PARTICLE SIZE DISTRIBUTION AND QUALITATIVE/QUANTITATIVE ANALYSIS OF TRACE METALS IN THE COMBUSTION GAS AND FLY ASH OF COAL/REFUSE DERIVED FUEL

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This work includes two different areas of research. Both areas are related to the combustion of the binder-enhanced densified refuse derived fuel (bdRDF) with high sulfur coal and examining trace elements. The first area of this work involved studying the trace metals in the combustion gas of bdRDF/coal blend and the effect of the binder, $Ca(OH)_2$, on reducing the trace elements emissions. The second area of work involved studying the trace elements in the fly ash and the effect of the dRDF and the binder on trace metals.

Each individual person disposes of an average of four to six pounds of garbage each day. Cities are running out of space for landfill sites. America disposes of an average of 160-200 million tons of Municipal Solid Waste (MSW) a year and 90% of it goes into landfills. One way of reducing the volume of landfills is to burn MSW after turning it into RDF. A binder was added to the RDF in order to improve the quality and produce a good fuel. One concern in this development is the release of pollutants in the combustion process.

The $Ca(OH)_2$ binder enhanced dRDF pellets satisfies the requirement of environmental acceptability, chemical and biological stability, and better storability. The trace elements in the combustion gas were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), and in the fly ash using Energy Dispersive X-ray microanalysis (EDX). The results indicates that some of the trace metals were reduced with the use of dRDF and binder. A particle size distribution was also studied using EDX to show the increase and the decrease of trace metals in relation to eight different particle sizes.

The results indicates that the use of binder enhanced dRDF instead of sulfur-rich coal is promising in reducing some of the trace metals and many different kinds of organic and inorganic emissions. The use of bdRDF is environmentally and economically safe, and it reduces the number of landfills needed to dispose of waste.

PREFACE

This work encompasses two areas of reasearch. The first three chapters involve the work with densified refuse derived fuel (dRDF), and the effect of $Ca(OH)_2$ binder in reducing toxic trace metals during the combustion of a dRDF/coal mix. The fourth chapter involves the analysis of economizer fly ash for trace metals using SEM/EDX and ICP-AES.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

Garbage is an inexhaustible source. It is estimated that each American discards, directly or indirectly, an average of four to six pounds of garbage every day (1). There are over 200 million tons of garbage produced annually in the United States (2,3). This amount of garbage, which continues to grow, is causing many problems. During the summer of 1987, a 3,000 ton barge from New York traveled the coast searching for a landfill site to dump a load of garbage. During the same year the city of Philadelphia planned to ship their garbage to Houston, but the plan was turned down once the residents of Houston learned about it (30).

In the summer of 1988, the beaches of New Jersey were closed because of infectious waste that was washed up on the shore. It was caused by some of the garbage that was dumped on the Staten Island's Fresh Kills Landfill which fell into the ocean and drifted over to New Jersey's shores (6). The Staten Island's Fresh Kills Landfill is the largest landfill in the world, covering 3,000 acres (6).

Municipal Solid Waste

Municipal Solid Waste (MSW) is one of the least used by-product resources in the United States (1). The disposal of refuse is an increasing concern of municipalities and state governments throughout the United States. In the year 1990, it was estimated that 160-200 million tons of MSW was disposed from the residential, commercial, and institutional sectors (2,3). Each ton of municipal solid waste is equivalent in energy content to a barrel of oil (4). The disposal of MSW is increasing yearly, and it is an inexhaustible source.

Cities are running out of space for landfills. One of the attractive solutions to landfills is incineration. In the early 1970s, environmental concern began to rise causing citizens to become increasingly cautious of residing near landfill sites. Due to air pollution, the garbage or MSW was no longer burned. At that time there were many landfills, and new landfill sites were available for disposal of garbage. Those landfills are either full, or becoming full and new landfills are expensive and difficult to site. Burning MSW causes environmental concern, yet the population is still growing.

Americans dispose of eighty to ninety percent of their MSW into the landfills filling them very quickly. The landfills in America have been reduced from 10,000 in 1980 to 6,500 in 1988 (5). Not only is the air polluted because of MSW, but the ground water is polluted as well when the garbage decomposes. Changes in the weather and rainfall are major factors contributing to garbage decomposition. It has been estimated that water polluted today will be affected for hundreds of years (6).

In 1989, the Environmental Protection Agency (EPA) proposed regulations for stricter control of new and preexisting landfills. These measures, which should go into effect in 1991, will help in solving the problem, but are costly. It is estimated that it will cost over 800 million dollars per year to implement these methods nationwide. The regulations and controls include monitoring ground water for contamination, allowing for the controlled escape of methane which forms as the garbage decomposes, and permanently sealing landfills after they are filled (7).

Sources of Municipal Solid Waste:

Municipal refuse is a heterogeneous mixture of organic and inorganic wastes discarded by homes, schools, hospitals, and a variety of other sources in the community. The major contributers to solid waste are (8):

a) Domestic: single and multiple dwellings,

b) Commercial: offices and retail stores,

c) Entertainment centers: restaurants, hotels and motels, and service stations,

d) Institutional: schools, hospitals, and municipal buildings,

e) Municipal services: demolition and construction, street and alley cleaning, landscaping, catch basin cleaning, parks and beaches, and waste treatment residues.

Contents of Municipal Solid Waste:

Municipal solid waste is an aggregate mixture of waste materials that can be classified as an organic fraction, an inorganic fraction, and moisture. The organic fraction, which makes up to 30% of the waste, is primarily cellulose (wood fibers). It is considered a major source for energy recovery. The inorganic fraction is noncombustible. It can be either recyclable or after combustion constitutes the ash residue. Table I shows the summary of the chemical characterizations of MSW.

Another aspect or objective of many of the recovery processes of MSW is to utilize its thermal energy. The heat content of MSW is important. The heat content of the as-received refuse can reach 3,500 to 5,500 Btu/pound (8). A reduction of the moisture or inert contents will increase

Table I: Chemical Analysis of MSW (8)

Compound	% wt	%Moisture	%Inorganic	%Organic
Paper	38.0	8.0	3.0	27.0
Wood	3.5	0.5	0.3	2.7
Textile	1.5	0.5	0.0	0.0
Yard waste	14.0	6.0	0.7	7.3
Food waste	16.0	10.0	0.9	5.1
Rubber & leather	2.5	0.5	0.4	1.6
Plastics	3.0	0.4	0.3	2.3
Metals	10.0	1.0	9.0	0.0
Glass	10.0	1.0	9.0	0.0
Miscellaneous	1.5	0.1	1.4	0.0
Total	100.0	28.0	25.0	47.0

%Organics	
Cellulose, fat, wax, oil	79.0
Starch, protein	13.0
Rubber, leather	3.0
Plastics	5.0
Total	100.0

Table I continued....

<u>%Elements</u>

Carbon	23.4
Hydrogen	3.0
Nitrogen	0.3
Oxygen	20.0
Sulfur	0.1
Others	0.2
Inerts	25.0
Water	28.0
Total	100.0

<u>%Proximate component analysis</u>

Volatile matters	42.0
Fixed carbon	5.0
Moisture	28.0
Inert	25.0
Total	100.0

the heat content. Decreased quantities of plastics will also decrease the heat content of MSW (9).

There are many solutions that have been proposed for the problem of growing landfills and the increase in MSW. These solutions include mass burning, burying, recycling, and use as energy source using Refuse Derived Fuel (RDF).

Burning Municipal Solid Waste:

Burning MSW does not only reduce the volume of garbage by 80% but also provides a source of usable energy. MSW can be burned in three different ways:

1. Direct combustion, Mass burn: the MSW is fed into the furnace through a moving grate where the temperature reaches 2400°F. The problems with the mass burn incinerators are the cost of the incineration facility and the emissions.
2. Conversion of MSW into liquid or gaseous fuel by means of pyrolysis, biodegradation, or hydrogenation. The liquid or gaseous fuel produced can then be easily cofired with coal or oil.
3. Burning of the combustible portion of MSW, Refuse Derived Fuel (RDF), after separating the incombustible portion.

The incombustible portion of MSW and the ash are discarded in landfills which create a new problem, pollution. Ash contains some organic constituents and some trace elements at different levels. Ash is considered hazardous if the levels of toxic constituents are high.

Burying MSW:

Sanitary landfills were increased in 1976, when the Resource Conservation and Recovery Act (RCRA) gave the Environmental Protection Agency (EPA) the authority to close open landfills and upgrade the quality of sanitary landfills. Sanitary landfills are typically huge depressions lined with clay to minimize leakage of pollutants into the groundwater. Heavy equipment is used to spread the MSW out and compress it every day. After the landfill has been packed to capacity, a layer of dirt and/or plastic is used to cover the day's haul.

Sanitary landfill operators follow strict guidelines. They control and monitor methane gas generation, surface water runoff, and groundwater contamination by the landfill.

Refuse Derived Fuel

Refuse Derived Fuel, shredded MSW with most glass and metals removed, is an attractive solution since it also addresses another problem affecting the United States: depleting energy reserves. One ton of RDF has the energy equivalent of one barrel of oil (10). RDF also has a 7,000 to 8,000 Btu/pound heat content. The powdered RDF, embrittled and pulverized refuse, will even have a higher heat content of over 8,500 Btu/pound (8).

There are some problems associated with burning RDF. These problems include technical and environmental aspects. This study focused on trying to solve one of the environmental problems, toxic trace metals emissions. Those emissions, which are generated from the combustion of coal and binder enhanced dRDF/coal blend, were studied to see the effect of adding dRDF to coal. Another aspect was to study the binder ($Ca(OH)_2$), which was added to the RDF before pelletization to see if it has any effect on the trace metals emissions.

Refuse Derived Fuel (RDF) Technology:

The starting material of RDF is MSW. The exact composition of MSW varies according to the area, the time of the year it was collected, and the make-up of that particular community. Refuse Derived Fuel refers to the heterogenous mixture of the combustible portion of municipal solid waste (12). Table II gives a breakdown of the composition of MSW of Denton, Texas (31,41).

The concept of RDF has existed since the early 1970s (13). There are seven forms of RDF that have been defined as described in Table III (12). RDF is commonly used in two forms, fluff (RDF-1) and densified (RDF-5; d-RDF).

There are several problems with using RDF-1 that makes it less attractive, such as: it is hard to handle, it is usually burned in suspension, and RDF-1 often causes problems in handling ash since much of it remains unburned (6). On the other hand the main benefits of using RDF rather than raw refuse are (2):

- **RDF** when properly processed, can be stored for an extended period of time,
- **RDF** technology allows for the recovery of saleable material.
- **RDF** can be combusted in a wide range of existing boilers, fluidized bed combustors, gasifiers, and cement and brick kilns,
- **RDF** can also be used as a feedstock for anaerobic digesters to produce methane gas,
- **RDF** can easily be transported from one location to another,
- **RDF** can be burned in supplemental basis with other fuel, such as coal or wood,

Table II: Municipal Solid Waste composition in Denton, Texas 1981

a. Combustible	
Paper	52%
Plastic	14%
Wood	5%
Garden waste	4%
Food waste	3%
Rubber	1%
Leather	1%
b. Non-combustible	
Glass/ ceramic/ stones	9%
Ferrous	6%
Aluminum	2%
Industrial/commercial	2%
Residual dirt	1%

Table III: Types of Refuse Derived Fuel

RDF-1	Waste used as fuel in as-discarded form
RDF-2	Waste processed to coarse particle size with or without ferrous metal separation
RDF-3	Shredded fuel derived from MSW that has been processed to remove metals, glass, and other inorganic materials (95 wt% passes 50-mm square mesh)
RDF-4	Combustible waste processed into powder form (95 wt% passes 10 mesh)
RDF-5	Combustible waste densified (compressed) into a form of pellets, slugs, cubits, or briquettes (d-RDF)
RDF-6	Combustible waste processed into liquid fuel
RDF-7	Combustible waste processed into gaseous fuel.

.**RDF** is more homogeneous, yielding less variability in fuel characteristics, thereby making combustion control easier to implement. It also burns more evenly at a higher sustained temperature,

.**RDF** has a lower percentage of unburnable residuals such as metals and glass, and this has a higher heat content per weight than does unprocessed solid waste,

.**RDF** when burned in a dedicated boiler has a greater thermal efficiency (8-10 percent greater),

.and finally **RDF** can have a beneficial effect on air emissions and ash residue.

In order to effectively utilize the combustible portion of MSW, known as RDF, it is necessary to densify the RDF in order to transport it economically and easily. It is then called Densified Refuse Derived Fuel (dRDF). This densification step can increase the density of RDF from 2 to 3 pounds per cubic foot to 20 to 25 pounds per cubic foot (4). If dRDF is going to be stored for a period of time longer than several days, a binder must also be added. Calcium hydroxide ($Ca(OH)_2$), which was proven to be the best binder, is added to RDF before densification. The binder delays biological and chemical degradation for years (14).

Manufacture of Binder-Enhanced Densified Refuse Derived Fuel (bdRDF) Pellets

At first large items such as car batteries, refrigerators, and other hazardous items are removed from MSW. The recyclable items such as aluminum cans, glass, and cardboard are handpicked from the top of a conveyer. The material then goes through a shredder to reduce the particle size. The ferrous materials are picked up by a magnetic separator. The non-ferrous materials proceed to an air classifier and the lighter fraction of this goes onto a second shredder. After the second shredder, the material was then mixed with $Ca(OH)_2$, as a binder, until equally distributed in the RDF. The binder is added at different percentages forming different runs. The mixed material is then densified and formed into cylinderical pellets. It is then called Binder-Enhanced Refuse Rerived Fuel (bdRDF).

This procedure produces pellets that are usually denser and have a higher heating value compared to pellets which are produced by a lesser step process (12). That is the type of pellet that was used in the combustion test for this project.

bdRDF combustion:

Binder-enhanced densified refuse derived fuel was fired in conjunction with pulverized coal in a suspension-type boiler. The bdRDF and coal were mixed and conveyed to a bunker and burned over the grate in a fireball created by the combustion of pulverized coal. The most important problem to be addressed is the pollutants that are emitted when the pellets are combusted. These products include (16): Organic compounds, such as Poly Aromatic Hydrocarbons (PAHs), Poly Cyclic Biphenyls (PCBs), Dioxins, and Furans; acid gases including sulfur oxides, nitrogen oxides, and hydrogen chlorides; and trace metals including lead, mercury, nickel, cadmium, chromium, copper, beryllium, antimony, arsenic, barium, selenium, zinc, and thallium. Each of these compounds potentially pose an environmental threat to society. Some of the organic compounds such as dioxins are listed among the most toxic compounds known today (30). Others such as PAHs are linked to lung cancer. Acid gases contributes to the acid rain problem (40). The thirteen most toxic trace metals were also monitored in this study. They are considered toxic because of their effect on the biological systems.

Many of these pollutants are the product of incomplete combustion. They are more prevalent when they are burned at insufficient temperatures, when they are not burned long enough, or when too much or too little air is added to the fire. Hence, the operation of the facility and the efficiency of combustion become major factors in controlling air pollution.

These types of pollutants are also emitted, to some extent, in the combustion of coal. In using bdRDF there are two things to be evaluated. The first is whether burning a mix of bdRDF and coal pollutes the environment less than burning coal. The second involves evaluating the amount of pollutants generated by combusting bdRDF and disposing the ash in landfills.

This portion of the bdRDF project deals with the issue of pollution and involves the analysis of toxic trace metals in order to determine the effect of bdRDF and the effect of calcium hydroxide ($Ca(OH)_2$) binder on toxic trace metals emissions. This method was designed to collect a wide range of metals which may occur in the particulate and/or gaseous phases. The samples were collected isokinetically with an Anderson Universal Sampler equipped for Modified Method EPA 5 sampling.

Fly ash

Many cities dispose of their municipal solid waste by incineration. Incineration is one of the attractive solutions to landfills (14,18,32-34). However, mass burn incineration produces ash residues mounting up to 25 percent by weight and up to 10 percent by volume of the incoming MSW (18,32). Some of the main problems of using MSW as a feedstock have been variability, biological and chemical instability, and poor fuel quality (14,33).

There are many ways to dispose and use fly ash, the following which are frequently used (38):

1. construction products (cement mixture)
2. asphalt additive
3. soil modifier
4. mineral resources
5. coal mine reclamation
6. ocean disposal
7. ash pond disposal
8. landfill disposal

Fly ash consists of 70-95% inorganic matter, and 5-30% organics. It is important to know the toxic constituents; organic and inorganic.

Fly ash, a fine particulate effluent from burning municipal incinerators, is the major by-product produced from burning municipal waste (35,36). Approximately 1-2 percent of fly ash escapes into the atmosphere (37). There are about 35,000 tons of fly ash produced for each million tons of waste incinerated.

Since fly ash is the major by-product of incineration (35,36), and incineration is the main attractive solution to landfills that are growing daily (14,33,34,39), physical and chemical characteristics of fly ash are becoming more and more important in determining their method of disposal (8). Trace metals are important in the ash because of their toxicity, which plays a major role in characterizing the fly ash as hazardous and how and where it will be used.

Metals

Studying metalloenzyme systems indicates the importance of certain metals in chemical reactions within living organisms. Certain metals are essential in that they are absolutely necessary for life process (17-20). Other elements are nonessential, since if they are absent, other elements may serve the same function. Although metals have many physical properties in common, their chemical reactivity is quite different and their toxic effect on biological systems is even more diverse. Metals can be regarded as toxic if they injure the growth or the metabolism of cells when they are present above a specified concentration (18).

The toxicity of a metal depends on the chemical compound with which it is bound. The combination of a metal with an organic compound may either increase or decrease its toxicity. All metals are considered toxic at high concentrations, and some are considered highly toxic even at very low concentrations. The source of metallic contamination is the release of metal from fossil fuels such as coal or oil when burned. A considerable amount of lead, cadmium, mercury, nickel, chromium, vanadium, and copper enters the atmosphere or deposit on the ash because of their presence in the fuel.

The following is a summary of the thirteen trace metals which were studied in this portion of the project (17-28):

Beryllium:

Beryllium has a short and long term fatal effect. It causes a chemical pneumonitis effect, dermatitis, mucous membrane irritation, and a respiratory disorder (17,19-21,26,27).

Antimony:

Animals exposed to fumes of antimony oxide develop pneumonitis, fatty degradation of the liver, decreased leucocyte counts, and damage heart muscles. Humans may face skin membrane irritations. Generally antimony and its compounds are considered very toxic (17,19,20,21,27).

Chromium:

Chromium is essential for the normal metabolism of glucose. Its compounds are suspected carcinogens, as evidenced by the cancer rate in the chromate-producing industry. Chromium causes infection of the nasal septum, congestion, hyperemia, emphysema, tracheitis, pharyngitis, bronco-pneumonia, dermatitis, and metal fume fever (17,19,20,23,27).

Arsenic:

Exposure or poisoning by arsenic can result in diarrhea, severe colic, bloody feces, reproductive system problems, cirrhosis of the liver, nerve disorder, kidney disorders, and skin disturbances (17,19,20,21,27).

Cadmium:

Cadmium reduces growth, and reduces the protein and fat digestion and absorption. The most notorious case of cadmium toxicity was the disorder known as Itai-Itai disease which occurred in Japan. Itai-Itai disease, caused by chronic-cadmium poisoning, makes bones so fragile that they can be broken by a hand shake. Cadmium causes hypertension and cardiovascular problems and is retained in the kidney and the liver (17,19,20,22,23,25,27).

Copper:

Copper is considered an essential element in trace amounts. Its toxic symptoms, if present at high levels, lie in the form of metal fume fever, respiratory disease, and other systemic disturbances (17,19,20,22,23,25-28).

Lead:

Lead is deposited in the bones and the soft tissues, particularly the brain, where it results in reduced functioning. Lead can cause structural damage to the nephrons of the kidneys resulting in the loss of amino acid, glucose, and phosphate in the urine. Lead has also been linked to increase dental caries, intestinal colic, peripheral neuropathy, and encephalopathy. Symptoms of lead poisoning include headache, fatigue, and weight loss (17,19,20,22,25-27).

Nickel:

Nickel is considered an essential element in trace amounts. Nickel and its compounds cause cancer of the lungs, dermatitis, sinus disturbances, and other respiratory diseases (17,19,20,22, 25-27).

Selenium:

Long exposure to selenium may lead to gastrointestinal disorders and disturbances of the nerve system. Selenium is connected to an increase in dental caries in children and irritation of the eyes, nose, throat, and respiratory tract (17,19,20,21,27).

Mercury:

Mercury poisoning often goes unnoticed because of its initially vague symptoms. Preliminary symptoms include fatigue, headache, and irritability followed by numbness in the extremities, blurring of vision, deterioration of muscular coordination, emotional disturbances, atrophy of muscles, and eventually death (17,19,20,27).

Zinc:

Generally, zinc and its compounds are considered nontoxic, but high concentrations of zinc can be harmful. Zinc is an essential element. Zinc is commonly associated with various other metals such as lead, copper, and cadmium, which makes the effects of zinc difficult to distinguish. The most common effects of zinc are metal fume fever, nausea, aching, vomiting and diarrhea (17,19-23,25-27).

Thallium:

Thallium accumulates in the kidneys, bones, and soft tissues. It is considered toxic and an accumulative poison which affects the nervous system causing various disorders (17,19,20,27).

Barium:

Experiments suggest that barium sulfate may contribute to the endotoxemia by generating bradykinin. Other barium salts such as acetate, carbonate, chloride, hydroxide, nitrate, and sulfide are highly toxic by ingestion. The pneumoconiosis, baritosis, results from inhalation of sulfate and oxide salts as fine dusts. Barium initially stimulates striated, cardiac, and smooth muscle and depresses serum potassium which is forced intracellularly. Subsequent muscle weakness may result from a direct depolarizing effect and neuromuscular blockade (17,19-21,26,27,42,43,44).

Combustion effect on trace metals

Combustion of bdRDF affects metals in various ways. The major portion of mercury, cadmium, lead, and chromium follows the combustion flue gases due to volatilization. The metals either go with the flue gas or become part of the collected fly ash. The lead and cadmium in paper and plastics is mostly vaporized.

The management of combustion, air control and flame temperature determines, to a significant extent, how much of these metals are vaporized. The same is true for furnace systems using flue gas recirculation to reduce flame temperatures in the combustion zone. The particulate emissions were greatly reduced by optimum combustion air settings, lifting of the particulate from the bed, lowering the height of the flame, and reducing flame penetration into the boiler (29).

As the combustion gas cools, the metals condense on the particulate matter. The presence of chlorine and sulfur in the bdRDF causes mercury, lead, and cadmium to form chlorides and sulfates. Lime injection, an alkaline material, can substantially inhibit these reactions.

Summary

Combustion of MSW is an attractive alternative to landfilling. The benefits of incineration come from reducing the number and the size of landfills as well as recovering energy from the waste. Burning MSW reduces the volume by 80-95 percent. One of the challenges in developing MSW as a source of energy is the amount of pollutants released during the combustion. These pollutants include inorganic acid gases, heavy metals, and toxic organics.

Refuse derived fuel, shredded MSW with most of the glass and metals removed, is an attractive way, since it produces more energy than MSW. In order to effectively utilize the RDF, it is necessary to densify it to produce more energy. Densified refuse derived fuel (dRDF) will be easily and economically transported.

A binding agent was developed for pelletized densified refuse derived fuel (dRDF). The study showed that calcium hydroxide ($Ca(OH)_2$) is effective in reducing the rate of biological and chemical degradation of dRDF pellets. It is also believed that calcium hydroxide has the potential to reduce the production of the pollutants and as well reduce the amount of pollutants that goes into the atmosphere.

This study was conducted to provide information on heavy metal emissions in order to demonstrate that it is possible to reduce these emissions. The most toxic heavy metals of concern are As, Ba, Be, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn.

The binder can reduce the trace metals emissions as well as other harmful emissions, such as dioxins, furans, PCBs, and PAHs, and acid gases. The bdRDF technology could become the answer to the society's landfilling problems as well as the energy problem.

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CHAPTER II

EXPERIMENTAL PROCEDURES

The Refuse Derived Fuel project, which was started at the University of North Texas (UNT), involved many phases, each with its own experimental procedures. The first phase, that was done a few years ago, was the selection and development of an appropriate binder for the densified refuse derived fuel (dRDF) pellets. The second phase was the collection, extraction, and analyses of the samples from the cofiring of dRDF and coal blend. The binder had a great effect on the pellets and on the whole study in general. It is worth while to begin with a history of development of the binder enhanced dRDF.

Binder Selection

The work to select the best binder for this project started in 1984 with a contract between the University of North Texas (UNT), our group, and Argonne National

Laboratory (ANL). After extensive library research and consulting with industry experts, 150 binders and binder combinations were selected. The preliminary evaluation of the binders eliminated more than half of these, either because of the cost, the environmental acceptability, or the effectiveness of it as a binder (1).

The remaining sixty seven binder candidates were then subjected to further studies, tests and protocols. The candidates included glue, oil, kiln dust, and wax. The protocols consisted of laboratory and environmental studies (2). The laboratory studies included binder ash content, binder Btu content, pellet's durability, pellet's water sorbability, and pellet's weatherability. The environmental protocols included the toxicity and the potential of harmful emissions of the binder. Each of the tests was given a certain amount of points which were totalled at the end of the protocol. The binders were then ranked by the assigned values of each protocol. At the end of this testing, the binders were reduced to thirteen candidates.

The remaining thirteen binder candidates were tested in a large scale pelletization process in July of 1985. The test was conducted at the Jacksonville, Florida Naval Air Station. About seven tons of RDF were used in the study; six and a half tons of which came from the Ames, Iowa facility, and a half ton from the Pompano Beach facility in Florida.

Fifty-four pelletization runs were produced at about two hundred fifty to three hundred pounds of RDF each.

The pellets, after being returned to UNT, were subjected to a series of tests including bulk density, integrity of the pellets, moisture loss with respect to time, durability, water sorbability, Btu content, and ash content. Based on all of these tests, it was determined that calcium hydroxide ($Ca(OH)_2$) was the top ranking binding agent.

The Co-firing of bdRDF and Coal

Preliminary Burn Test:

A preliminary burn test was conducted in May 1987 at Argonne National Laboratory, before a full scale cofiring, to ascertain and evaluate any potential problems. Eight and a half tons of Thief River Falls bdRDF pellets were cofired with coal in the same boiler that would be used during the full scale test burn.

The test consisted of ten percent bdRDF, by Btu content, with high sulfur Kentucky coal. Information was obtained pertaining to various sites handling, laboratory techniques, methods of blending the coal with bdRDF, and determining the consumption rate of the coal and bdRDF by the boiler. Also preliminary procedures for collecting, examining, and analyzing the various samples were arranged.

This information was returned to UNT, studied very well, and a plan was put forth for the six week full scale cofiring of the coal/bdRDF blend. That study minimized mistakes and problems of working with the fuel blend and collecting the samples.

The Full Scale Burn Test:

In the full scale cofiring combustion test, the fuels consisted of sulfur-rich Kentucky coal and bdRDF. Coal and bdRDF were blended at different bdRDF ratios by Btu content. The bdRDF contained different levels of calcium hydroxide as a binder.

The coal/bdRDF mixes were fired in the power plant of ANL during a six week period in June/July of 1987. With each different blend of fuel, the boiler was allowed to reach a steady state of operation before sampling took place. Background information was collected by sampling and collecting data during the firing of one hundred percent coal.

bdRDF Fuel

The University of North Texas and Argonne National Laboratory conducted the full scale cofiring of bdRDF and high sulfur Kentucky coal at ANL Boiler #5. About 1500 tons of coal and 600 tons of bdRDF were burned during the six weeks burn test. The bdRDF pellets were provided by two sources, the Future Fuel, Thief River Falls, facility and the Reuter facility.

The Future Fuel is a small scale, on-line dRDF processing facility which produces 60 to 80 tons per day of dRDF. This facility uses Lundell equipment and had been in use for nearly a year since the pellets used for this study were made.

Approximately 300 tons of pellets were produced during the end of 1986 and were stored at their facility until the summer of the 1987 combustion test. Calcium hydroxide ($Ca(OH)_2$) was used as a binder in manufacturing the pellets. About 75 tons of 0% binder bdRDF pellets, 50 tons of 4% binder pellets, and 75 tons of 8% binder pellets were made by Future Fuel facility.

The Reuter facility, which is capable of manufacturing 400 tons of dRDF per day, uses Buhler-Miag equipment. The plant was opened about a month before the burn test started. About three hundred tons of pellets, having the same binder content composition as the Future Fuel pellets, were obtained from the Reuter facility. An extra seventy-five tons of dRDF pellets, which had some of the plastic removed from it, was also obtained from this facility. Those pellets contained 0% and 4% calcium hydroxide binder. The exact amount of plastic removed was not determined.

Kentucky Coal

ANL is currently burning high-sulfur Kentucky coal brought from local (Chicago-area) vendors having storage yards within 25 miles of ANL. These yards receive coal transported from the mines by barge. Delivery of the coal to ANL is by 30 to 40 ton truckloads. A maximum of three to four truckloads per day is delivered. A typical coal sample analysis taken on January 8, 1987 is given in Table IV.

During the test runs, samples were taken at each of the two weight scales at two hour intervals, composited, and hand-sorted to determine the percentage, by weight, of coal and bdRDF. These fuel samples are being analyzed for the coal, bdRDF, and bdRDF/coal mixtures for: proximate analysis, ultimate analysis, heat value, ash fusion temperature, bulk density, and fuel content (e.g. percent by weight or heat input of bdRDF and coal).

Boiler Configuration

The boiler plant at Argonne National Laboratory consists of five boilers that provide the steam requirement for the entire laboratory. The steam produced by the five boilers is used primarily for space heating but also for refrigeration and for driving emergency electrical turbo-generators. The newest and largest boiler is Boiler #5, which was used to conduct this burn test. It is the only one which is a spread-stoker coal fired boiler; the others use a combination of gas and oil burners.

This boiler was built by the Wickes Boiler Company and was installed in 1965. It has a rated capacity of 170,000 pounds of steam per hour at a gauge pressure of 200 psig saturated. This is equivalent to about 212 x 10^6 Btu/hour. At its maximum capacity, this boiler uses nine tons of coal per hour rated at 11,600 Btu/lb. A rate of 4.1 tons of coal per hour was needed for the boiler to operate at its average capacity of 8,500 lb/hour. The boiler had never been operated over 13,000 lb/hour, although its capacity is 170,000 lb/hour. The combustion test was done at the capacity that was needed at the time and not the maximum boiler capacity. During the test run, the average operating capacity was between 90,000 and 100,000 lb/hour. Further

Table IV: Sample Analysis of Kentucky Coal

Proximate Analysis	As Received	Dry Basis
% Moisture	6.28	xxxx
% Ash	8.15	8.70
% Volatile	37.28	39.78
% Fixed Carbon	48.29	51.52
	100.00	100.00
BTU/lb	12,461	13,296
% Sulfur	2.70	2.88

Ultimate Analysis	As Received	Dry Basis
% Moisture	6.28	xxxx
% Carbon	69.17	73.81
% Nitrogen	1.49	1.59
% Hydrogen	4.79	5.11
% Chlorine	0.01	0.01
% Sulfur	2.70	2.88
% Ash	8.15	8.70
% Oxygen (diff.)	7.41	7.90
	100.00	100.00

Bulk Density = 41.96 lb/ft^3
Free Swelling Index = 4

Ash Fusion Temperature	Reducing	Oxidizing
Initial Deformation	1950°F	2380°F
Softening (H=W)	2175°F	2500°F
Softening (H=1/2W)	2285°F	2585°F
Fluid	2390°F	2650°F

design performance data of Boiler #5 was shown in Table V. A schematic drawing of the boiler is shown in Figure 1.

Pollution Control Equipment

The air pollution control equipment associated with Boiler #5, at ANL, consists of a mechanical multiclone collector followed by a spray dryer absorber and a fabric filter baghouse. As the gases and associated particulates depart the boiler, they first enter the multiclone collector which is also called a multiple cyclone. The cyclone causes the gas stream to change direction while the particulates, which are heavier, continue in the same direction and become separated from the gas stream. The multiclone collector at ANL was built by Western Precipitation Inc. and contained 105 individual cyclones with a removal efficiency of 90% of the particulate from the gas flow. The multiclone is the most popular type among mechanical collectors.

Table V: Test Boiler (Boiler #5) Design Performance Data

Manufacturer: Wickes Boiler Company (now Combustion Engineering Company)

Date Installed: 1965

Boiler Area: 17,647 ft^2

Economizer Area: 11,900 ft^2

Water Wall Area: 1,345 ft^2

Furnace Volume: 9,600 ft^3

Turndown Capability Ratio: 3.3 : 1

Firing Equipment: Hoffman Stoker-Grates

Performance Based on Fuel of Not Less Favorable Analysis Than: Bituminous Coal

Moisture	13.0%
Vol. Matter	36.5%
Fixed Carbon	41.1%
Ash	9.4%
Total	100.0%
Btu/lb (as fired)	11,200
Fusion Temp of Ash	2050°F

Load Fuel	1/2 MCR* Coal	MCR* Coal
Steam Output, 10^{6}lb/hr	85.0	170.0
Press, in Boiler Drum (psig)	200.0	200.0
Temp. Feed Water Entering Feed water Heater	228°F	228°F
Temp. Feed Entering Econ.	292°F	270°F
Temp. Feed Leaving Econ.	350°F	347°F
Temp. Air Entering Unit	100°F	100°F
Temp. Gas Leaving Boiler	500°F	582°F
Temp. Gas Leaving Econ.	331°F	346°F
Excess Air-Boiler Exit	37%	30%
Excess Air-Econ. Exit	38%	31%
Wet Gas at Boiler Exit, 10^6#/hr	113.10	217.00
Wet Gas at Econ. Exit, 10^6#/hr	114.00	219.00
Air Weight Entering Unit, 10^6#/hr	100.00	191.00
Draft in Furnace, H$_2$O	0.10	0.10
Draft Loss thru Boiler, H$_2$O	0.27	1.00

* Maximum Continuous Rating

Table V .....continue...

Draft Loss thru Collector, H_2O	0.65	2.20
Draft Loss thru Econ., H_2O	0.33	1.20
Draft Loss thru Glass, Baffle, H_2O	0.22	0.80
Draft Loss thru Flues, H_2O	0.19	0.70
Draft Loss Total	1.76	6.00
Air Press. Loss thru Burners, H_2O	-	-
Air Press. Loss thru Damper Ducts, H_2O	0.20	0.70
Air Press. Loss thru Stoker, H_2O	0.55	1.10
Air Press. Loss Total	0.75	1.80
Water Press. Loss thru F.W. Htr., $\#/in^2$	2.10	8.20
Fuel Burned, $10^6\#/hr$	8.99	18.00
Liberation, $Btu/hr/ft^3$	10,450	22,500
Heat Losses		
Dry Gas (%)	5.94	6.01
H_2 & Moist. in Fuel (%)	5.21	5.24
Moist. in Air (%)	0.15	0.15
Unburned Combustible **	1.30	2.30
Radiation	0.90	0.40
Manufacturer's Margin	1.50	1.50
Total Losses	15.00	15.60
Efficiency	85.00	84.40

** Based on 50% Recovery

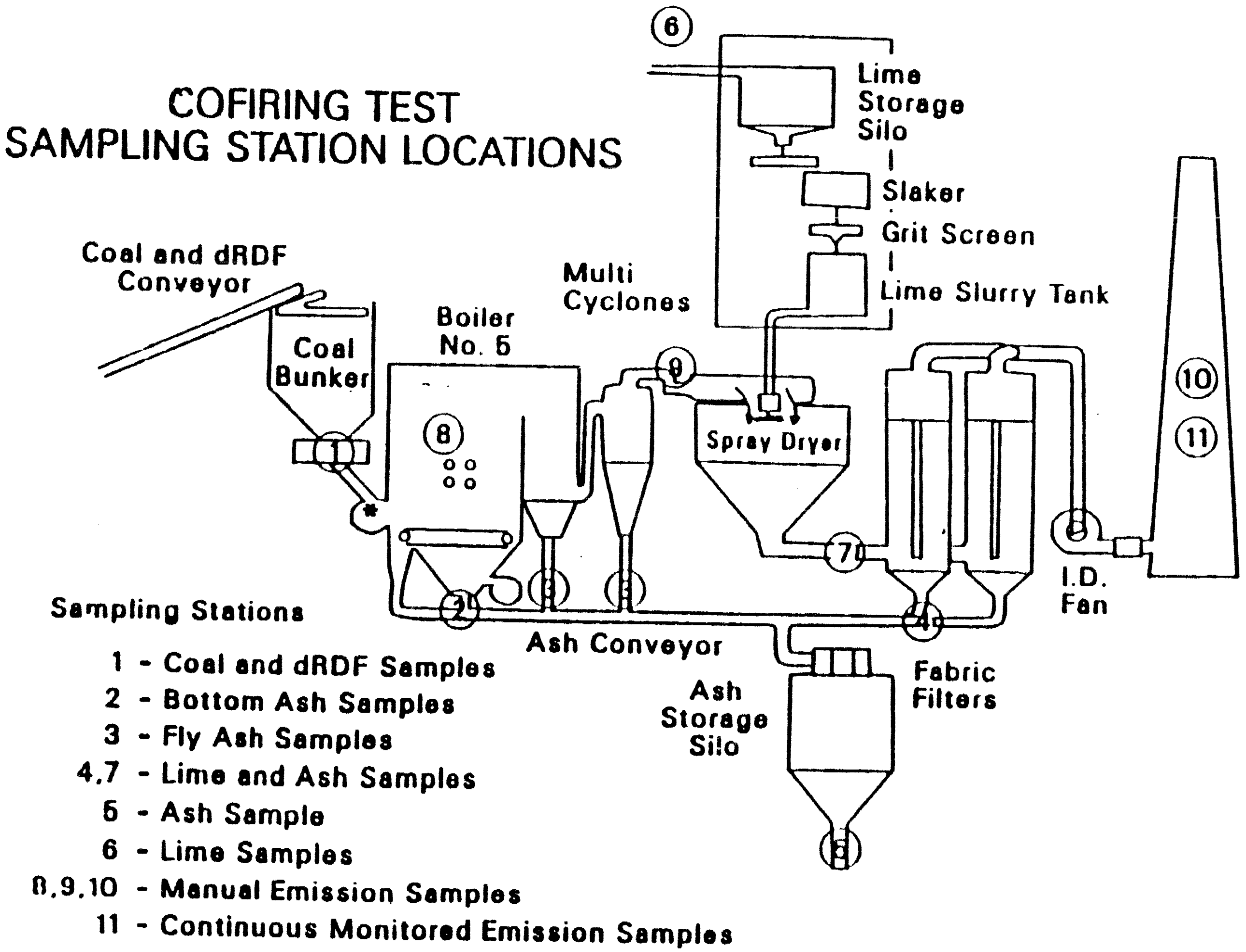

Fig. 1 Schematic Arrangement of Test Boiler and Pollution Control Equipment

The efficiency of the multiclone collector decreases as the particle size decreases, since it is difficult to separate the particulate from the gas stream when they are smaller and lighter. Generally the literature places the value of the collector efficiency to be in the range of 65-75 percent (4). The multiclone at ANL has a higher efficiency of 90% for the removal of particulate for a gas flow rate of both 50,000 and 25,000 SCFM. The actual efficiency value lies in between the two extremes.

