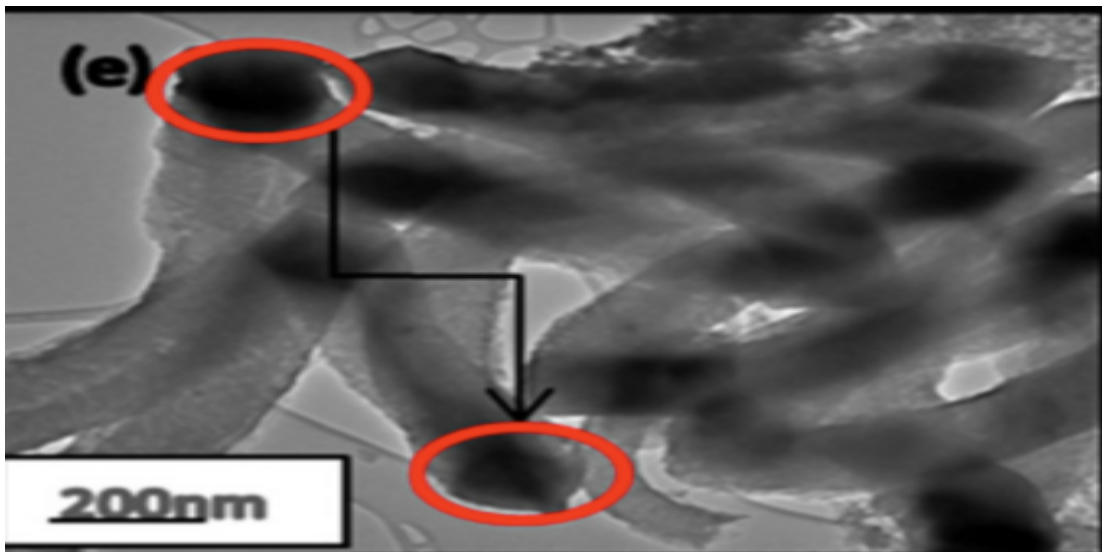


Figure 3. SEM images of different magnifications, well-defined CNFs, apparently formed by tip growth, were clearly visible as seen by the red-colored circles, at 700 °C [32].

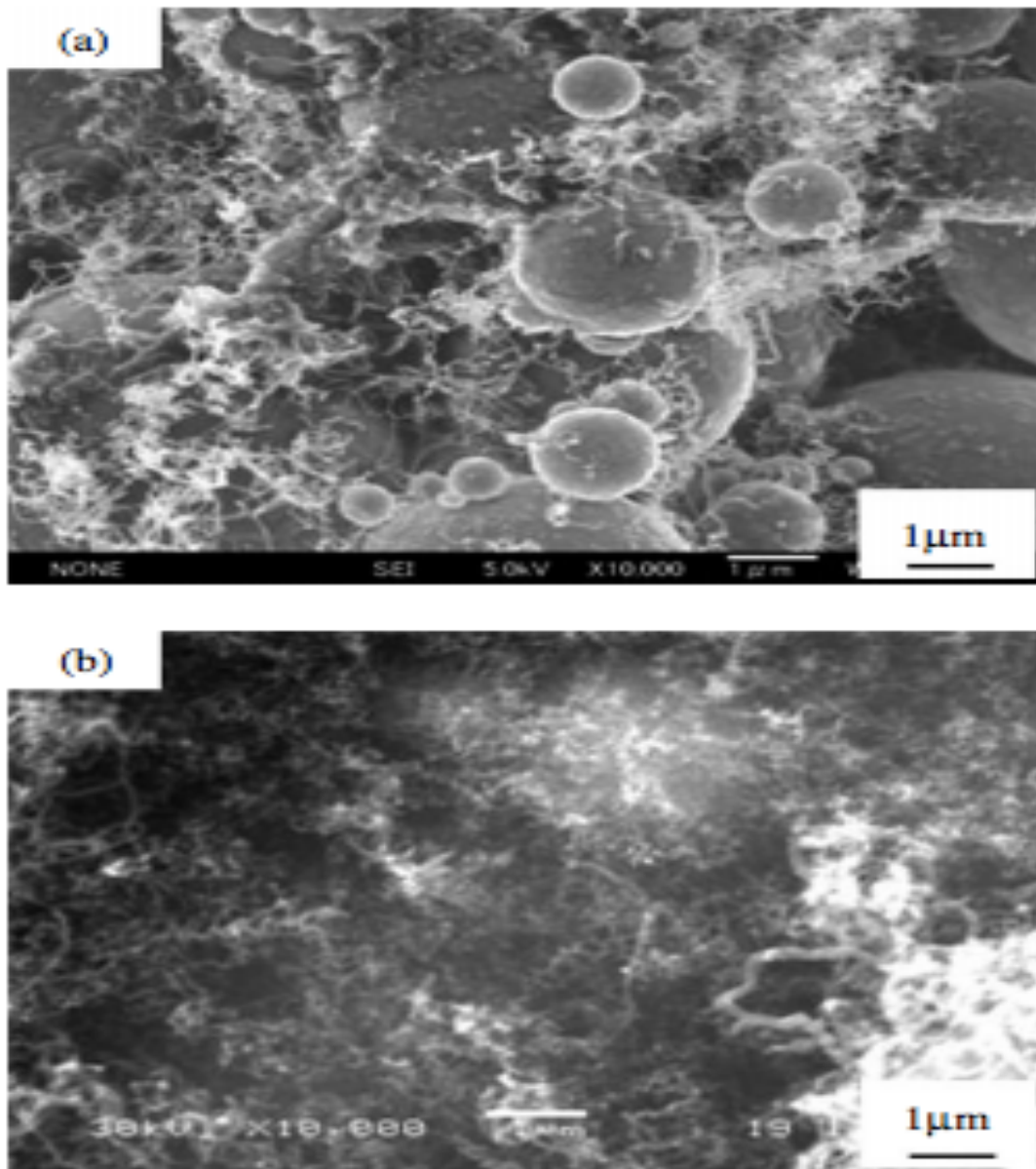


Figure 4. SEM images of carbon nanotubes grown (a) with methane at 1170 K and (b) with ethanol at 1070 K <sup>[33]</sup>.



Figure 5. SEM images of Multi Walled Nanotubes (MWNTs) and Carbon Nano Fibers (CNFs) covering the surface of 5 wt % Fe loaded fly ash <sup>[22]</sup>.

## **B- Making Use of Coal Waste**

As stated previously, fly ash is a combustion by-product from fossil fuels, such as coal and biomass. As energy needs have grown over the past few years, fly ash has been produced in increasing quantities and there have been challenges about how to effectively dispose of it without having a negative effect on the environment <sup>[7]</sup>.

In the USA, coal ash is, by mass, the largest form of waste associated with energy production. Currently, there is over 100 million tons of coal ash waste produced every year. This waste product contains various toxic chemicals such as lead, arsenic, mercury and radioactive uranium. Methods that have been used to dispose of fly ash safely in the environment include using it as an additive in materials such as cement, concrete, grout, or as a fill material in stabilization projects and in roadbeds. It is estimated that about 43% of the fly ash produced in the USA is recycled by being a replacement for Portland cement. However, this recycling process has been criticized by building experts. Fly ash

use in concrete buildings is dangerous because its use in these buildings is inferior in terms of a quality <sup>[8]</sup>. In addition, it may lead to indoor air contamination due to the possible leaching of chemicals or cause caustic reactions with other materials. The reason for this is that there are variations in the chemical composition of the fly ash from different sources of compounds and could make the final concrete products too weak for proper use of various structures <sup>[9]</sup>.

Fly ash consists of various small particles called precipitators that are categorized as cenospheres, which are small hollow particles, and plerospheres that are thin-walled hollow spheres. It is important to note that the high thermal stability, low-bulk density, and their spherical shape make them suitable for use in the large-scale fluidized bed reactors <sup>[18]</sup>.

Fly ash has the following physical properties, a whitish gray color, a bulk density of 0.994 g/cm<sup>3</sup>, moisture content is about 3.14%, and an average particle size of 6.92 micrometers <sup>[10]</sup>.

### C- Class C and Class F Fly Ash

Class F fly ash is produced from burning harder, older anthracite and bituminous coal. The chemical composition of Class F fly ash includes silicon dioxide,  $\text{SiO}_2$ , aluminum oxide,  $\text{Al}_2\text{O}_3$ , and iron oxide,  $\text{Fe}_2\text{O}_3$ . Class C fly ash is produced from burning younger lignite and subbituminous coal. Class C fly ash contains silicon dioxide,  $\text{SiO}_2$ , aluminum oxide,  $\text{Al}_2\text{O}_3$ , and iron oxide,  $\text{Fe}_2\text{O}_3$ , but the percentage total of these compounds tends to be less than in Class F fly ash (see Figures 6,7,8, and 9 to note differences in chemical compositions) <sup>[11][12]</sup>.

## Classes

Class C



Class F



**Class F –  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 70\%$**

**Class C –  $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \geq 50\%$**

Figure 6. Showing differences of fly ash and colors in the sample <sup>[11][12]</sup>.

Fly Ash				
Class F Burning of Bituminous & Anthracite			Class C Burning of Lignite & Sub Bituminous	
Low Fe	High Fe	Components	Low Ca	High Ca
46-57	42-54	SiO <sub>2</sub>	46-59	25-42
18-29	17-24	Al <sub>2</sub> O <sub>3</sub>	14-22	15-21
6-16	16-24	Fe <sub>2</sub> O <sub>3</sub>	5-13	5-10
2-6	1-4	CaO	8-16	17-32
0.7-2.1	0.3-1	MgO	3-5	4-12
2.0-3.0	2.1-2.7	K <sub>2</sub> O	0.5-1	0.3-1.6
0.2-1	0.2-1	Na <sub>2</sub> O	1-4	1-6
0.4-3	0.5-2	SO <sub>3</sub>	0.5-3	0.5-5
0.6-5	1.2-5	LOI	0.1-2	0.1-1
1-2	1-2	TiO <sub>2</sub>	<1	<1

Other elements present in traces: Hg, Cd, Sb, Se, Ti, V (1-10 ppm)  
 As, Cr, La, Mo, Ni, Pb, Th, U, Zn (10-100 ppm) B, Ba, Cu, Mr, Sr(100-1000ppm)

Figure 7. Class F and Class C fly ash, showing components of fly ash and other elements present <sup>[11][12]</sup>.

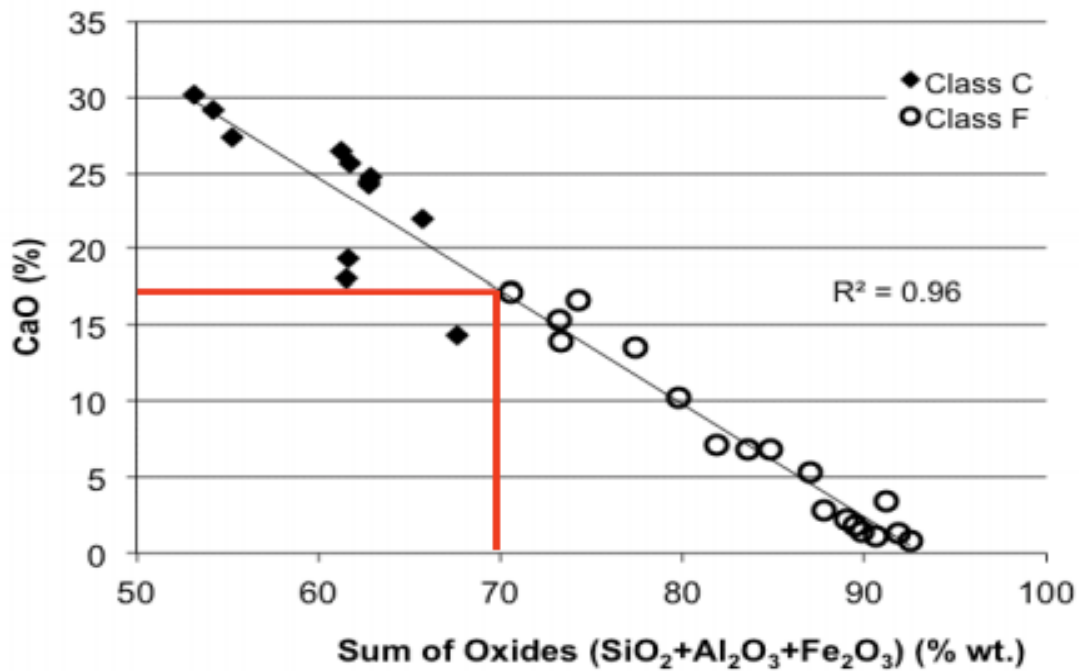


Figure 8. Class F and Class C fly ash, showing chemical classification <sup>[11][12]</sup>.

Differences - density of class fly ash

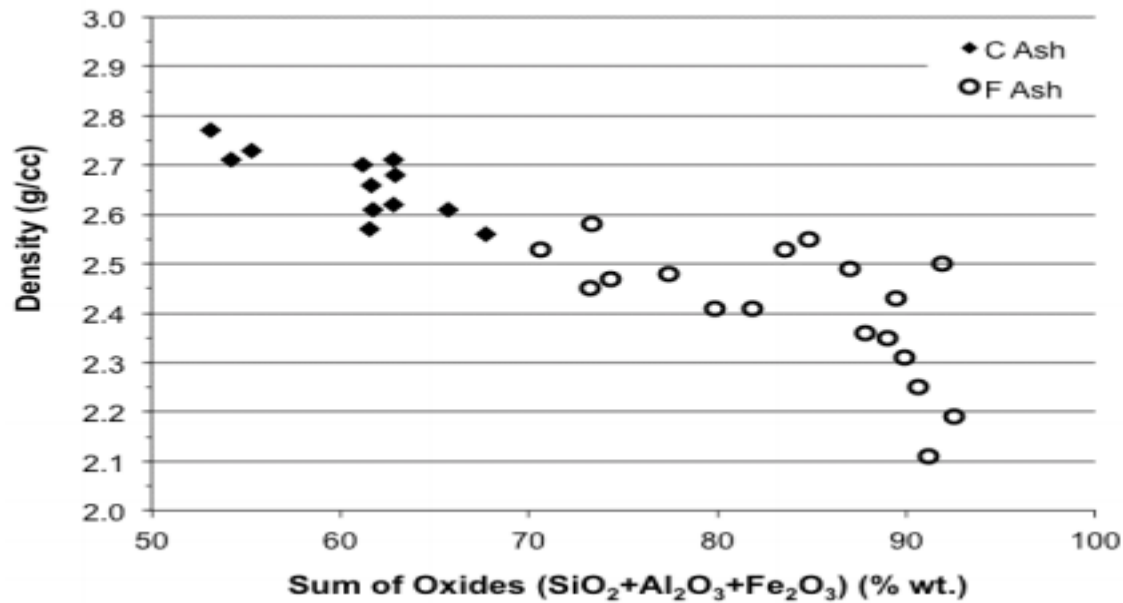


Figure 9. Class F and Class C fly ash, showing differences in density <sup>[11][12]</sup>.

Shcherban, et al., provide the following description of fly ash. Fly ash is typically comprised of the following constituents: approximately 1.5-2 times less aluminum oxide than the common aluminum raw materials, i.e., 20-35% Al<sub>2</sub>O<sub>3</sub> in ash in comparison to 50-62% Al<sub>2</sub>O<sub>3</sub> in bauxite, an aluminum ore. It has a high level of silica, i.e., 40-65% SiO<sub>2</sub>, and this makes it impossible to process for aluminum extraction by the Bayer method or using direct alkaline alumina extraction. The table that follows shows chemical composition of fly ash from three different power plants in Russia. The fly ash depends on silica and alumina content to produce CNTs.

Power Plant	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	LOI (Loss on ignition)	Total
Pavlodar	59.82	27.79	5.48	1.65	1.20	0.72	0.40	0.62	4.50	97.68
Ermak	60.50	27.20	5.05	1.90	1.60	0.58	0.30	0.60	4.00	97.73
Troitsk	58.48	30.21	4.78	1.95	1.12	0.66	0.30	0.55	0.80	98.05

TABLE 1. Chemical Analysis Of Fly Ash From Three Different Power Plants In Russia

Due to technology differences used at Russian plants, different power plants produce fly ash that has different chemical constituents <sup>[13]</sup>. Fly ash is mainly composed of small glassy aluminosilicate spheres that are between one to one hundred micrometers in diameter. The spheres are formed because of rapid cooling of the molten mineral matter in the pulverized coal at high combustion temperatures <sup>[14]</sup>. The fly ash applications that have been successfully implemented are in agriculture and soil management <sup>[15]</sup>. It is used as absorbents for heavy metals, waste stabilization, and as catalysts for waste gas cleaning, hydrogen production, and for gas phase oxidation. Although fly ash has been successfully implemented in these processes, it is not used on a large scale, i.e., only small quantities are used in these processes <sup>[16]</sup>. Our research is being conducted to examine if there is a possibility that fly ash can be used effectively as a catalyst support in carbon nanotube synthesis (CNT).

#### **D- The CVD Process**

The CNT market is projected to be a multi-billion dollar industry within the next ten years. Research has been conducted showing the fluidized bed chemical vapor deposition method (FBCVD) is the best method for large-scale CNT synthesis. The chemical vapor deposition process is a CNT synthesis technique whereby the gaseous carbon source (such as ethylene or acetylene) is decomposed at moderate temperatures of less than 1200 degrees Celsius in the presence of a metal catalyst. This method mainly uses a transition metal on a porous substrate as its best catalyst <sup>[17]</sup>.

In the FBCVD method, a gas mixture flows vertically through the bed of catalyst particles, resulting in increased bed mixing, and a ‘fluid-like’ behavior of the particle bed. The result of this process is an increase in the transfer of mass and heat in the reaction zone <sup>[22]</sup>.

In the CVD process, hydrocarbon gas is allowed to flow over a heated layer of catalyst particles. The CVD process does not require the use of high temperature, i.e., temperatures of between 500-1100 degrees Celsius can be effective. By using this



process, huge quantities of nanotubes are produced. One drawback when using this method is that the metal catalysts that are needed in the CNT synthesis increase the overall expense. The yield may not be high enough to warrant the cost of production. There are various research processes that are being undertaken seeking to produce a rapid, efficient and low-cost CNT synthesis method while using the CVD method [22].

Other advantages of CVD are continuous production, lower energy requirements, and greater control over the reaction parameters. The substrates that are used in the synthesis of CNTs are  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$  and  $\text{MgO}$ . The transition metals that are favorable in this process are Fe, Co, and Ni, which are often doped with Mo so that one can improve the overall yield and selectivity. In this process, one can achieve about one to fifteen percent metal by weight in terms of the total [22].

However, even though the catalysts and substrates give a decent fluidizing medium and support CNT growth, they are not recycled because they are destroyed by the CNT purification process, which uses strong acids or bases for treatment purposes. There is a need to conduct further research in order to determine a catalyst that will be more environmentally and resource friendly for large-scale production to be adopted. Different researchers have proposed the use of naturally occurring materials, for example, minerals, magma, and organic hydrocarbons as suitable components in the production of CNTs [18].

The use of waste materials such as oil fly ash as a catalyst support in the production of CNTs provides a cheaper alternative to porous silica and helps in the preservation of the environment. Fly ash is cheaper because it is an abundant raw material that is a waste product derived from the combustion of fossil fuels [19].

The focus of the research presented in this thesis is on fly ash as a means for the production of CNTs because fly ash has a similar composition to many of the previously used laboratory catalyst supports for CNT synthesis. Therefore, fly ash has the potential to be used as a catalyst or catalyst support for CNT growth without using a chemical treatment or having to impregnate fly ash with Fe in order to increase its metal loading [20].