ANL uses other types of pollution control with the multiclone, since it does not meet the pollution control codes by itself. However, the multiclone increases the efficiency of other pollution control equipment by removing the bulk of the particulate from the gas stream before it encounters the remaining equipment (4).

After the flue gases exit the multiclone collector, they are ducted into the spray dryer absorber (SDA) through a system of two gas dispersers. While passing though the two dispersers, the flue gas contacts a fine spray of absorbent (lime feed slurry). The SDA has the ability to remove particulate and gaseous pollutants including vapor phase organics and acid gases (1,4,5). The mechanisms of particulate removal are varied and include inertial impaction, direct interception, and diffusion (Brownian movement) (5). In all mechanisms the particulate and the vapor phase gases are eventually absorbed on the droplets of absorbent. Water evaporation causes the droplets to dry; causing the gas stream to cool. In the cooler gas stream, remaining vapor phase species, especially the trace elements and organics, are condensed and can be absorbed onto the remaining droplets or onto the dried solid particulate (6). Control of the gas distribution, lime feed rate, temperature and pressure within the SDA module assures that the reacting droplets reach their desired level of dryness before they leave the SDA chamber. A portion of the dry product, consisting of fly ash, calcium sulfite, calcium sulfate, and unreacted lime, falls to the bottom of the absorption chamber. The material is then conveyed to the recycled material disposal silo. The efficiency of an SDA depends on many variables including the droplet size of the absorbent, the diameter of the particulate, and the design variances of each particular unit. The SDA at ANL is designed to remove a minimum of 78.3% of the SO_2 contained in the flue gases exiting the boiler multiclone system when the total boiler flue gas flow rate varies from 87,600 pounds per hour (35% MCR) to 219,000 pounds per hour (100% MCR) (1). Design specification data for the SDA that was used during the burn are listed in Table VI.

While the SDA removes the possible pollutants, the primary task of it is the removal of SO_2 and HCL. The

Table VI: SDA Design Performance Data

Maximum Continuous Rating (% MCR)	35**	70**	100
Flue gas to absorber			
(ACFM)	28,869	53,677	73,608
(lb/hr)	87,600	153,300	219,000
Flue gas inlet temp. to absorber (°F)	330	346	346
Flue gas outlet temp. from absorber	146	148	148
Flue gas ACFM to baghouse	24,415	43,059	61,519
Flue gas inlet temp. to baghouse	146	148	148
Flue gas outlet temp. from baghouse	136	138	138
Flue gas dew point temp. outlet from baghouse	12	128	128
Flue gas ACFM from baghouse	24,620	43,415	62,035
Barometric pressure(mm Hg)	760	760	760
Sulfur in fuel* (%)	3.5	3.5	3.5
SO_2 from boiler (lb/hr)	441	882	1,260
SO_2 leaving bag filter at 78.3% removal (lb/hr)	95.7	191	272
Outlet leading baghouse (GR/ACF)	0.01	0.01	0.01

Flue Gas Analysis (volume %)

	35% MCR	75% MCR	100% MCR
O_2	6.74	5.00	5.00
N_2	75.73	74.90	74.90
CO_2	10.32	11.82	11.82
H_2	6.95	8.02	8.02
SO_2	0.23	0.26	0.26

	35% MCR**	75% MCR**	100%MCR**
Raw Pebble (lb/hr)	479	838	1,198
Water	11.6	19.4	26.4
Ayomizer KW	50	82	111
Disposable material(lb/hr)	1,074	1,970	2,814

* As specified

** These figures are calculated with the assumption that the flue gas flow in the 70% case is in direct proportion with the 100% figure supplied and that the flue gas flow in the 35% is equal to 40% of the flow in the 100% case.

reaction of these processes are given below (38):

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$

The treated and cooled fuel gases are exhausted from the SDA module and flow to the baghouse. The flue gases pass through a filtration system, the bags, where the remaining particulates in the flue gases are filtered out. This removes the fly ash and entrained spent dry chemicals. The clean, scrubbed flue gases exit the baghouse and pass through the inducted draft fan and stack, escaping to the atmosphere. Table VII gives the performance design data for the baghouse.

Fuel Handling and Storage

The bdRDF pellets, as previously mentioned, were obtained from two sources: the Future Fuel Inc. and the Reuter Inc. facilities. In a six week period from June 3 to July 7, 1987, twenty-six shipments were delivered to ANL. There were ten shipments totaling approximately two-hundred and twenty five tons from the Future Fuel facility, and sixteen shipments totaling approximately three hundred and fifty-two tons from Reuter Inc. Nearly all shipments contained over twenty-tons of dRDF pellets each. The pellets were manufactured with $Ca(OH)_2$ as a binder at 0, 4, and 8 percent. Table VIII shows the deliveries of bdRDF.

The two different types of pellets had different bulk densities. The Future Fuel pellets typically had bulk densities of 25-27 lb/ft^3, compared to the Reuter pellets which had bulk densities of 40-45 lb/ft^3 (7,35,38). The greater the bulk density of the pellets, the more mechanically durable they are. To maintain the integrity of the pellets, during the combustion test, the pellets were handled as little as possible.

The pellets were stored outdoors at ANL covered by tarpaulin to minimize the exposure to outside elements. But the tarpaulin trapped all the moisture coming from the pellets. The moisture condensed under the cover and settled on the top layer of the pellets. The tarpaulin covers were therefore removed hours before using the pellets to allow them to dry as much as possible.

Table VII: Baghouse Design Data

	35% MCR	70% MCR	100% MCR
Gas volume (ACFM)	24,415	43,059	61,519
Temperature (°F)	146	148	148
Bag fabric			Huyck Glass Fiber
Number of compartments			4
Bags per compartment			280
Bag diameter (inches)			6
Bag length (feet)			12
Total filter area per compartment (sq. ft.)			5,278
Total air-to-cloth ratio			
Gross	1.2:1	2.2:1	3.03:1
Net (with 1 comp. off-line)	1.6:1	2.8:1	4.04:1
Hopper outlet clearance to ground			4.0 feet
Length			48.1 feet
Width			30.0 feet
Height			45.0 feet

Table VIII: Deliveries of bdRDF

TRF = 224.68t
MIN = 352.33t

Date	(#/cu. ft.) Bulk Density	Type	% Binder	Tons
3 June 87	40.4	MIN	0	23.57t
4 June 87	27.3	TRF	0	20.42t
5 June 87	44.1	MIN	4	23.85t
5 June 87	27.4	TRF	4	19.39t
11 June 87	45.9	MIN	8.5	23.85t
11 June 87	29.6	TRF	8	23.38t
3 June 87	52.7	Coal		
11 June 87	53.9	Coal		
15 June 87	26.5	TRF	0	23.75t
15 June 87	26.5	TRF	0	23.20t
15 June 87	42.6	MIN	0	23.78t
16 June 87	42.9	MIN	0	21.84t
19 June 87	45.6	MIN	8	23.37t
20 June 87	45.6	MIN	8	23.23t
22 June 87	24.7	TRF	4	23.98t
22 June 87	24.7	TRF	4	23.95t
23 June 87	44.1	MIN	4	23.21t
24 June 87	25.6	TRF	8	21.43t
24 June 87	27.0	TRF	8	23.69t
24 June 87	44.1	MIN	4	22.70t
25 June 87	25.1	TRF	8	21.49t
26 June 87	43.3	MIN	4	23.27t
29 June 87	41.2	MIN	4	23.88t
29 June 87	42.8	MIN	4	21.98t
1 July 87	40.8	MIN	0*	19.72t
2 July 87	41.5	MIN	0*	19.44t
7 July 87	43.3	MIN	4*	21.68t
7 July 87	43.9	MIN	4*	13.25t

* Less Plastic

Coal/bdRDF blend

Following the successful combustion test of 8.5 tons of the Future Fuel binder-enhanced dRDF pellets, which were burned at ANL during May of 1987, much was learned about the blending of bdRDF with coal. For example bdRDF appears to have less of a dust problem than the coal presently being used. A four cubic yard front end loader was used to blend the coal with bdRDF. It was determined that three volumes of coal with one volume of bdRDF pellets produced a blend close to 10% bdRDF by Btu content. The coal/bdRDf was blended until the material looked roughly homogeneous. This was accomplished by approximately four turnings by the front end loader.

The pile was moved to the coal pit and then transported by a conveyer to the coal bunker. From the coal bunker, the mixture went to the boiler passing through the coal scale, which measures and controls the rate at which the mixture is introduced into theboiler. The rate at which the coal/bdRDF mixture was burned was based on the amount of heat required by the system at that time.

The burning test consisted of twelve different runs. The actual coal/bdRDF run schedule is shown in Table IX, indicating the time, date, run number, composition of coal/bdRDF in Btu content, and the calcium hydroxide (binder) percentage. Two runs were made by firing one hundred percent coal in order to establish base line data. The Future Fuel and Reuter Inc. pellets were burned back to back, but they were kept separated so that any difference in the performance characteristics or emission amounts between the pellets could be detected.

Collection plan

During the six week test, over 1500 samples of flue gas emissions, fly ash, bottom ash, and feed stock samples were collected during the 12 runs given in Table IX. Sampling stations are shown in Figure 1. The organic emission samples were collected at sampling stations 8, the boiler; 9, the duct; and 10, the EPA observation port. The trace metals were taken at sampling stations 9 and 10. The inorganic acid gas samples were collected from the sampling station 9. The fly ash samples were collected from the multicyclone and from the economizer, sampling station 3.

The bottom ash samples were collected from undergrate and through the grate, sampling station 2. The feedstock samples were taken at the coal scale A and B every two hours to determine the percentage of bdRDF in the coal/bdRDF mixture, and to be analyzed for proximate analysis, heat content, and ash fusion temperature. Lime and ash samples

Table IX: Coal/dRDF Test Run Scheduale

Run #	Date	Composition/Pellet Source	%Binder
1	1-5 June	Coal	xxxxx
2	5-7 June	Coal, 10% dRDF	0
2	7-8 June	Coal, 10% dRDF	0
3	8-10 June	Coal, 10% dRDF	4
3	10-12 June	Coal, 10% dRDF	4
4	12-13 June	Coal, 10% dRDF	8
4	13-15 June	Coal, 10% dRDF	8
1	15-18 June	Coal	xxxxx
5	18-20 June	Coal, 20% dRDF	0
5	20-23 June	Coal, 20% dRDF	0
7	23 June	Coal, 20% dRDF	4
6	23-25 June	Coal, 30% dRDF	8
6	25-26 June	Coal, 30% dRDF	4
7	26-28 June	Coal, 20% dRDF	4
8	28 June-1 July	Coal, 20% dRDF	8
12	1-4 July	Coal	xxxxx
11	4-5 July	Coal, 50% dRDF	4
12	5-6 July	Coal	xxxxx
9*	6-7 July	Coal, 30% dRDF	0
10*	7-8 July	Coal, 30% dRDF	4
12	8 July	Coal	xxxxx

* reduced plastic content dRDF pellets

were taken three times a day from sampling stations 4 and 7. Also, the moisture, CO_2, and O_2 content were determined by a Fyrite or an Orsat analyzer during the twelve test runs.

Ash and feedstock samples were analyzed for EP toxicity and for trace metals content (37). The organic flue gas emission samples were analyzed for PolyChlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), and Dioxins and Furans using Gas-Chromatography/Mass Spectrometry (GC/MS)(35,38). The inorganic flue gas emission samples were analyzed for SO_x, NO_x, CO_2, HCl, HBr and HF using High Performance Liquid Chromatography (HPLC)(36).

The main focus of this work involved the analysis of toxic trace elements emission samples which were collected from sampling station 9. Thirteen elements were studied and analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP/AES). The elements of most environmental concern are:

As	Arsenic	Tl	Thallium
Cd	Cadmium	Ba	Barium
Hg	Mercury	Be	Beryllium
Pb	Lead	Cr	Chromium
Sb	Antimony	Cu	Copper
Se	Selenium	Ni	Nickel
Zn	Zinc		

Trace Elements Collection Apparatus

Trace elements emission samples were collected with an EPA Modified Method 5 (EPA MM5) sampling train (39). Figure 2 shows a schematic diagram of the sampling train.

The sampling train was designed to collect samples isokinetically. Isokinetic sampling is accomplished by uniform sampling of both particulate and gases in the stack. In order to achieve this sampling state, the velocity being drawn into the sampling train by the vacuum must equal the velocity of the gas stream. The velocity of the gas stream in the stack was measured by pitot tubes. If the gas stream velocity changes, the sampling train vacuum must also be changed in order to maintain an equal velocity of gas entering the train.

The sampling train employed five impingers to assist in cooling down the gas stream and provide a means to collect the trace elements. Cooling the gas stream was done by keeping the impingers in an ice bath with the water a little below the top of the impinger. Collecting the trace metals was accomplished by aqua regia solutions that the impengers contain.

The first two impingers initially contained 100 mL each of aqua regia (HNO_3/HCL), as an oxidizing agent. The third

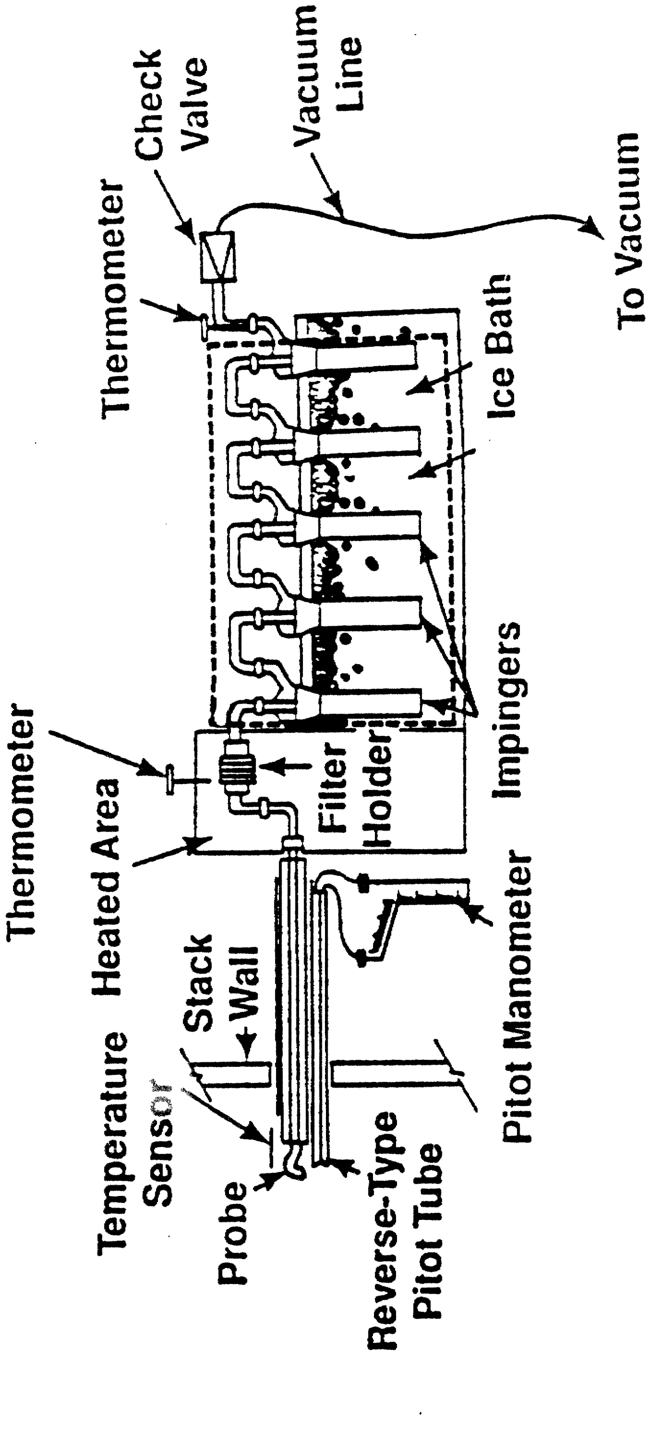

Figure 2. EPA MM5 Sampling Train

impinger contained 200 mL of 2% potassium permanganate ($KMnO_4$), an oxidizing agent, in 10% sulfuric acid (H_2SO_4), as an acidic medium. The fourth impinger was empty, and the fifth impinger contained 200-500g of silica gel desiccant to absorb the moisture from the flue gas before it enters the vacuum system. All five impingers were kept in an ice bath during the sampling run. The temperature of the last impinger was kept below 70°F.

The impingers and glass connectors were cleaned before being used by soaking them in a hot detergent bath. The glassware was then rinsed and allowed to soak in hot chromic acid. Then it was rinsed off with water, distilled water, and pesticide grade acetone. Finally the glassware was wrapped in aluminum foil andstored until needed.

The probe and particulate filter were maintained at a temperature between 225°F and 275°F to prevent condensation of trace metals inside the probe. A quartz liner with electric wire taped around it was used to heat and control its temperature. A glass fiber filter was used to collect the particulates. The filter was set in a temperature controlled oven to keep it at a constant temperature during the whole sampling run.

Sample Recovery

Collecting an individual sample lasts about one hour. This corresponds to about 1-2m^3 of gas sampled each time. The samples were recovered on site immediately after sampling was completed. The probe liner and nozzle were rinsed thoroughly with 10% aqua regia followed by acetone. Any particulate matter which had accumulated in the liner was brushed, then washed out and stored with the aqua regia rinse. Also stored with this were the filter and connector glassware rinses. The filters were stored separately in a Petri dish.

The first impinger with its connectors glassware were washed with aqua regia. The rinse was stored in a separate container. The second impinger was also washed and stored in a third container. The third and fourth impingers with their connectors were washed with aqua regia and stored in a fourth container. The resin was removed from the fifth impinger to be dried and reused again. The filter which was stored in a Petri dish was sealed and wrapped in aluminum foil immediately after the filter was placed in it.

The Teflon containers, containing the rinses, were then packed and shipped back to UNT's laboratories for analysis. The samples were arranged on the shelves according to their run number and dates.

Sample Analysis

All the samples were analyzed with a Perkin-Elmer Inductively Coupled Plasma (ICP) Atomic Emission Spectrometer (AES) model 5500. The samples were introduced to the plasma through the ICP torch by a nebulizer.

The sampling method was designed to collect a wide range of metals which may occur in gaseous or in particulate phases. The samples were collected isokinetically with an Anderson Universal Sampler equipped for modified Method 5 Sampling (40). The samples collected were analyzed using the ASTM Method 200.7 ICP/AES method for trace elements analysis (41).

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP/AES)

Historical Aspects:

The development of ICP began in 1984 when a successful operation of ICP at atmospheric pressure was accomplished (8-10). In 1960 an isolation of the plasma was done by R.T. Reed (11,12). The introduction of ICP as a source of analytical atomic emission spectrometry, done in 1963, constituted a revolutionary advance in this field (13). The first independent publications on using ICP started in 1964.

The performance characteristics of ICP-AES, namely its versatility, wide applicability, and ease of use are almost unparalleled among other methods of elemental analysis (18). Basically, using ICP-AES determines any element in the sample except the injector gas (32).

The application of ICP-AES to simultaneous determination of major, minor, and trace level elements in various matrices has been well documented (14-18). ICP offered several advantages as an alternative approach for the analysis of geochemical and environmental samples (19-24). A number of studies have concentrated on developing methods for isolating trace elements from complex matrices including co-precipitation (25), chelation (26-27), chromatography (28), and conversion into hydrates (29). In all of these isolation methods, large volumes of additional chemicals are brought into contact with the samples, and thus may introduce contaminating or interfering species. In addition, some of these techniques are time consuming and tedious (30,31).

Instrumentation of ICP:

The ICP instrument is comprised of five fundamental parts: a radio frequency (RF) generator, ICP source, spectrometer sample introducer, and data analyzer. A schematic of a Perkin-Elmer ICP-AES/5500 is shown in

Figure 3. The instrumental operating parameters together with the analytical lines used are given in Table X.

In the ICP-AES, the radio frequency power is transferred to the plasma through a coil wound around the torch. The coil inductively couples the energy to the plasma. The RF does not come into direct contact with the plasma eliminating the problem of elemental contamination from the electrode. This coil, once it is energized with the RF power, induces an electromagnetic field within the torch. This field inductively heats the formed plasma to temperatures exceeding 5,000 K. The gas that sustains the plasma is initially made electrically conductive by Tesla sparks before a self sustained plasma results.

The torch consists of a series of annular tubes made of quartz. The various tubes make the torch carry the gas at different flow velocities through the RF coil region. In this region, the gas is rapidly heated and subsequently ionized. The outer stream flows at a high rate and serves to sustain the plasma. It also carries away the heat that is dissipated by the plasma to the inside walls of the torch. A centrally located gas stream flowing at a low rate carries an aerosol sample up through the existing plasma. After penetrating the hot core of the plasma, the aerosol is desolvated, dissociated, atomized, and excited. Upon passing

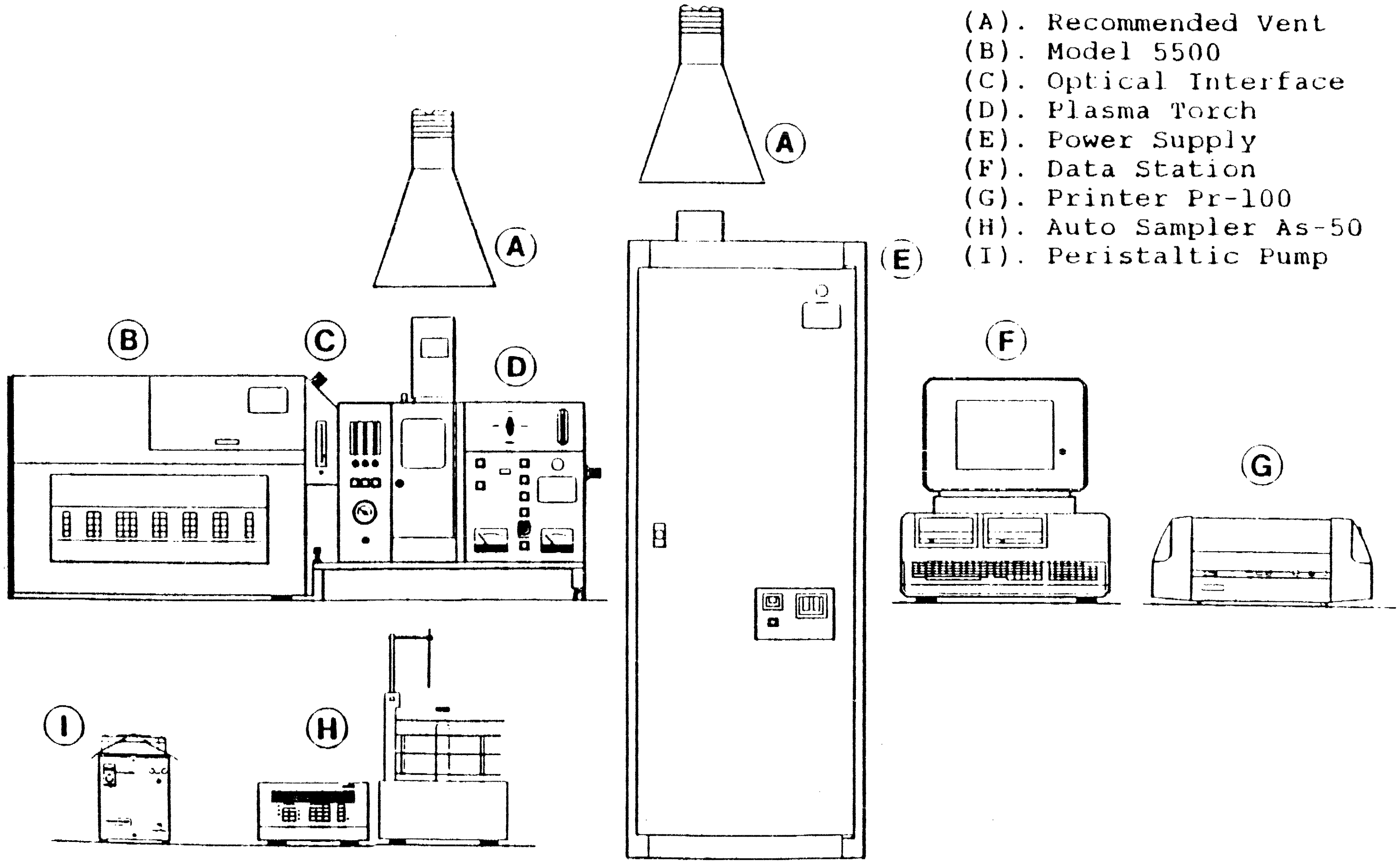

Fig. 3 Schematic of a Perkin-Elmer ICP/5500

Table X: Analytical Conditions for ICP-AES

Argon gas was used for Plasma, Nebulizer, and Auxiliary gas.

Instrument Parameters:

Incedent Plasma Power	1250 W
Reflection Power	< 5 W
Plasma Gas	14 L/m
Auxiliary Gas	0.8 L/m
Nebulizer Pressure	25 psi
Viewing Hight	15 mm above R.F. coil

Element Parameter:

Element	Wavelength nm	Background Correction
As	193.70	-0.05+0.05
Ba	455.40	-0.05+0.05
Be	313.04	-0.05+0.05
Cd	214.44	-0.05+0.05
Cr	267.72	-0.05+0.05
Cu	324.75	-0.05+0.05
Hg	194.23	-0.05+0.05
Ni	231.60	-0.05+0.05
Pb	220.35	-0.05+0.05
Sb	196.03	-0.05+0.05
Se	190.86	-0.05+0.05
Tl	190.89	-0.05+0.05
V	290.88	-0.05+0.05
Zn	213.86	-0.05+0.05

through and out of the plasma, the various ionic and atomic species relax to their ground states, emitting characteristic radiation (33,34).

Sample Introduction

Many methods of sample introduction have been developed for ICP-AES. A nebulizer in conjunction with an aerosol discrimination chamber to form a fine mist of droplets was used to introduce the samples. The mist was then transported and injected into the plasma. The droplets go into the waste.

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CHAPTER III

RESULTS AND DISCUSSION

The results of the 13 trace metals analysis are shown in Tables XI through XXII. In the tables the columns denoted with (S) symbol shows the analysis of Site 2 samples and the column with (EPA) symbol shows Site 3 samples. There were a total of 46 Site 2 samples and two Site 3 samples analyzed. Appendix E shows the detection limits for ICP of the gas samples analyzed.

The samples were analyzed for trace metals including As, Be, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Sb, Se, Tl, and Zn using ICP/AES. The data collected were studied to show the effect of $Ca(OH)_2$ binder on the trace elements. Four areas will be discussed in this chapter: 1) the difference between the Reuter pellets and the Future Fuel (Thief River Falls pellets); 2) the difference between Site 2 and Site 3 trace metals; 3) the effect of bdRDF on trace metals; and 3) the effect of binder on trace metals.

The data in this chapter will be used to point out differences between runs and the effects on trace metals, not to represent absolute values. In this type of analysis,

Table XI: TRACE ELEMENTAL ANALYSIS of RUN # 1; Coal

ELEMENT	S1	S2	S3
As	0.48	BDL	BDL
Hg	BDL	0.67	BDL
Se	BDL	BDL	BDL
Cr	BDL	0.33	BDL
Sb	BDL	BDL	BDL
Be	BDL	BDL	BDL
Cu	BDL	BDL	BDL
Tl	0.07	4.36	12.37
Zn	BDL	0.05	BDL
Cd	BDL	BDL	BDL
Pb	BDL	2.11	0.98
Ni	0.67	2.44	0.98
Ba	0.09	BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XII: TRACE ELEMENTAL ANALYSIS of RUN # 2, Coal/ 10% dRDF (0% Binder)

ELEMENT	S1	S2	S3	S4
As	BDL	BDL	3.20	0.92
Hg	BDL	BDL	0.40	0.23
Se	BDL	BDL	0.38	BDL
Cr	BDL	BDL	0.09	3.10
Sb	BDL	BDL	0.64	BDL
Be	BDL	BDL	BDL	BDL
Cu	3.08	2.04	BDL	BDL
Tl	0.06	13.09	4.50	5.77
Zn	0.16	1.00	0.04	0.08
Cd	BDL	BDL	0.03	BDL
Pb	1.52	1.11	BDL	BDL
Ni	3.30	1.82	1.12	1.17
Ba	BDL	BDL	0.02	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XIII: TRACE ELEMENTAL ANALYSIS of RUN # 3; Coal/ 10% bdRDF (4% Binder)

ELEMENT	S1	S2	S3	S4	S5
As	0.58	BDL	0.63	0.49	BDL
Hg	0.57	BDL	0.26	0.50	BDL
Se	0.70	BDL	0.54	0.62	0.40
Cr	0.27	BDL	0.21	0.23	BDL
Sb	BDL	0.22	BDL	BDL	0.23
Be	BDL	BDL	BDL	BDL	BDL
Cu	BDL	0.37	BDL	BDL	0.43
Tl	1.38	10.85	2.81	2.45	9.67
Zn	0.04	0.06	0.04	0.05	0.03
Cd	BDL	BDL	BDL	BDL	0.03
Pb	0.37	1.07	1.46	1.24	1.21
Ni	0.91	1.52	0.63	0.46	0.95
Ba	BDL	BDL	BDL	BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XIV: TRACE ELEMENTAL ANALYSIS of RUN # 4; Coal/ 10% bdRDF (8% Binder)

ELEMENT	S1	S2	S3	S4	S5
As	BDL	BDL	1.76	1.30	BDL
Hg	BDL	0.04	0.29	BDL	0.65
Se	BDL	BDL	0.28	0.73	0.90
Cr	BDL	BDL	0.07	0.18	0.22
Sb	BDL	BDL	0.30	0.66	BDL
Be	BDL	BDL	BDL	BDL	BDL
Cu	2.62	0.87	BDL	BDL	BDL
Tl	12.33	12.13	3.32	6.17	6.05
Zn	0.08	0.96	BDL	BDL	0.12
Cd	BDL	BDL	0.04	0.04	BDL
Pb	1.13	0.46	BDL	BDL	3.42
Ni	2.41	1.71	0.39	0.60	0.90
Ba	BDL	BDL	BDL	BDL	BDL

(BDL) - Below Detection Limits

Units- mg/m^3 gas sampled

Table XV: TRACE ELEMENTAL ANALYSIS of RUN # 5; Coal/ 20% bdRDF (0% Binder)

ELEMENT	S1	S2	S3	S4	S5	S6
As	BDL	BDL	3.05	1.24	1.57	BDL
Hg	0.20	BDL	0.22	0.72	BDL	0.20
Se	BDL	BDL	0.79	0.40	1.57	BDL
Cr	BDL	BDL	0.14	0.30	0.08	BDL
Sb	BDL	BDL	0.84	BDL	1.16	BDL
Be	BDL	BDL	BDL	0.01	BDL	BDL
Cu	1.16	1.89	BDL	BDL	BDL	0.56
Tl	11.53	13.14	13.71	1.99	15.99	12.56
Zn	0.28	0.43	BDL	0.06	BDL	3.71
Cd	BDL	BDL	0.05	BDL	0.16	BDL
Pb	1.62	1.20	0.30	0.94	BDL	1.57
Ni	1.83	0.93	1.46	1.67	0.76	0.67
Ba	BDL	BDL	BDL	BDL	BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XVI: TRACE ELEMENTAL ANALYSIS of RUN # 6; Coal/ 30% bdRDF (8% Binder)

ELEMENT	S1	S2	S3	S4
As	BDL	BDL	0.90	1.59
Hg	0.25	BDL	BDL	0.63
Se	BDL	BDL	0.84	BDL
Cr	BDL	BDL	0.28	0.29
Sb	BDL	BDL	BDL	BDL
Be	BDL	BDL	BDL	BDL
Cu	0.62	0.26	BDL	BDL
Tl	11.69	13.02	4.13	5.59
Zn	BDL	0.40	0.05	0.04
Cd	BDL	BDL	BDL	BDL
Pb	1.86	1.79	2.18	3.48
Ni	0.26	BDL	1.18	0.77
Ba	BDL		BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XVII: TRACE ELEMENTAL ANALYSIS of RUN # 7; Coal/ 20% bdRDF (4% Binder)

ELEMENT	S1	S2	S3	S4
As	BDL	BDL	BDL	BDL
Hg	BDL	BDL	BDL	0.62
Se	BDL	BDL	BDL	BDL
Cr	BDL	BDL	BDL	0.35
Sb	BDL	BDL	BDL	BDL
Be	BDL	BDL	BDL	BDL
Cu	1.69	2.00	1.03	BDL
Tl	1.23	16.53	10.40	4.18
Zn	0.02	BDL	0.02	0.72
Cd	0.02	BDL	BDL	BDL
Pb	BDL	BDL	BDL	1.58
Ni	1.92	1.22	1.44	0.54
Ba	0.8	1.07	BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XVIII: TRACE ELEMENTAL ANALYSIS of RUN # 8; Coal/ 20% bdRDF (8% Binder)

ELEMENT	S1	S2	S3	S4	S5
As	BDL	BDL	BDL	1.59	2.62
Hg	BDL	BDL	BDL	BDL	BDL
Se	BDL	BDL	BDL	0.36	0.42
Cr	BDL	0.04	BDL	0.12	0.12
Sb	BDL	BDL	0.29	0.28	0.58
Be	BDL	BDL	BDL	BDL	BDL
Cu	1.68	1.19	1.31	BDL	BDL
Tl	11.91	6.36	6.29	9.73	2.14
Zn	0.03	0.02	BDL	BDL	BDL
Cd	BDL	BDL	BDL	BDL	BDL
Pb	0.06	BDL	BDL	BDL	BDL
Ni	0.55	0.31	0.18	0.68	0.20
Ba	0.06	0.05	0.03	BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XIX: TRACE ELEMENTAL ANALYSIS of RUN # 9; Coal/ 30% bdRDF (0% Binder Less plastics)

ELEMENT	S1	S2	S3
As	BDL	0.59	0.62
Hg	BDL	0.80	BDL
Se	BDL	BDL	BDL
Cr	BDL	3.29	BDL
Sb	BDL	BDL	BDL
Be	BDL	BDL	BDL
Cu	1.05	BDL	BDL
Tl	3.86	2.65	2.55
Zn	BDL	0.65	BDL
Cd	BDL	BDL	BDL
Pb	BDL	3.06	BDL
Ni	014	1.31	0.58
Ba	0.02	BDL	BDL

(BDL) - Below Detection Limits

Units- mg/m^3 gas sampled

Table XX: TRACE ELEMENTAL ANALYSIS of RUN # 10;

Coal/ 30% bdRDF (4% Binder Less plastic)

ELEMENT	S1	S2
As	BDL	BDL
Hg	0.26	0.33
Se	BDL	BDL
Cr	BDL	0.12
Sb	0.15	.23
Be	BDL	BDL
Cu	1.70	1.75
Tl	2.91	3.30
Zn	0.02	0.02
Cd	BDL	0.16
Pb	3.81	3.28
Ni	1.36	0.84
Ba	0.06	0.02

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XXI: TRACE ELEMENTAL ANALYSIS of RUN # 11; Coal/ 50% bdRDF (4% Binder)

ELEMENT	S1	EPA	S3	EPA
As	BDL	BDL	1.49	BDL
Hg	0.15	BDL	0.38	0.47
Se	BDL	BDL	0.38	0.42
Cr	BDL	0.09	0.17	0.38
Sb	BDL	BDL	BDL	BDL
Be	BDL	BDL	BDL	BDL
Cu	1.07	1.04	BDL	BDL
Tl	5.62	5.29	3.30	3.50
Zn	0.07	0.07	0.11	1.49
Cd	BDL	BDL	0.04	0.02
Pb	1.75	1.73	BDL	BDL
Ni	1.17	1.10	0.24	1.68
Ba	0.02	BDL	BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

Table XXII: TRACE ELEMENTAL ANALYSIS of RUN # 12; Coal

ELEMENT	S1	S2	S3
As	BDL	BDL	3.09
Hg	BDL	0.28	BDL
Se	BDL	BDL	0.93
Cr	BDL	BDL	0.13
Sb	0.17	BDL	1.25
Be	BDL	BDL	BDL
Cu	0.83	0.95	BDL
Tl	5.74	5.26	4.70
Zn	0.03	0.05	BDL
Cd	BDL	BDL	BDL
Pb	2.17	2.15	BDL
Ni	1.37	1.39	BDL
Ba	0.02	BDL	BDL

(BDL)- Below Detection Limits

Units- mg/m^3 gas sampled

variability in results is quite common (1-5). Large variability, in organic and inorganic analysis, has been reported in studies involving different incinerators and the same feedstock (2). It is also observed using the same incinerator, same feedstock, but on different days (3). In another study, values for organics varied by a factor of five to ten and in some cases by as much as one hundred (4).

These results were considered to be comparable. All of these studies were done using the same feedstock. The fact that the data from this study shows some variability is not surprising. Appendix F shows an example of statistical analysis for runs 2 and 5 with some interpretations.

The difference Between Reuter Pellets and The Future Fuel Pellets:

The bulk density of the pellets is important to look at since it gives an idea of how to transport the pellets, how good is the pelletization process, and the amount and distribution of binder in the pellets. It is known that as the amount of binder in the pellets increases, the bulk density of the pellets should increase. The data concerning the pellets, which has been reported elsewhere (1,5,6), shows that this was the case with Reuter Pellets. The pellets with zero percent binder had bulk densities averaging 42.0 lb/ft^3, the four percent binder pellets had bulk densities averaging 43.3 lb/ft^3, and the eight percent binder pellets averaging 45.7 lb/ft^3 in bulk density. In contrast, the Future Fuel pellets had bulk densities of 26.8 lb/ft^3 for zero percent binder, 25.6 lb/ft^3 for four percent binder, and 26.8 lb/ft^3 for eight percent binder.

Two tests run on the pellets were ash and Btu content. It Was necessary to grind the pellets before conducting any of these tests. The results were reported elsewhere (1) and shown in Appendix A. The results show a slight difference between the two types of pellets. The Reuter pellets ground up fairly easily. Future Fuel pellets were not so easy to grind since they contain a large quantity of plastic. The plastic has to be removed before grinding the pellets, because it is very difficult to grind.

This difference in the bulk density of the Future Fuel pellets raises questions about the pellets and their use. This variability is unclear, and it may be due to the variability in the pelletization process or the binder level.

The Reuter pellets bulk densities were consistent with what was expected. They had a higher bulk density which increased with an increase in binder level. The ash and Btu analysis were off a little in the Future Fuel pellets which proves that the Reuter pellets were more homogeneous. This makes the use and the data collected from Reuter pellets more reliable.

Table XXIII shows the average of trace metals analysis in mg/m^3 gas sampled for all runs which will be used for all illustrations and comments. The averages were taken from the previous tables XI-XXII. Appendix B shows the standard deviation of the trace metals analyzed using Inductively Coupled Plazma for all runs.

Site 2 and Site 3

Figure 4 illustrates the trace metals collected from Site 2 and Site 3. The samples were collected from run 11 which was 50% bdRDF and 4% binder. Only two samples were collected from Site 3, which makes it hard to judge and study the difference between Site 2 and Site 3. It is also very difficult to study the pollution control equipment from such few data.

It should also be noted that the Site 2 samples were taken after the first stage of the pollution control equipment, the multiclone. The multiclone is capable of removing ninety percent of all particulates, which means that nearly all the metal that is bound to particulates will be removed at this point.