Research shows that the favorable compositions of the fly ash will offer the advantage of reducing the use of what are termed virgin resources, i.e., the components that cannot be recycled in the CNT synthesis and, in addition, lower the costs that have been associated with the CNT catalyst manufacture. Use or production of recyclable materials helps preserve the environment. Our method used Class C coal fly ash as a catalyst support in the fabrication of carbon nanotubes. Class C fly ash, which is produced from the combustion of younger lignite coal, has not been previously reported in the literature as a catalyst support for CNT synthesis. The goal is to grow CNTs of one micron or more in length <sup>[21]</sup> <sup>[22]</sup>.

## 2. Materials and Methods

### A- Materials

Class C fly ash was obtained from the Jeffrey Energy Center at no cost. Reagent grade iron (III) nitrate nona-hydrate and 95% ethanol were used. Other materials included watch glasses, beakers, alumina sample boats, crucibles, spatulas, pipets, and filter paper.

### B- Instruments

Neutron activation analysis (NAA)

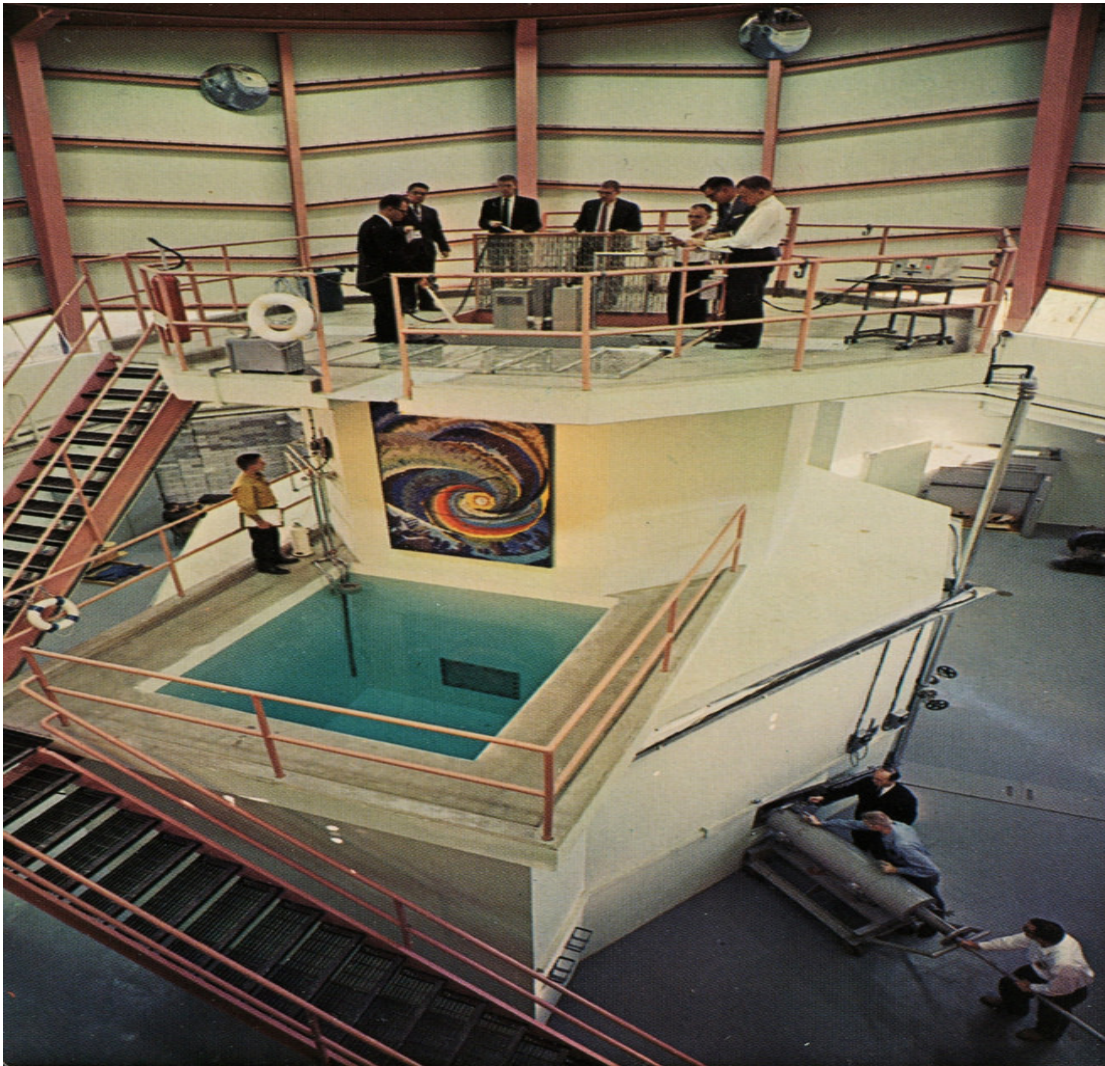


Figure 10. The Triga Mark II Uranium Fission Reactor at Kansas State University <sup>[34]</sup>.

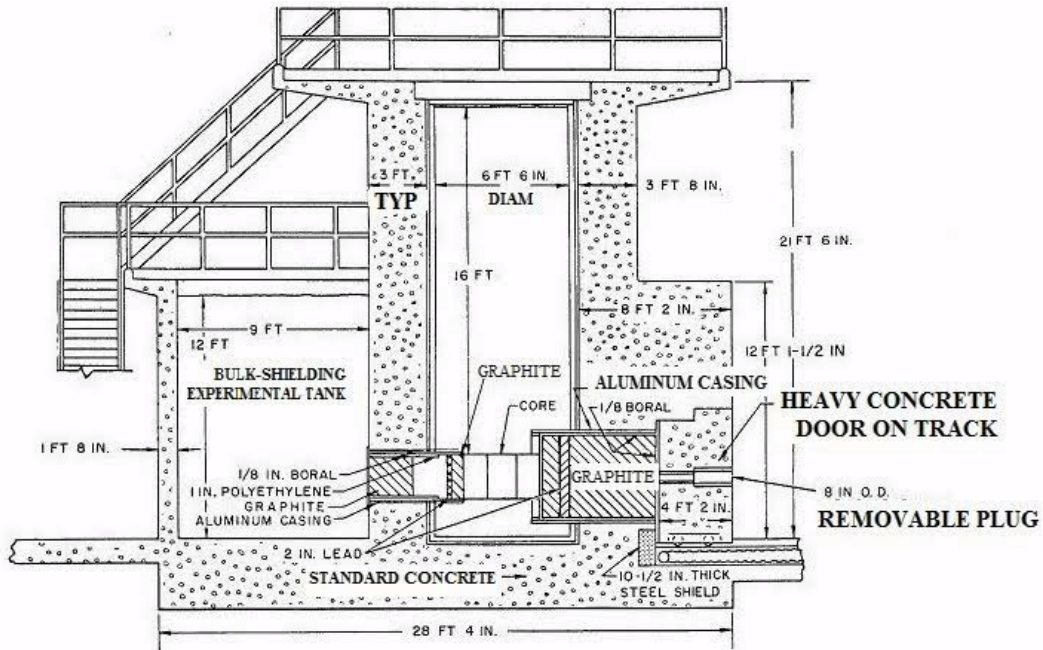


Figure 11. Scheme of Triga Mark II Uranium Fission Reactor at Kansas State University <sup>[34]</sup>.

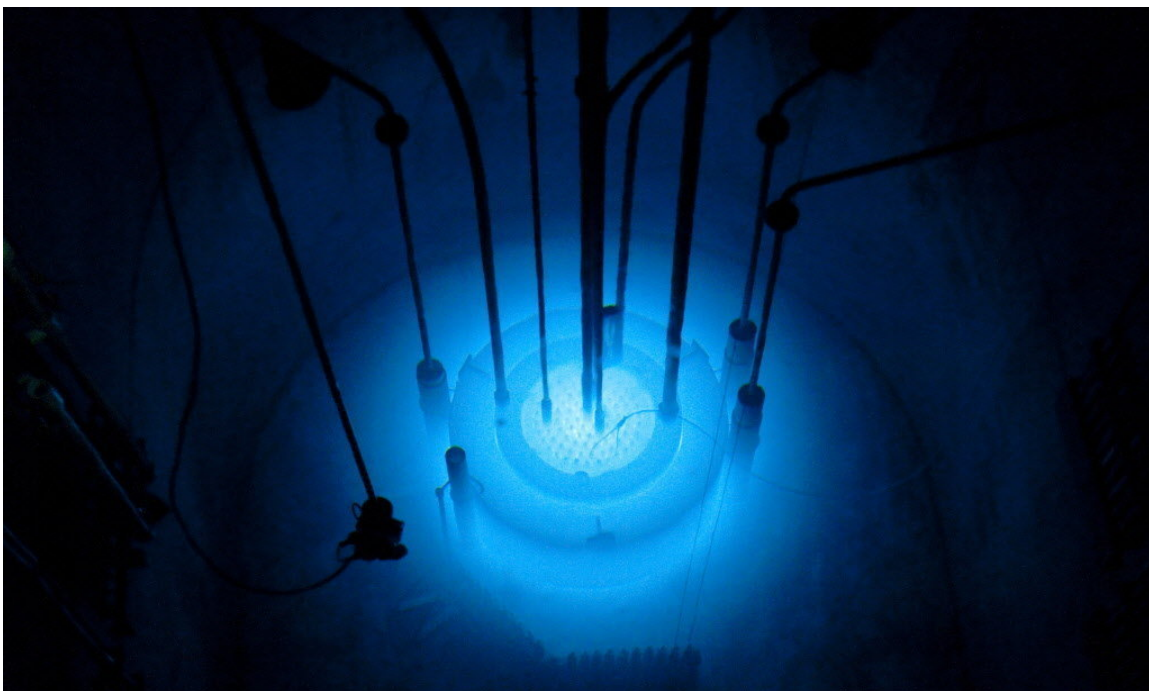


Figure 12. Neutron activation analysis (NAA) was performed to identify elements present in the sample. This is the reactor core <sup>[34]</sup>.

## Raman spectroscopy

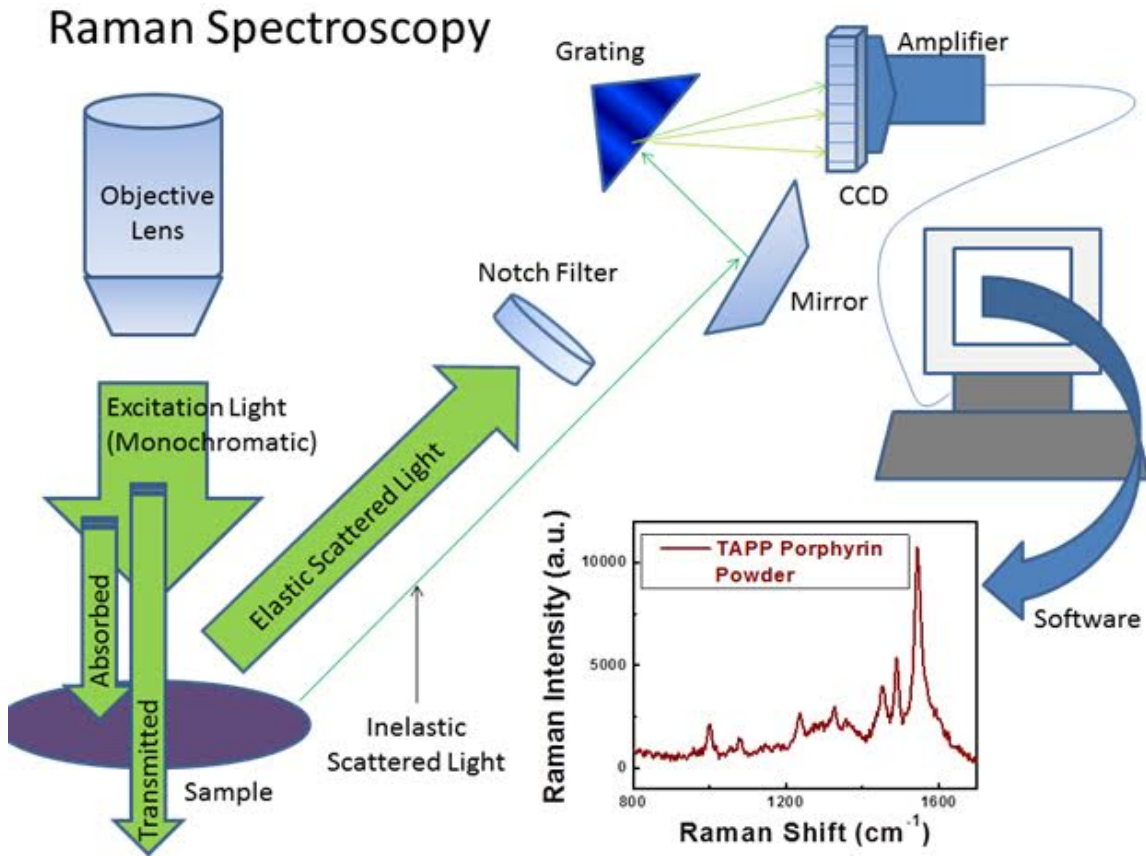


Figure 13. Schematic diagram of Raman spectroscopy, which was used to study CNTs

[35].

Scanning electron microscopy (SEM)



Figure 14. SEM at the University of Kansas, Microscopy and Analytical Imaging Lab, KU Research. Photo by Eric L. Trump, Ph.D., Emporia State University.

## **C- Experimental Section**

The method used to prepare samples was based on a procedure reported by Dunens, et al, in which catalysts were prepared via wet impregnation, i.e., soaking the fly ash in a solution. The  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in ethanol and then the process of sonication prepared an emulsion down to 1/100 of a micron was applied for a period of fifteen minutes. Weighed amounts of sieved fly ash substrate in their appropriate proportions were added to the catalysts that had a total iron load of either 2.5 or 5 weight percent (wt %). This mixture was then stirred and air-dried at 40 degrees Celsius for fifteen hours prior to calcination in air at 800 °C for about 12 hours <sup>[22]</sup>.

### **1- Sample Preparation**

Based on the work of Dunens, et al., the idea was to prepare the catalysts by wet impregnation, i.e., soaking the fly ash in a solution of the metal catalyst. To prepare the first sample (see Figure 15),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (1.81 g) was weighed on a balance and transferred to a beaker. In the fume hood, 5.0 mL of ethanol was added to dissolve the iron (III) nitrate. Class C fly ash (10 g) was added to the beaker and the mixture was sonicated for 15 minutes.



Figure 15. First sample 2.5 (wt %) Fe loaded fly ash, sandy to yellow color.

The second sample (see Figure 16), was prepared in a manner similar to the first one, but used 14.5 g of Iron (III) nitrate nona-hydrate, 5.0 mL of ethanol, and 8.0 g of Class C fly ash.



Figure 16. The second sample 20 (wt %) Fe loaded fly ash. Note the darker brown color.

## **2- Heating the Sample**

Samples were heated for 15 hours at 40 degrees Celsius. Then they were calcined in a furnace at 800 degrees Celsius for 12 hours (see Figure 17). The furnace was turned off and the samples were allowed to cool slowly for 4 hours before opening the furnace and removing them.





Figure 17. 2.5 (wt %) Fe loaded fly ash, after heated for 12 hours at 800 °C.



Figure 18. Tablets of 2.5 (wt %) Fe loaded fly ash.

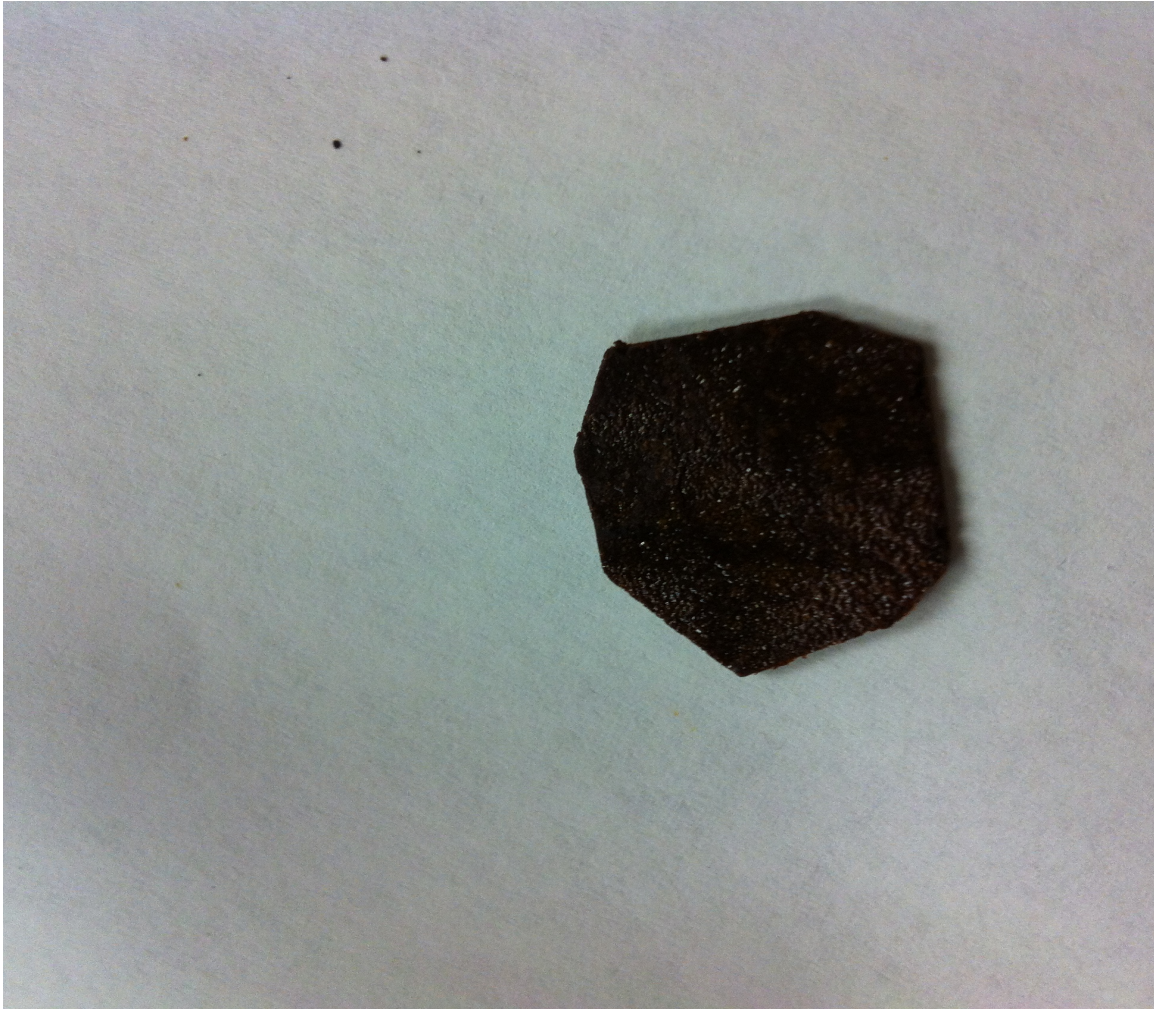


Figure 19. 20 (wt %) Fe loaded fly ash, after heating for 15 hours at 40 °C.

Class C fly ash has a whitish sandy color (see Figure 6). This study used different iron concentrations in fly ash by using two samples. The first sample 2.5 (wt %) Fe loaded fly ash was sandy to yellow color (see Figure 15). After heating the sample it solidified (see Figure 22). The samples were pressed into get round tablets (for more details see Figures 17,18,19, and 20). In addition, the second sample 20 (wt %) Fe loaded fly ash was a brown color (see Figure 16). After heating the sample we got powder (see Figure 21).