Table XXIII:

Average concentrations (mg/m^3 gas sampled) of trace metals for all run samples collected.

	Run 1	Run 2	Run 3	Run 4
As	0.16	1.03	0.34	0.61
Hg	0.22	0.21	0.27	0.20
Se	BDL	0.10	0.38	0.38
Cr	0.11	0.80	0.14	0.09
Sb	BDL	0.16	0.11	0.19
Be	BDL	BDL	BDL	BDL
Cu	BDL	1.28	0.20	0.70
Tl	5.58	5.86	5.43	8.00
Zn	0.02	0.28	0.04	0.23
Cd	BDL	0.01	0.01	0.02
Pb	1.03	0.66	1.07	1.00
Ni	1.36	1.85	0.89	1.20
Ba	0.03	0.01	BDL	BDL

Table XXIII Continue.......

Average concentrations (mg/m^3 gas sampled) of trace metals for all run samples collected.

Element	Run 5	Run 6	Run 7	Run 8
As	0.89	0.62	BDL	0.84
Hg	0.22	0.22	0.16	BDL
Se	0.46	0.21	BDL	0.16
Cr	0.09	0.14	0.09	0.06
Sb	0.33	BDL	BDL	0.23
Be	BDL	BDL	BDL	BDL
Cu	0.60	0.22	1.18	0.84
Tl	11.49	8.61	10.37	7.29
Zn	0.75	0.12	0.19	0.01
Cd	0.04	BDL	0.01	BDL
Pb	0.94	2.33	0.40	0.01
Ni	1.22	0.55	1.28	0.28
Ba	BDL	BDL	0.63	0.03

Table XXIII Continue.......

Average concentrations (mg/m^3 gas sampled) of trace metals for all run samples collected.

Element	Run 9	Run 10	Run 11	Run 12	Run 11 EPA
As	0.40	BDL	0.75	1.03	BDL
Hg	0.27	0.43	0.27	0.09	0.24
Se	BDL	BDL	0.19	0.31	0.21
Cr	1.10	0.06	0.09	0.04	0.24
Sb	BDL	0.19	BDL	0.47	BDL
Be	BDL	BDL	BDL	BDL	BDL
Cu	0.35	1.73	0.54	0.59	0.52
Tl	3.86	2.91	4.46	5.23	4.40
Zn	0.22	0.02	0.09	0.03	0.78
Cd	BDL	0.08	0.02	BDL	0.01
Pb	1.02	3.55	0.88	1.44	0.86
Ni	0.68	1.10	0.71	0.92	1.39
Ba	0.01	0.04	0.01	0.01	BDL

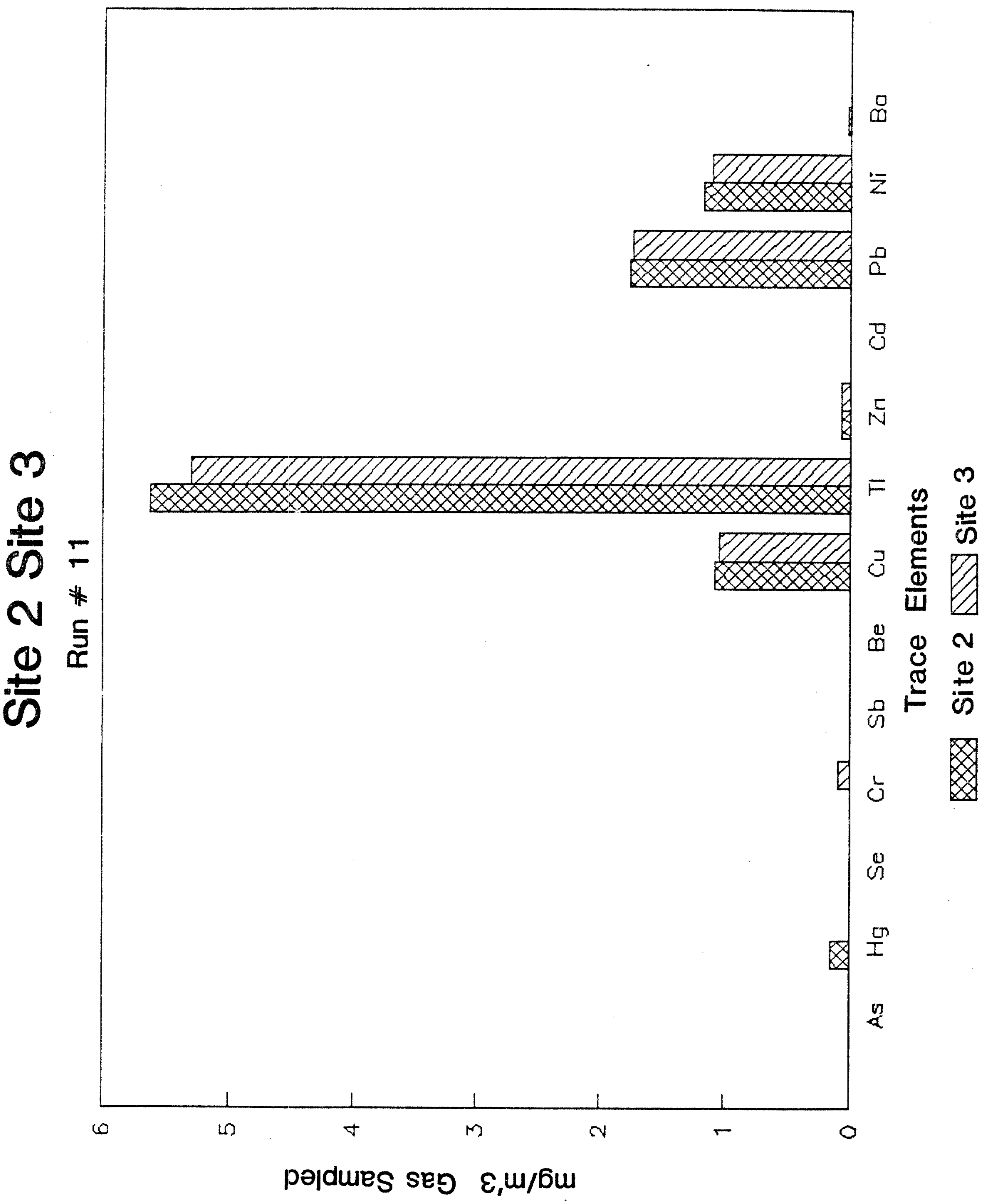

Figure 4: Run # 11(50% bdRDF, 4% binder). Comparison between site 2 and site 3 (EPA Observation)

The figure illustrates the following:

- the elements As, Se, Sb, Be, and Cd were below the detection limits in both Site 2 and Site 3;
- the element Zn was almost the same in both sites;
- the element Cr is more in Site 3;
- and the elements Hg, Cu, Tl, Pb, Ni, and Ba were lower in Site 3 sample.

The difference between Site 2 and Site 3 is due to the pollution control equipment which reduces the elements that go into the air. The elements Zn and Cr are volatile and travel with the flue gas.

Effect of bdRDF on Trace Metals

Although the processing of MSW into RDF removes much of the unwanted noncombustible materials, the dRDF fuel is still considered to be heterogeneous from the microscopic point of view (7). The metal content of the flue gas after burning bdRDF/Coal mix is expected to be affected by the different percentages of bdRDF input. Elements such as Cd, Cr, Cu, Hg, Pb, and Zn are known to be enriched in RDF relative to coal (8-11).

Figure 5 illustrates the comparison between run 2 (ten percent bdRDF/zero percent binder) and run 5 (twenty percent bdRDF/zero percent binder). Appendix F shows the statistical

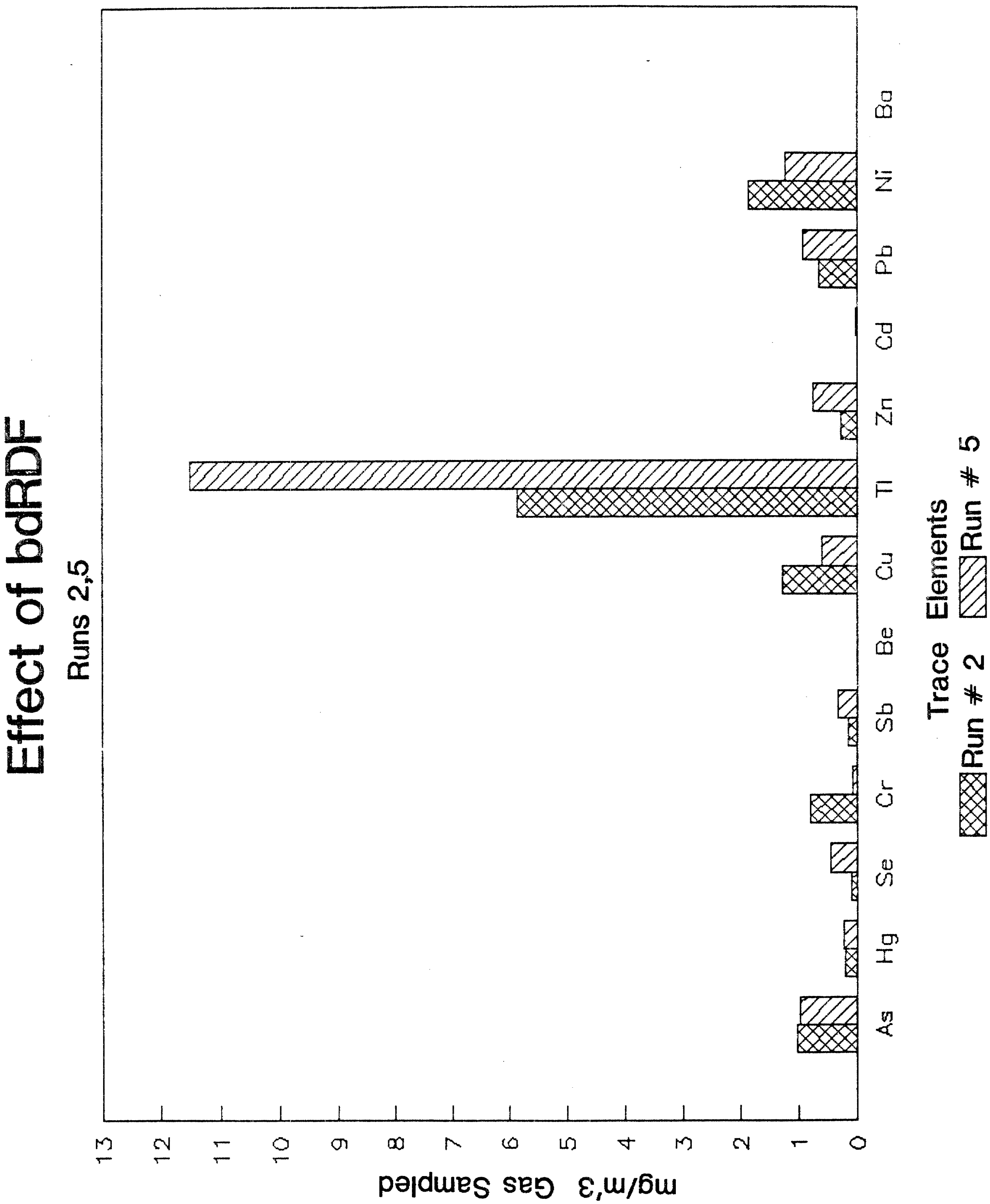

Figure 5: Run # 2(10% bdRDF, 0% binder), Run # 5(20% bdRDF, 0% binder)

analysis of the collected data using the "Comparison of Two Experimental Means" method as an example for the interpretations of the data. Figure 6 illustrates the comparison between run 3 (ten percent bdRDF/four percent binder), run 7 (twenty percent bdRDF/four percent binder), and run 11 (fifty percent bdRDF/four percent binder). Figure 7 illustrates a comparison between run 4 (ten percent bdRDF/eight percent binder), run 8 (twenty percent bdRDF/eight percent binder), and run 6 (thirty percent bdRDF/eight percent binder). All of these figures show the effect of an increase in bdRDF on trace elements.

By looking and examining the three figures, the following can be realized:

- the elements As and Sb were slightly increased with an increase in bdRDF;
- the element Hg almost remained the same, or it varied just a little, meaning that it was not affected by the increase in bdRDF;
- the elements Se and Cr slightly decreased with an increase in bdRDF;
- the elements Cd, Ba, Cu, and Ni decreased with an increase in bdRDF;
- the elements Tl and Pb increased with an increase in bdRDF;

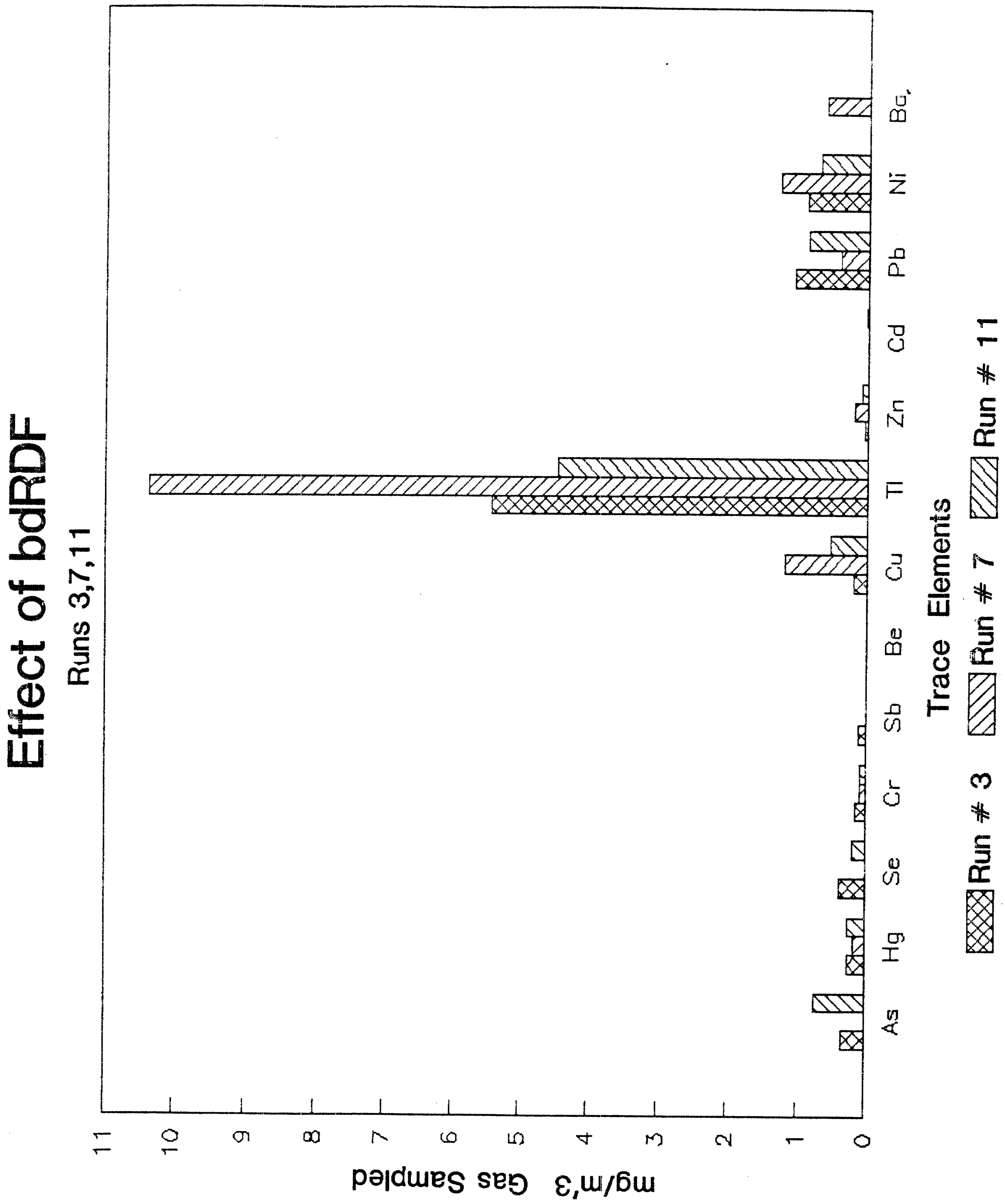

Figure 6: RUn #3 (10% bdRDF,4% binder), Run #7 (20% bdRDF, 4% binder), Run # 11(50% bdRDF,4% binder)

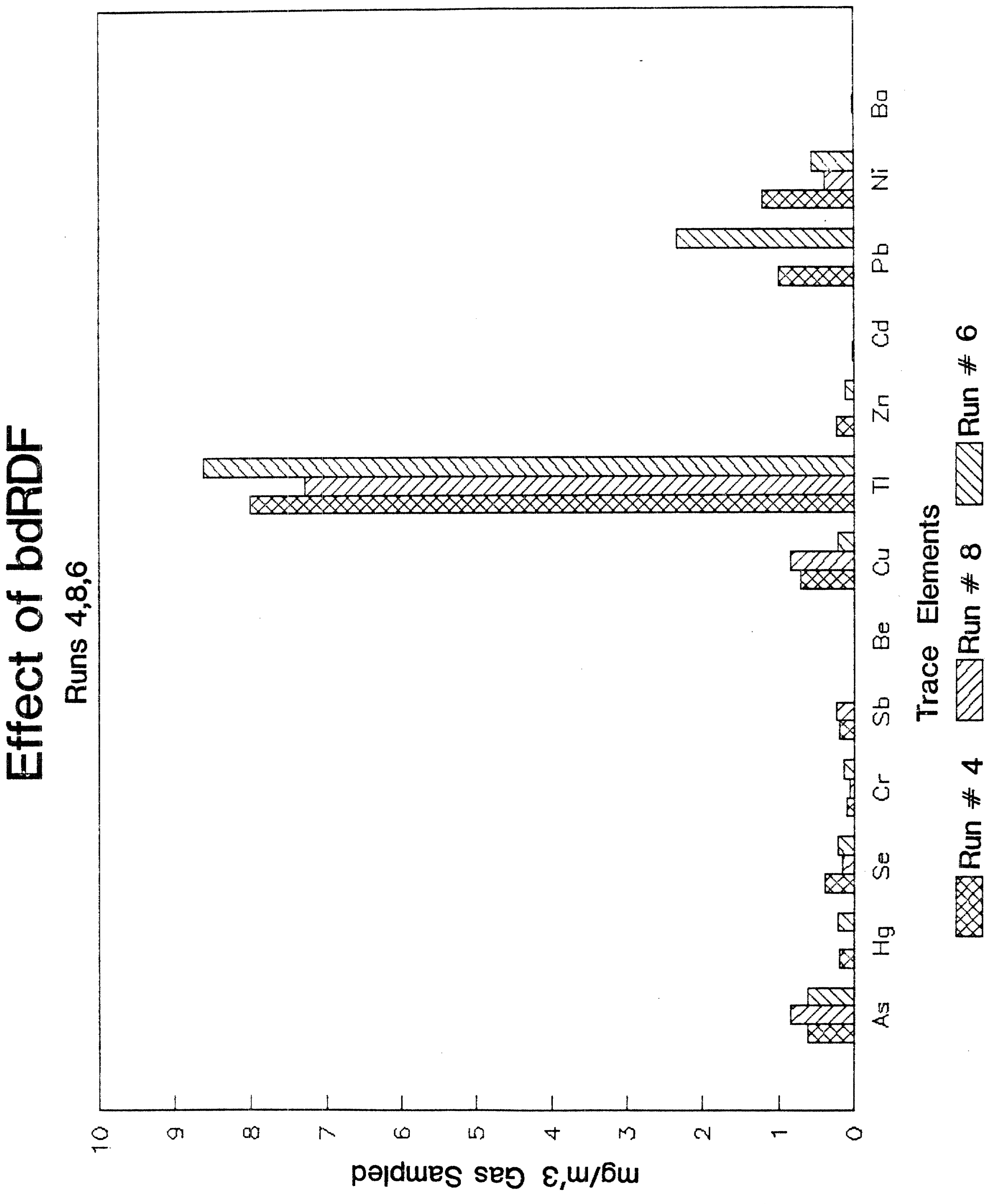

Figure 7: Run #4 (10%bdRDF, 8% binder), Run #8(20% bdRDF, 8% binder) Run #6 (30% bdRDF, 8% binder)

- the element Be was below the detection limit in all samples;
- the element Zn varied with an increase in bdRDF, so it was difficult to judge if it was increased or decreased.

The increase of some elements such as As, Sb, Tl, and Pb is due to their presence in the bdRDF more than coal. Other elements such as Se, Cd, Ba, and Ni decreased due to their lower presence in bdRDF in comparison to coal. The elements Cr, Cu, and Cd decreased due to their condensation on the ash particulates.

Effect of Binder on Trace Elements

Calcium Hydroxide was used as a binder in the manufacture of bdRDF pellets. It was expected that the binder would decrease the trace metals and other emissions when bdRDF was co-fired with sulfur-rich coal. However, the effect of the binder content on the metals is still unknown.

Table XXIII and Figures 8, 9 and 10 illustrate the effect of $Ca(OH)_2$ binder on trace metals at constant bdRDF Btu content. Figure 8 shows the effect of binder in 10% bdRDF with 0, 4, and 8 percent binder. Figure 9 shows the 20% bdRDF with 0, 4, and 8 percent binder. Figure 10 shows the 30% bdRDF with 0, 4 percent binder and less plastic.

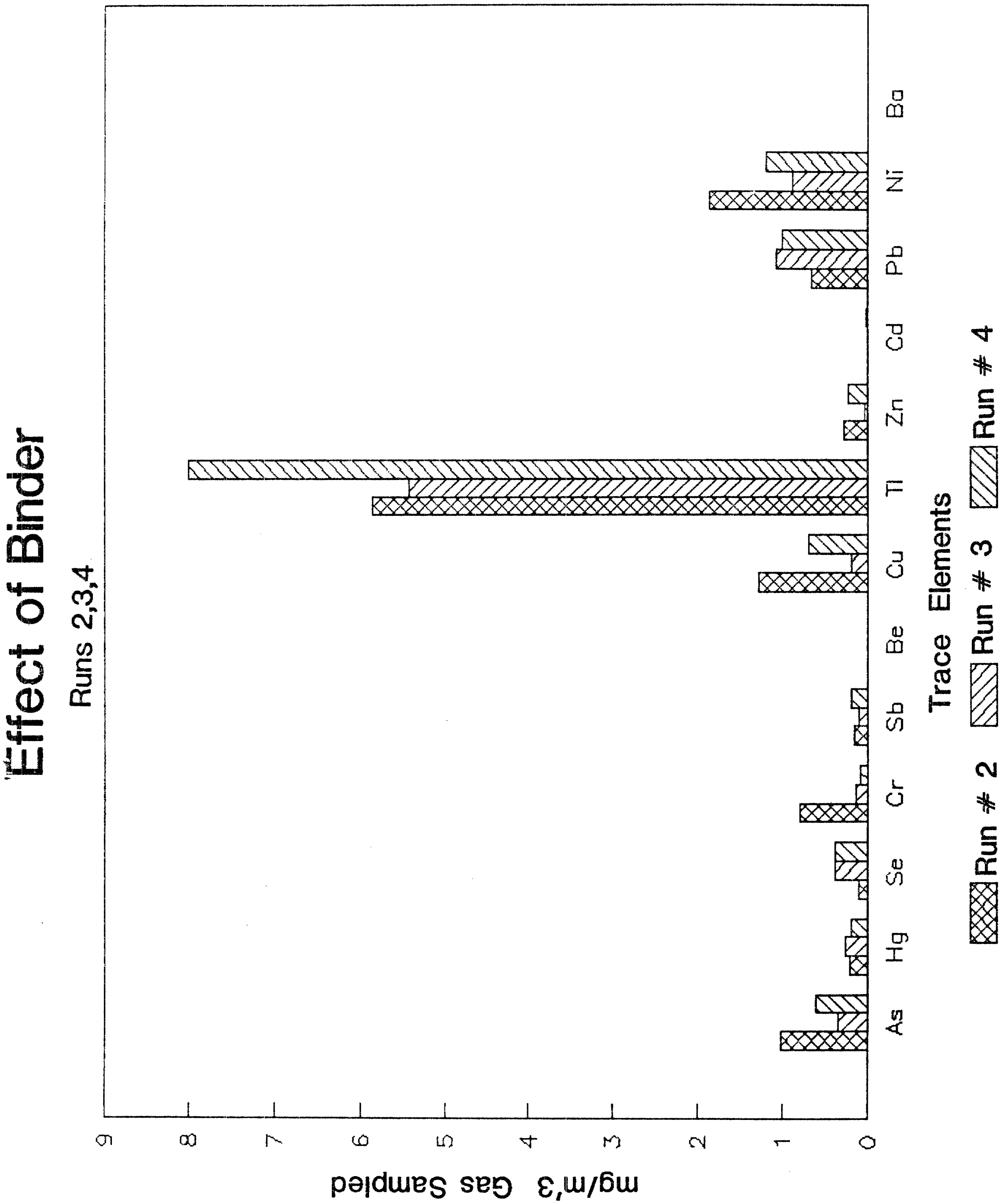

Figure 8:Run # 2 (10% bdRDF, 0% binder), Run # 3 (10%bdRDF 4% binder) Run # 4 (10% bdRDF, 8% binder)

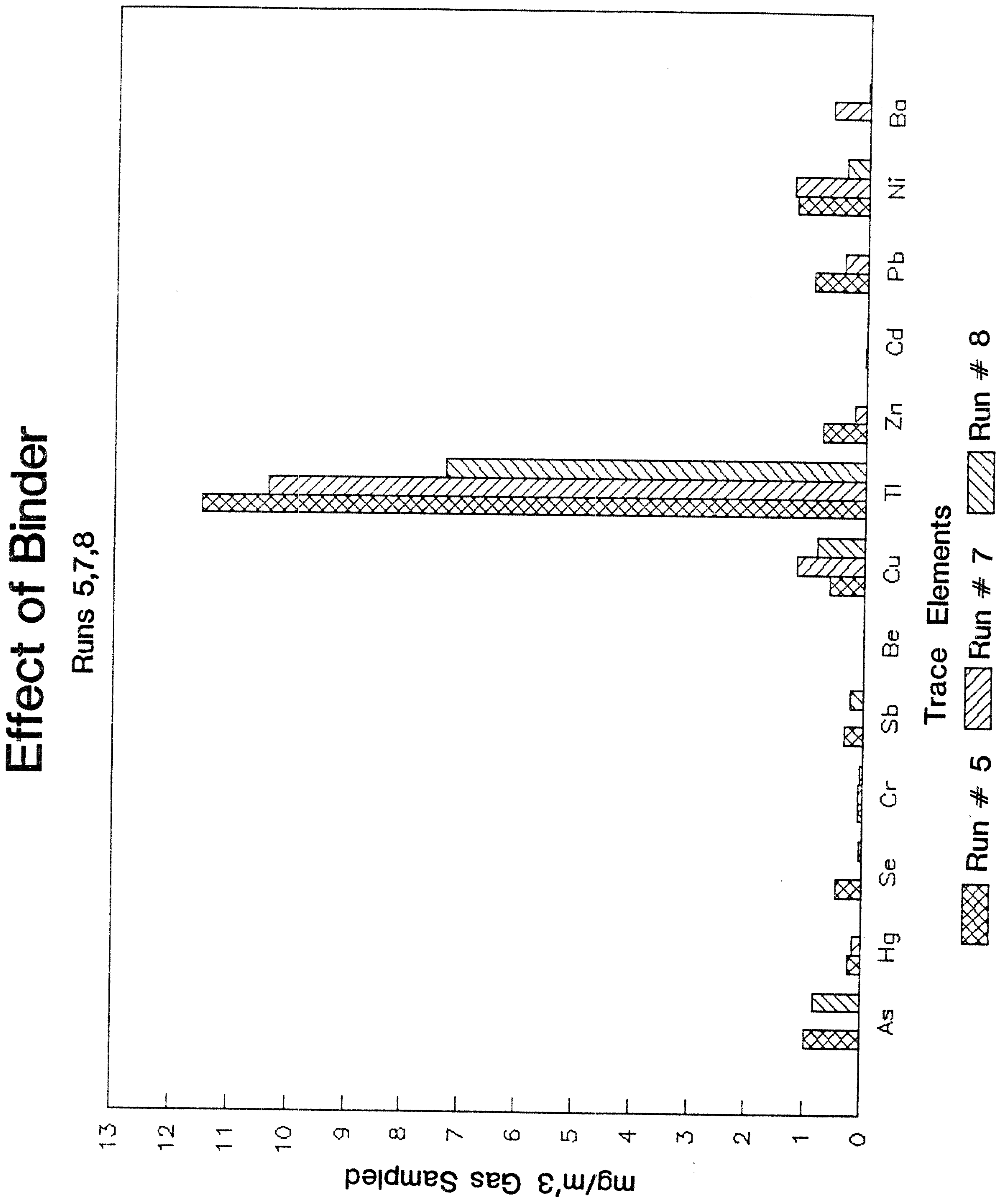

Figure 9: Run # 5(20% bdRDF, 0% binder), Run # 7(20% bdRDF 4% binder), Run # 8(20% bdRDF, 8% binder)

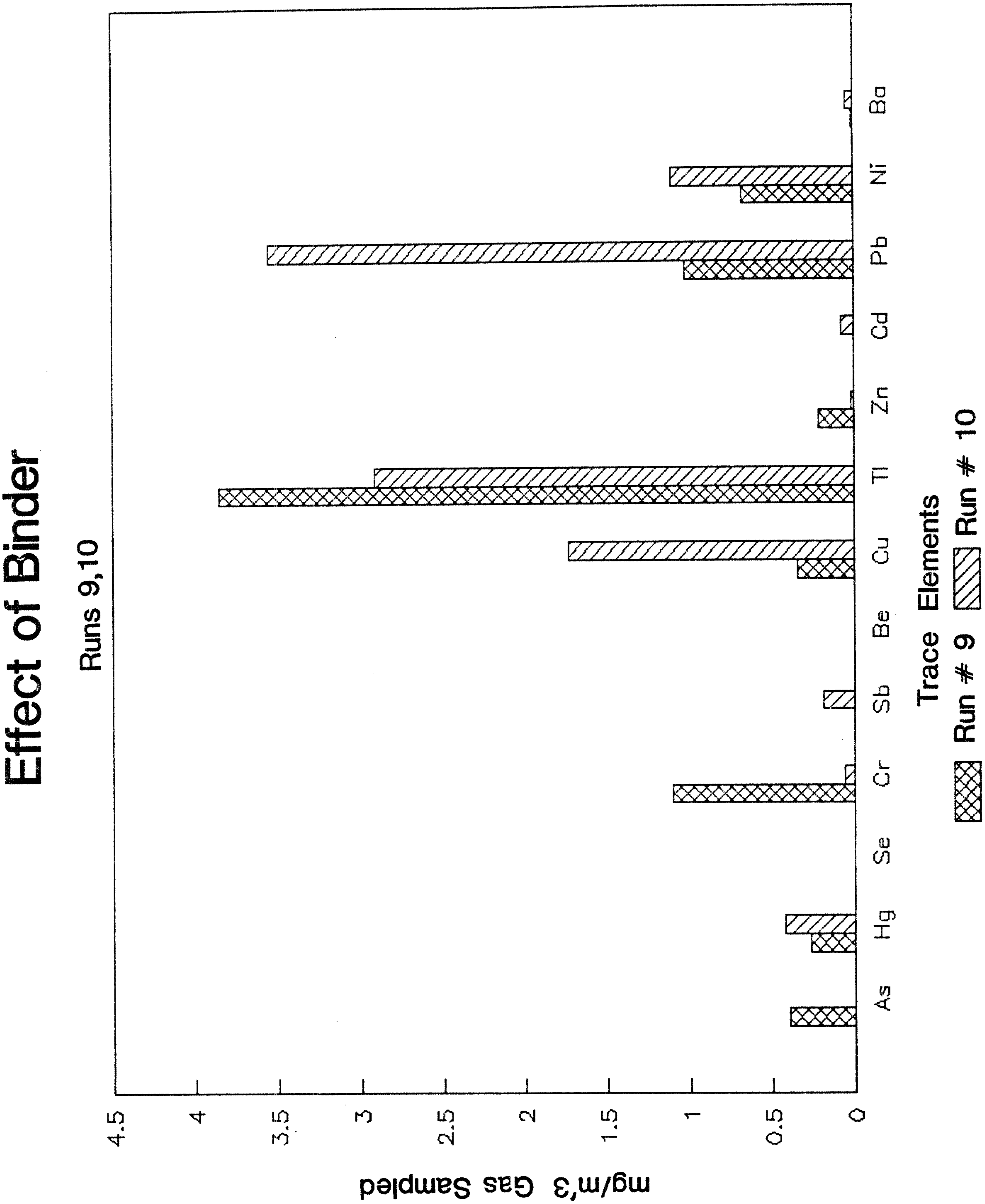

Figure 10: Run #91(30%bdRDF, 0% binder), Run # 10(30% bdRDF, 4% binder) (Less Plastic)

The graphs illustrate the following:

- the elements As, Cr, Zn, Ni, Ba, Hg, Sb, and Cu decreased with an increase in binder;
- the element Se slightly increased;
- the elements Be and Cd below the detection limit;
- the elements Pb and Tl decreased in case of the 20% bdRDF;
- there was an abnormal increase in Pb concentration in the case of the 10% bdRDF, and there was an increase in Tl concentration only in the case of 10% bdRDF / 8% binder.

As mentioned before, variability is quite common.

Figure 10, which contains less plastic, shows less trace element concentration. The elements As, Cr, Tl, and Zn decreased with an increase in binder content. The elements Hg, Sb, Cu, Pb, Ni, and Ba increased with an increase in binder content. Figure 11 illustrates a comparison between run 11 (50% bdRDF/4% binder) and run 12 (coal).

The increase or decrease of the element in these samples was due to the presence of the binder. Calcium hydroxide contains some elemental impurities which might affect the elemental concentration of some elements. It also has a great effect in reducing the trace elements in the

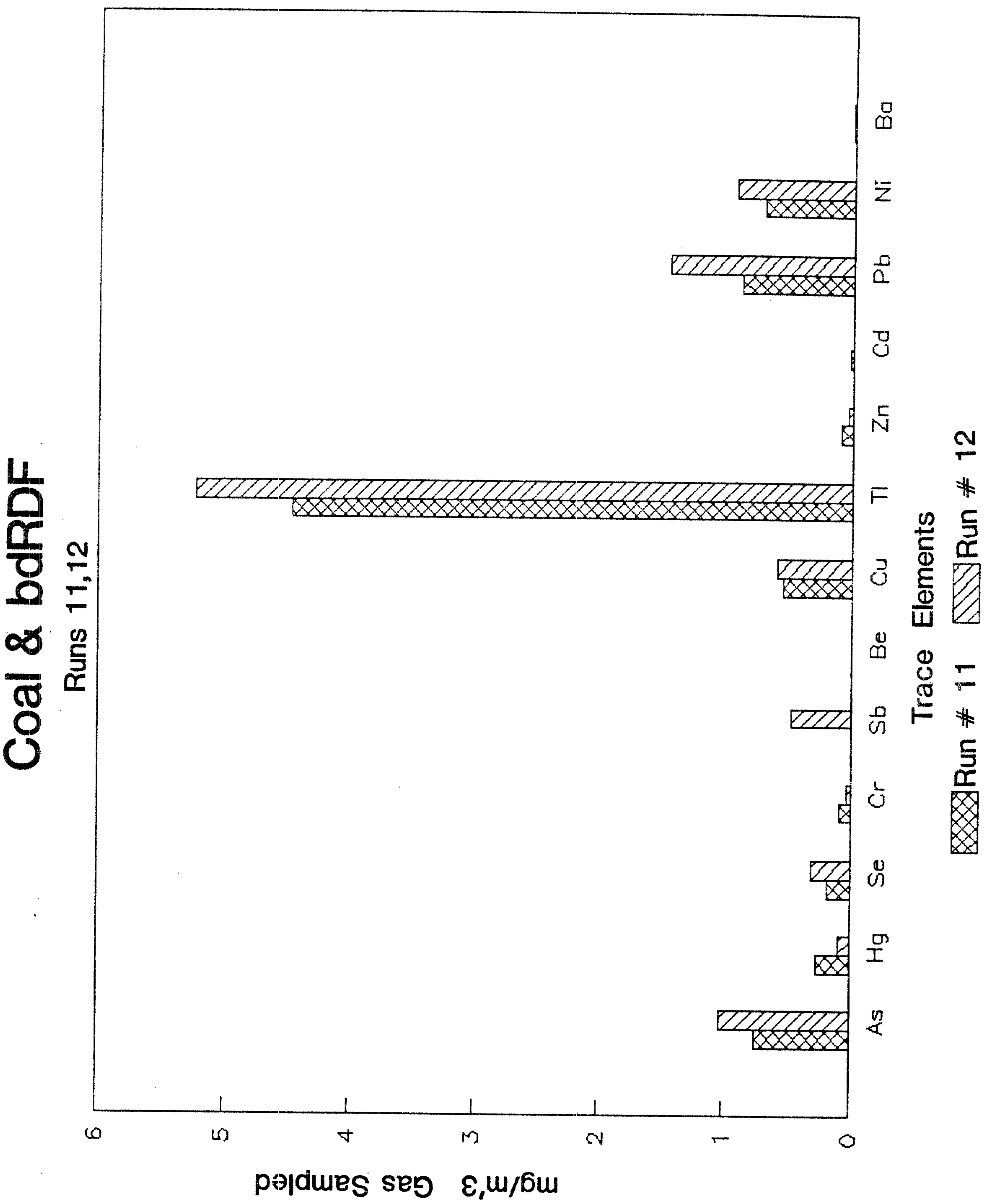

Figure 11:Run # 11(50%bdRDF, 4% binder), Run # 12(COal))

flue gas. The pollution control equipment contains a sprayer which sprays lime to reduce the particulate and at the same time reducing the trace elements present in the flue gas.

To fully understand and explain the collected data, it is important to detail the conditions under which the samples were collected. First the coal/bdRDF mixture was observed going into the boiler hours before it was calculated to come through. This occurred because the middle portion of a solid moves through the conical feed faster than the side portions. Because of this, it was impossible to predict when a run was going to start or finish; therefore, the test became a series of continuous runs instead of discrete runs as was originally planned. The exact composition of the feedstock was determined by taking samples of as it went through the coal scales. To help insure the integrity of the samples, sampling was conducted a few hours after the run had been underway, thus ensuring that the transition between runs had been completed.

It was not feasible to use pure coal in between runs to clean the bunker from bdRDF and to clean the boiler from the binder residue. Thus the binder residue increased with time. The build up of binder residue decreased the effect of the binder on trace metals.

Conclusion

The question of using bdRDF as a source of fuel and its effect on trace metals has been answered. Using $Ca(OH)_2$ as a binder and its effect on reducing trace metals has been studied. The test burn showed that it is possible and effective to use bdRDF with coal to be co-fired even at levels of up to 50% Btu content. Generally, bdRDF reduced the toxic trace metals, making it an effective and safe fuel.

There is much evidence in this study pointing toward the fact that bdRDF is indeed environmentally and economically safe and viable. Finding landfill sites is becoming increasingly difficult and cities are running out of space for landfills. Almost every week or every month we hear about this problem in the news, but it has not yet reached a crisis point.