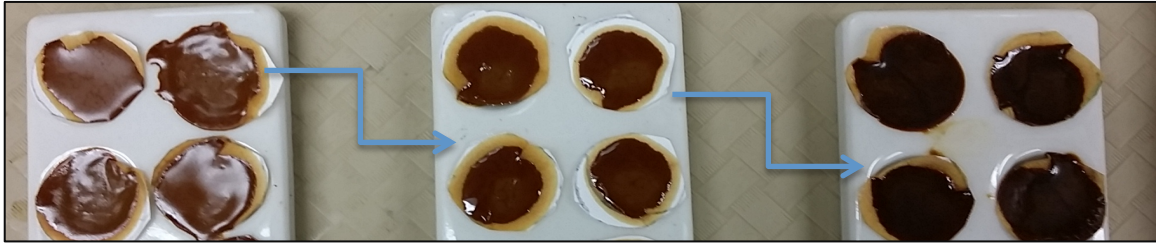


Figure 20. 20 (wt %) Fe loaded fly ash; the color of the sample changed from light brown solution to dark brown solid.

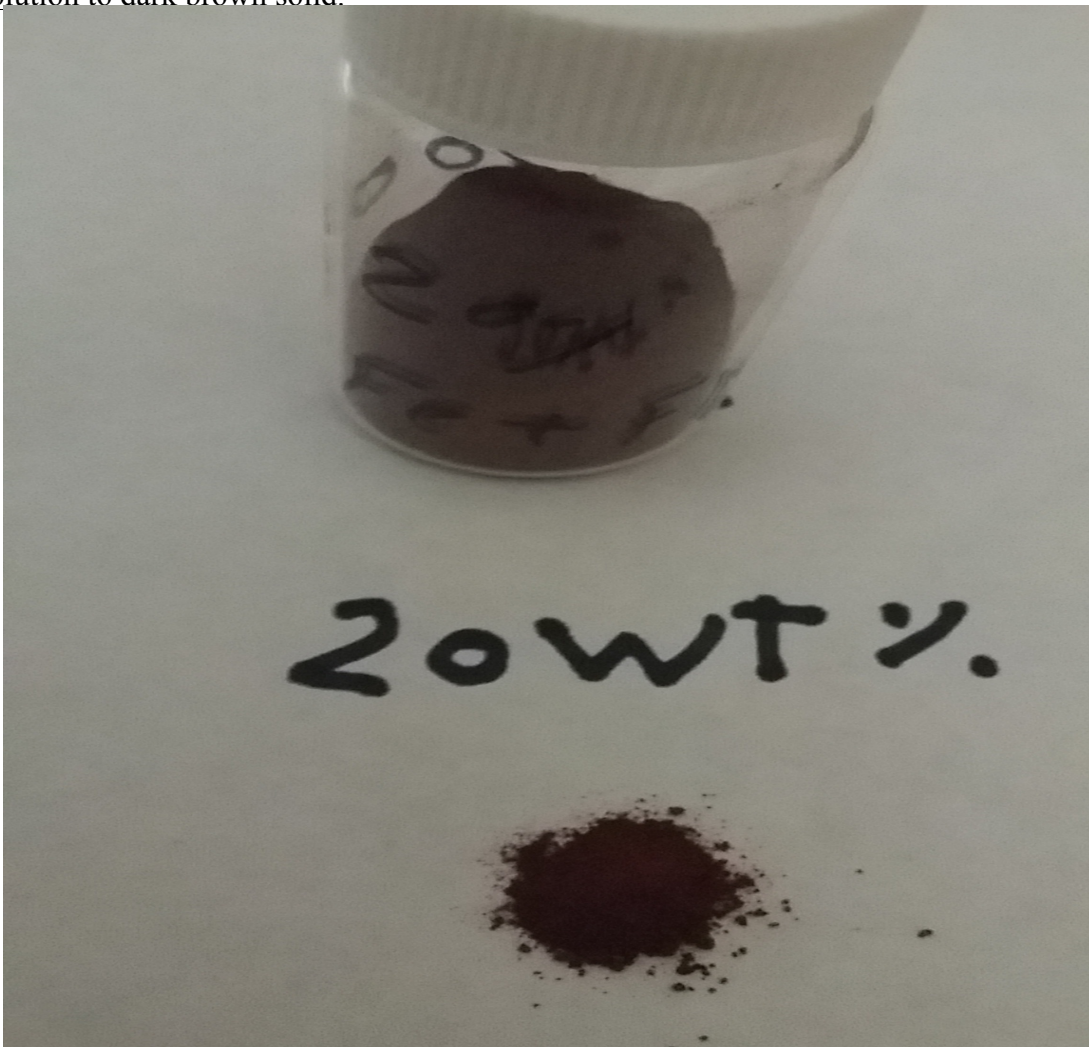


Figure 21. 20 (wt %) Fe loaded fly ash. After heating the sample, powder was obtained.

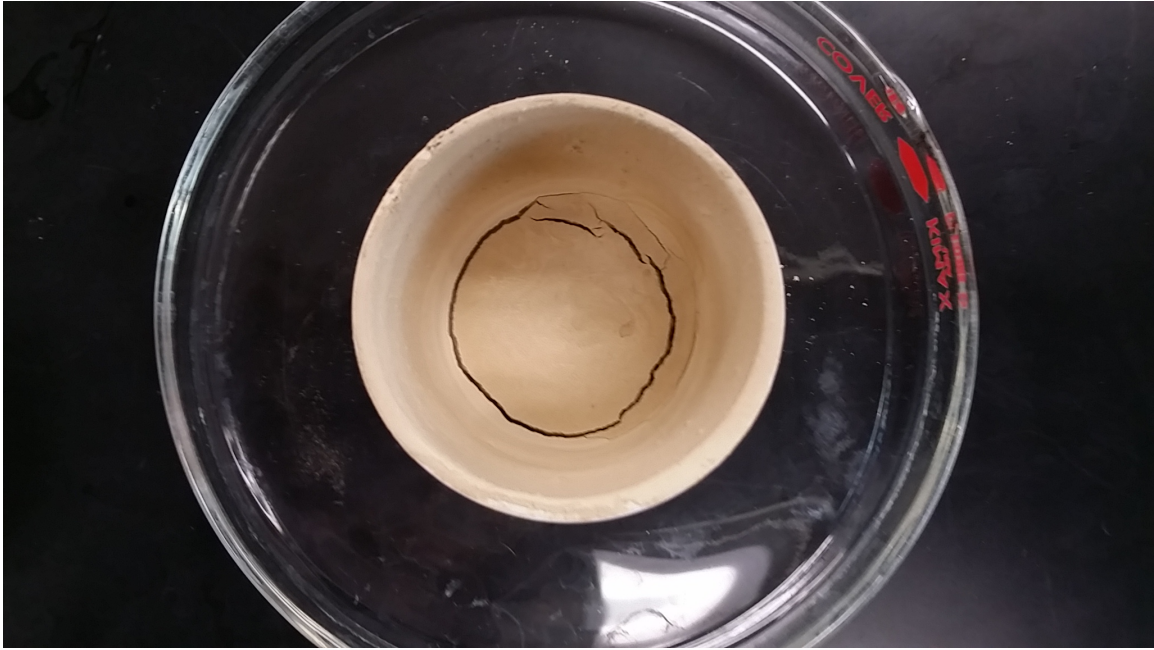


Figure 22. 2.5 (wt %) Fe loaded fly ash. After heating the sample a solid pellet was obtained.

#### **D- The CVD Process**

Four samples each of 2.5 wt %, 10 wt %, and 20 wt % iron loaded Class C fly ash were used in the CVD process in an attempt to grow carbon nanotubes. The CVD process was carried out in a manner similar to that described by Dunens, et al., using an Inconel 601 instrument at the Chemical Engineering Department at Kansas State University (see Figure 23). The instrument consisted of a cylindrical fluidized bed reactor that had a diameter of 52 mm and was 1,000 mm long, and is enclosed in a high temperature ceramic furnace. The expansion unit had the following dimensions of 100 mm diameter and 500 mm height and was installed at the top of CVD apparatus in order to minimize incidences of particle entrainment. To ensure that the process was carried out under the required environmental parameters, various particle scrubbers were used for the treatment of the effluent gases prior to their release <sup>[22]</sup>.



Figure 23. Sample tablet being introduced into the CVD apparatus at Kansas State University. Photo by Eric L. Trump, Ph.D., Emporia State University.

Gas flow to the reactor was controlled using the Alicat Scientific 16 series mass flow controllers. For measuring the temperature of the particle bed in-situ, a type-K thermocouple was used. In all of the experiments, a catalyst was introduced into the reactor at room temperature under an Ar flow of 1 standard liter per minute (SLPM). The reactor was heated to 750 °C for 30 minutes under a flow of Ar at 1 SLPM. The temperature of the furnace was reduced to 650 degrees Celsius under a flow of H<sub>2</sub>/Ar at 1 SLPM prior to reaction with ethylene for 10 minutes at 500 standard cm<sup>3</sup> / min (SCCM). Growth conditions consisted of 100 SCCM of C<sub>2</sub>H<sub>4</sub> flow, 250 SCCM of H<sub>2</sub> flow rate of 1 SLPM for a duration of 15 minutes. Cooling, post reaction, was carried out using an Ar flow of 3 SLPM (see Figure 24) <sup>[22]</sup>.

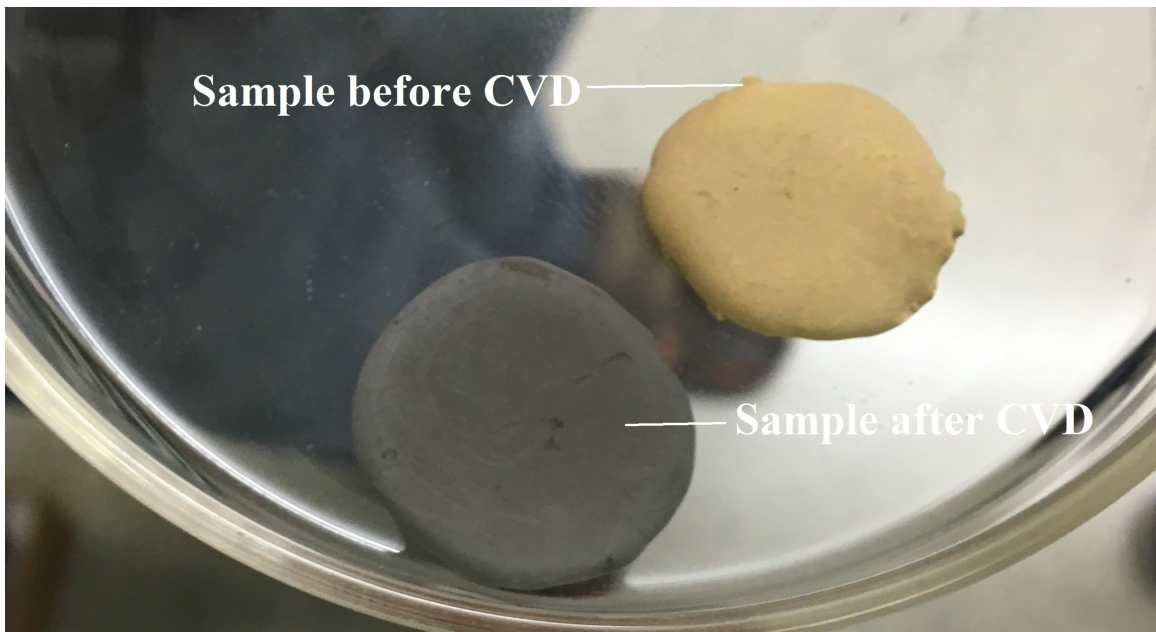


Figure 24. A comparison of samples before and after CVD. Note the black color, indicating that carbon was deposited. Photo by Eric L. Trump, Ph.D., Emporia State University.

### 3. Results and Discussion

#### A- Neutron Activation Analysis (NAA)

Class C fly ash was obtained from Jeffrey Energy Center near St. Mary, Kansas on 9/10/2015, at no cost. Neutron activation analysis (NAA) was performed to identify elements present in the fly ash. Table 2 shows results obtained from the Class C fly ash using the Triga Mark II Uranium Fission Reactor at Kansas State University (see Figures 10, 11). The neutron activation analysis (see Figures 12, 25) is a radiochemical method of analysis whereby neutron irradiation of the sample is used to convert elements into radioactive isotopes. The radioactive elements are then detected and quantified through the use of gamma ray spectroscopy. The analysis was performed not only to verify the presence of silica and alumina, but also to determine the presence of other elements such as Fe and Co. This analysis is important to show the presence of silicon and aluminum, which have a role in the growth of CNTs.

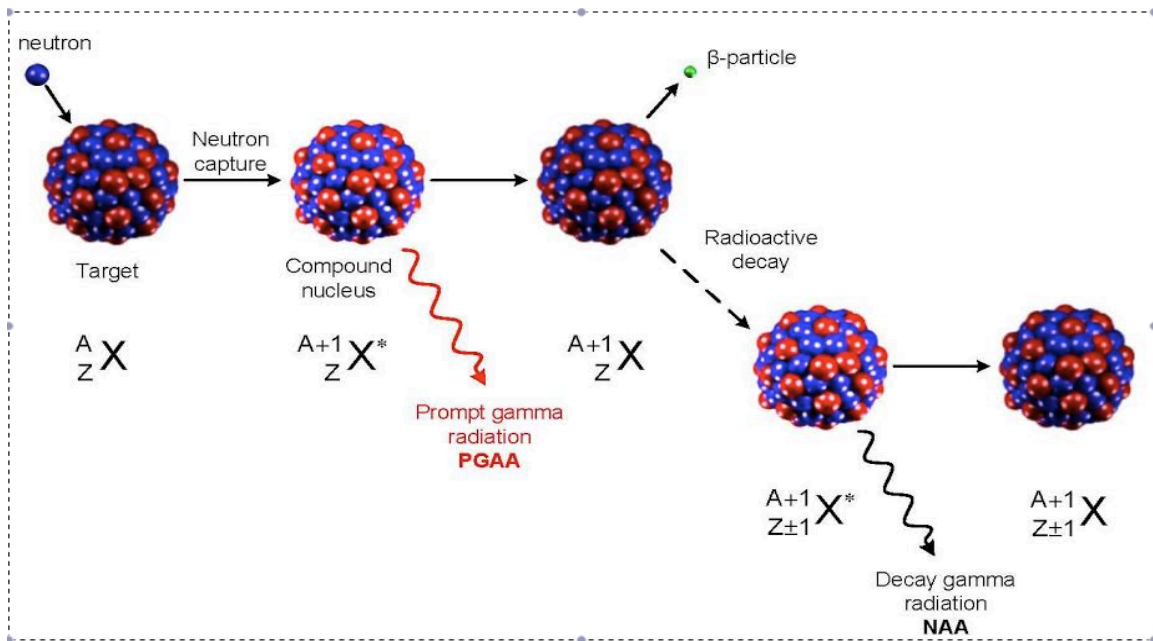


Figure 25. During neutron activation analysis, neutron capture transforms certain stable isotopes of elements into radioactive isotopes<sup>[34]</sup>.

	KeV	Isotope	Corrected mass, g	Uncertainty, g
Peaks ID'd manually	843.5	Mg-27	1.61E-03	3.75E-05
	846.8	Mn-56	5.29E-05	6.89E-07
	1369	Na-24	4.21E-03	2.11E-05
	1780	Al-28	5.16E-02	4.43E-04
		Fe	0.00E+00	
Peaks ID'd by software		Si-32	4.66E-02	8.94E-03
		Ca-47	5.55E-05	6.69E-05
		CR-51	2.31E-03	1.23E-04
		GA-72	3.89E-06	1.08E-06
		ZR-95	1.40E-01	2.70E-02
		CE-139	2.13E-01	1.79E-03
		LA-140	2.25E-05	1.89E-07
		EU-152x	2.24E-08	5.57E-09
		GD-153	5.68E-04	3.00E-05
		GD-159	1.37E-04	4.25E-06
		Hg-203	1.38E-03	4.16E-04
	TOTAL	4.61E-01	3.89E-02	

TABLE 2. Elements Identified by Neutron Activation Analysis.



The neutron activation analysis (NAA), showed the presence of silicon and aluminum, which was expected. We did not expect to see the significant amounts of zirconium and cerium (see Table 3.), since these were not reported in other studies [13]. The absence of iron was unexpected. Iron might be present, but was not detected. Possible reasons might include the low natural abundance of Fe-57 (2.12%) and the long irradiation time required. Iron-56, the most abundant isotope of iron does not have a favorable cross-section for neutron capture.

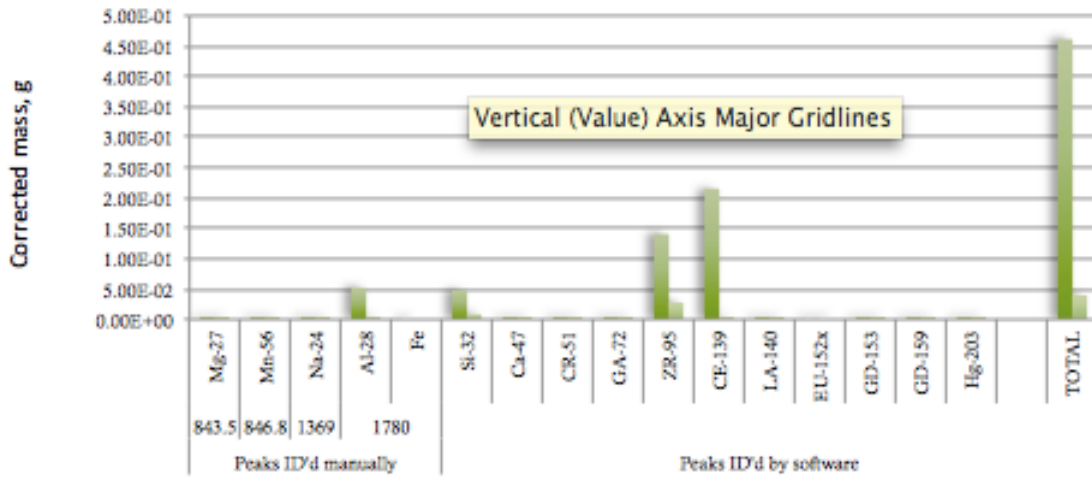


TABLE 3. Elements detected by NAA. Note the significant amounts of cerium and zirconium.

## B- Scanning Electron Microscopy (SEM)

Figures 26 and 27 show scanning electron microscopy (SEM) images of different magnifications for the CNTs on the surface of 2.5 weight percentage (wt %) Fe loaded fly ash. The images were obtained from the University of Kansas, Microscopy and Analytical Imaging Lab, KU Research. The results are fragments of small particles with sizes in the range of (206.2-276.9  $\mu\text{m}$ ) shown in the Figure 27 (d). Furthermore, Figure 28 compares (a) 2.5 weight percentage (wt %) Fe loaded fly ash and (b) 20 weight percentage (wt %) Fe loaded fly ash. The white arrow shows the locations of small Carbon nanotubes.