This test has also shown conclusively that the addition of the binder to the RDF pellets reduced the amount of some trace metals emissions that occurred from the combustion of the pellets. The trace elements which were reduced or varied with an increase of bdRDF were reduced with an increase of binder content.

In conclusion, this study has demonstrated that it is feasible to use dRDF as an alternate energy source. It also showed that it is possible to reduce the toxic trace metals emissions through the use of $Ca(OH)_2$ binder. In this way, the problems of landfills and energy alternatives will be solved along with the environmental and economical problems.

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CHAPTER IV

FLY ASH ANALYSIS

PREFACE

This chapter is conserned with methods for studying and analyzing economizer fly ash. Both parts of the study were conducted at UNT. The first study involved Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX), using a semi-quantitative software program. The particle size of the fly ash with relationship to trace elements, and the binder effect on trace elements and its relationship to particle size were studied in this part of work.

The second analysis was done by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). ICP was used to analyze fourteen elements in the economizer fly ash and study their relationship to particle size and binder percentage.

FLY ASH ANALYSIS

INTRODUCTION

The disposal of refuse is an increasing concern of municipalities and state governments throughout the U.S. By the year 2,000, the existing landfills will become filled to capacity, and new landfills will be more costly to site (1-3). The development of an attractive disposal method is becoming critical. Incineration is one of the solutions (4-8).

Mass burn, which many cities use to dispose of their MSW, produces ash residue mounting up to 25 percent by weight and up to 10 percent by volume of the incoming MSW (5,6). Fly ash is the major by-product of burning MSW (9,10). Approximately 1-2 percent of fly ash escapes to the atmosphere (3,11). Fly ash consists of 70-95% inorganic matter and 5-30% organics (3). Physical and chemical characteristics of fly ash are becoming important for determining the method for disposal or use (3,12).

Trace element concentration in ash is of great interest because of its relationship to regulatory criteria under the Resource Conservation and Recovery Act (RCRA) regarding toxicity. Fourteen elements were studied in this part of the work. More details about fly ash, trace metals and their toxic effect were previously mentioned in Chapters I and II.

Ash Sampling

A total of 567 tons of bdRDF pellets were co-fired with 2,041 tons of sulfur-rich Kentucky coal in 12 test runs (224.7 tons of bdRDF from the Future Fuel facility and 352.3 tons from the Reuter facility). The runs were classified according to the difference in Btu content of bdRDF in the fuel, and the different binder content of bdRDF. Runs 1 and 12 were performed with one hundred percent coal in order to establish baseline data. Coal runs were also performed in between the different runs to avoid cross-contamination and to clean out bdRDF from previous runs. Details of test sampling locations and descriptions have been published (13-16) and were mentioned previously in Chapter II.

Over 1,500 samples of flue gas emissions, fly ash, bottom ash, and feedstock were collected during the 12 runs. A total of 190 bottom ash samples were collected from the traveling grate: from under the grate and through the grate. A total of 176 fly ash samples were collected from the multi-cyclone and from the economizer. Random ash samples were taken every eight hours. The samples were collected either by one of the UNT research teams or one of the operators at the specific time. Aluminum containers were used to collect the ash samples. After the samples cooled down they were transferred into ziplock bags which were then labeled with the date, run number, and the time the sample was collected. The ash samples were then packed and transported to UNT where they were arranged according to the run number, date, and time of collection.

PART I

FLY ASH STUDY BY SEM/EDX

EQUIPMENT

Vacuum Evaporator:

The ash samples, after being separated into different particle sizes, were mounted on a carbon sample holder and coated with carbon. A JEOL JEE-4X vacuum evaporator was used for this task.

Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Analysis (EDX):

The SEM/EDX is comprised of three fundamental parts: the scanning electron microscope, the X-ray analyzer, and the data station for controlling and handling the collected data. A JEOL JSM-T300 Scanning Microscope and Tracor Northern TN 5500 X-Ray analyzer data station with an 8510 Model printer was used to study the fly ash samples.

Sample Analysis

A representative homogeneous economizer fly ash sample, about 40 grams, was taken and separated into eight different particle sizes using sieves. The sieves were arranged on top of each other according to their sizes from the smallest (bottom) to the largest (top). The sample was placed in the top sieve (1000 u) and the cover was placed on the top of the sieve. The samples were then placed on a shaker for 10 minutes each. The different particle sizes were then carefully taken, weighed, and placed in separate glass vials. Vials were labeled with the run number, type of ash, particle size, the date the sample was collected, and the date it was separated. The different particle sizes are represented with the numbers 1 through 8 in the graphs as follows:

size 1 represents (<45u) particle size
size 2 represents (>45-(63)u) particle size
size 3 represents (>63-(75)u) particle size
size 4 represents (>75-(125)u) particle size
size 5 represents (>125-(250)u) particle size
size 6 represents (>250-(500)u) particle size
size 7 represents (>500-(1000)u) particle size
size 8 represents (>1000u) particle size

A representative homogeneous sample was taken from each one of the vials, mounted on a carbon holder, and coated with carbon under high vacuum. The samples, after being coated, were analyzed using SEM/EDX.

SEM/EDX is a multi-element analysis with quantitative and qualitative capabilities (17-19). The advantage of using SEM is that it is a nondestructive technique that can be used to screen the samples for some other analytical technique which gives an idea where and how to use fly ash. By knowing approximately the constituents of fly ash, disposing and using it will become easier and constructive with very little danger. The use of EDX in conjunction with SEM can potentially increase its sensitivity to trace elements that have been electro-deposited (17-20).

Appendix C shows a copy of the printout of the SEM/EDX analysis of the 20% bdRDF/4% binder. Eight analysis with eight graphs are shown for the eight different particle sizes. Appendix D shows four pictures of fly ash taken from different samples.

To evaluate the collected ESM/EDX data one of the samples was analyzed five times, five different areas, for a statistical analysis. Table XXIV shows the trace elemental analysis of size 1, 20% bdRDF/4% binder, and Table XXV shows the statistical analysis of the values. The analytical percentages collected seems to be consistant and reasonable.

Table XXIV: SEM/EDX analysis of economizer fly ash of 20% dRDF/4% BINDER

SIZE 1 ANALYZED 5 TIMES FOR STATISTICAL ANALYSIS.

	1	1	1	1	1
Al	16.14	17.74	17.72	17.01	17.78
Si	28.80	31.86	32.54	28.35	29.67
S	06.48	06.53	06.95	05.72	06.47
K	03.65	04.13	04.01	03.36	03.48
Ca	16.95	15.74	16.00	16.13	18.14
Ti	01.82	01.26	01.65	01.64	01.39
Fe	24.27	21.54	19.33	26.60	21.19
Cu	01.88	01.48	01.80	01.19	1.87
Mg	00.00	00.00	00.00	00.00	00.00

Table XXIV: Statistical analysis

	Sum.X	Av.	SD
Al	86.66	17.33	0.54
Si	151.22	30.24	1.67
S	33.15	6.63	0.00
K	18.63	3.73	0.30
Ca	82.96	16.59	0.87
Tl	7.76	1.15	0.20
Fe	112.93	22.59	2.55
Cu	8.22	1.64	0.27

Results and Discussion

The coal/bdRDF ash chemical composition depends on the following factors:

- .the origin and composition of bdRDF
- .the bdRDF ratio in the blend
- .the geological and geographic factors related to coal deposits
- .the combustion conditions
- .and the air control device efficiency.

Calcium hydroxide was used as a binder in the manufacture of binder-enhanced dRDF pellets. The binder has many advantages among which are that it affects the pellets by making them more dense, odorless, allowing them to be stored for years without being chemically or biologically affected. By making the pellets more dense, transporting them will be easier, and the heat content of the pellets will increase producing a better fuel than the unprocessed MSW or dRDF without binder.

It was expected that the binder would decrease the emissions in general and the trace metals in particular, since the bdRDF contains much less sulfur (approximately 0.1%) than the currently used sulfur-rich (3.5%) low grade Kentucky coal. The coal/bdRDF blend was made with 10, 20, 30, and 50% by Btu heat content of bdRDF. Accordingly the ash, which will be a mixture of coal ash and bdRDF ash, should be less hazardous depending on the bdRDF percent and the binder percent used.

The only fly ash samples investigated, thus far, were those from the economizer. The SEM/EDX was used to study in particular the following fourteen elements: Tl, Ba, Be, Cr, Cu, Ni, V, As, Cd, Hg, Pb, Sb, Se, and Zn. The results summarized in the tables XXVI-XXXVI. The graphs also gives a better idea of the effect on trace elements. They are divided into two parts: the particle size determination and relationship to trace elements, and the binder effect on trace elements.

Particle Size Determination of Fly Ash and Relationship to Trace Elements:

In this part, the weight percent of elements versus the particle size were evaluated. The results summarized in the Tables XXVI through XXXVI and the following graphs 12 through 22 suggest the following:

- In general, Cu, Tl, K, Al, S, and Zn increased with an increase in particle size of fly ash
- The elements Si, Fe, Mg, and Ca decreased with an increase in particle size
- Some elements like Ti and V were at very low

Table XXVI: SEM/EDX analysis of economizer fly ash of 10% dRDF/0% BINDER

	1	2	3	4	5	6	7	8
Al	21.76	21.28	17.47	21.12	18.62	21.61	10.05	11.05
Si	35.43	35.17	27.66	31.98	28.60	36.31	17.22	13.37
S	08.85	07.20	04.50	04.17	03.94	05.33	16.90	30.11
K	04.36	03.76	03.40	03.62	02.85	04.73	03.23	00.00
Ca	06.26	06.70	05.11	06.68	05.00	03.59	06.20	01.13
Ti	00.96	01.73	02.13	02.44	01.85	03.33	06.17	00.00
Fe	22.38	23.83	39.82	29.53	38.73	23.90	30.06	43.17
Cu	00.00	00.34	00.00	00.00	00.00	00.75	03.34	00.26
V	00.00	00.00	00.00	00.37	00.77	00.43	03.82	00.73

Table XXVII: SEM/EDX analysis of economizer fly ash of 10% dRDF/4% BINDER

	1	2	3	4	5	6	7	8
Mg	02.92	02.18	02.10	02.24	01.25	03.73	00.00	00.00
Al	17.04	14.24	16.21	19.29	19.39	20.71	16.10	19.45
Si	26.21	25.49	27.62	34.07	34.65	35.27	19.90	26.24
S	05.44	06.53	04.63	03.66	05.05	04.54	13.97	13.18
K	02.43	02.75	02.88	03.65	04.59	04.14	03.06	02.98
Ca	16.44	29.97	12.16	09.84	06.71	11.07	11.08	04.88
Ti	00.93	00.96	01.62	01.79	02.05	02.79	03.51	02.27
Fe	26.85	15.57	31.00	24.07	23.98	15.40	22.06	23.02
Cu	01.74	02.31	01.79	01.39	02.32	02.35	06.67	07.98
Zn	00.00	00.00	00.00	00.00	00.00	00.00	03.65	00.00

Table XXVIII: SEM/EDX analysis of economizer fly ash of 10% dRDF/8% BINDER

	1	2	3	4	5	6	7	8
Al	13.87	16.44	15.51	18.68	19.97	19.24	16.65	13.32
Si	20.62	23.87	28.74	31.33	35.10	28.93	29.32	27.00
S	06.78	05.87	05.07	04.83	05.03	08.01	07.39	18.04
K	02.76	02.92	03.12	03.46	04.48	03.41	03.61	03.97
Ca	27.85	28.96	16.41	16.23	10.13	10.42	12.52	05.39
Ti	01.20	01.36	01.42	01.65	02.38	01.96	01.89	03.44
Fe	20.40	12.82	21.49	17.93	17.23	21.60	18.98	22.45
Cu	02.84	01.63	01.40	01.39	02.08	02.12	03.56	06.37
Mg	03.69	06.13	04.84	04.50	02.33	02.16	02.85	00.00
Zn	00.00	00.00	00.00	00.00	01.26	02.26	03.24	00.00

Table XXIX: SEM/EDX analysis of economizer fly ash of 20% dRDF/0% BINDER

	1	2	3	4	5	6	7	8
Al	18.49	19.31	19.64	21.24	19.87	21.31	13.56	15.06
Si	28.44	32.09	32.17	31.78	31.26	36.92	22.77	26.94
S	05.06	05.45	03.33	04.26	04.52	10.55	15.39	13.61
K	03.21	03.57	03.48	03.80	04.07	04.05	02.61	04.38
Ca	18.49	14.71	08.86	08.12	09.56	03.98	16.53	04.77
Ti	02.03	02.27	01.90	02.25	02.99	02.61	01.92	03.81
Fe	21.40	20.02	29.53	28.54	27.75	20.58	22.22	28.36
Cu	02.88	02.58	01.09	00.00	00.00	00.00	00.00	00.00
Mg	00.00	00.00	00.00	00.00	00.00	00.00	04.99	03.08

Table XXX: SEM/EDX analysis of economizer fly ash of
20% dRDF/4% BINDER

	1	2	3	4	5	6	7	8
Al	17.78	17.81	20.07	20.51	21.20	20.81	15.87	19.21
Si	29.67	30.91	34.51	36.57	41.23	41.23	29.06	26.11
S	06.47	05.95	05.38	04.38	05.75	05.69	17.44	14.55
K	03.48	03.51	03.84	04.07	05.58	05.65	04.24	02.62
Ca	18.14	12.81	09.48	06.50	04.89	04.08	06.57	05.43
Ti	01.39	02.20	01.74	02.81	02.71	02.51	03.19	02.80
Fe	21.19	24.81	22.93	25.81	18.74	20.03	19.73	24.96
Cu	01.87	01.27	00.80	00.00	00.00	00.00	03.89	04.32
Mg	00.00	00.73	01.24	00.00	00.00	00.00	00.00	00.00

**Table XXXI: SEM/EDX analysis of economizer fly ash of
20% dRDF/8% BINDER**

	1	2	3	4	5	6	7	8
Mg	04.33	06.15	06.12	04.75	03.67	03.99	01.68	02.88
Al	13.00	16.22	15.46	18.52	17.63	19.95	16.87	15.69
Si	20.81	32.78	23.37	28.86	30.25	30.71	24.71	20.17
S	06.34	05.97	05.52	04.44	05.45	05.27	11.91	10.87
K	03.06	03.05	02.98	03.10	03.85	04.08	03.17	02.35
Ca	34.92	29.34	26.03	19.27	17.16	14.84	13.26	13.80
Ti	01.42	01.71	02.43	01.94	02.14	03.01	02.18	02.62
Fe	16.12	12.40	18.06	17.90	16.96	15.89	20.56	22.95
Cu	00.00	01.38	00.00	01.23	01.17	01.64	04.28	05.27
Zn	00.00	00.00	00.00	00.00	01.73	01.41	01.39	03.40

Table XXXII: SEM/EDX analysis of economizer fly ash of 30% dRDF/0% BINDER

	1	2	3	4	5	6	7	8
Al	15.30	16.08	16.30	19.88	18.87	19.06	13.68	06.78
Si	21.86	29.04	25095	34.73	34.00	36.69	36.79	12.63
S	04.63	05.05	03.89	03.05	02.65	04.67	05.08	18.87
K	04.35	04.49	04.15	04.74	04.35	06.39	06.18	01.48
Ca	31.40	21.70	20.67	09.82	11.39	06.10	06.70	38.38
Fe	16.37	16.37	21.82	21.67	19.98	21.05	28.16	09.67
Ti	03.08	04.61	04.08	03.89	06.84	03.59	03.41	02.48
Cu	03.01	2.67	03.15	02.21	01.92	02.46	00.00	06.41
Mg	00.00	00.00	00.00	00.00	00.00	00.00	00.00	02.90

Table XXXIII: SEM/EDX analysis of economizer fly ash of 30% dRDF/4% BINDER

	1	2	3	4	5	6	7	8
Mg	02.73	03.05	04.26	03.68	02.97	02.02	00.00	00.10
Al	13.29	14.69	15.88	16.51	18.33	18.12	18.10	26.31
Si	22.38	26.82	28.40	29.57	29.91	32.22	30.18	35.53
S	06.19	06.73	05.32	05.73	04.05	06.55	09.51	08.40
K	04.55	04.31	04.29	04.34	04.43	05.90	05.32	03.68
Ca	21.69	19.43	20.43	22.02	16.03	14.33	09.65	08.47
Ti	02.15	02.25	02.63	03.42	02.76	03.37	06.97	02.96
Fe	23.84	21.04	16.78	13.63	21.51	16.49	18.23	13.38
Cu	03.18	01.68	02.01	01.11	00.00	01.02	02.14	01.15

Table XXXIV: SEM/EDX analysis of economizer fly ash of 30% dRDF/8% BINDER

	1	2	3	4	5	6	7	8
Al	14.87	15.03	16.28	17.92	18.09	17.83	21.32	14.94
Si	22.95	23.85	25.87	27.10	27.55	28.33	27.51	26.83
S	07.36	06.61	06.02	04.76	04.13	05.40	10.19	17.24
K	03.09	02.89	02.95	03.33	03.49	03.18	04.14	02.69
Ca	19.59	21.07	18.83	18.97	15.34	26.01	14.34	05.25
Ti	01.88	02.19	01.57	01.74	02.08	02.13	02.93	01.57
Fe	22.95	21.77	21.19	17.99	21.79	09.82	15.19	30.66
Mg	05.91	06.60	07.28	08.19	07.54	07.29	03.84	00.82
Zn	01.41	00.00	00.00	00.00	00.00	00.00	00.00	00.0

Table XXXV: SEM/EDX analysis of economizer fly ash of 50% dRDF/4% BINDER

	1	2	3	4	5	6	7	8
Mg	02.83	02.70	03.95	04.29	03.55	02.24	00.00	03.41
Al	08.62	10.10	09.64	09.82	09.96	09.42	05.98	07.07
Si	11.55	13.03	13.39	12.79	13.24	10.65	05.53	08.21
S	02.06	01.73	01.04	01.58	00.90	00.91	01.21	01.97
K	01.38	01.44	01.38	01.26	01.43	01.13	00.45	00.59
Ca	11.75	08.55	08.85	10.74	07.08	07.32	01.47	05.31
Ti	00.47	00.74	00.83	00.94	00.67	00.88	00.58	00.89
Fe	10.96	08.26	08.36	08.09	07.39	04.16	03.48	02.14
Cu	29.86	31.73	30.61	29.82	32.24	36.69	46.98	40.98
Zn	20.52	21.71	21.95	20.66	23.54	26.60	34.31	29.43

Table XXXVI: SEM/EDX ANALYSIS OF 100% COAL

	1	2	3	4	5	6	7	8
Al	10.32	9.77	8.42	9.15	9.89	9.18	4.52	3.51
Si	13.49	11.79	9.35	10.87	12.67	10.78	5.46	3.04
S	1.82	1.46	0.94	1.20	1.39	1.76	1.46	1.54
K	1.07	0.95	0.61	0.74	1.07	0.86	0.58	0.00
Ca	2.74	1.75	0.92	1.69	1.78	1.14	0.40	0.47
Ti	0.18	0.00	0.00	0.12	0.00	0.00	0.24	0.00
Fe	6.74	6.20	7.96	6.35	9.55	6.91	4.29	2.72
Cu	36.52	38.93	41.23	40.28	36.81	40.00	48.22	51.69
Zn	27.13	29.16	30.57	29.60	26.83	29.38	34.81	37.03

concentrations. Thus, it was hard to predict whether the concentrations increased or decreased with an increase in particle size

- Some elements in some samples were not detected by SEM/EDX because they were below the detection limits of the instrument
- The concentration ranges for toxic metals in fly ash were significantly lower than levels typically found in ash from mass burn incineration.

Binder Effect on Trace Elements in Fly Ash and Relationship to Particle Size:

In this part of the work the binder was studied to observe its effect on trace elements emissions. Every particle size was looked at separately with the detected elements. Eight graphs were drawn for each type of bdRDF. The result summarized in the previous Tables XXVI-XXXVI and the following graphs 23-54 suggest the following:

- In any graph of the same particle size 1 through 8, the elements Al, Si, S, K, and Fe weight percent decreased with an increase in the binder percentage, the elements Ti, V, and Zn weight percent were not affected by an increase in binder level, and the

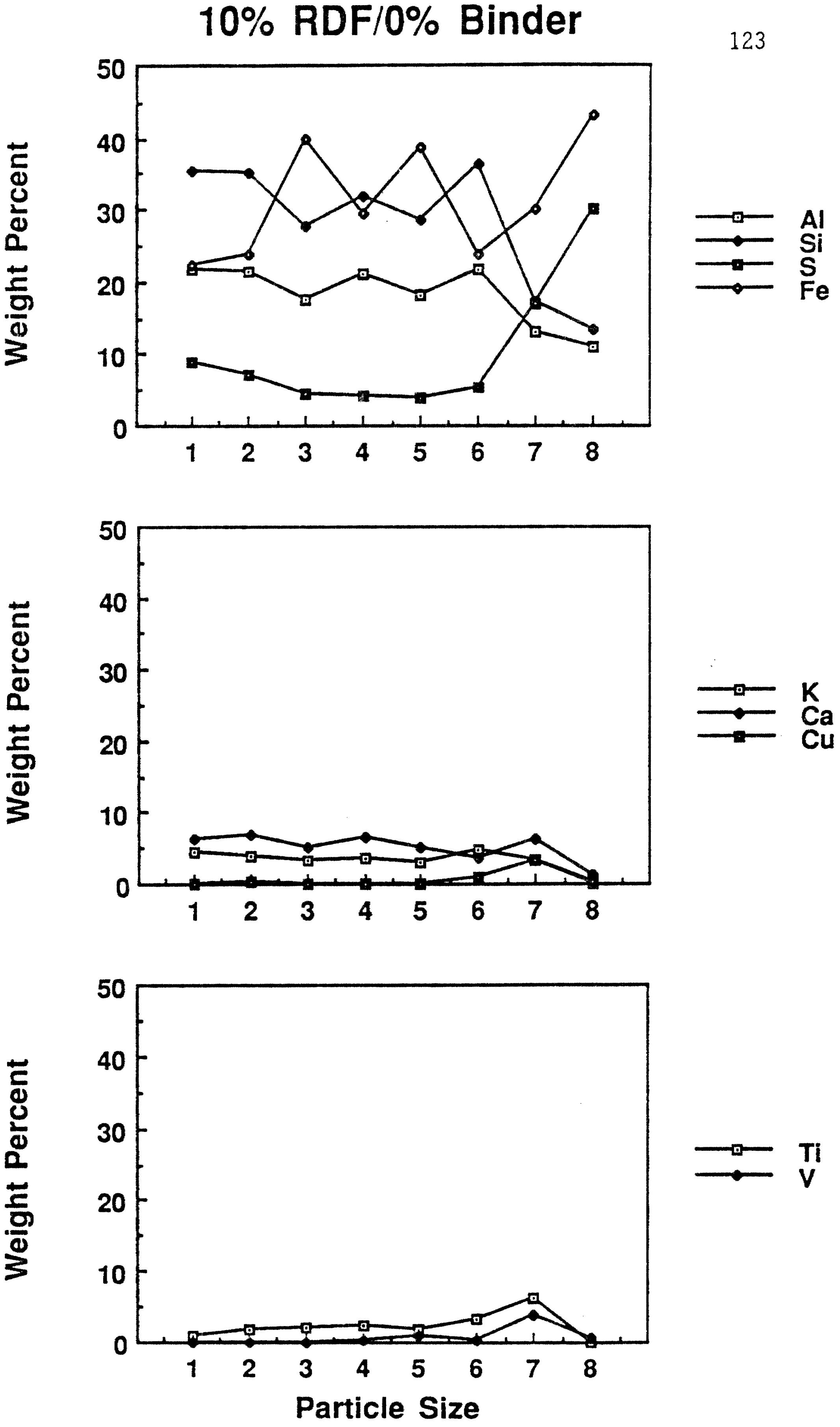


Figure 12. SEM/EDX Particle size distribution.

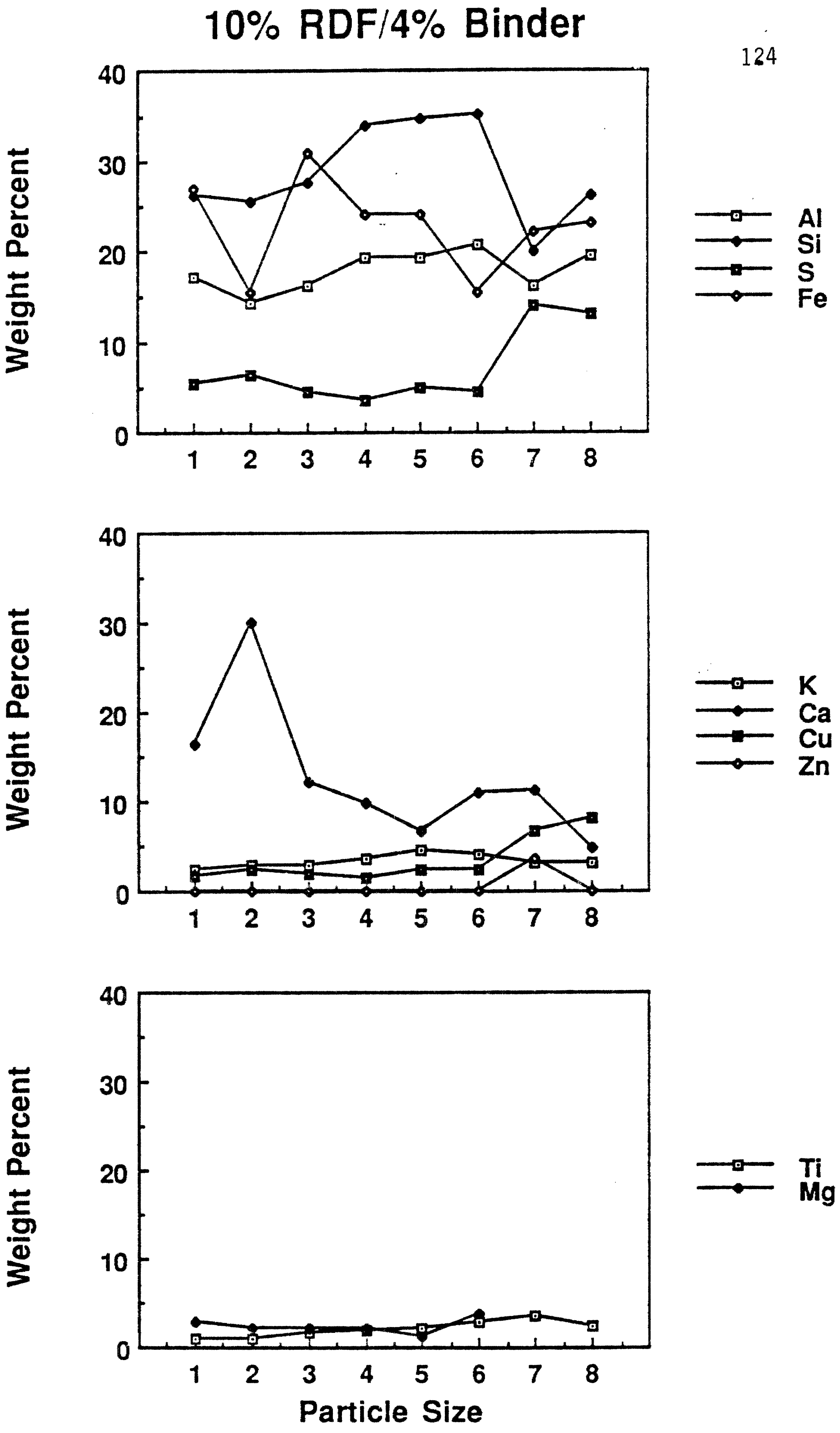


Figure 13. SEM/EDX Particle size distribution.

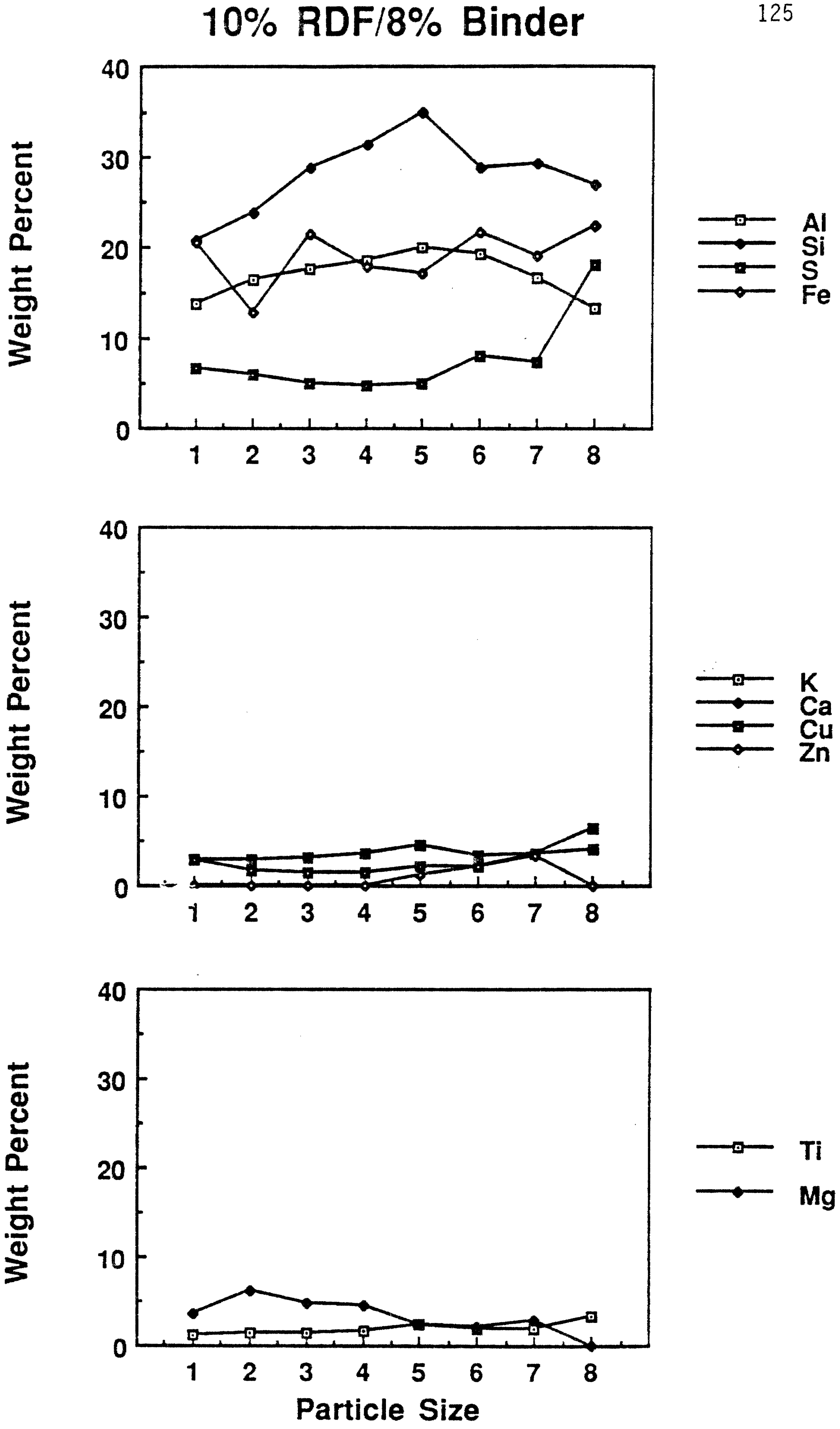


Figure 14. SEM/EDX Particle size distribution.

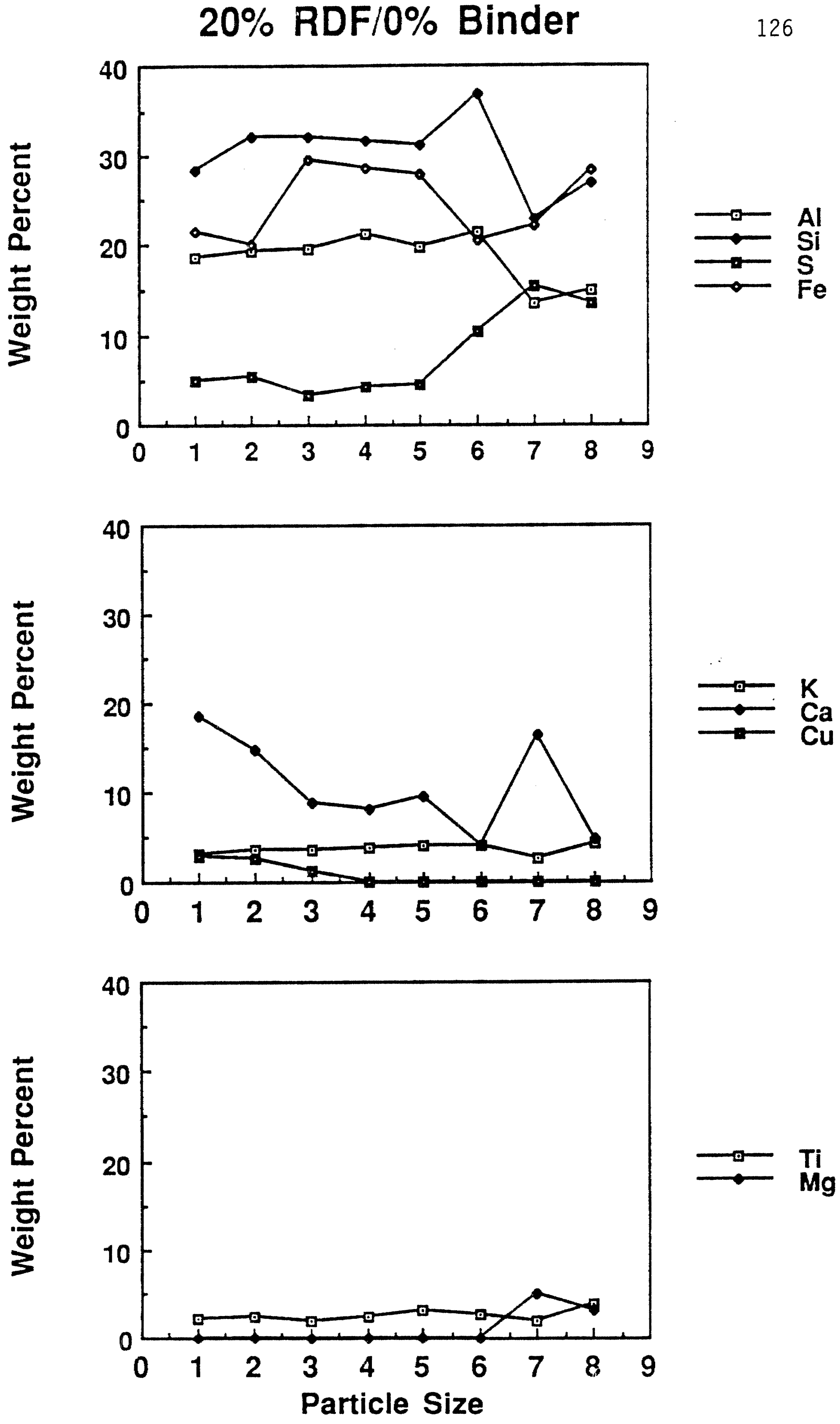


Figure 15. SEM/EDX Particle size distribution.

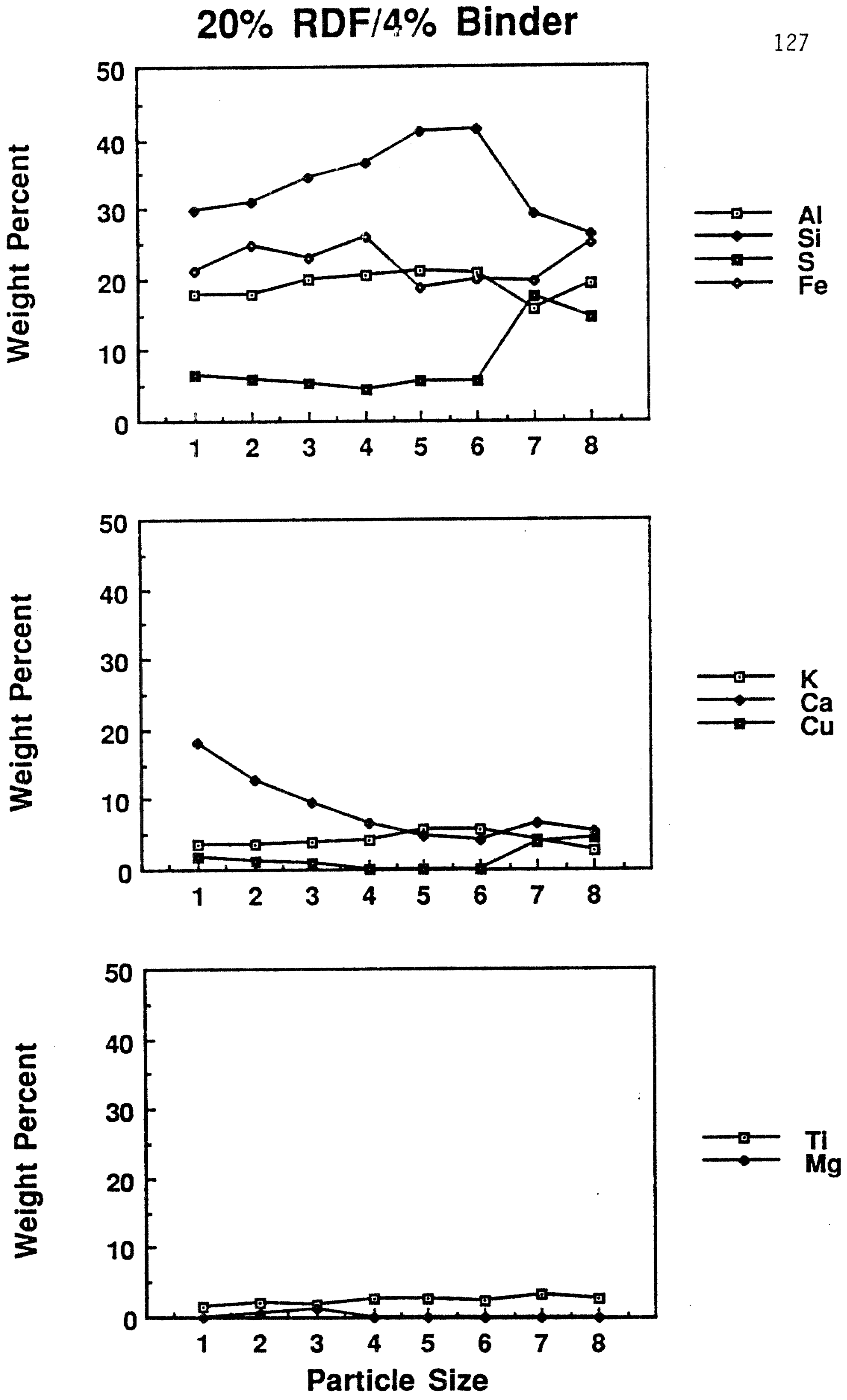


Figure 16. SEM/EDX Particle size distribution.