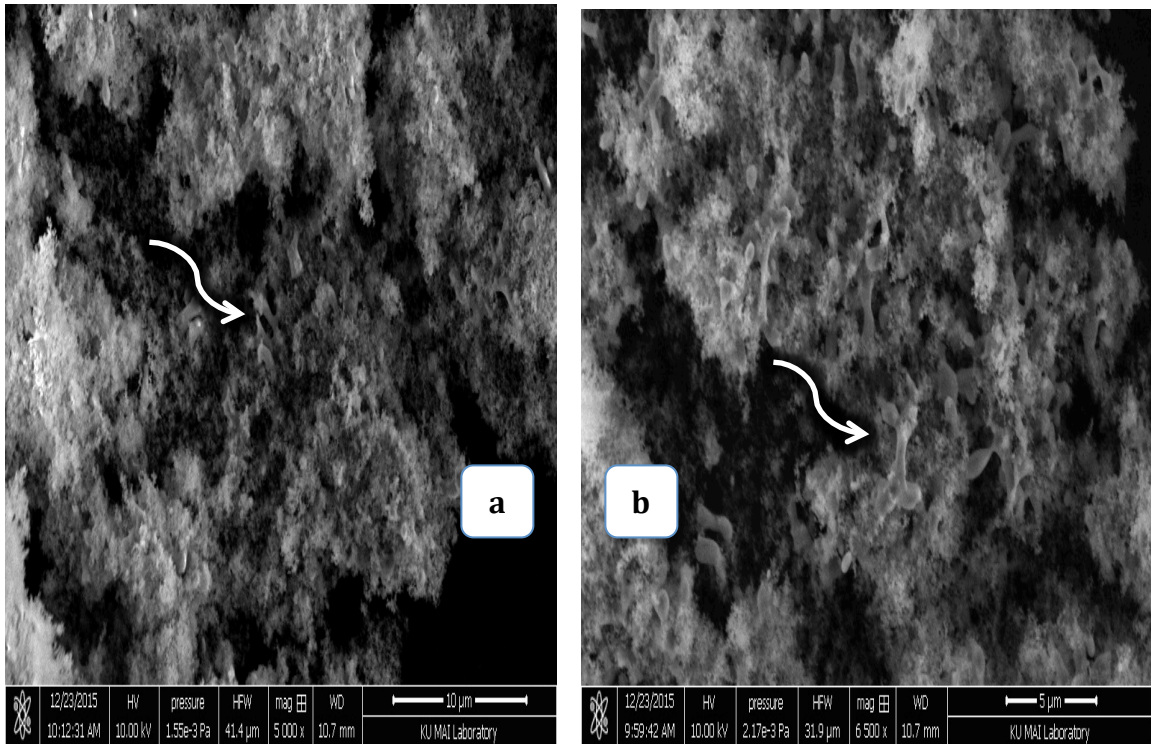


Figure 26. SEM images of 2.5 wt % Fe loaded fly ash (a) at 500x magnification. The arrow shows small CNTs. Image (b) is at 6500x magnifications.

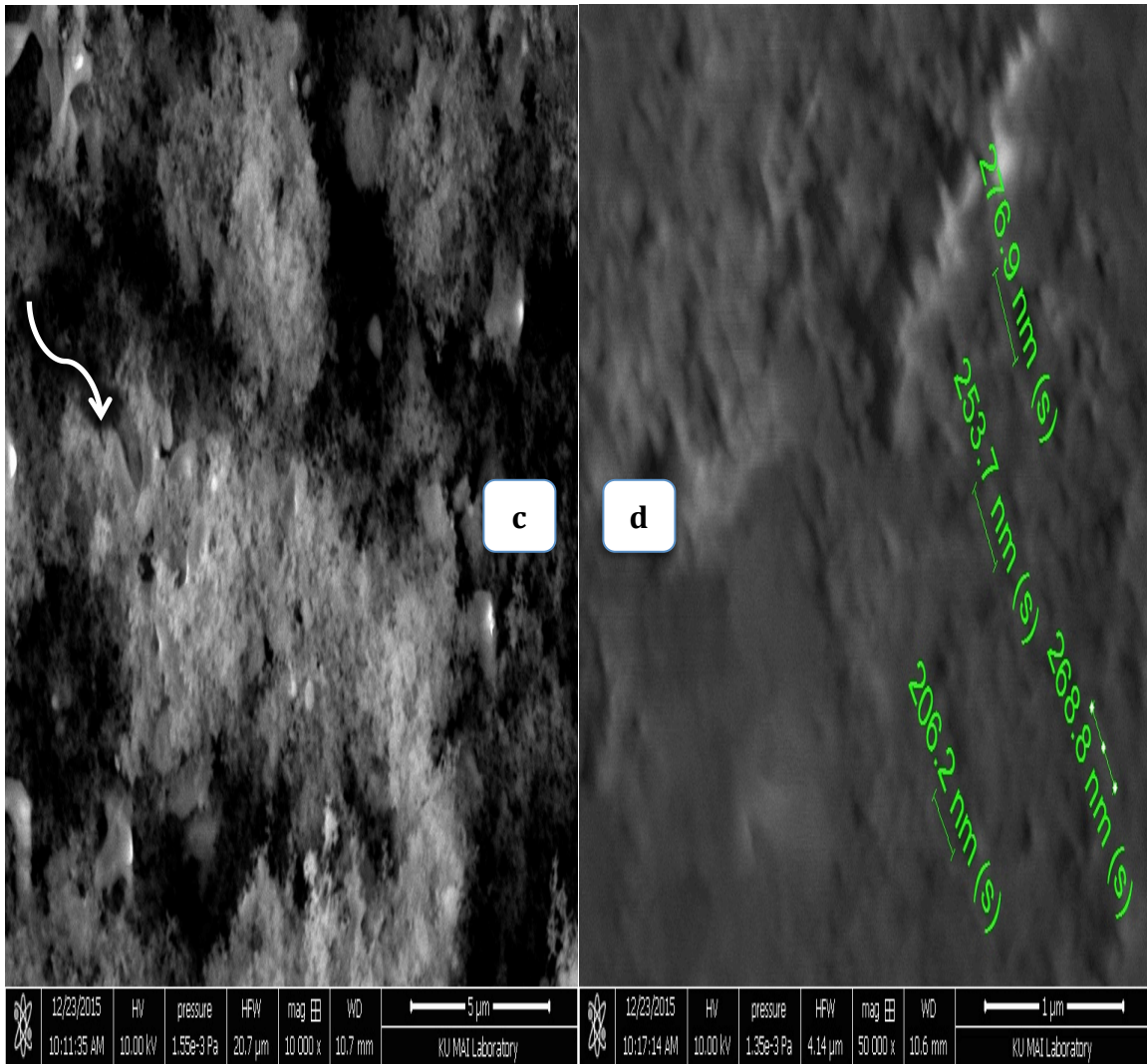


Figure 27. SEM images 2.5 of wt % Fe loaded fly ash (c) at 1000x magnification. The arrow in the left of the image shows CNTs growth. Image (d) shows CNTs at 50000x magnification.

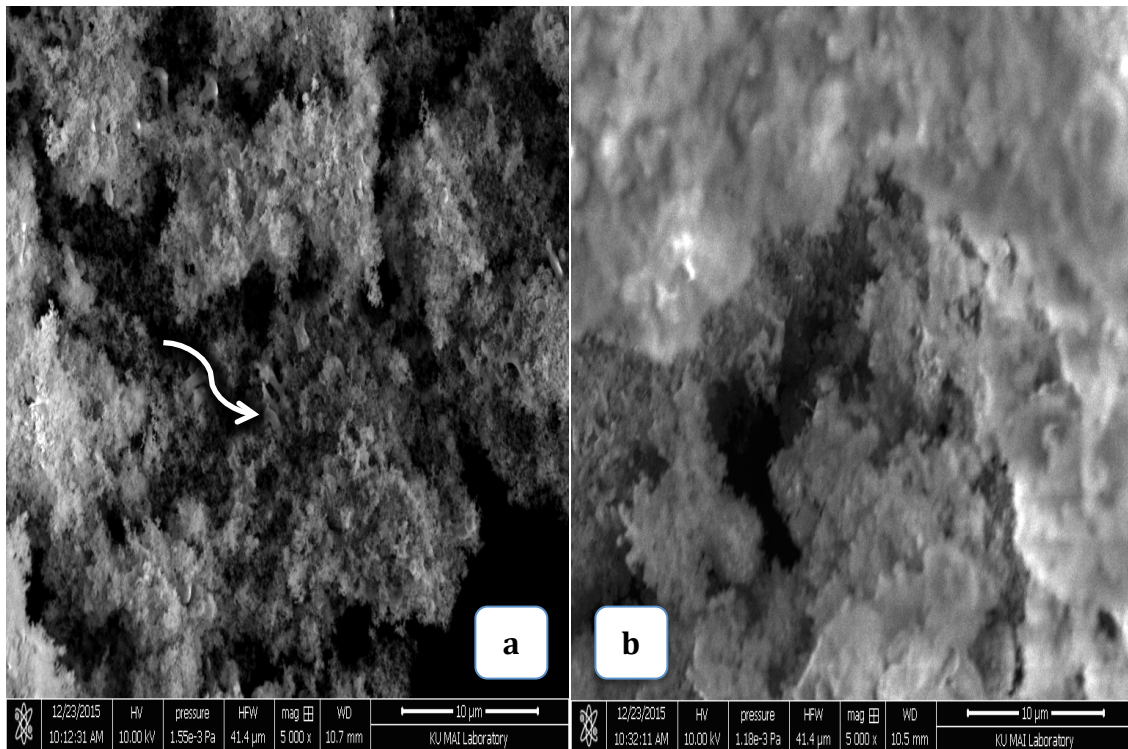
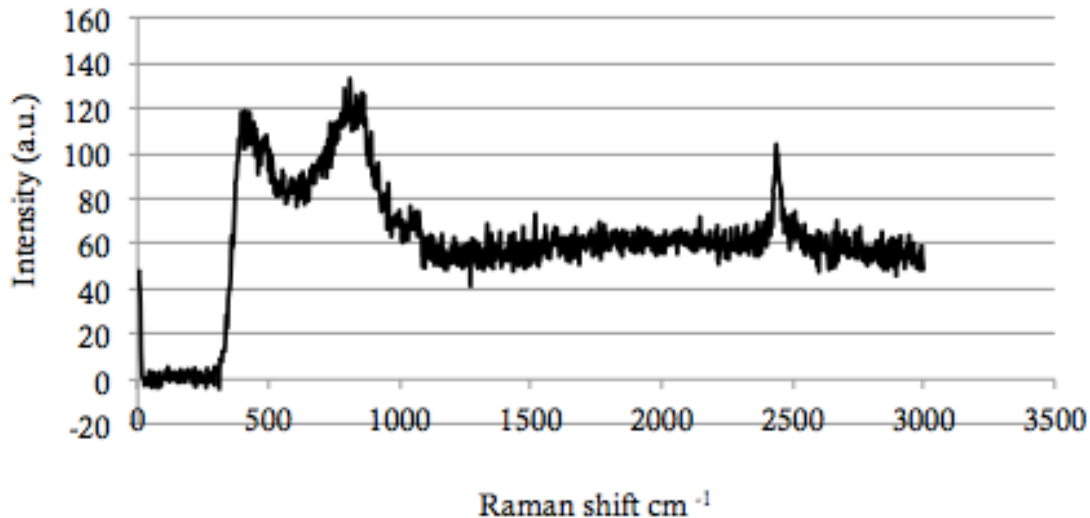


Figure 28. SEM images 2.5 wt % Fe loaded fly ash (a) at 500x magnification. The arrow shows small CNTs. In image (b) 20 wt % Fe loaded fly ash at 500x magnification shows that there were no CNT produced.