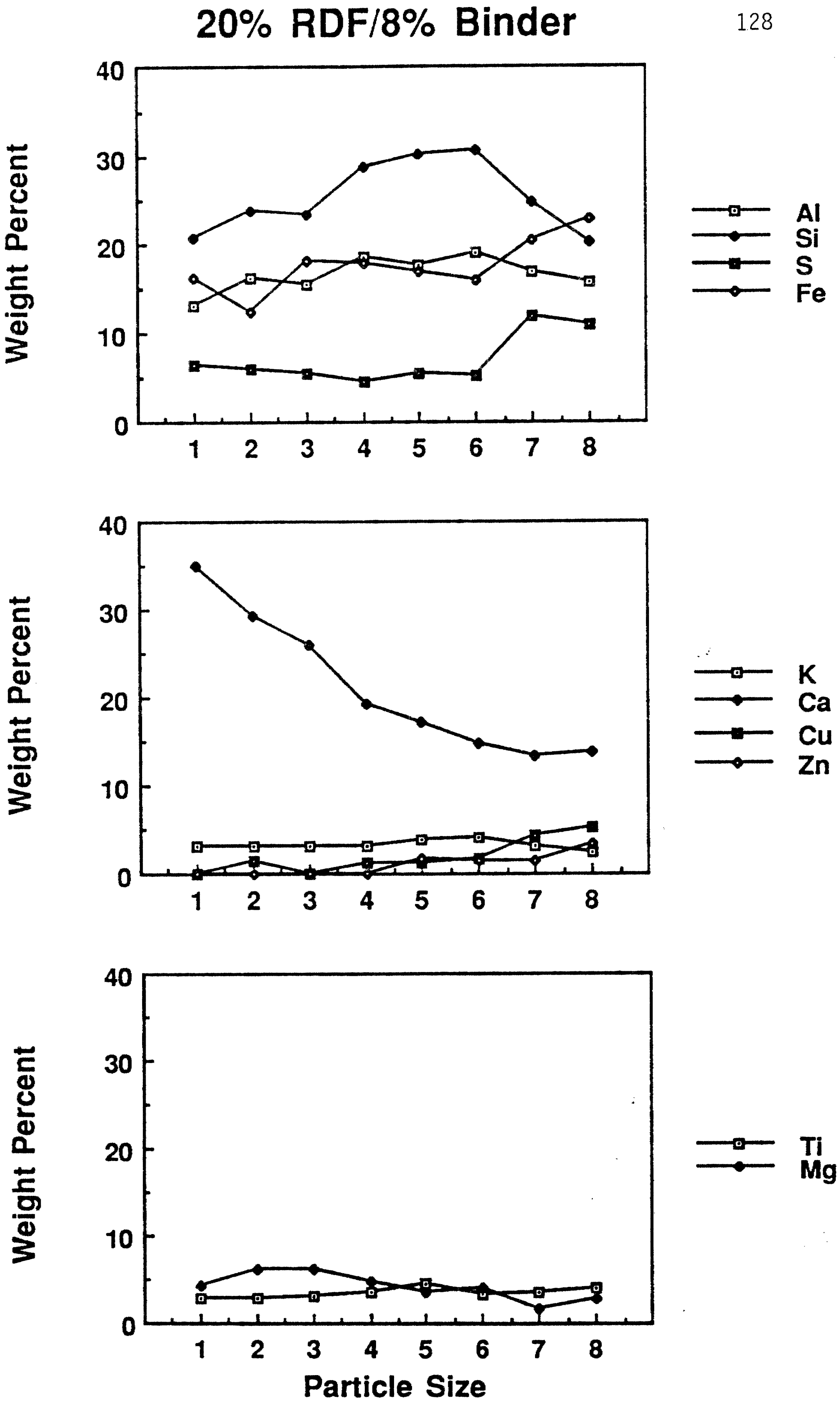


Figure 17. SEM/EDX Particle size distribution.

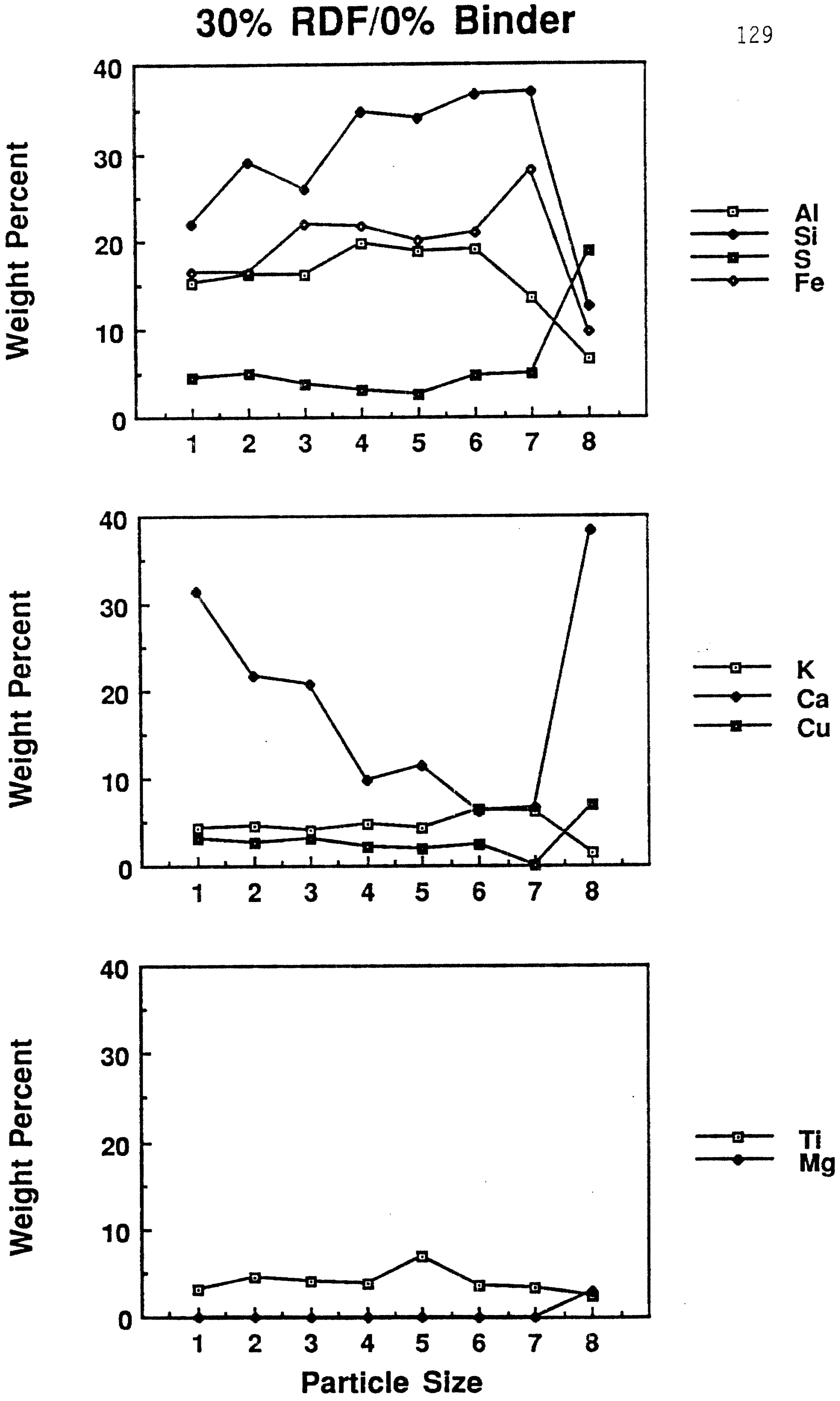


Figure 18. SEM/EDX Particle size distribution.

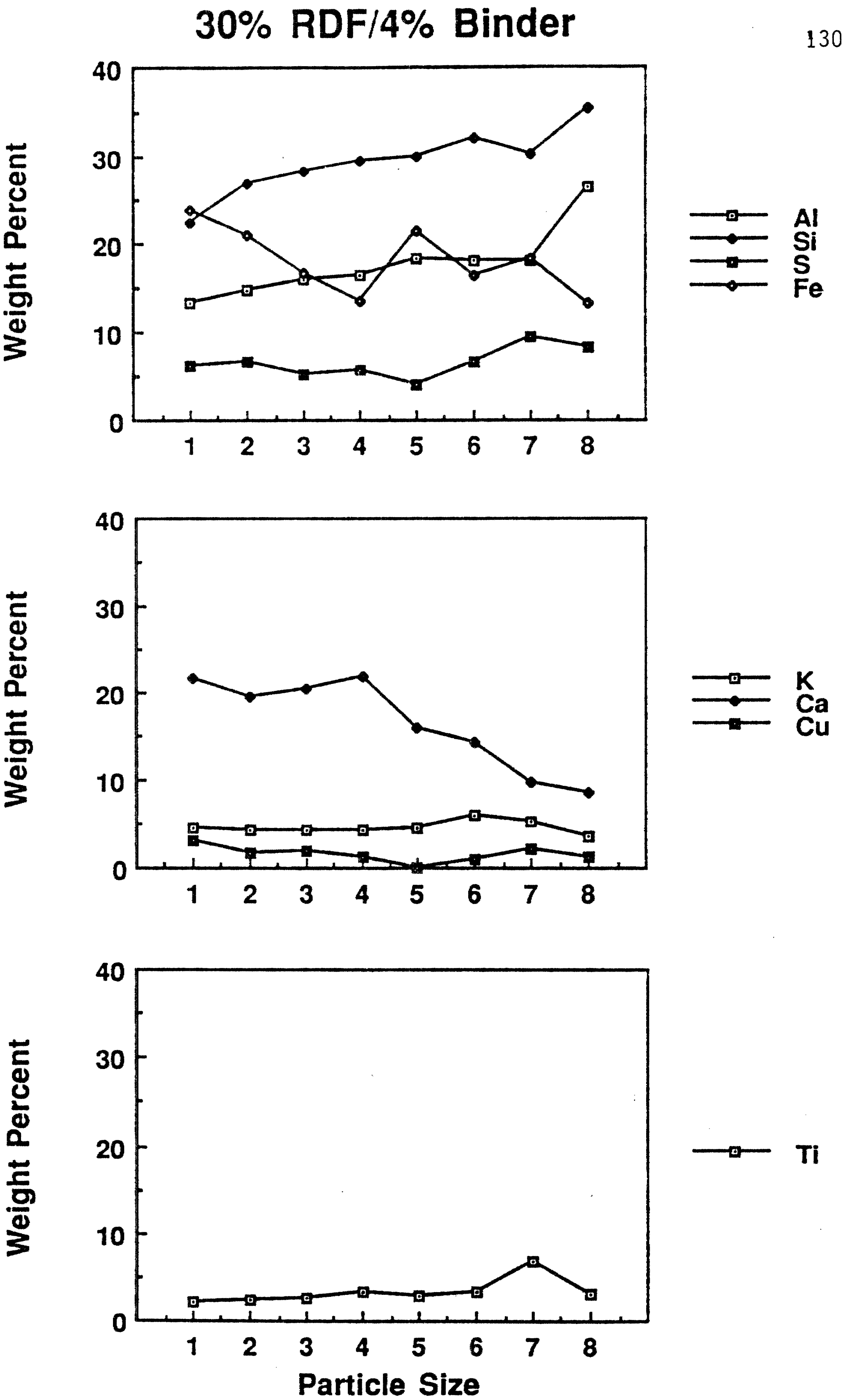


Figure 19. SEM/EDX Particle size distribution.

30%RDF/8% Binder

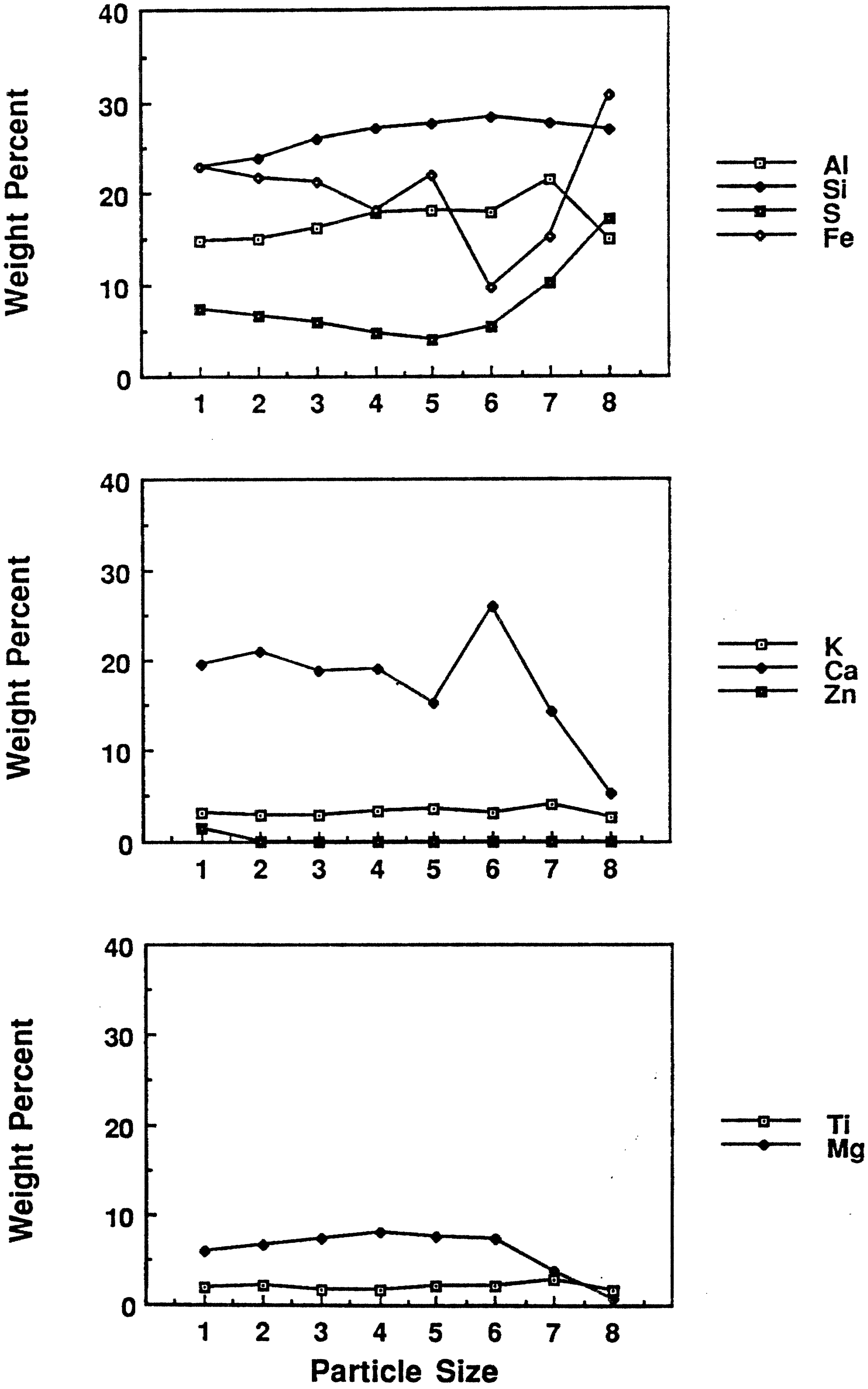
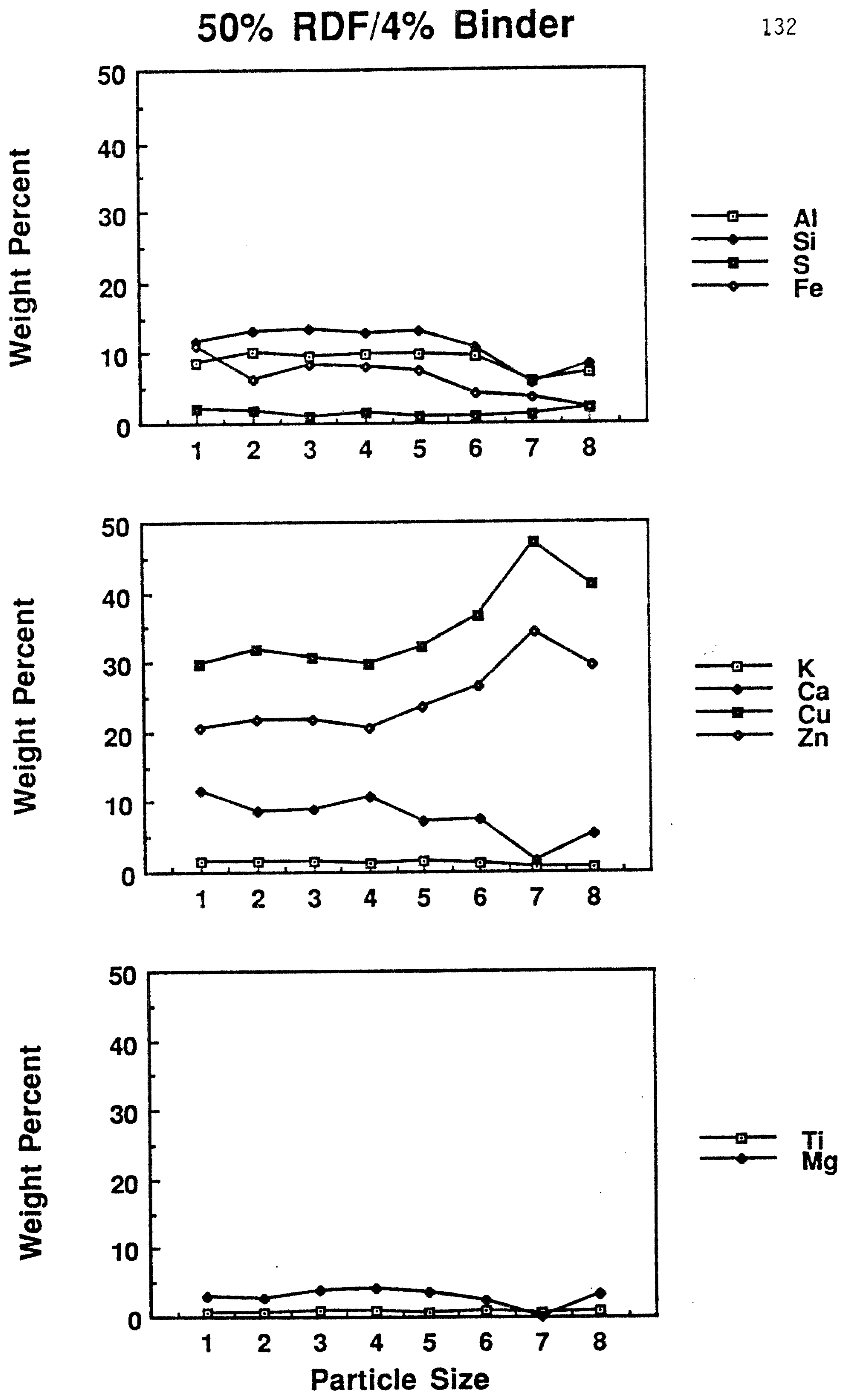


Figure 20. SEM/EDX Particle size distribution.



50% RDF/4% Binder

Figure 21.SEM/EDX Particle size distribution.

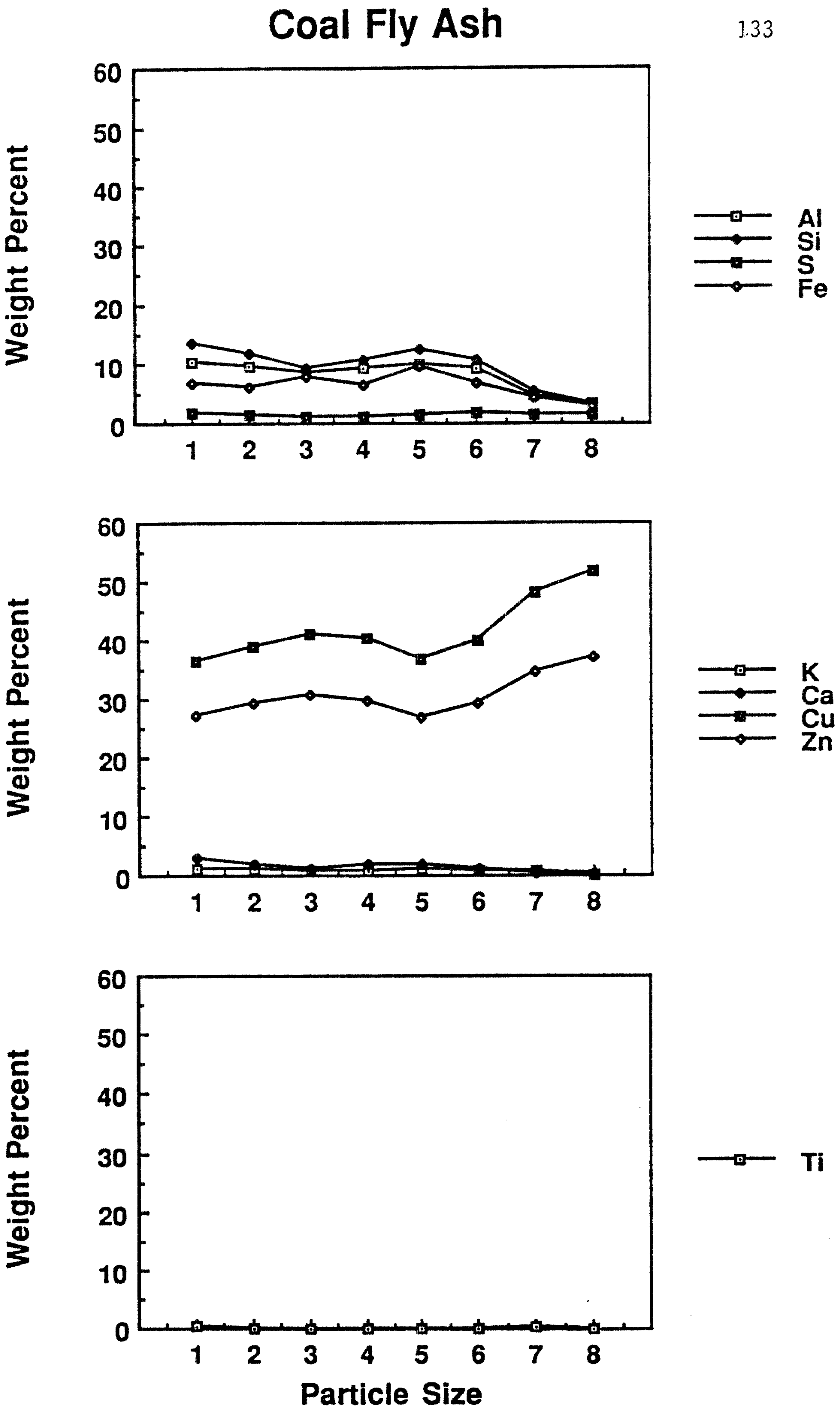


Figure 22. SEM/EDX Particle size distribution.

Figure 23. **Size 1 - SEM Analysis 10%**

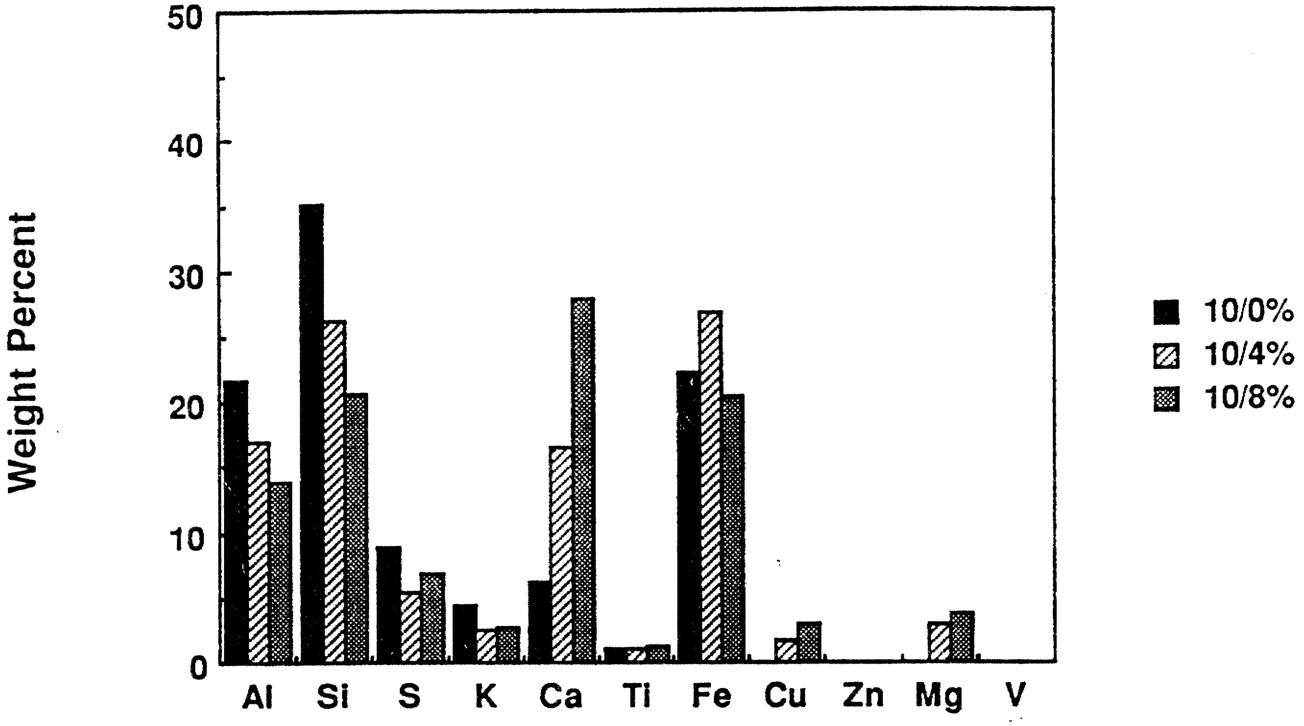


Figure 24. **Size 2 - SEM Analysis 10%**

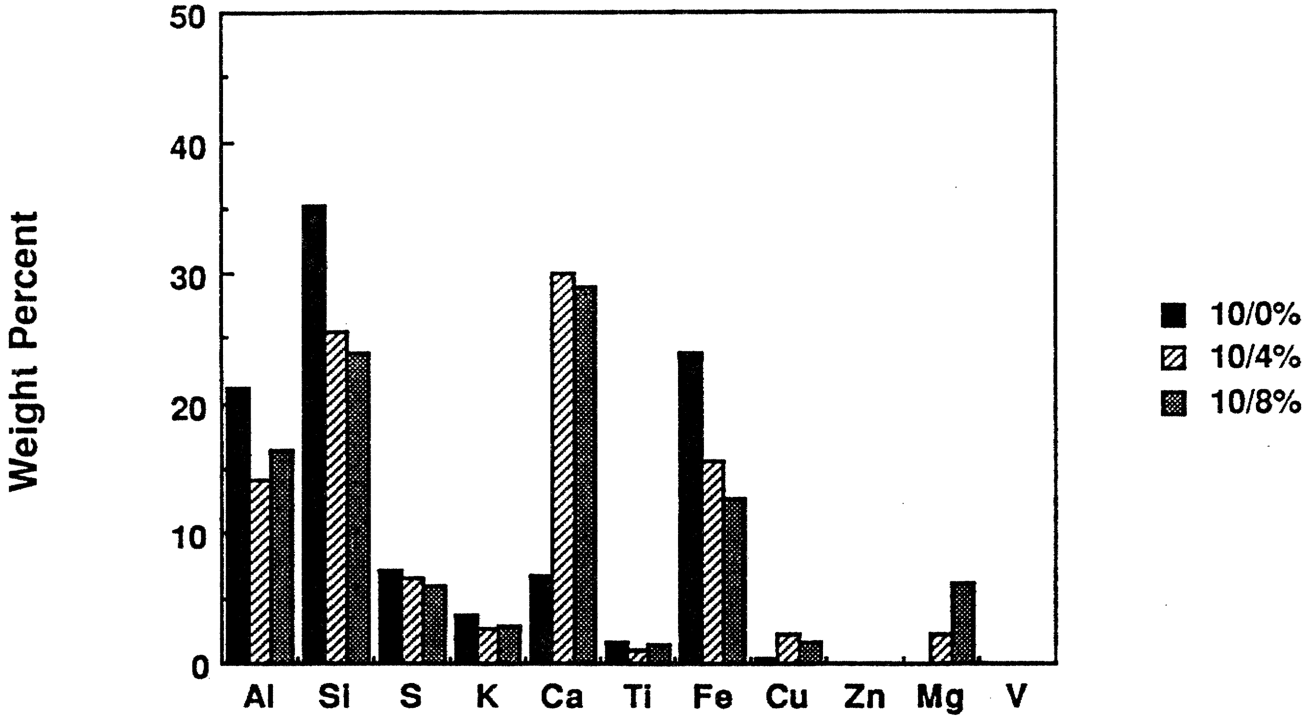


Figure 25. **Size 3 - SEM Analysis 10%**

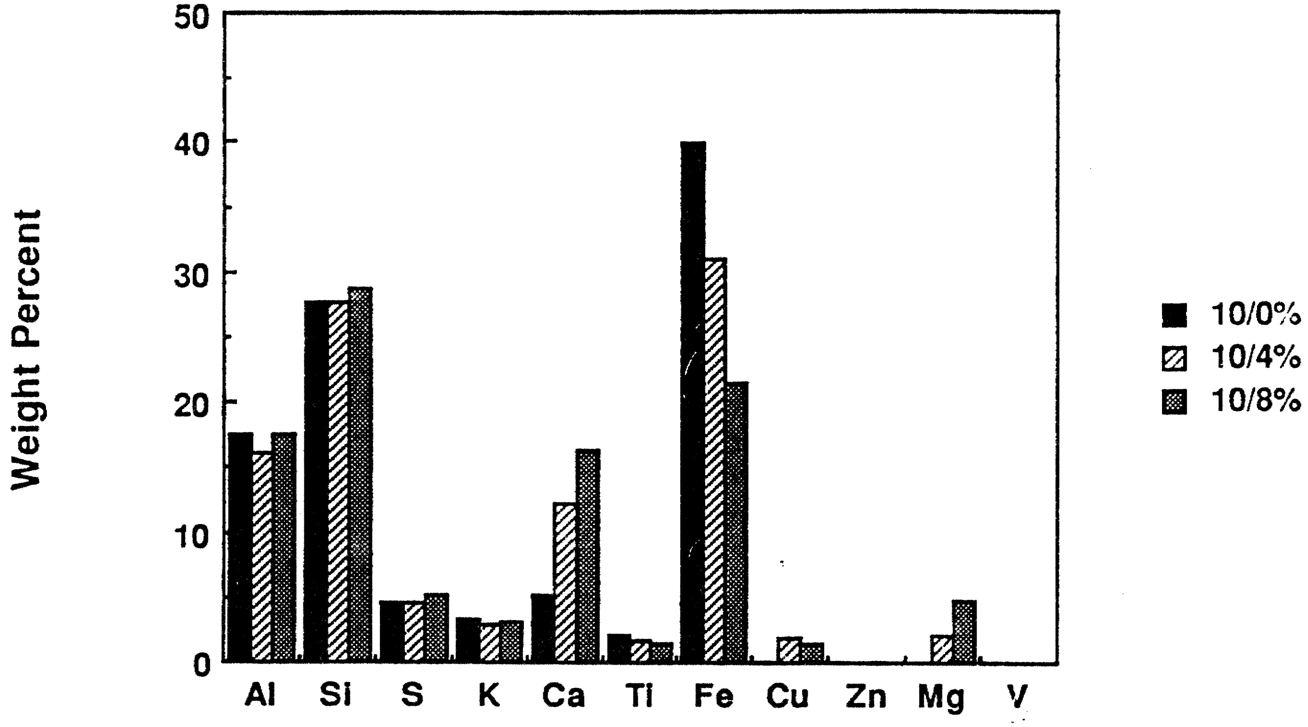


Figure 26. **Size 4 - SEM Anlysis 10%**

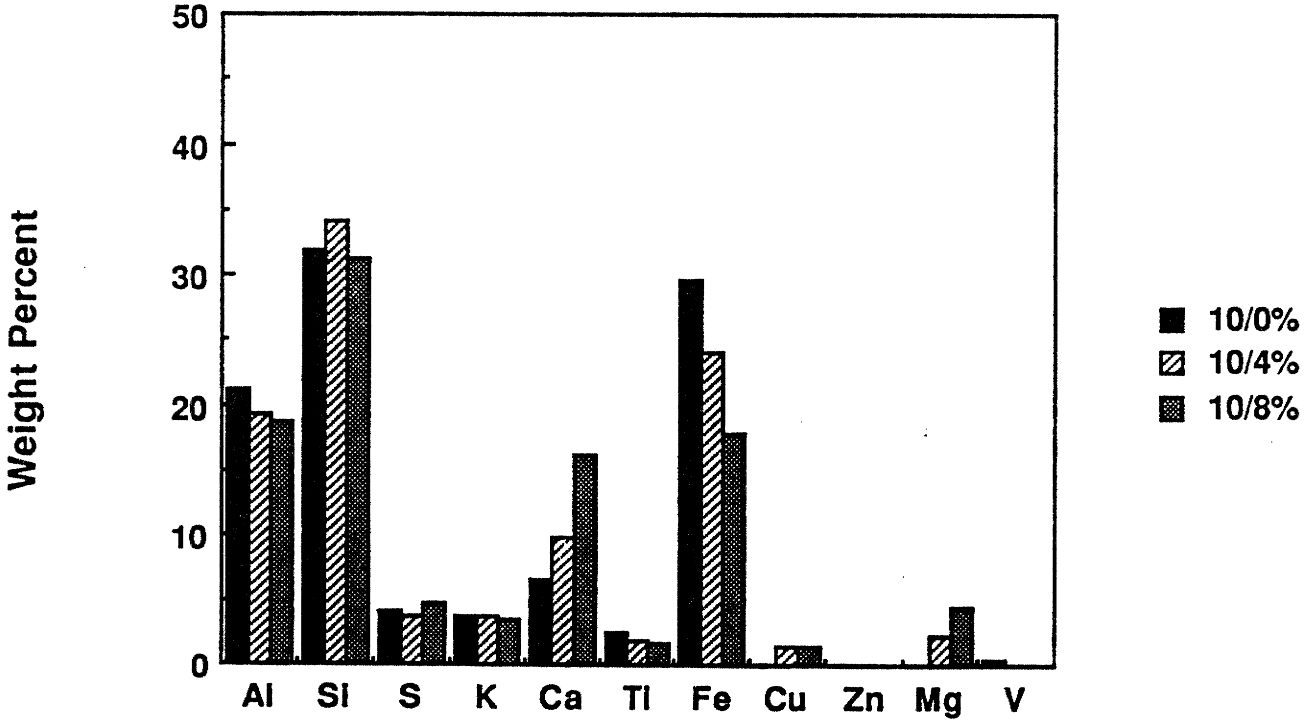


Figure 27 Size 5 - SEM Analysis 10%

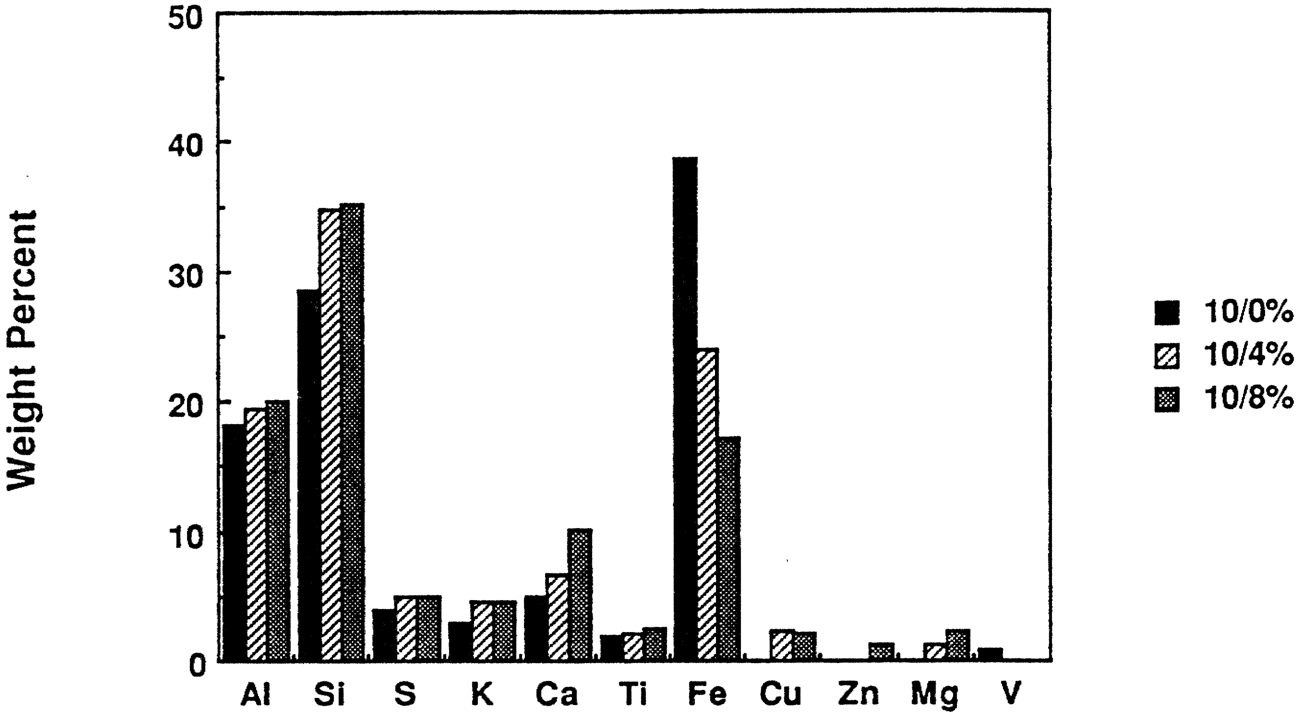


Figure 28. Size 6 - SEM Analysis 10%

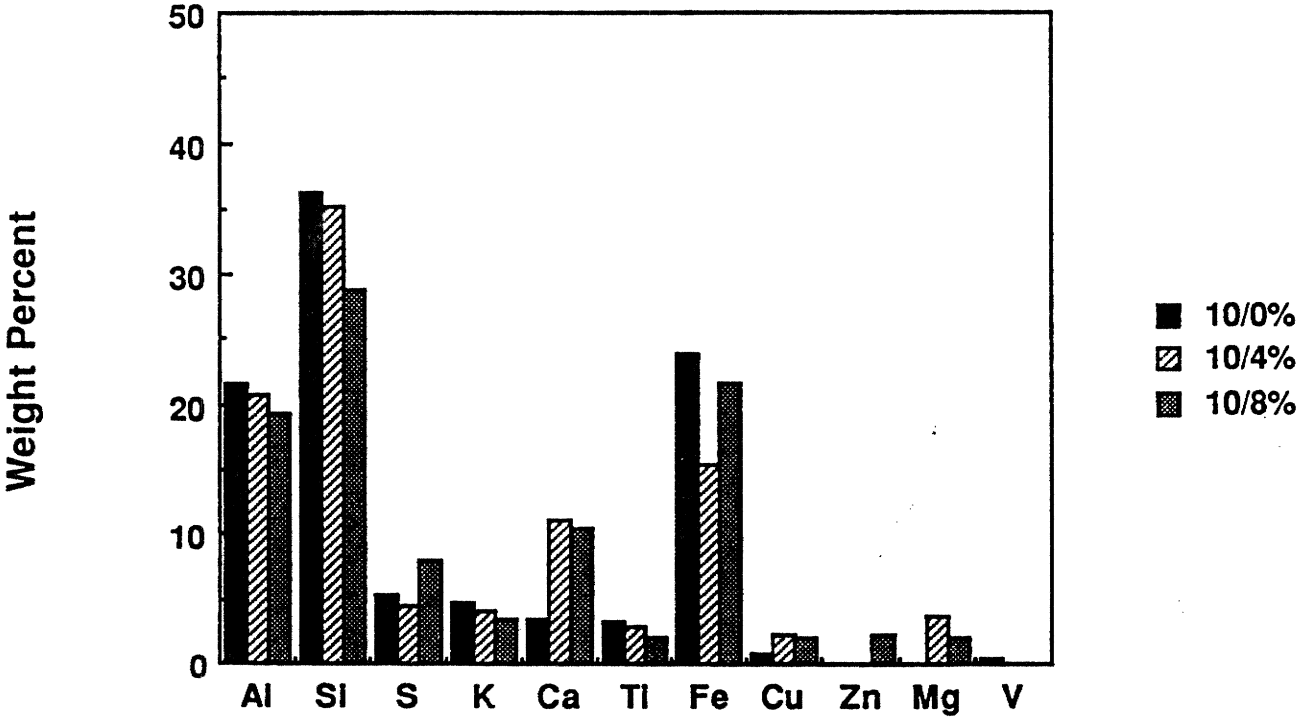


Figure 29. Size 7 - SEM Analysis 10%

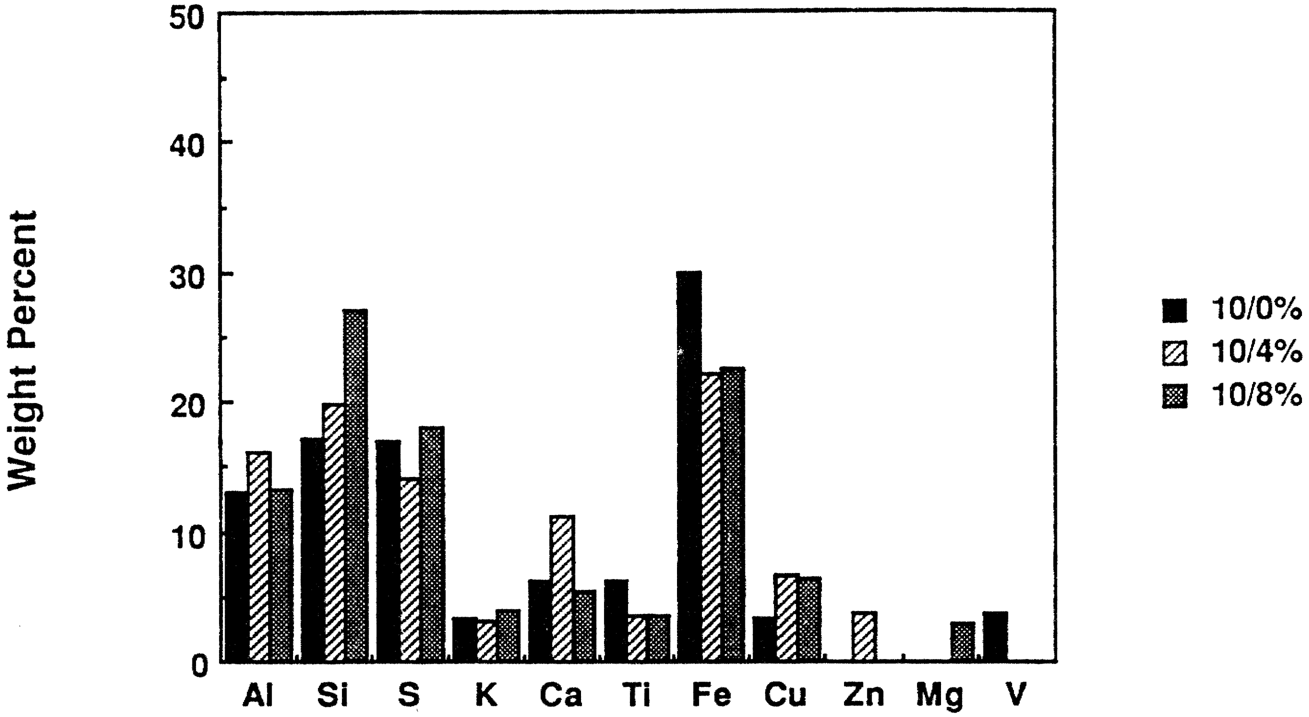


Figure 30. Size 8 - SEM Analysis 10%

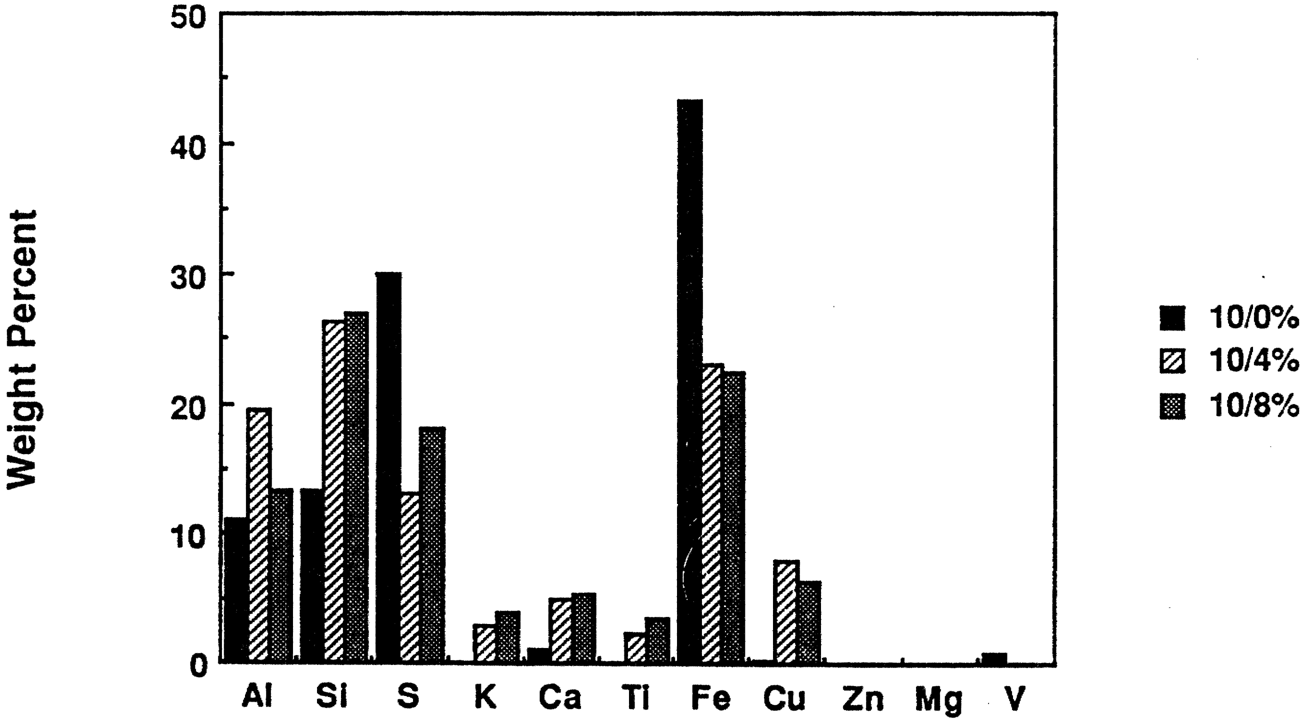


Figure 31. **Size 1 - SEM Analysis 20%**

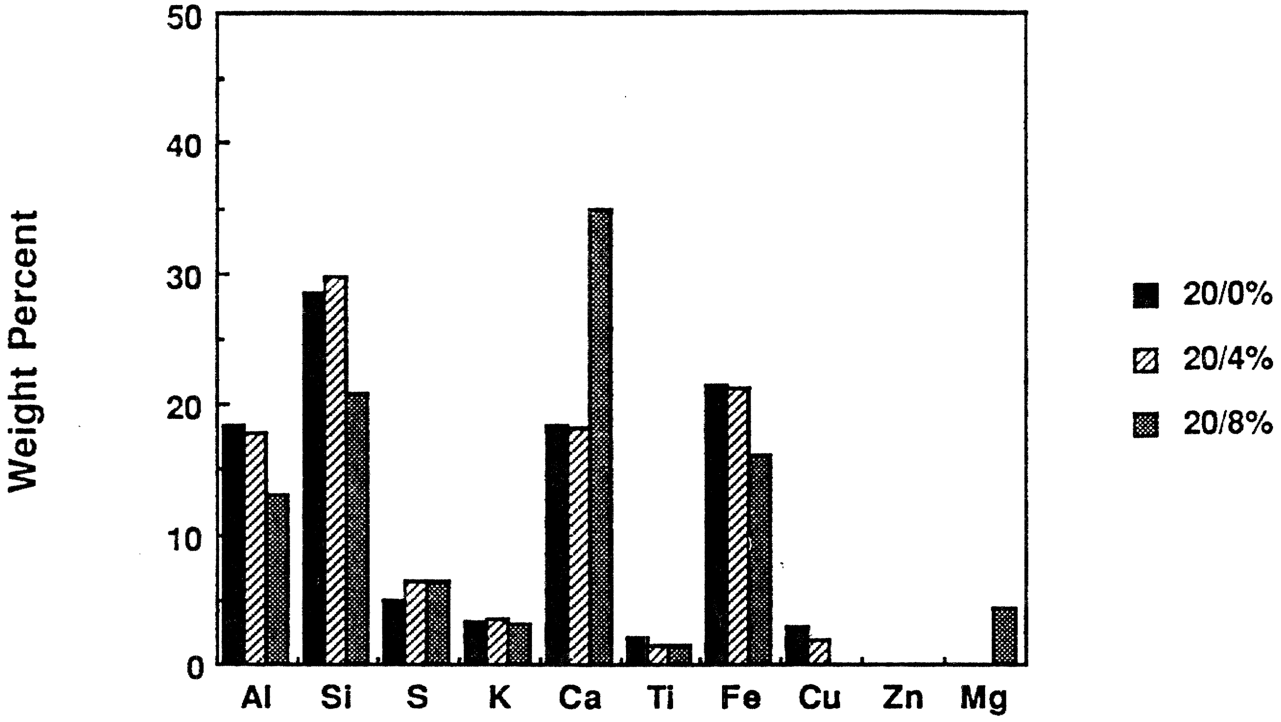


Figure 32. **Size 2 - SEM Analysis 20%**

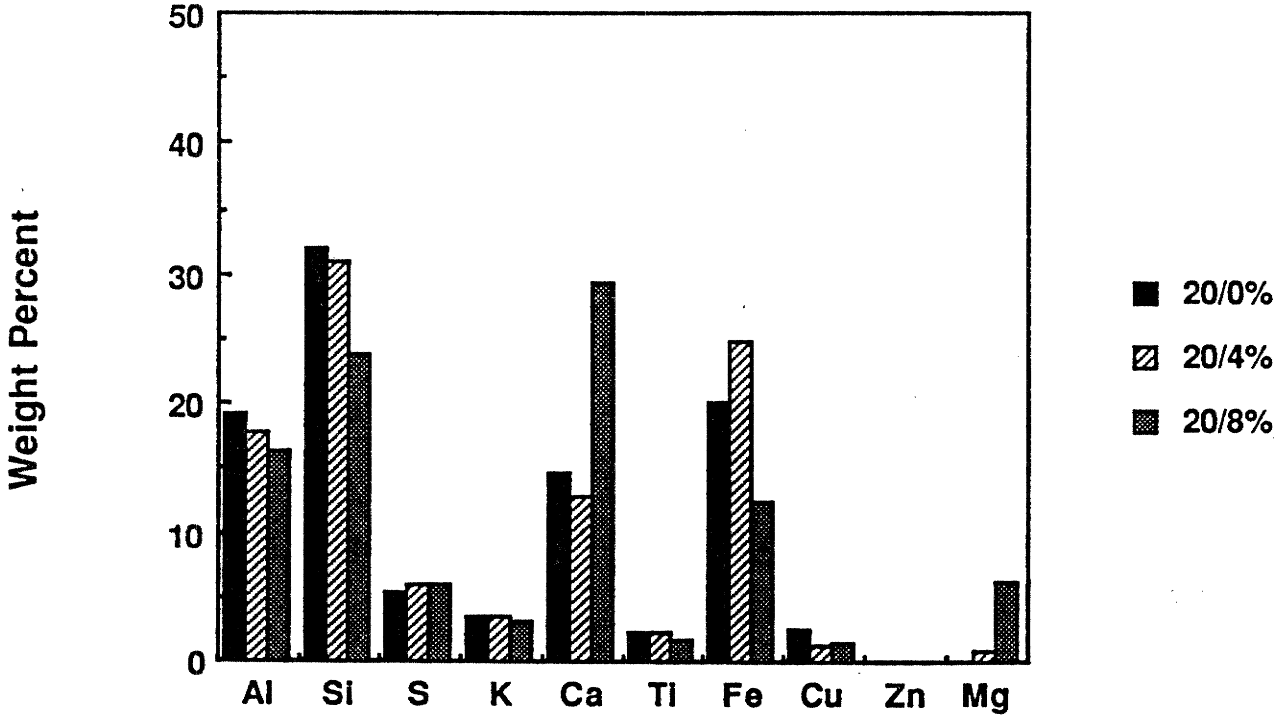


Figure 33. Size 3 - SEM Analysis 20%

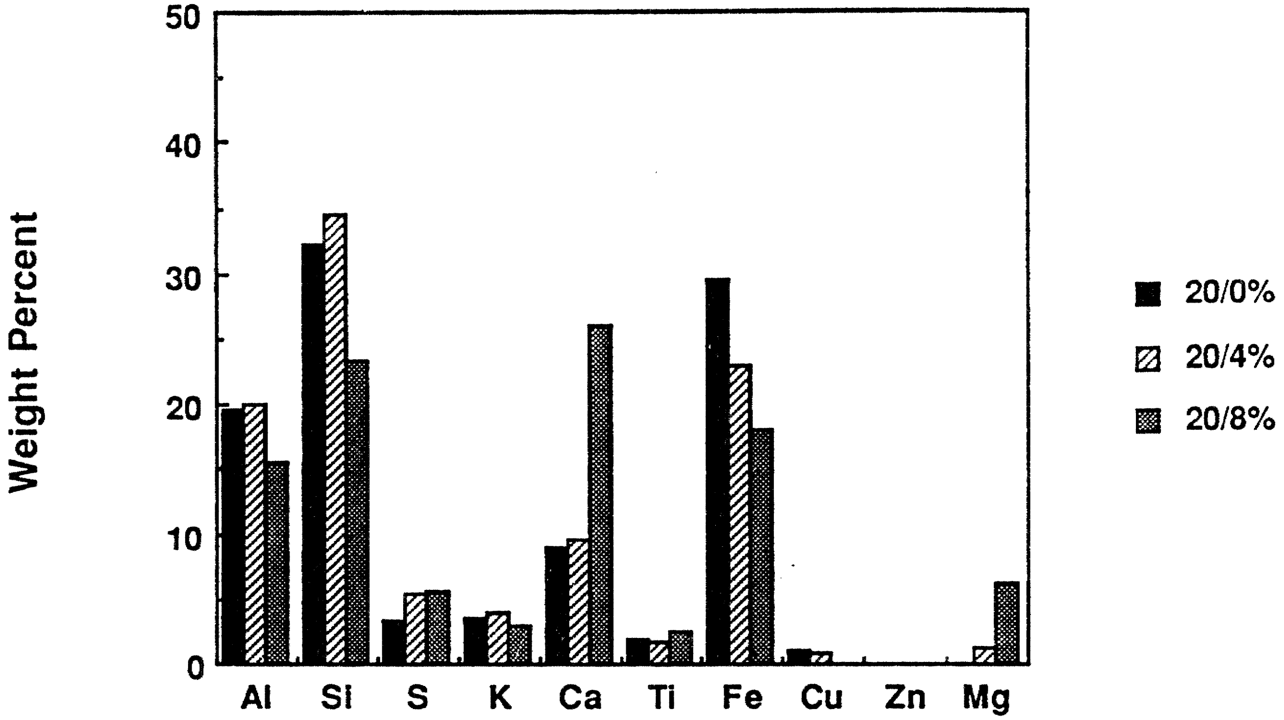
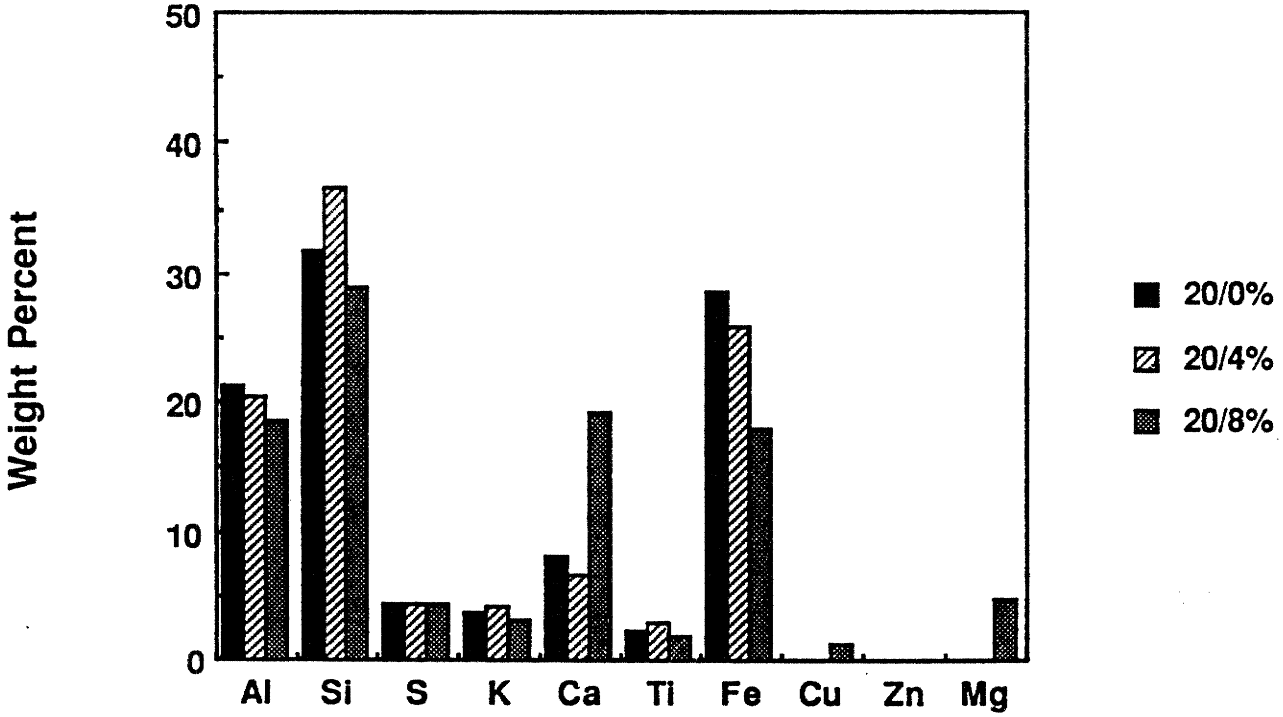


Figure 34 Size 4 - SEM Analysis 20%



Fgure 35 · Size 5 - SEM Analysis 20%

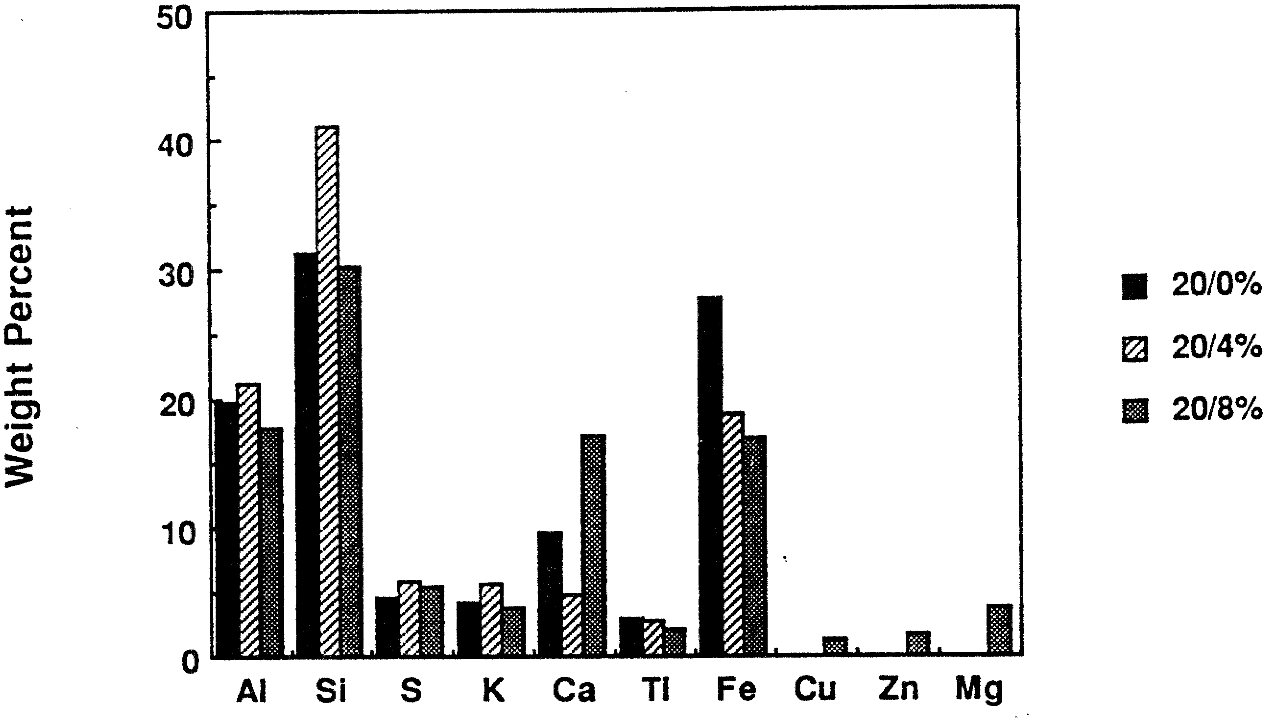


Figure 36. Size 6 - SEM Analysis 20%

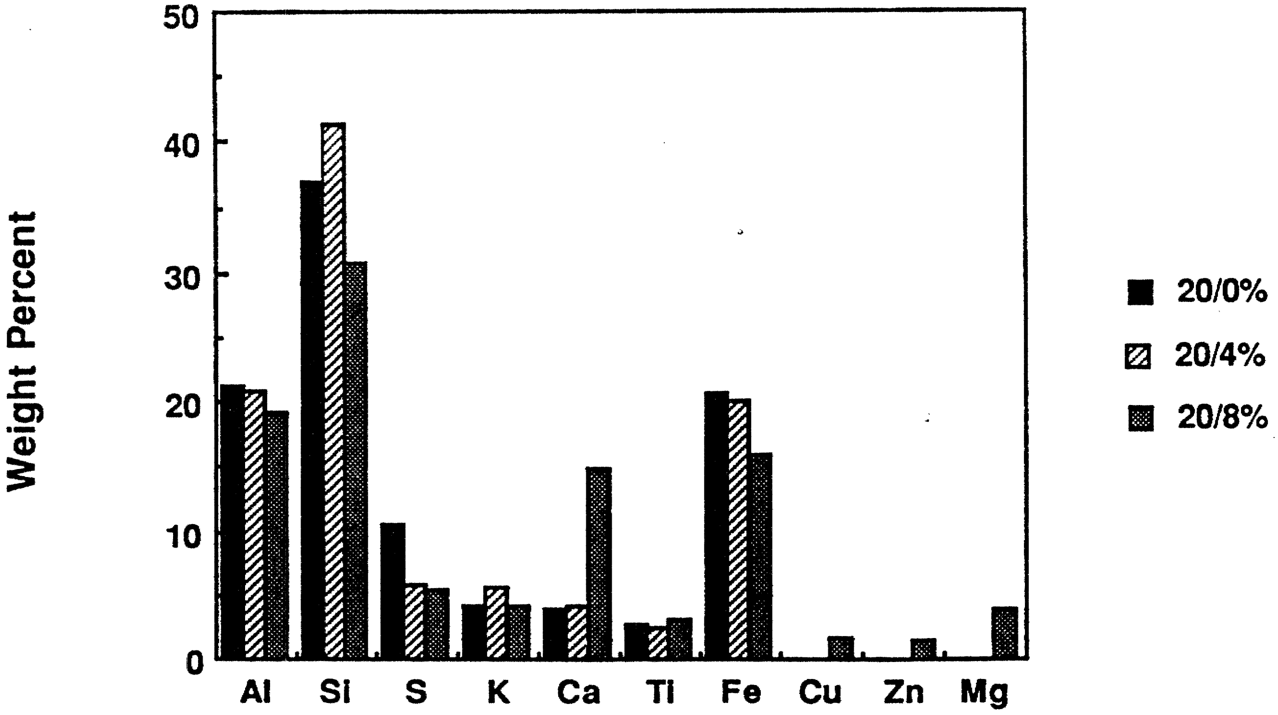


Figure 37. **Size 7 - SEM Analysis 20%**

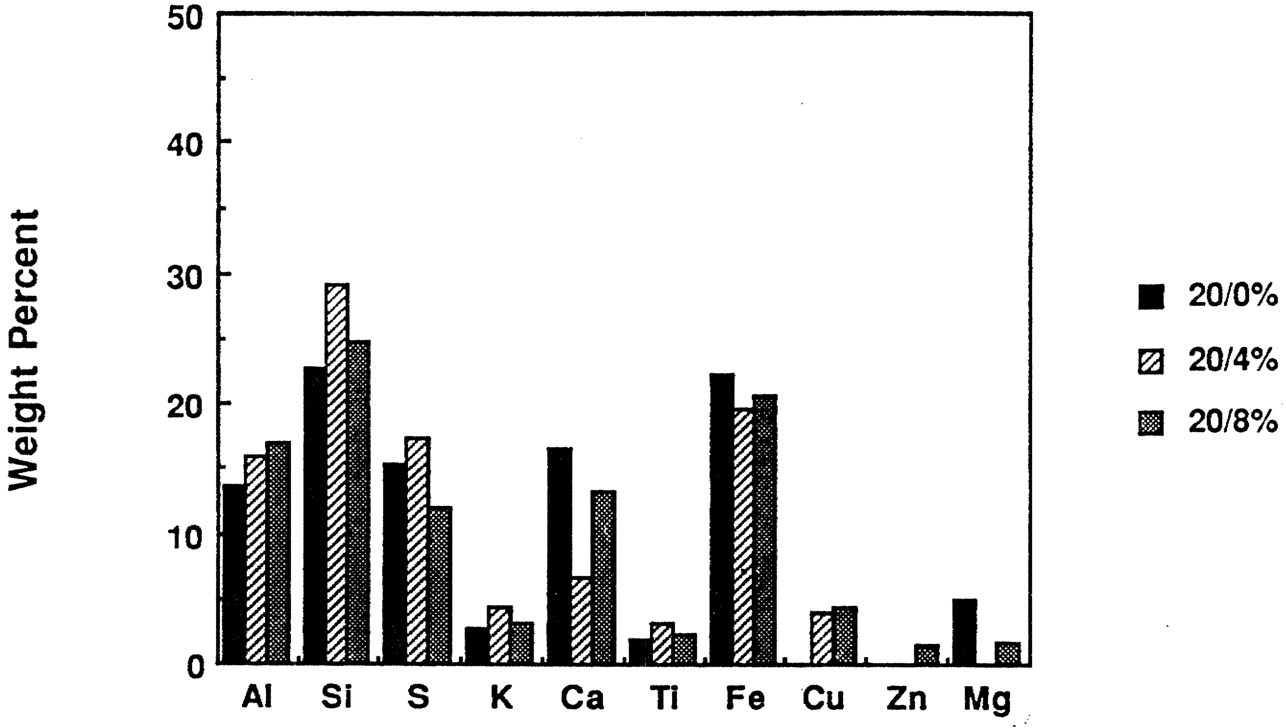


Figure 38. **Size 8 - SEM Analysis 20%**

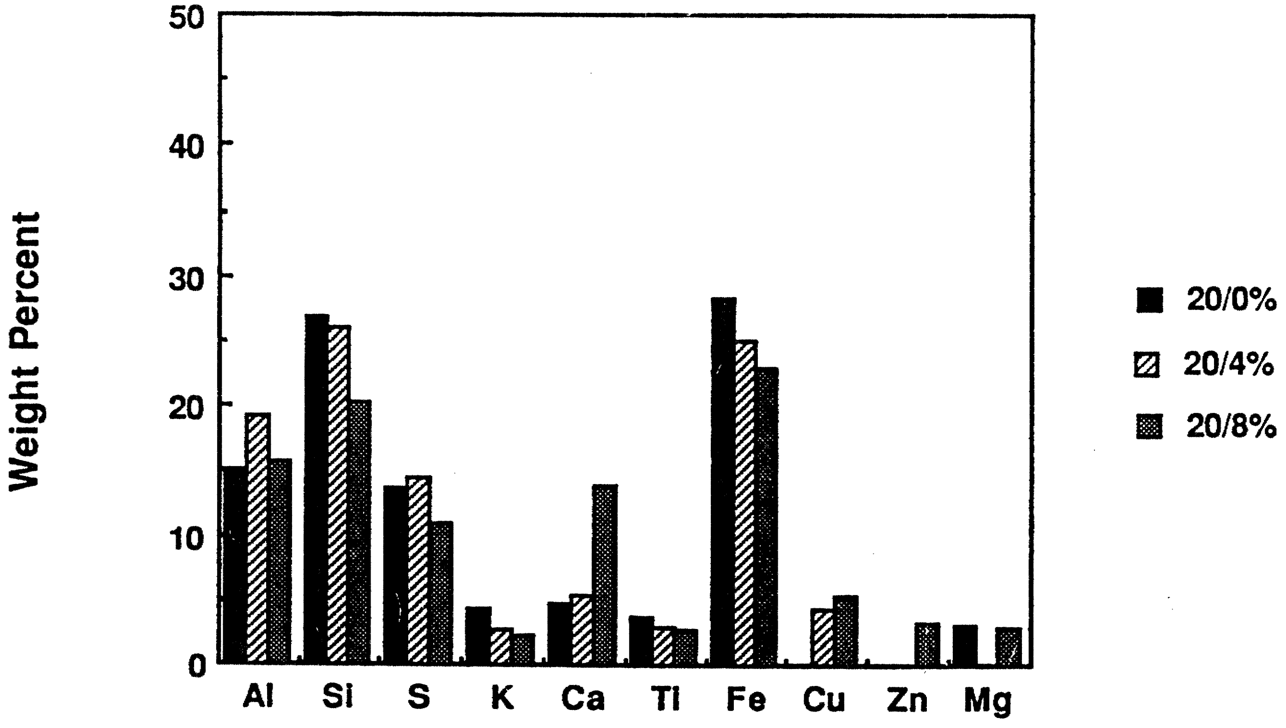


Figure 39. **Size 1 - SEM Analysis 30%**

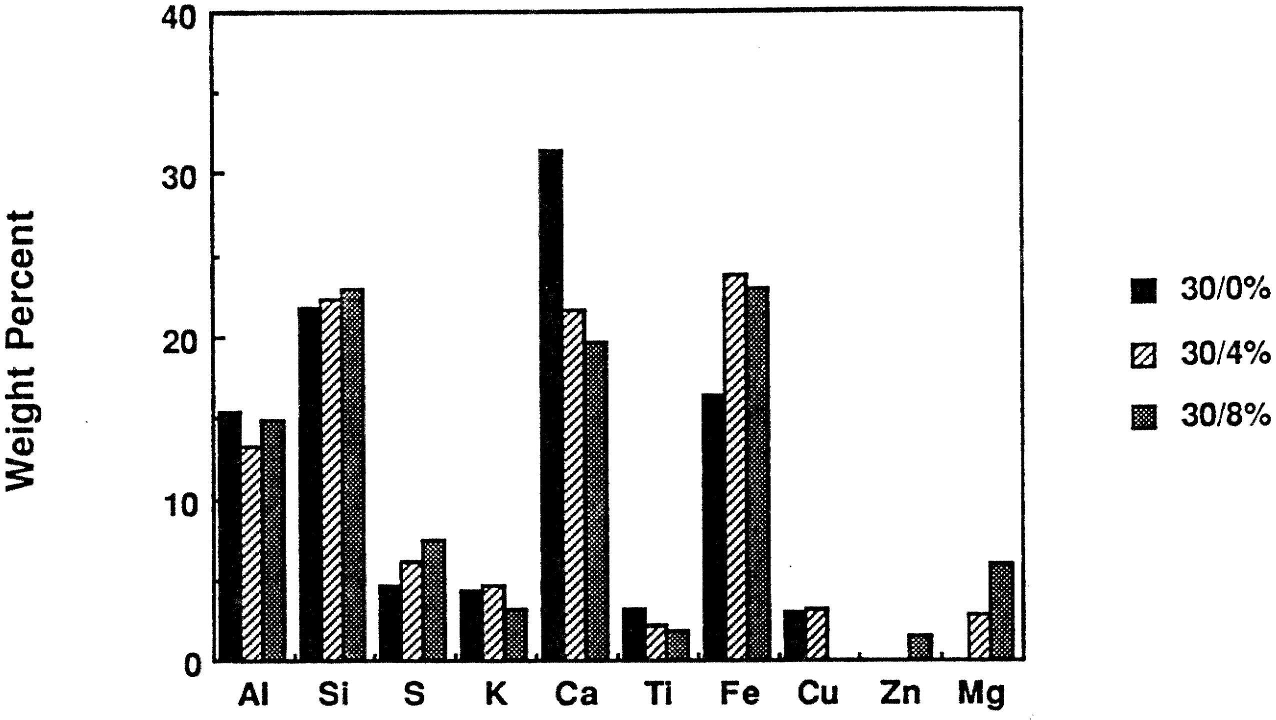
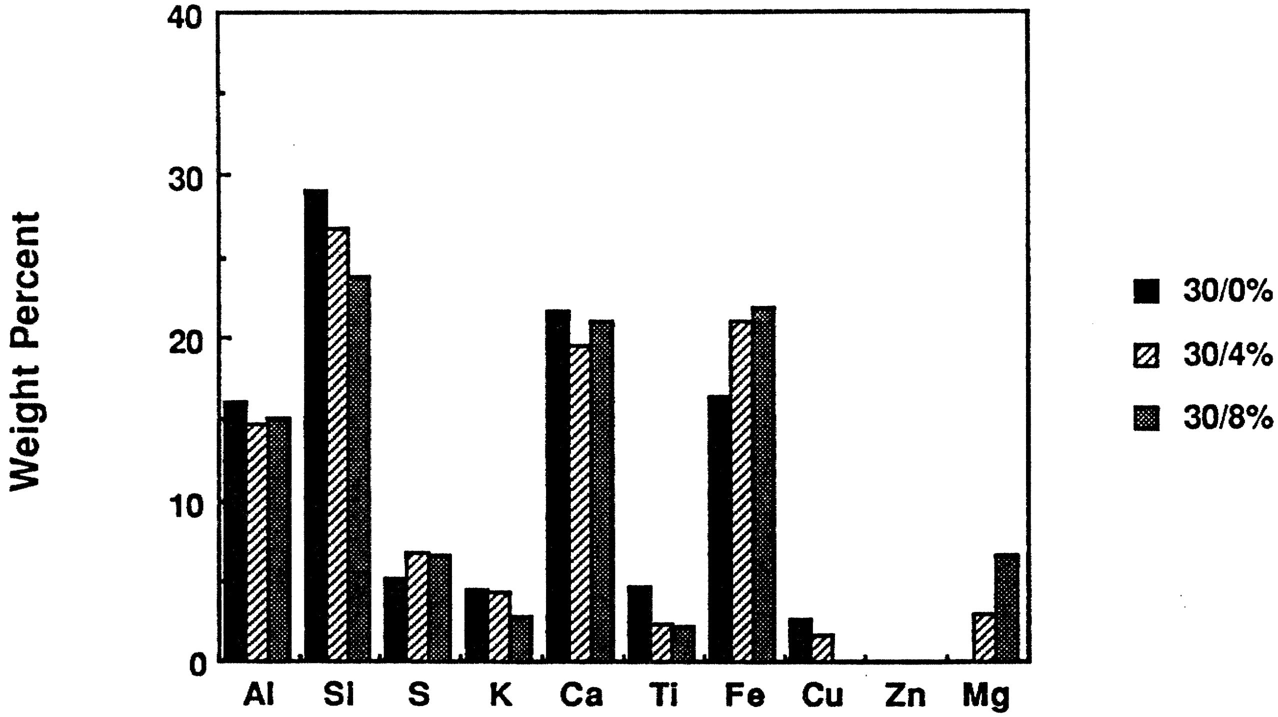