Close inspection reveals differences between the 2.5 wt % Fe and the 20 wt % Fe loaded fly ash. These experiments used low and high concentrations of iron nitrate to show which one resulted in greater production of CNTs. Figure 28a shows small carbon nanotubes, such as the one indicated by the white arrow. In Figure 28b the 20 wt % Fe white color shows that the catalyst is not uniformly distributed and the fly ash particles do not have a uniform size. The main challenge remains to obtain, according to Bakshi, et.al, <sup>[23]</sup> “a homogeneous distribution of CNTs in the matrix.”

## C- Raman Spectroscopy

Four samples each of the 2.5 wt %, 10 wt % and 20 wt % Fe loaded fly ash were subjected to the CVD process. The samples with in each wt. % showed consistent results when analyzed by Raman spectroscopy. The spectroscopic technique used to show a G and D band, observe vibrational, rotational, and other low-frequency modes in a system, by which molecules can be identified is shown in Figure 13. Raman spectra results are presented in Figure 29 using the sample of the 2.5 wt % Fe based on the little carbon nanotubes (CNTs) derived. For the 20 wt % Fe there was no yield in the results because there were no CNTs that were produced. Moreover, various analytical tests were conducted in order to see the amount of CNTs derived from the catalysts used.



**Figure 29. The Raman spectra for the 2.5 wt % Fe catalysts fly ash, (see text for more details).**

Figure 30 shows (a) 2.5 wt % Fe was able to generate results and the ratio of the intensity of the G peak (graphitic carbon) at (1518 cm<sup>-1</sup>) and D peak (defective carbon) at (1334 cm<sup>-1</sup>). This indicates the extent of graphitization of carbon in the reaction products (IG/ID). The Figure 30 image (b) shows 20 wt % Fe did not generate any results. Figure 30 image (b) 20 wt % Fe did not show any carbon nanotubes and, therefore, it did not produce the Raman shift. Dispersion was uneven because the metal catalyst and the fly

ash support showed weak interaction [24].

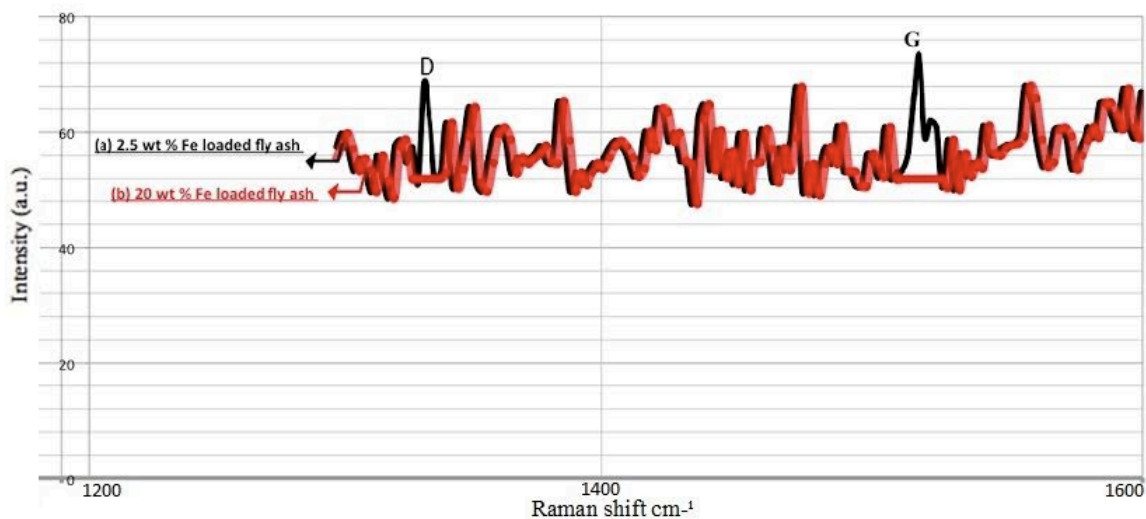


Figure 30. The Raman spectra for the two fly ash supported catalysts (a) 2.5 wt % Fe fly ash, and (b) 20 wt % Fe fly ash catalyst. The G peak (1518 cm<sup>-1</sup>) to D peak (1334 cm<sup>-1</sup>) intensity ratio indicates the extent of graphitization. The presence of the D and G bands indicates the presence of carbon nanotubes. The Raman Spectrum of 20 wt % Fe (shown in red) is superimposed on the other spectrum to emphasize the lack of CNTs produced. The 10 wt % (not shown) also had no CNT growth.

The CNT growth for the 2.5 wt % Fe has been attributed to the low strength interaction that exists between the metal and the support. In addition, there is a low G/D ratio, which is indicative of a low degree of wall graphitization and poor CNT quality. No CNTs were produced in the 20 wt % Fe catalyst. Studies have shown that the natural iron content in the fly ash is inactive during the process of CNT growth under the ideal reaction conditions. This has been attributed to the inherent heterogeneity of the location of iron and the composition of the fly ash [25]. However, metallic nanotubes are indicated if the light excitation energy is between 1.7 and 1.9 electron volts, and resonance is observed in the 1300-1700 cm<sup>-1</sup> wave number ranges. If the light excitation energy is above 2.2 electron volts or below 1.5, and resonance peaks are observed in the 1300-1700 cm<sup>-1</sup> wave number ranges, it is evidence of the semiconducting nature of

CNTs<sup>[26]</sup>.

Rafiei reports experiments are being conducted in order to determine whether CVD is an effective method for the synthesis of CNTs. The use of CVD represents one of the methods with the highest yield of the nanotube growth. However, the aim of this research was to fabricate vertically aligned CNTs with homogenous distribution on the surfaces and to create high uniformity. In previous studies, according to Rafiei, a silicon wafer was used as the substrate and nickel as a catalyst was deposited on the diffusion barrier from the Ni/Ti. The nickel dots were catalysts of about 1.6 micrometers and had about 200  $\mu\text{m}$  that had been patterned using UV and the e-beam lithography. In order to form CNTs, a triode plasma-enhanced chemical vapor deposition (PECVD) reactor was used with a gas ratio of  $\text{C}_2\text{H}_2$  over  $\text{H}_2$  or  $\text{NH}_3$  at a temperature of 620  $^\circ\text{C}$ . The positive ions in the cathode sheath were used in order to help in the growth of the CNTs<sup>[27]</sup>. In another experiment, Yamada, et al., used high efficiency water-assisted CVD in the synthesis of CNTs. They used iron as the catalyst for the synthesis of the CNTs and were able to achieve CNTs that had a carbon purity of 99.95%. Hence, these methods allow expanding of new techniques with best metallic catalyst particles to grow CNTs<sup>[28]</sup>. In this experiment, Fe clusters obtained at the various synthesis temperatures might vary in shape as well as in size.<sup>[36]</sup>

CVD is used as a preferred method for the preparation of CNTs in place of the arc discharge or laser ablation because CVD uses low temperatures. In addition, the orientation, nanotube length, alignment, purity, diameter, and density of the CNTs can be controlled when using this method. The catalyst in the CVD process helps ensured that there is decomposition of the carbon source. Hence, it is able to produce CNTs. The most frequently used catalysts in this process are iron, cobalt or nickel. These catalysts can be doped with other metals such as Au. Preferred carbon sources in the CVD process are hydrocarbons such as methane, ethane, acetylene, isobutene or ethanol<sup>[29]</sup>.

#### 4. Conclusion

Nanotechnology is an area of significant research based on the electrical and mechanical properties that have been attributed to CNTs. CNTs are suitable for use in a wide range of fields such as in medicine, engineering, manufacturing, military and for energy storage. With such diverse and important uses, it has led researchers to investigate how they can be efficiently produced. With the advent of its commercialization, it has led to various researchers looking for methods that they can incorporate in order to produce affordable CNTs.

One of the proposed methods has been the CVD process. Research has shown that the CVD process is a good method of growing nanotubes when using desired substrates. In the search for a desired substrate, Nath, et al., are exploring whether fly ash can be used to generate CNTs <sup>[30]</sup>. **The results of this research indicate that 2.5 weight percent iron is able to generate CNTs, albeit at a small lengths that cannot be commercialized.** High concentration (20 wt% Fe catalyst fly ash) did not produce CNTs. The significance of this project was the discovery that only low iron concentrations grew CNTs. Fe concentration should be between 2.5 or 5 (wt %). The Raman spectra in previous experiments done by Buckley, et al., have shown a G and D band intensity ratio of 1.4. However, in this experiment we were only able to achieve a G and D band intensity ratio of 1 <sup>[31]</sup>. Future research is needed to investigate ways that fly ash can be used efficiently to produce the required amount and quality of CNTs to be used for commercial purposes. In the future Ion Beam Deposition System (IBS) will be used to give a uniform distribution of the catalyst particles. Also, a different class of fly ash (from older anthracite coal) will be investigated. Other metals for use as catalysts could be promising.



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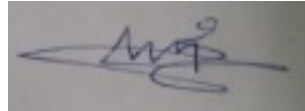
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