Figure 40. **Size 2 - SEM Analysis 30%**



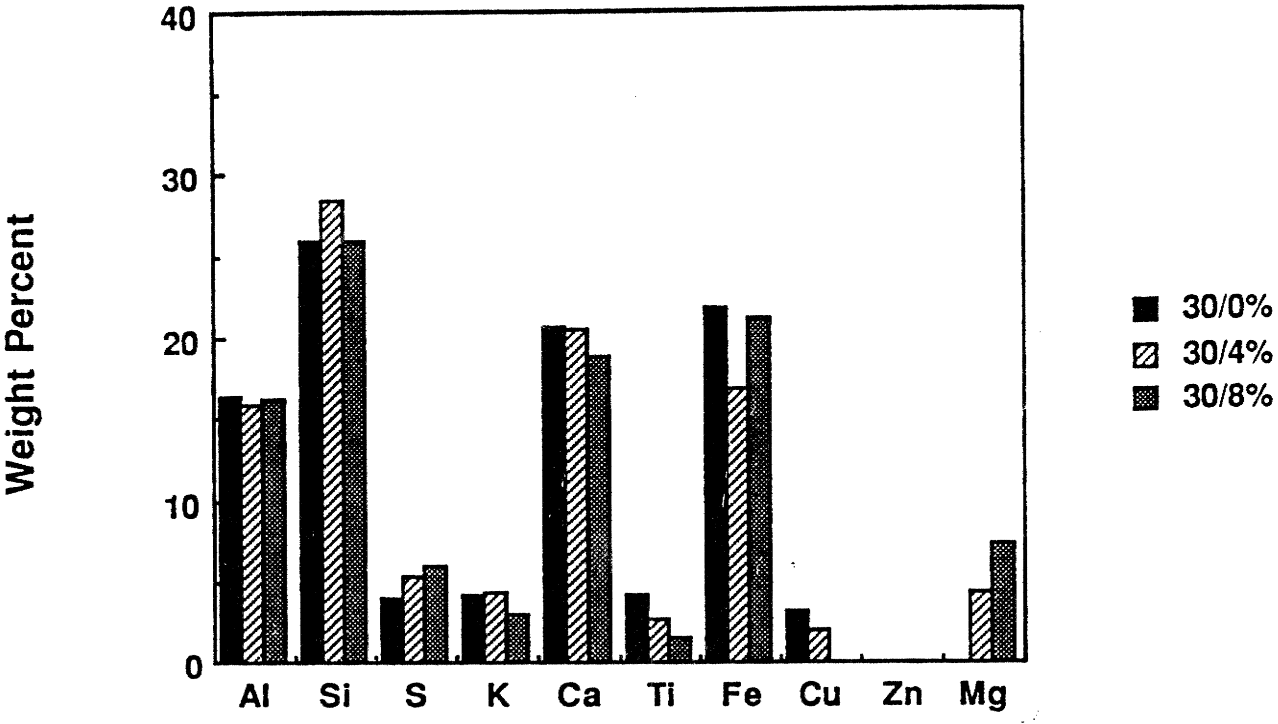


Figure 41. Size 3 - SEM Analysis 30%

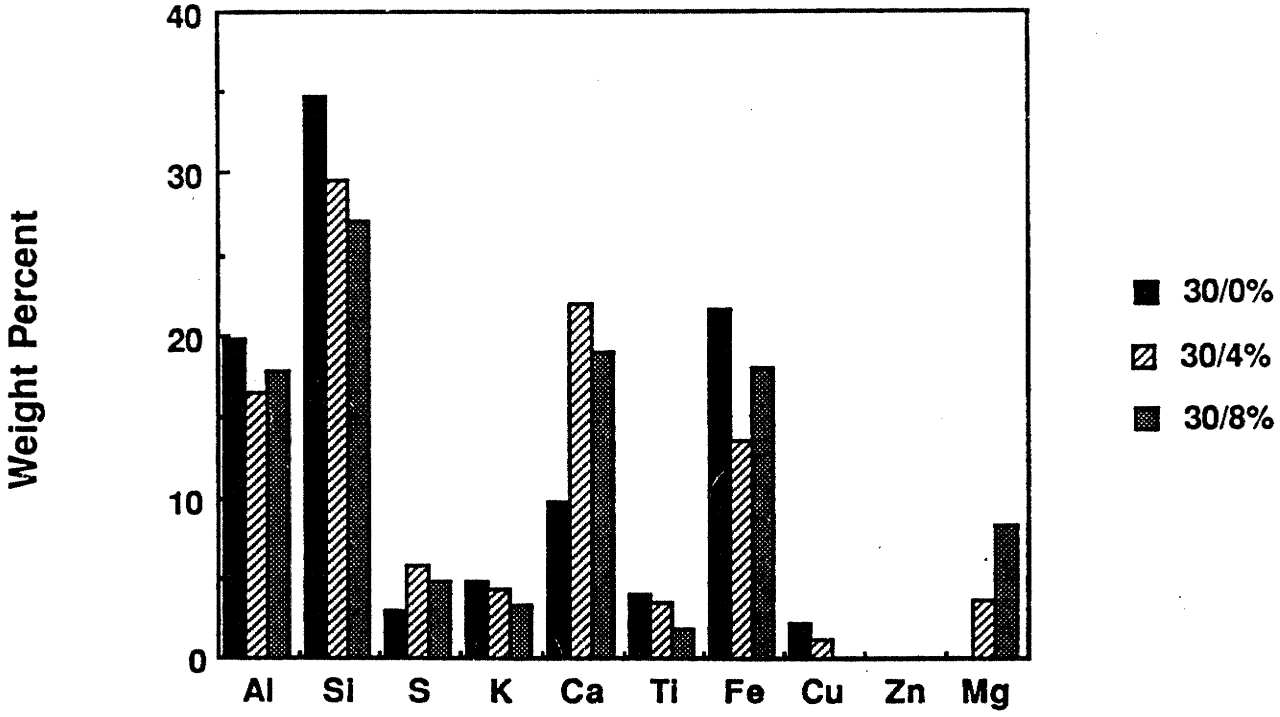


Figure 42. Size 4 - SEM Analysis 30%

Figure 43. **Size 5 - SEM Analysis 30%**

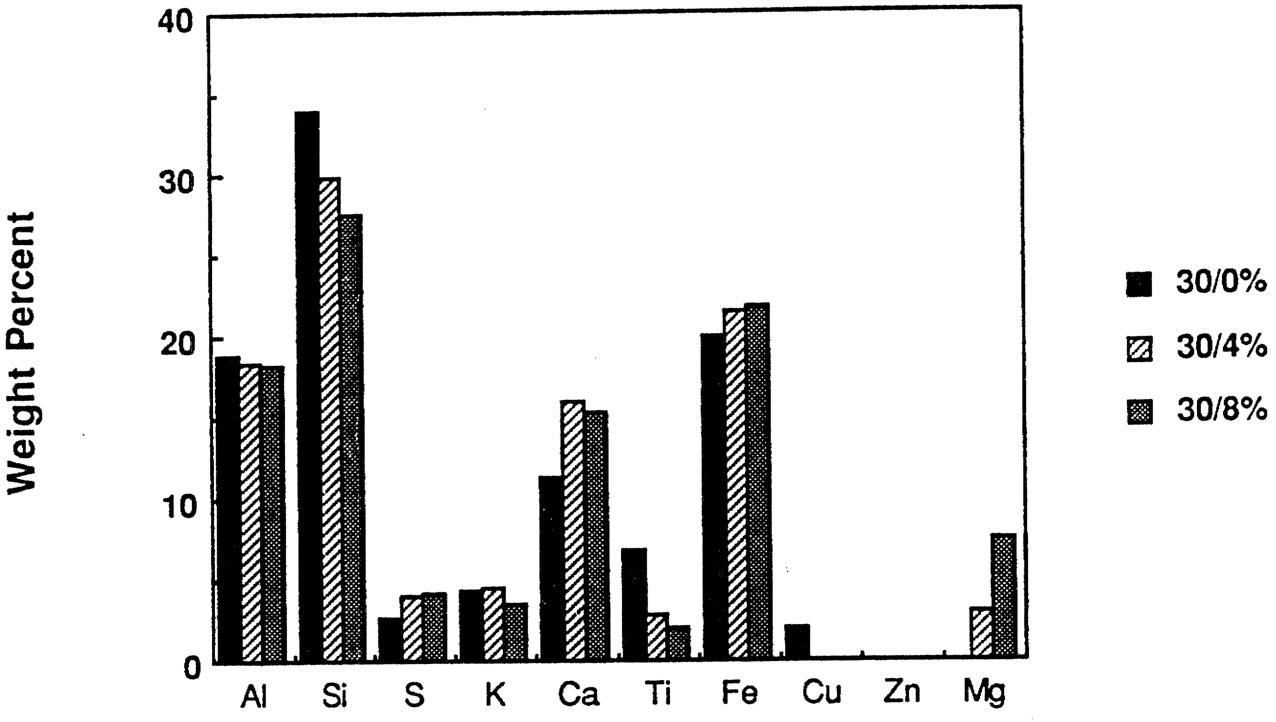


Figure 44. **Size 6 - SEM Analysis 30%**

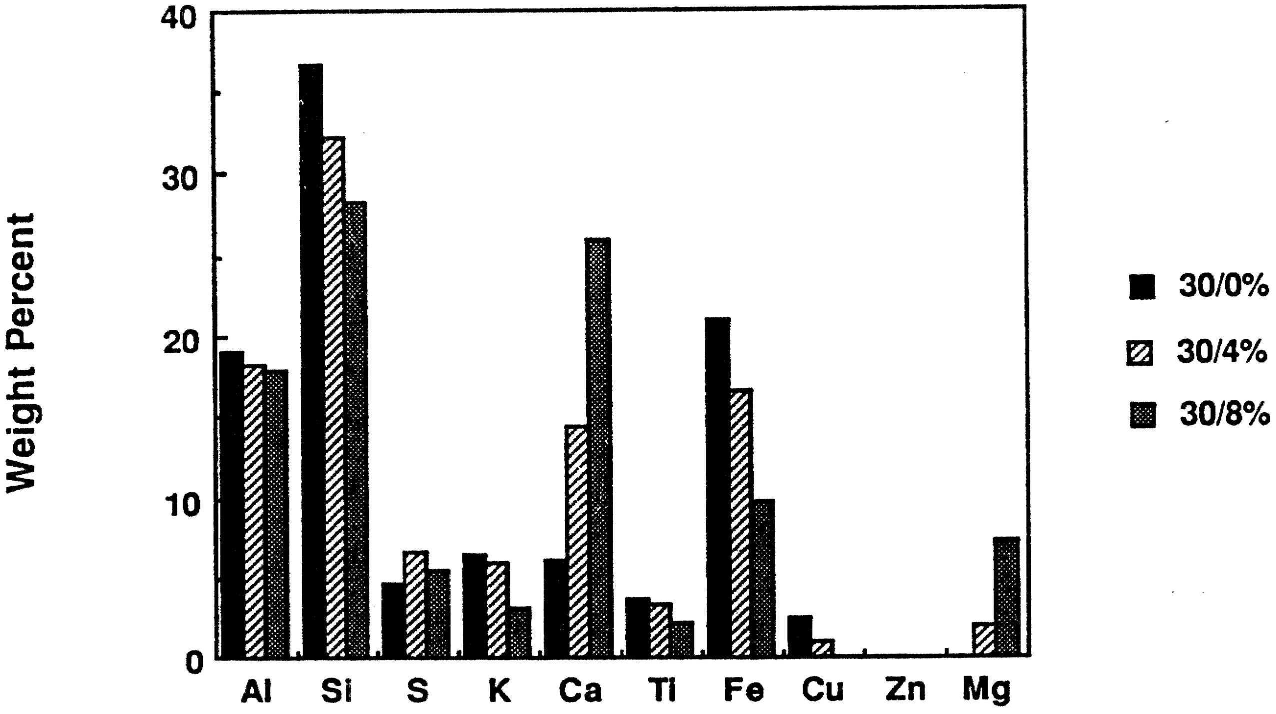


Figure 45. **Size 7 - SEM Analysis 30%**

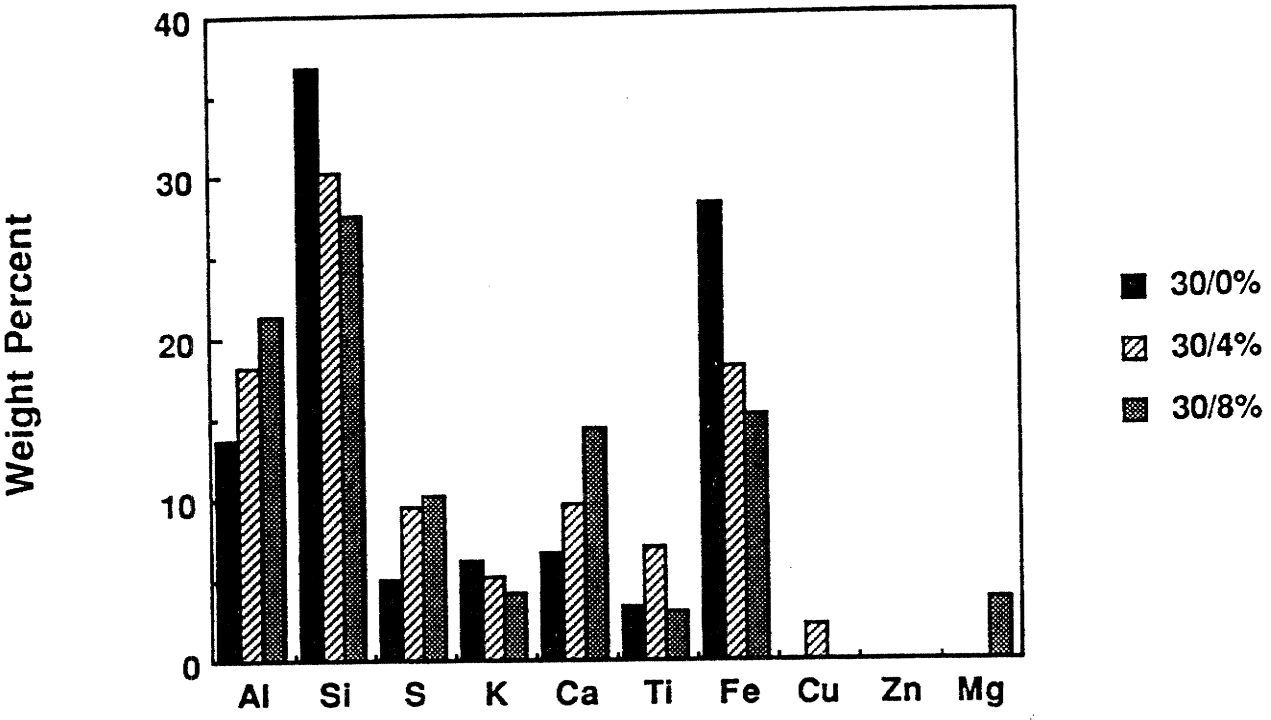


Figure 46. **Size 8 - SEM Analysis 30%**

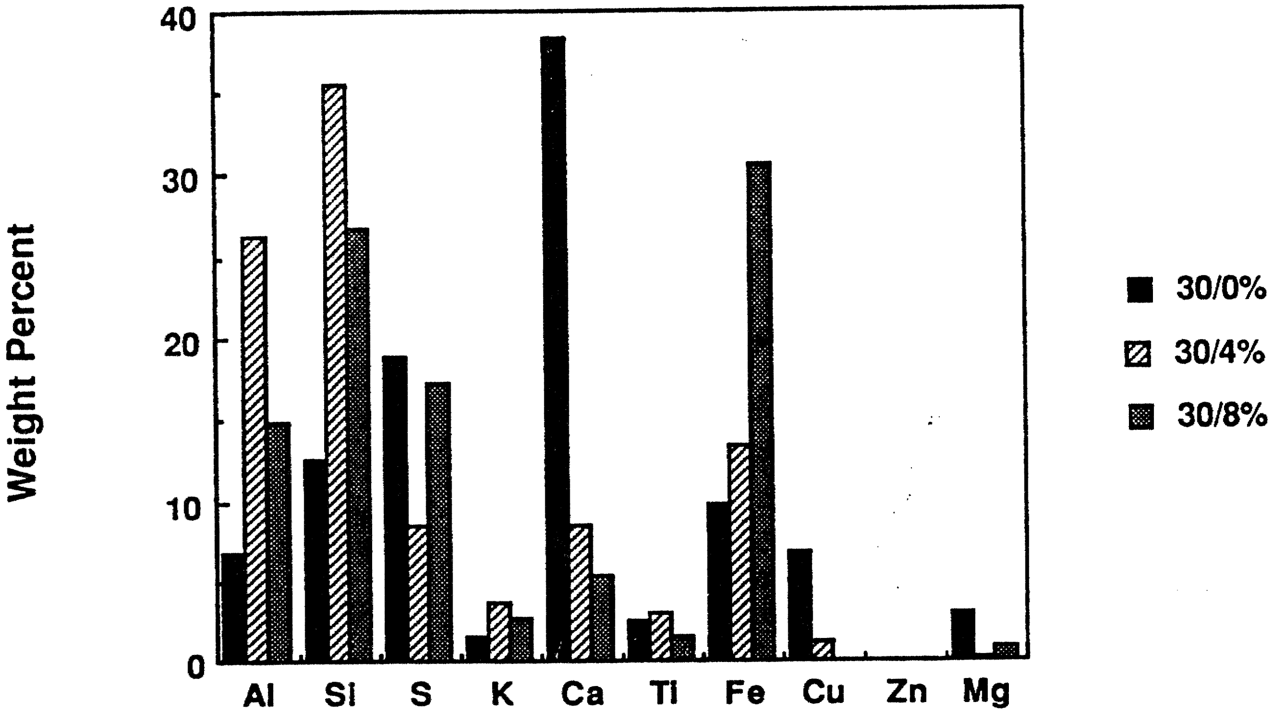


Figure 47. Size 1 - SEM Analysis 50%

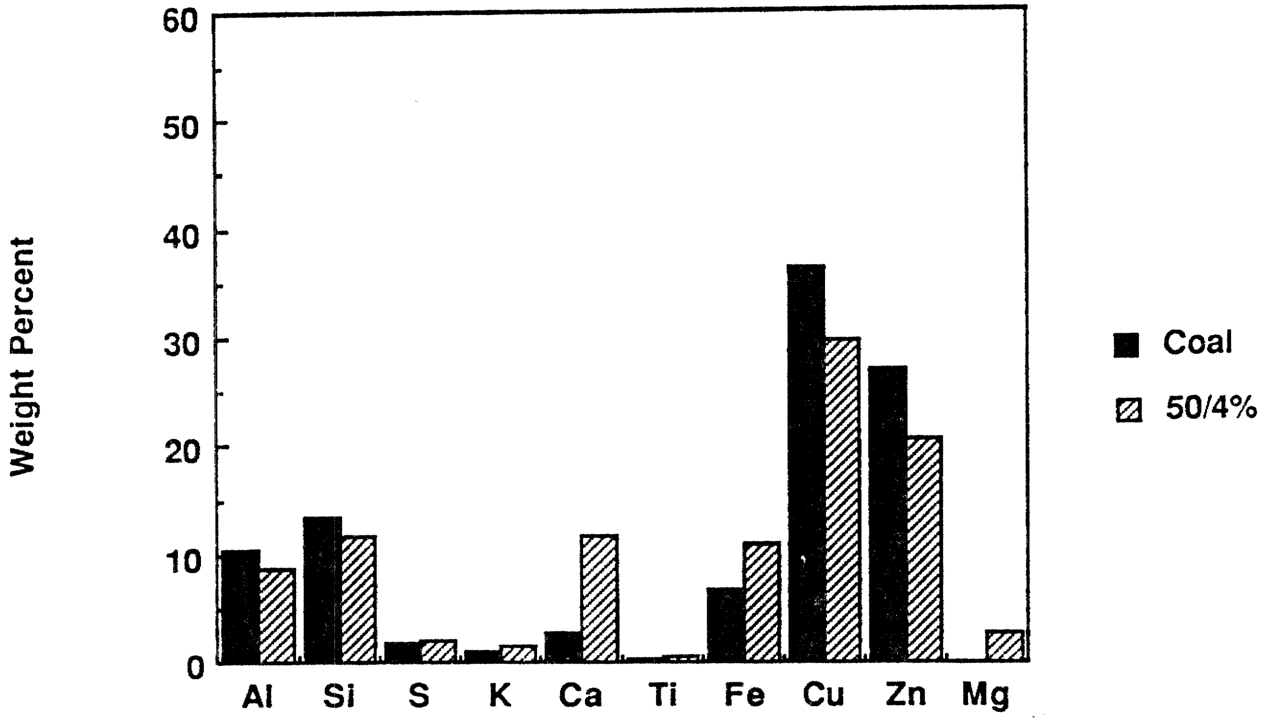


Figure 48. Size 2 - SEM Analysis 50%

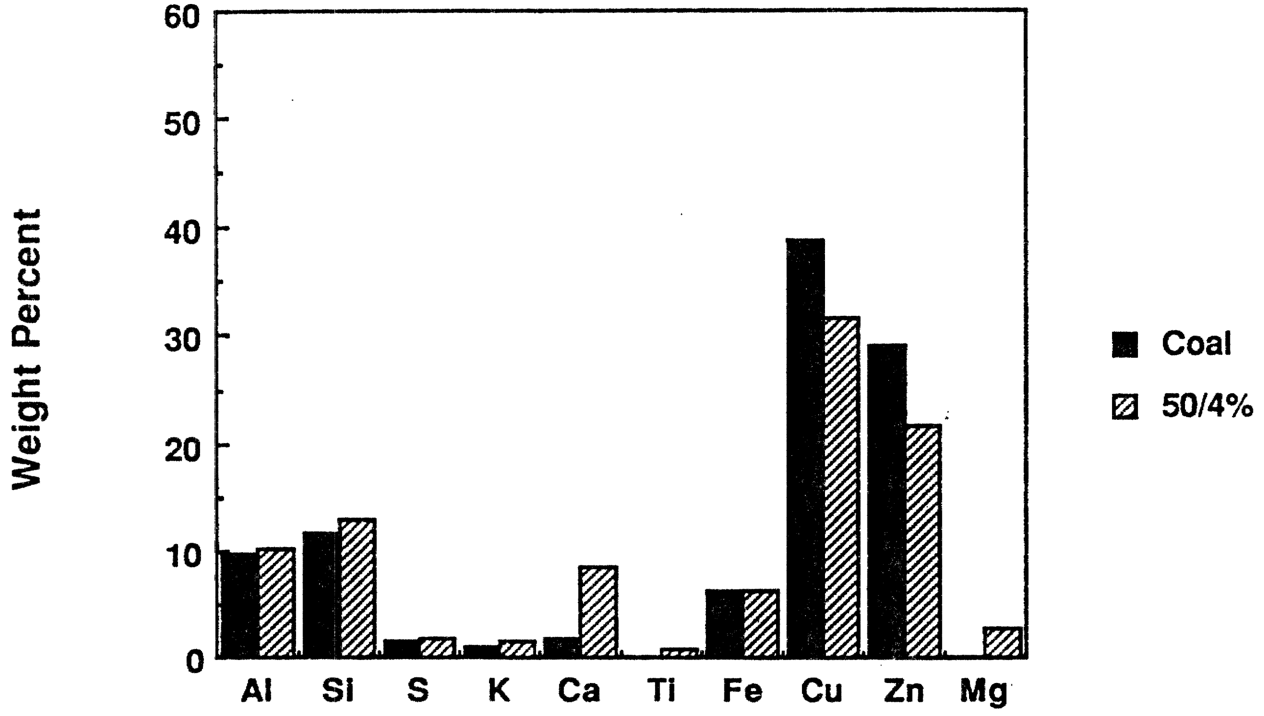


Figure 49. Size 3 - SEM Analysis 50%

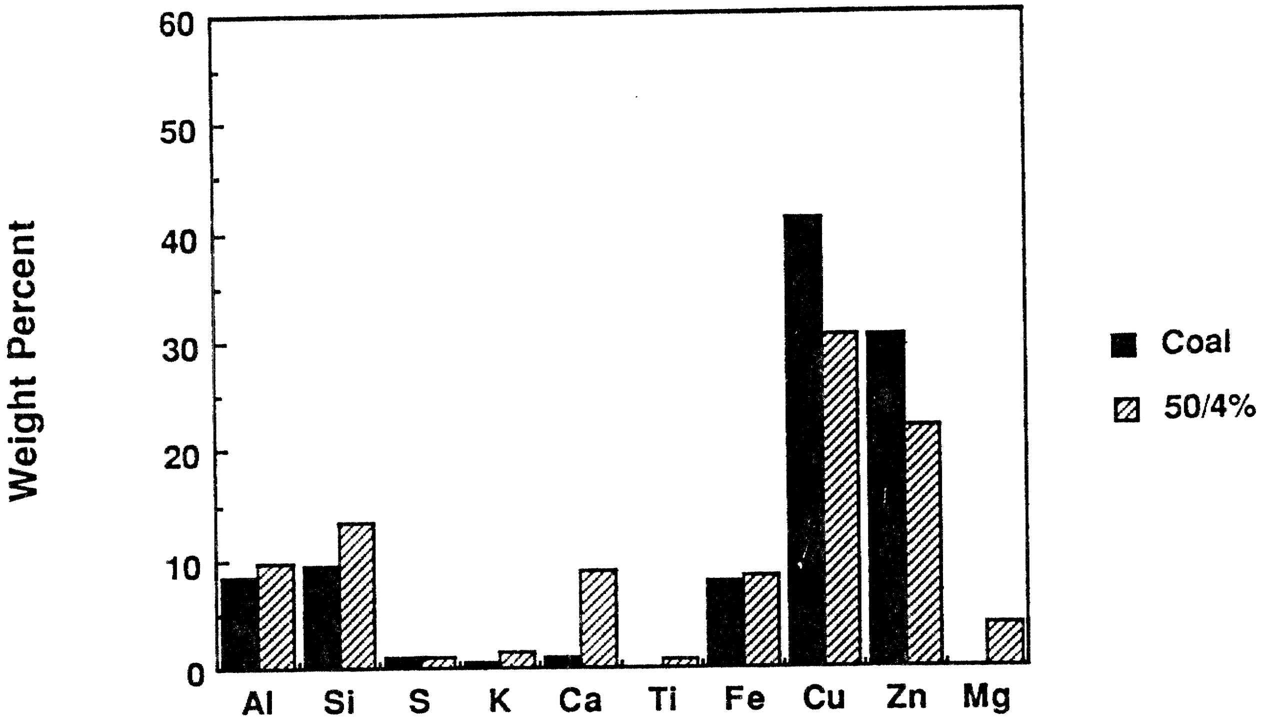


Figure 50. Size 4 - SEM Analysis 50%

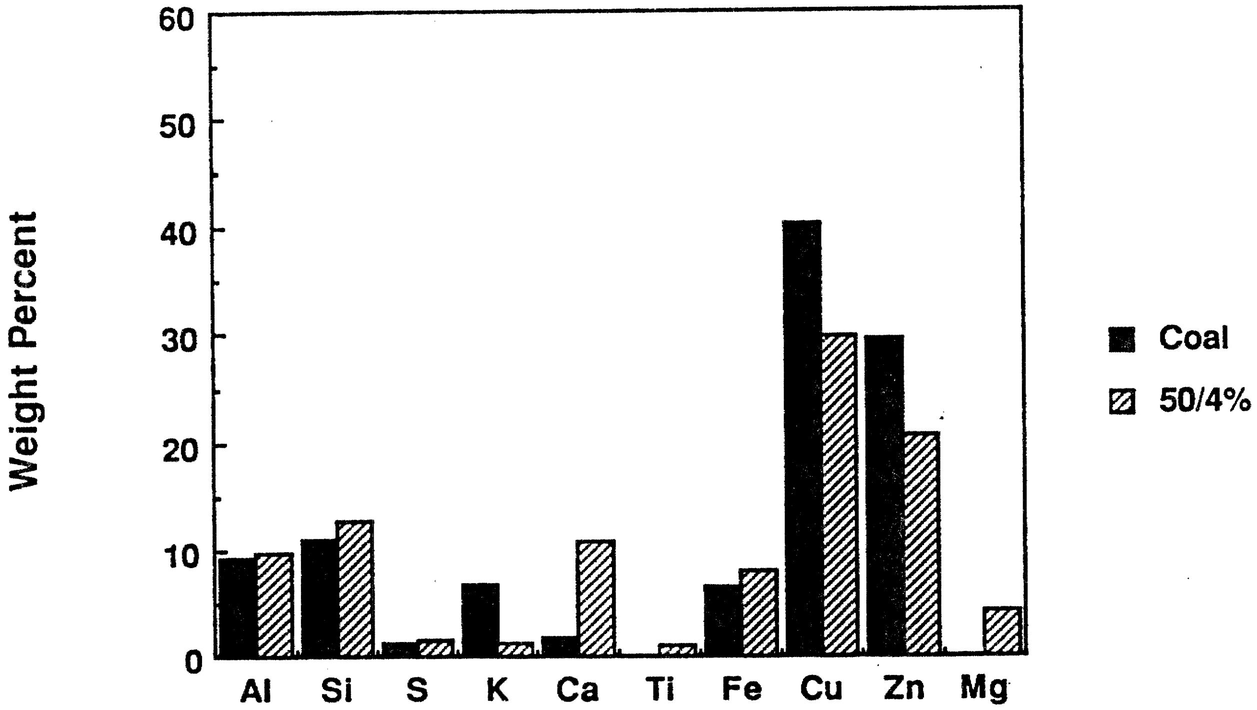


Figure 51.**Size 5 - SEM Analysis 50%**

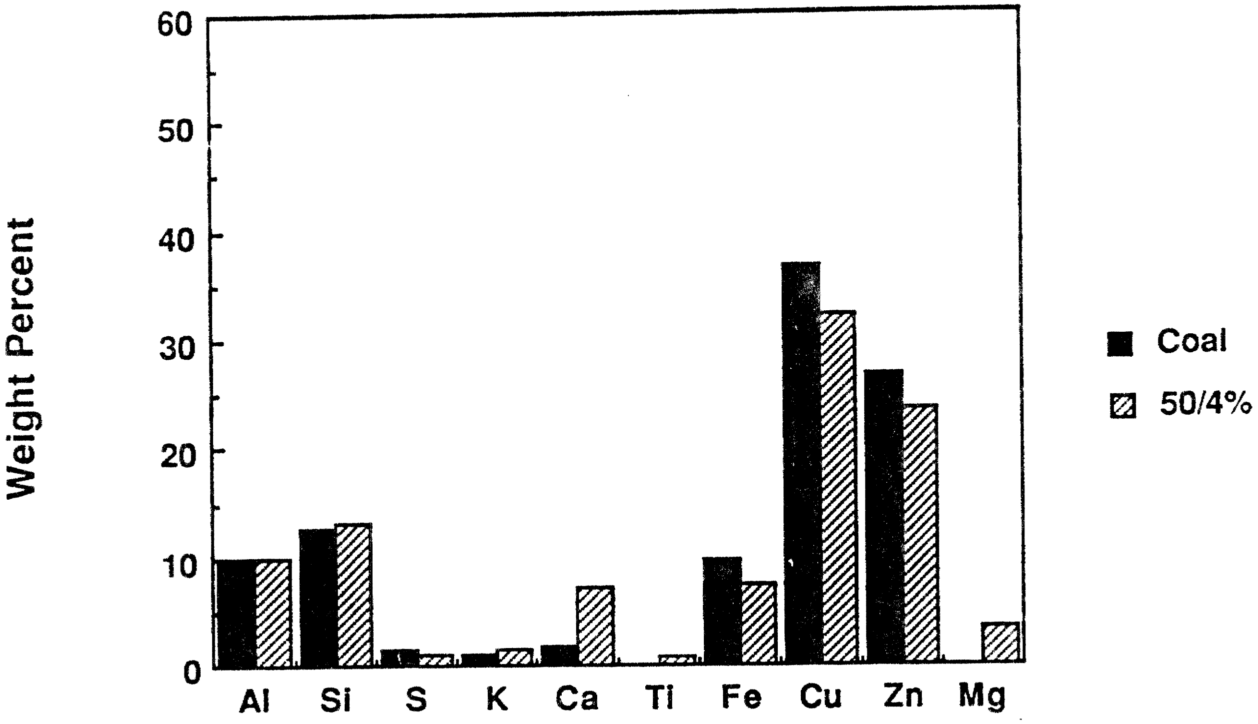


Figure 52.**Size 6 - SEM Analysis 50%**

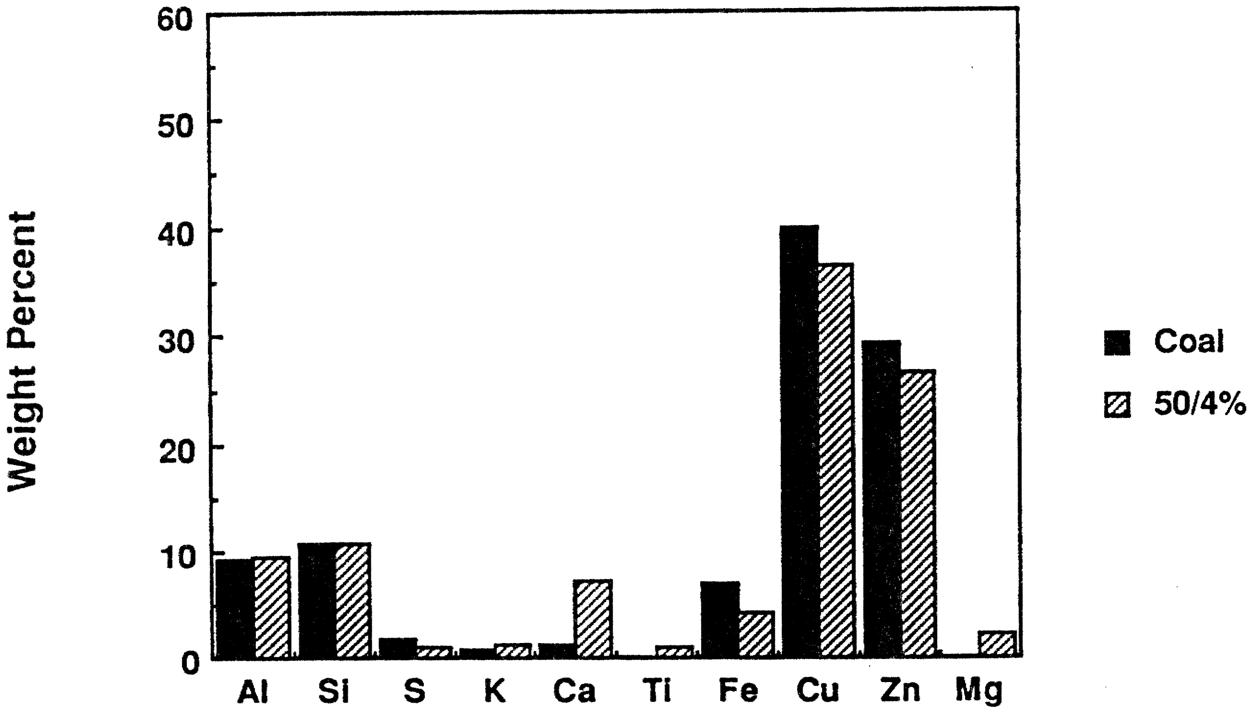


Figure 53. Size 7 - SEM Analysis 50%

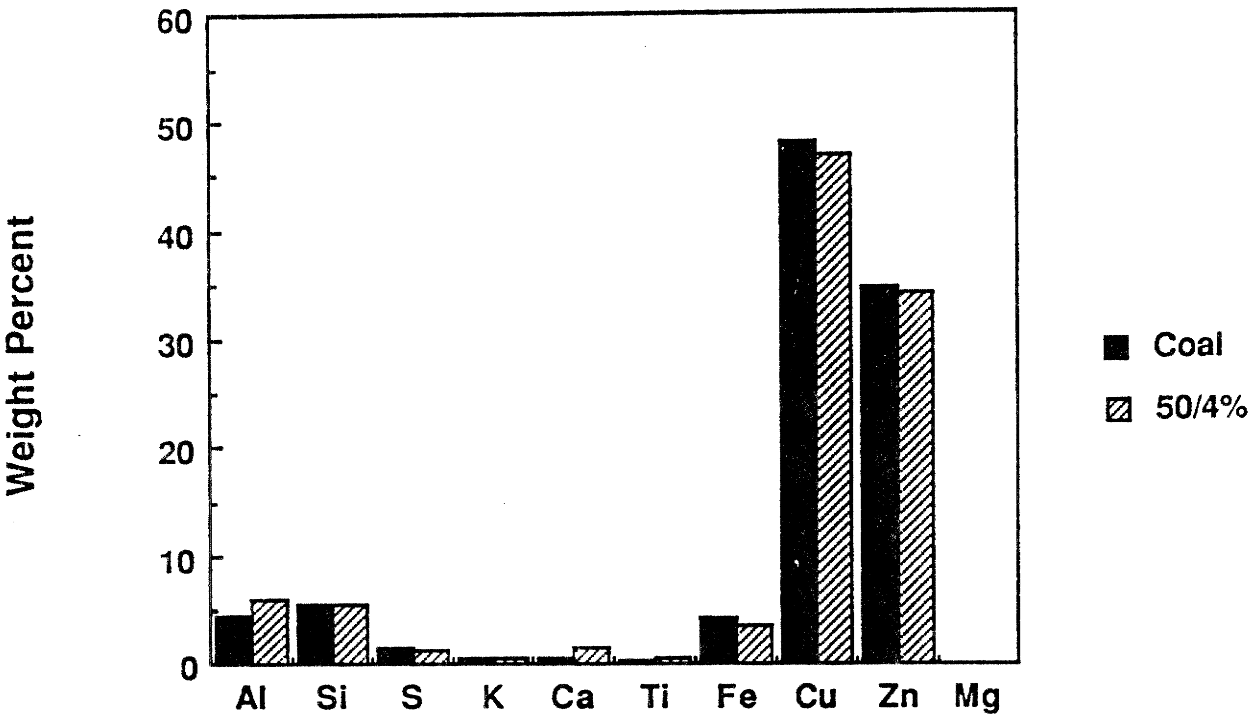
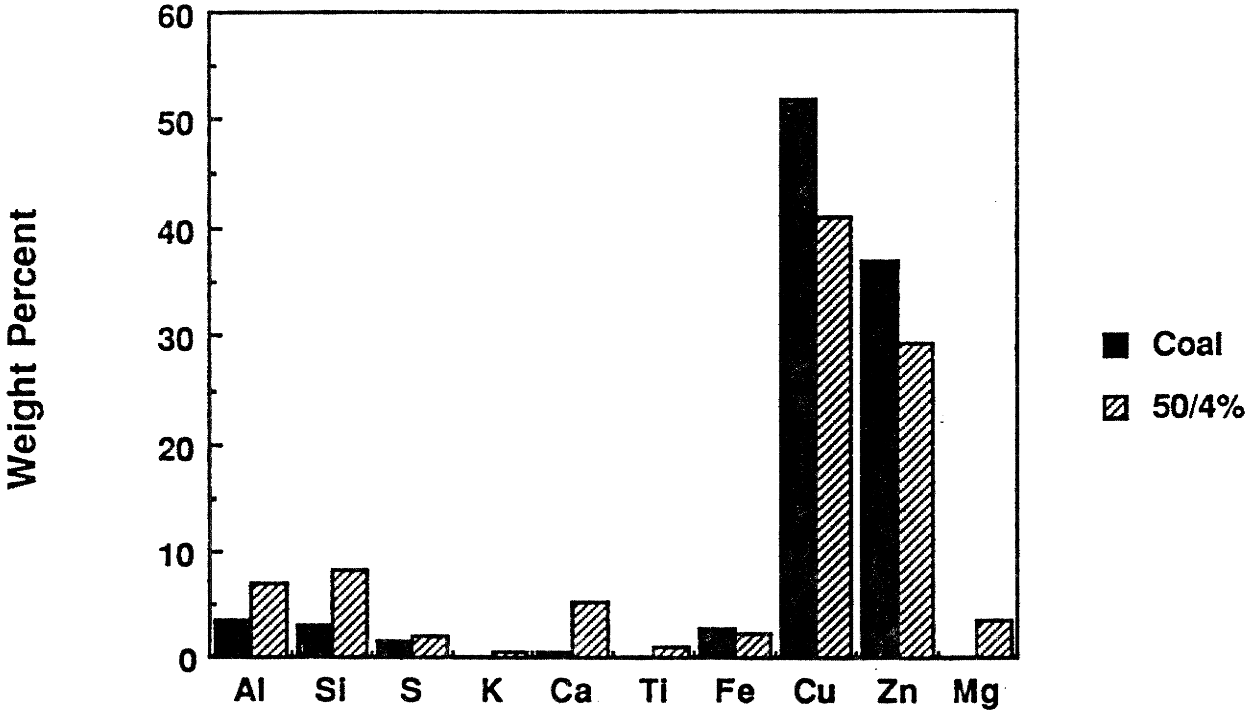


Figure 54. Size 8 - SEM Analysis 50%



elements Ca, Cu, and Mg weight percent increased with an increase in binder level.

- In any bdRDF Btu percentage (10, 20, 30, 50%) graph, the elements Ca, Si, and Al weight percent decreased with an increase in particle size, the elements Fe, and K weight percent were not changed with an increase in particle size increase, the elements S, Ti, and Cu weight percent were increased with an increase in the particle size, and the elements Zn, Mg, and V weight percent were very low. Because of the extremely low weight percent of Zn, Mg, and V, and the detection limits of the SEM/EDX, it was hard to predict if they were increased or decreased with the binder content or particle size.
- In general one can say that the trace toxic metals weight percent in economizer fly ash decreased with the increase in lime binder percentage, and the majority decreased with the increase in bdRDF Btu content percent.

PART II

FLY ASH ANALYSIS BY ICP-AES

EQUIPMENT

Parr Bombs:

Parr Teflon acid bombs were obtained from Parr Instrument Company. The bomb is made of a microwave transparent polymer (Figure 55). A compressible relief disc is built into the closure to release excessive pressure. Over 1500 psi, the relief disc will be compressed to a point where support for the O-ring will be lost, and it will rupture. In most cases all parts of the bomb were reusable except for the O-ring.

Microwave Oven:

A Kenmore commercial microwave oven was used in this work. The oven has a variable timing cycle from 1 second to 100 minutes and a variable heating cycle based on power setting from 10% through 100% full power (700 w).

Inductively Coupled Plasma Atomic Emission Spectrometry ICP-AES:

A Perkin-Elmer ICP-5500 Atomic Emission Spectrometer with a 27.12-MH_z RF generator was used in this analysis. A

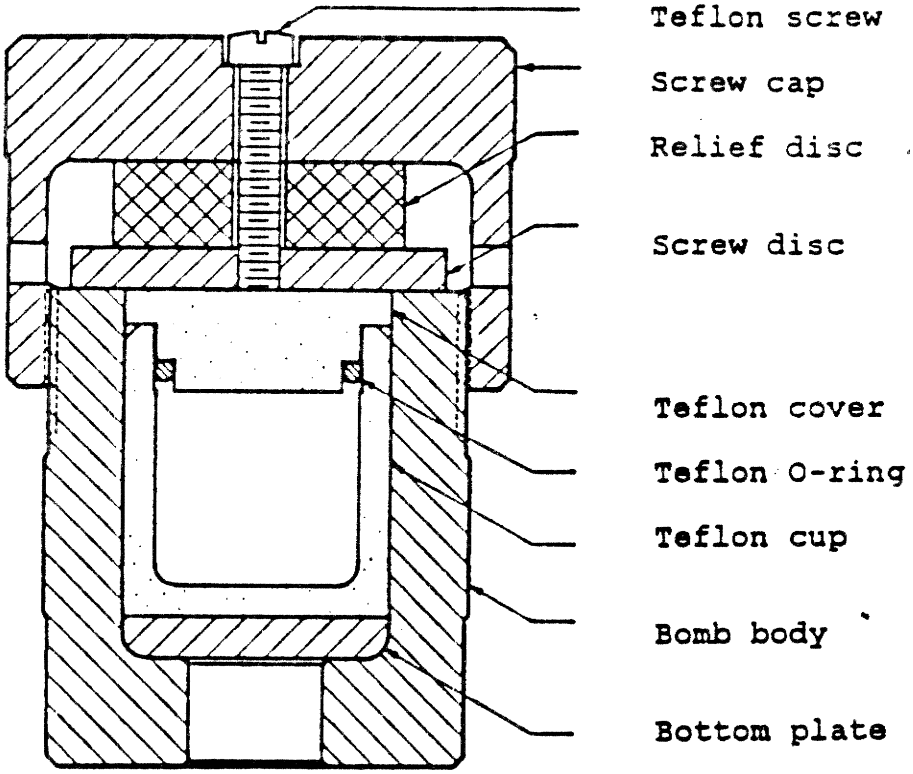


Figure 55 . **Schematic of a Parr bomb**

Perkin-Elmer Model-10 data station was used with a Pr-100 printer.

Sample Analysis

After the samples were returned to the laboratory, they were arranged on the shelves according to the dates and times they were collected. About 10 grams of a homogenous sample was ground to pass through, at least, a 75 mesh sieve. A 400 mg sample was placed in a poly-Teflon container and treated with 1 mL of hydrofluoric acid and 3 mL of aqua regia. The teflon container was then placed in the bomb and the bomb was tightly capped. The bomb was placed in the microwave oven and heated for 4 minutes and left for several hours to cool. After cooling, the teflon container was uncapped and 2 mL of saturated boric acid was added quickly. The container was then recapped, returned to the microwave oven and reheated for 1 more minute, then cooled again.

At this stage some uncombusted carbon remained in the solution. The solution with the residue was then filtered, washed with deionized water and the filtrate was diluted to 50 mL in a polyethylene volumetric flask. The microwave heating procedure has been used to determine minor and major constituents in the past (21-23).

The solution was finally analyzed by ICP-AES using a blank and a standard solution containing the same amounts of acids. Standards with varied concentrations of As, Hg, Pb, Sb, Se, Tl, Ba, Be, Cd, Cr, Cu, Ni, V, and Zn were used for the analysis.

Results and Discussion

The results are summarized in Table XXXVII. Fourteen elements were investigated: As, Cd, Hg, Pb, Sb, Se, Te, Ba, Be, Cr, Cu, Ni, V, and Zn. The metals As, Cd, Hg, Pb, Sb, Se and Tl are not included in the table because their concentrations were too low to be detected by ICP. Table XXXVIII shows the ICP detection limits of all elements studied.

Effect of bdRDF content on trace metals:

Processing of MSW to RDF removes much of the unwanted trace metals. The metal content of coal/bdRDF blend ash is expected to be affected by the different Btu percentages of bdRDF.

Elements such as Cd, Cr, Cu, Hg, Pb and Zn are known to be enriched in RDF related to coal. The first set of graphs 56-62 shows the percent bdRDF versus concentration (ug/g)

Table XXXVII : Summary of Toxic Metals Concentration in Economizer Fly Ash (ug/g).*

Run#	Ba	Be	Cr	Cu	Ni	V	Zn	Btu%dRDF	Binder%
1.	158.2	25.3	105.2	152.7	130.0	223.4	324.8	0	-
2.	240.1	27.7	111.3	199.5	135.3	234.1	338.5	10	0
3.	202.2	19.6	100.3	151.8	122.2	177.9	293.7	10	4
4.	144.4	14.7	94.9	143.7	100.8	160.7	390.8	10	8
5.	227.7	20.2	143.8	243.4	137.4	231.0	404.6	20	0
7.	155.7	11.3	108.3	208.5	149.0	187.1	478.2	20	4
8.	182.8	13.3	127.6	243.6	121.3	193.4	466.7	20	8
9.	160.1	11.4	114.4	360.6	92.7	181.3	443.6	30	0
10.	158.3	10.5	115.9	207.9	75.6	149.6	455.9	30	4
6.	190.2	10.5	112.2	227.6	130.5	161.3	470.8	30	8
11.	228.5	14.9	126.1	353.5	97.7	179.8	372.1	50	4
12.	177.4	16.6	93.5	217.1	97.8	171.6	240.3	0	-

* Average of Three Replicates.

Table XXXVIII: Detection Limits of ICP (ug/g) of Fly Ash.

As (ug/g)	62.50
Ba	12.50
Be	0.63
Cd	6.25
Cr	6.25
Cu	6.25
Hg	125.00
Ni	12.50
Pb	125.00
Sb	125.00
Se	62.50
Tl	125.00
Zn	6.25

for each element alone at a constant level, percent, of the binder. The top graphs shows 0, 10, 20, 30 percent bdRDF versus element concentration at 0 percent binder. The middle graphs shows the 10, 20, 30, 50 percent bdRDF versus element concentration at 4 percent binder. The bottom graph shows 10, 20, and 30 percent bdRDF versus element concentrations at 8 percent binder. The graphs shows how the elements increase or decrease in concentration with an increase in bdRDF.

The results summarized in table XXXVII and shown in graphs 56-62, suggest the following:

.The elements Be, Ba, Zn, V, Ni, Cu, and Cr were detected but the rest of the fourteen elements were not detected because they were below the detection limits (Table XXXVIII).

.The most prominent increase in concentration resulting from cofiring coal/bdRDF mixtures were Cu and Zn.

.The element Cr was increased slightly in economizer fly ash. This increase is due to this element being more enriched in RDF ash than in coal ash.

.The elements Be, Ba, Ni and V decreased in concentration with the increase in bdRDF percentage. Generally those concentrations were lower or close to those in coal ash.

Binder effect on trace elements:

The second set of graphs 63-69, shows the trace element concentration versus the binder percentage at a specific bdRDF Btu content 10, 20, 30, and 50%. The top graphs shows the trace element concentration versus the binder percentage at 10% bdRDF Btu content. The second middle graphs shows the trace element at 20% bdRDF. The third shows the same trace metal at 30% bdRDF Btu content.

The results summarized in the second set of graphs 63-69 suggest the following:

.The elements Be, Ba, V, Ni, Cu, and Cr were decreased with an increase in binder percentage.

.The element Zn increased in concentration with an increase in binder content.

The binder-enhanced dRDF is a promising technique for the future to be used as fuel or as a substitute for coal. It is an economical way of disposal of MSW in the sense that it reduces the heavy cost of landfilling, and this technique will generate extra income if sold as fuel. According to the results presented here it shows promise in reducing emissions, especially the trace elements emissions, making it safer to use as fuel.

Figure 56. Cr, in Economizer Fly Ash

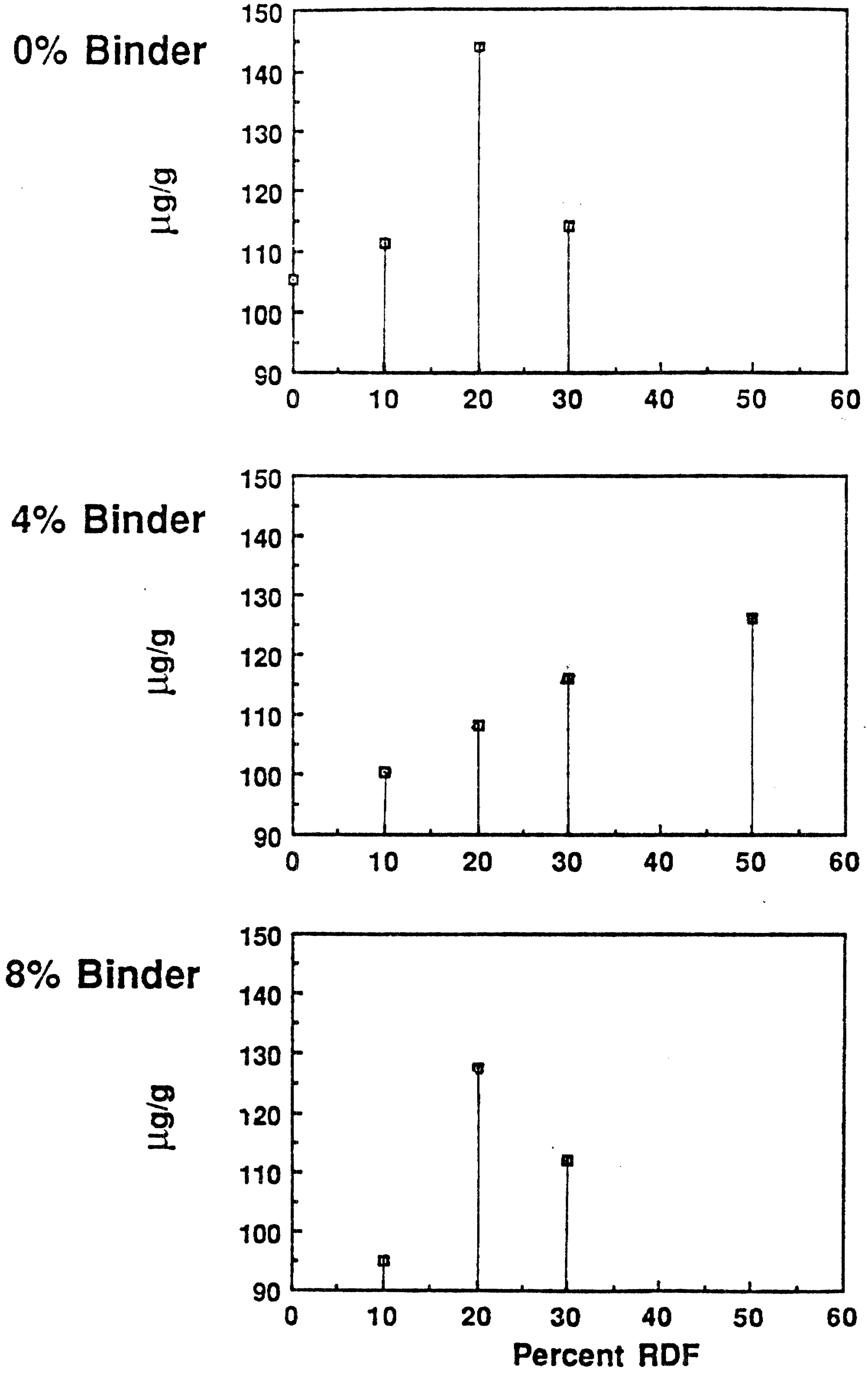
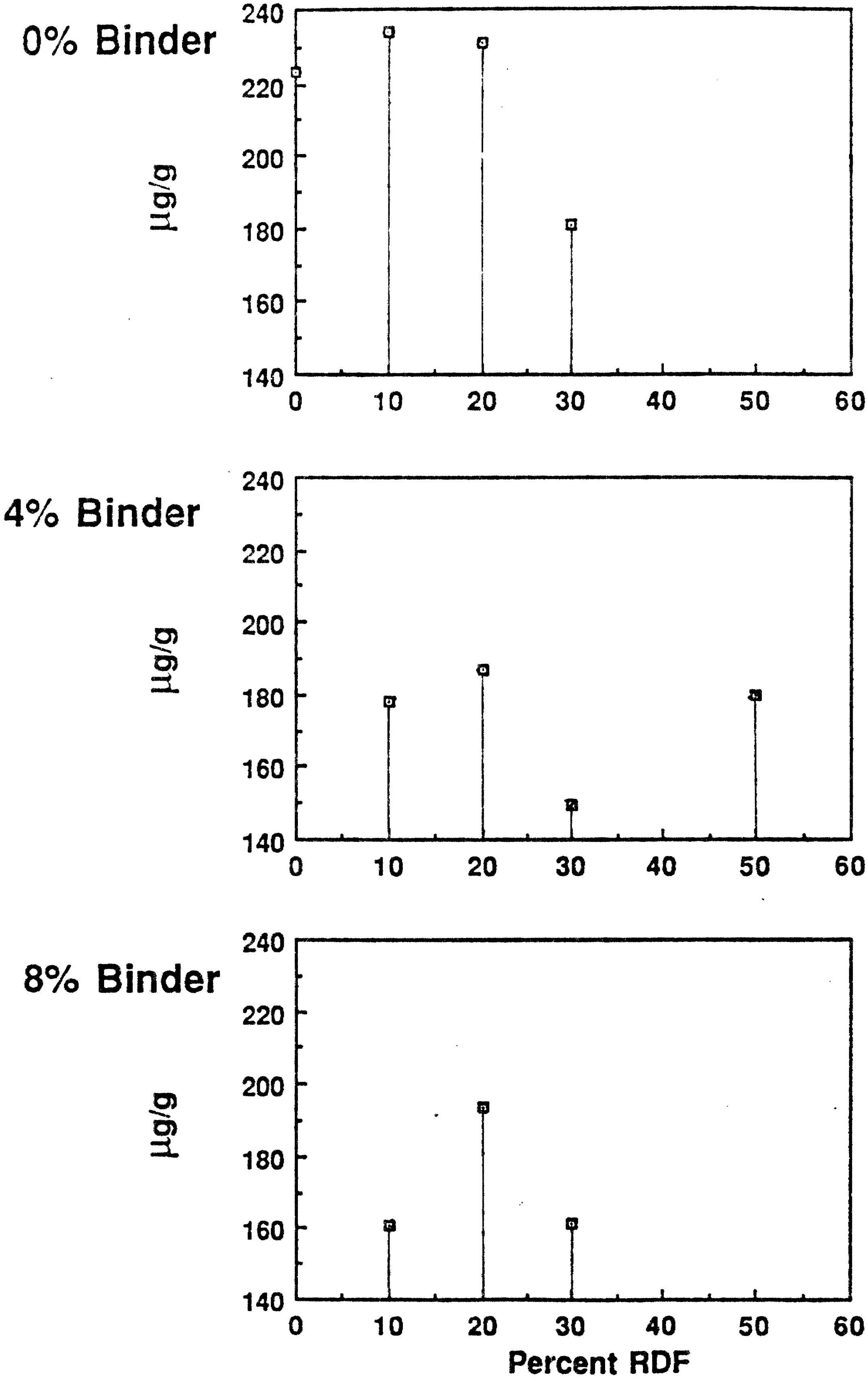


Figure 57. V, in Economizer Fly Ash



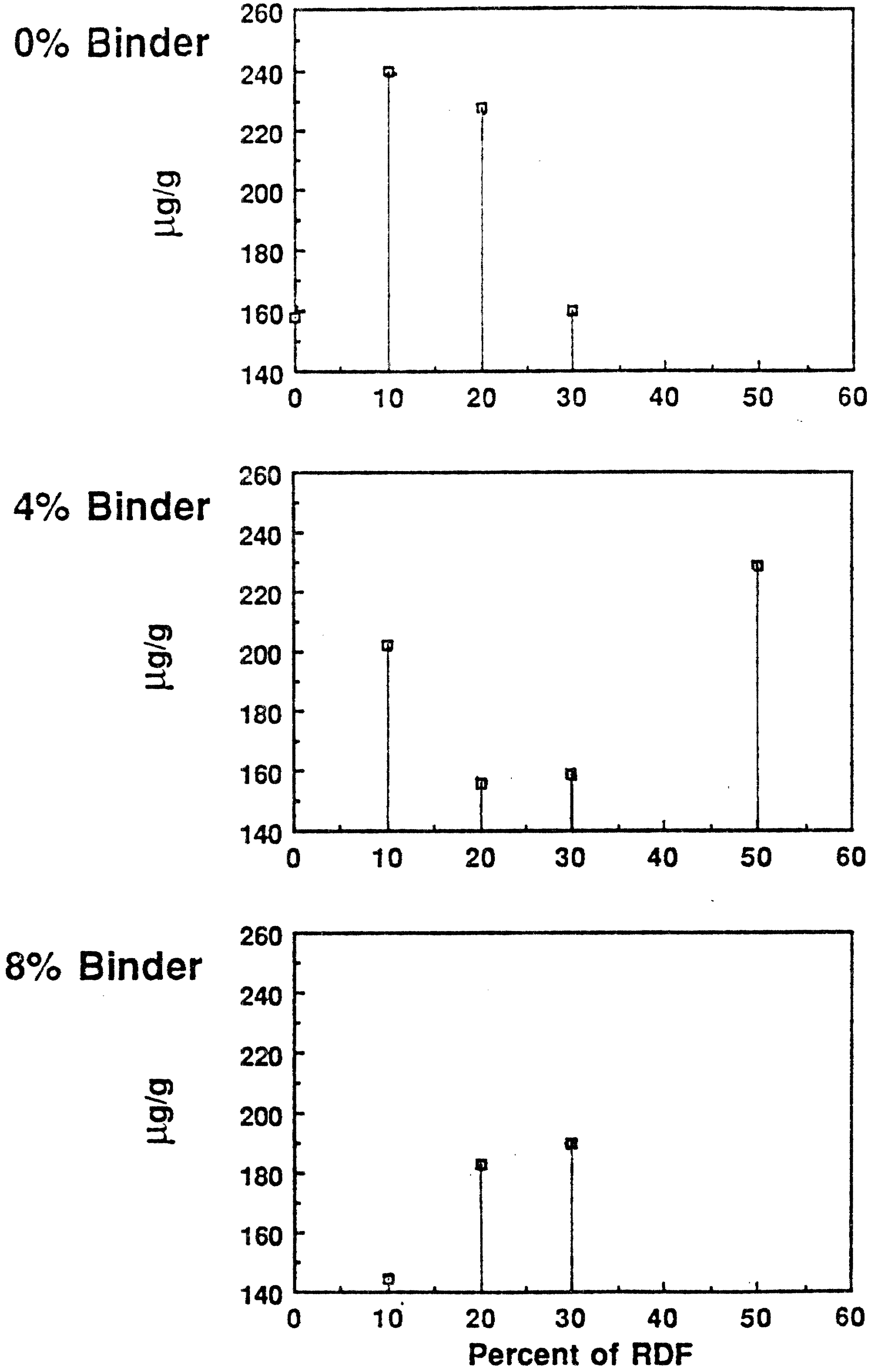


Figure 58.Ba, in Economizer Fly Ash

Figure 59. Be, in Economizer Fly Ash

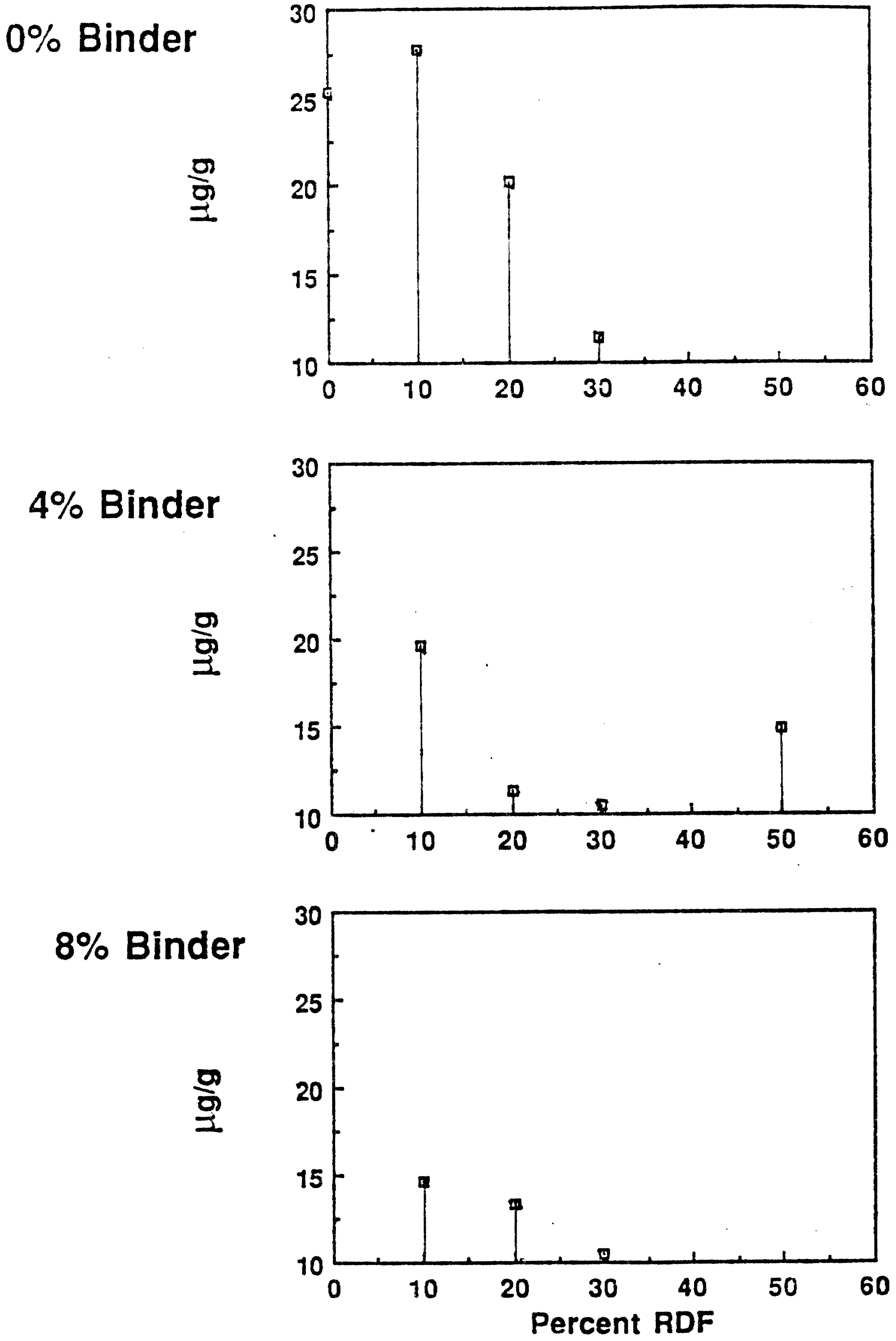
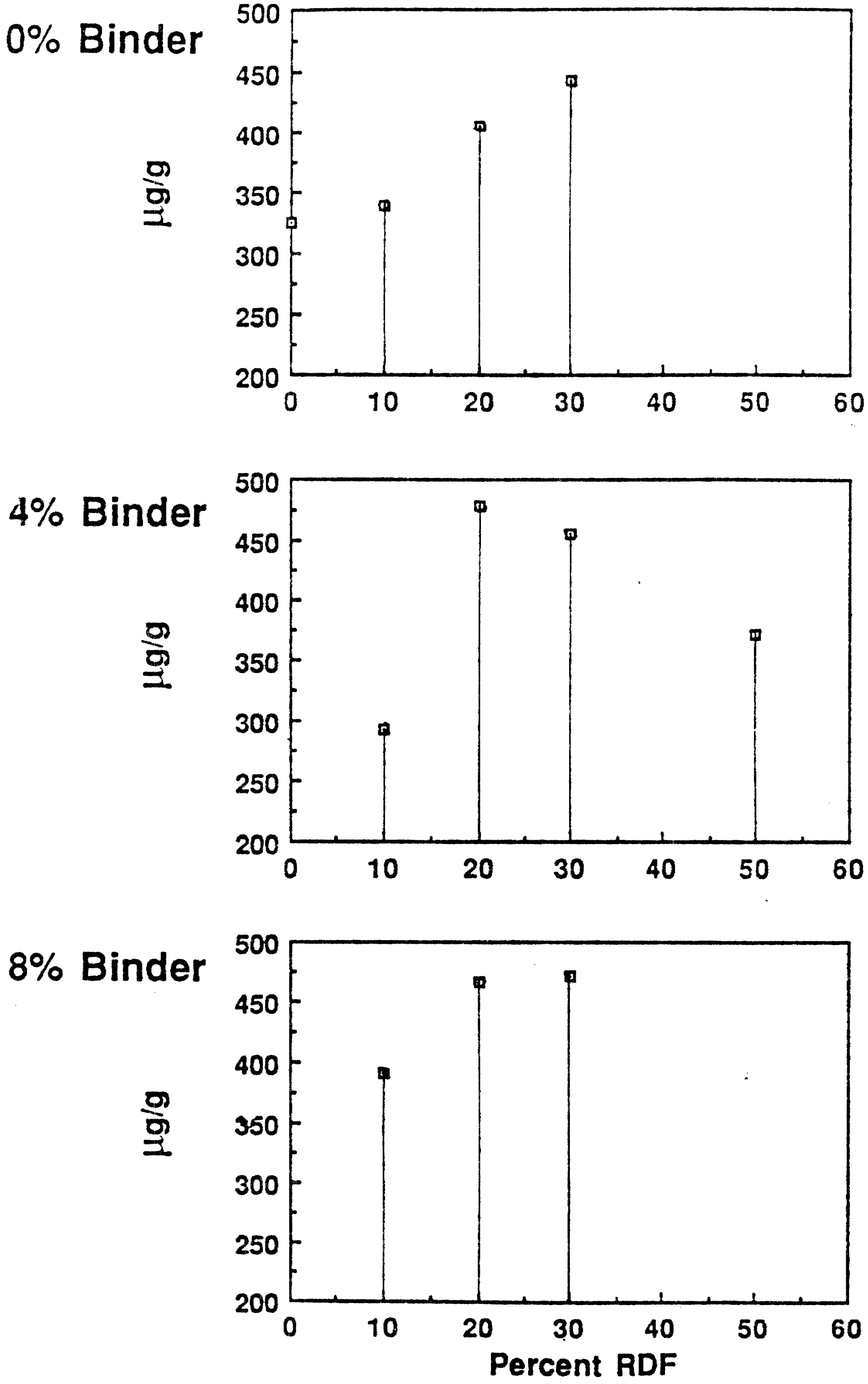


Figure 60. Zn , in Economizer Fly Ash



0% Binder

4% Binder

8% Binder

Figure 61. Cu, in Economizer Fly Ash

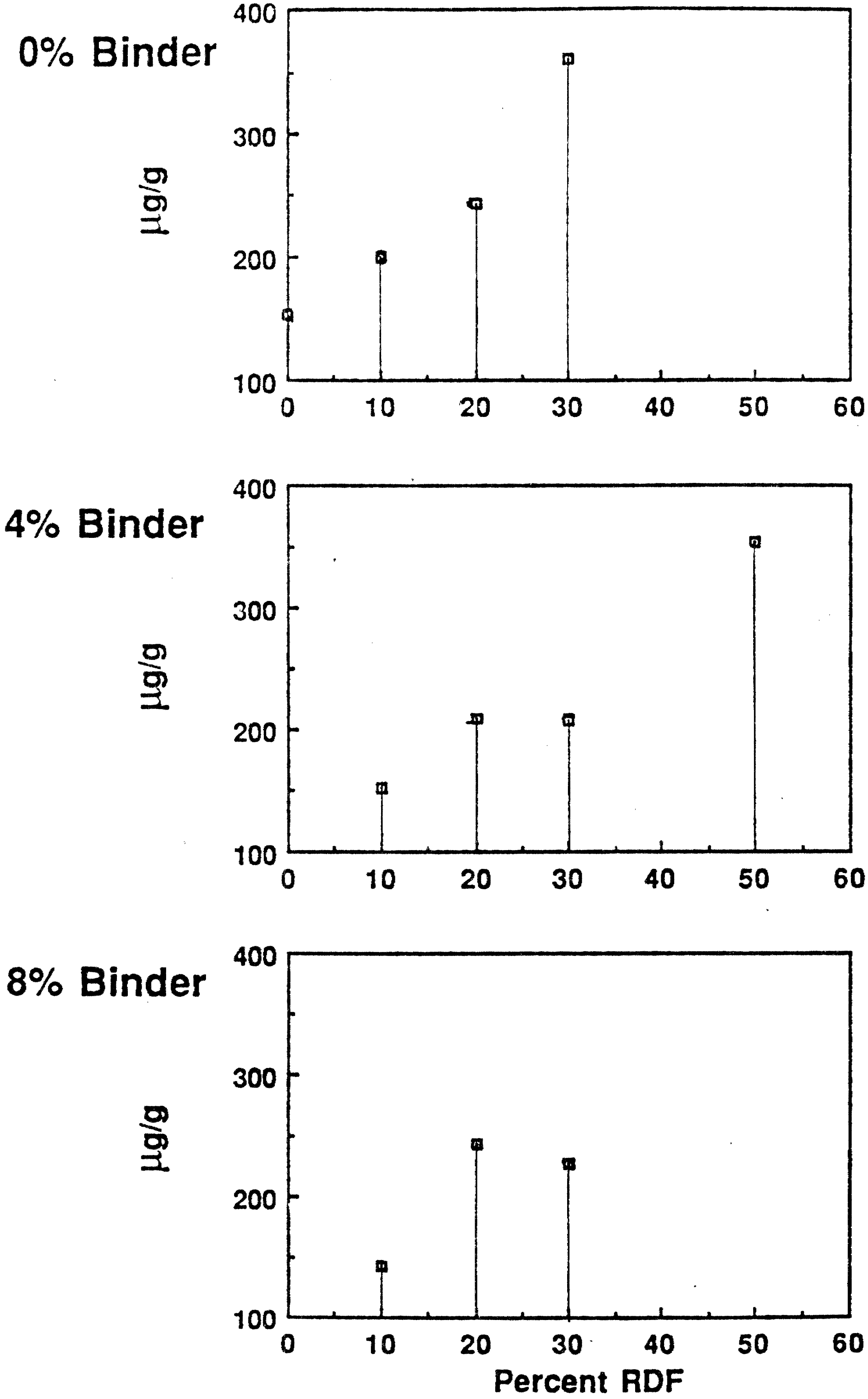


Figure 62. Ni, in Economizer Fly Ash

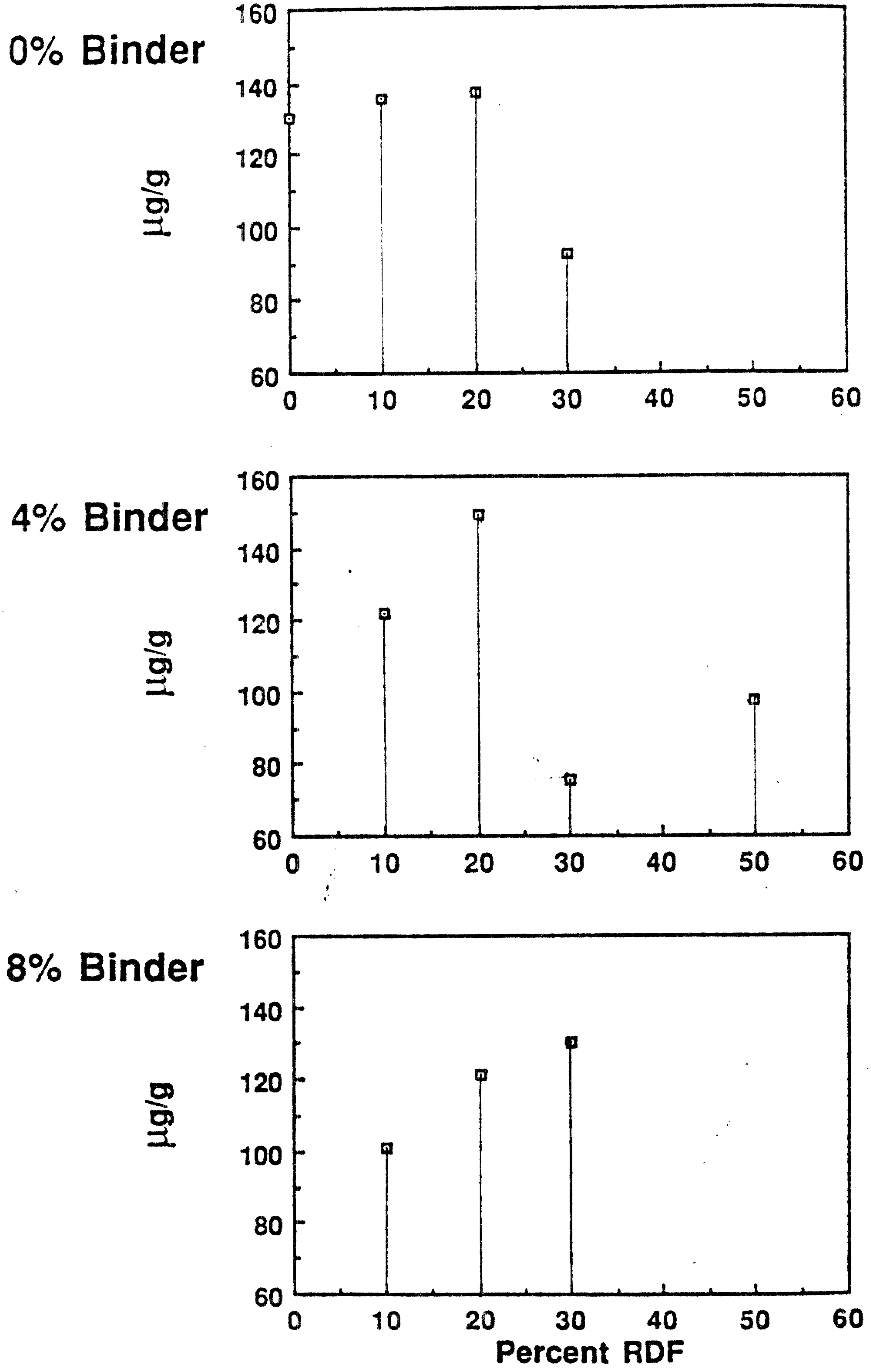
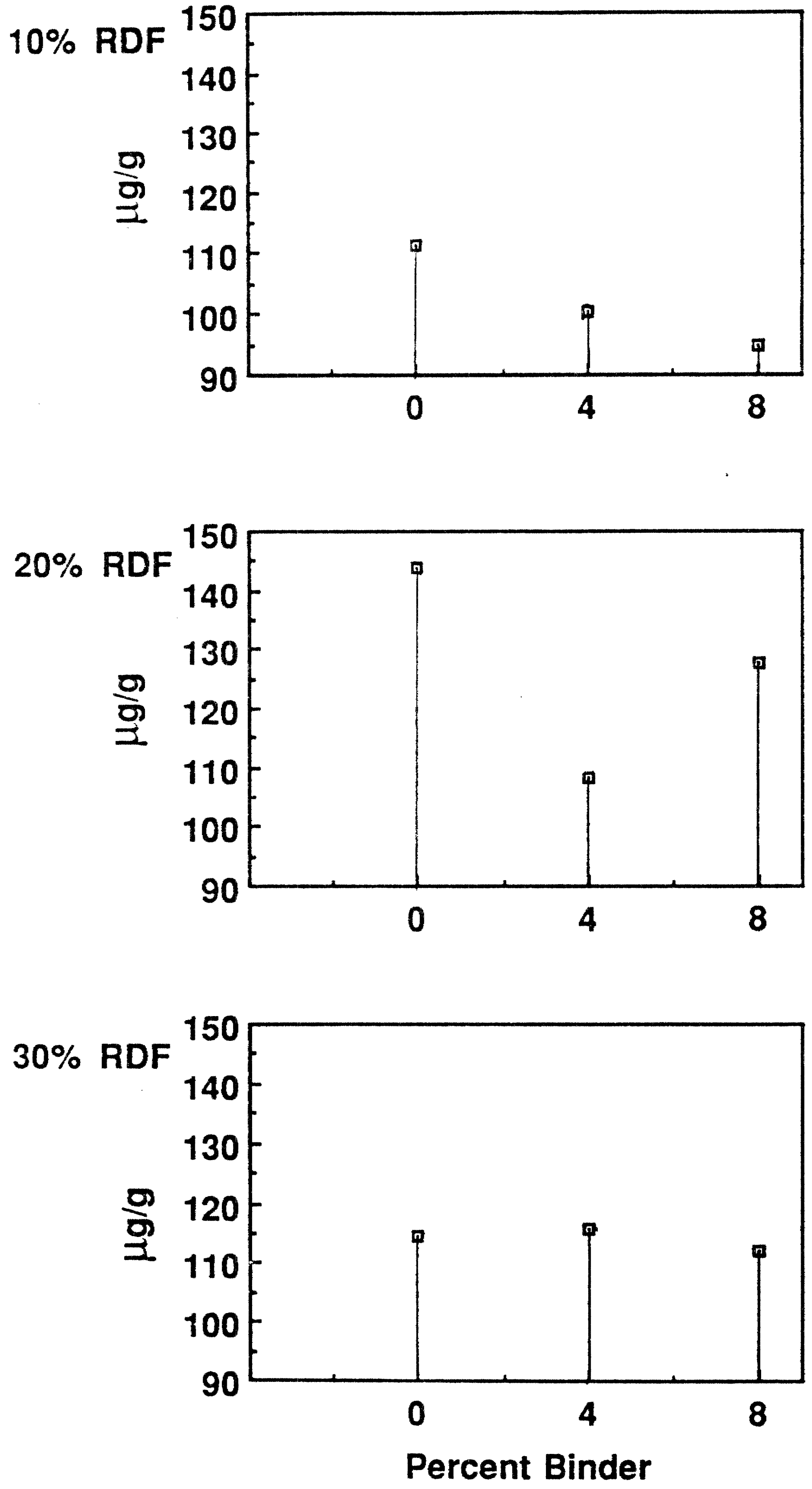


Figure 63.



Cr, in Economizer Fly Ash

Figure 64.

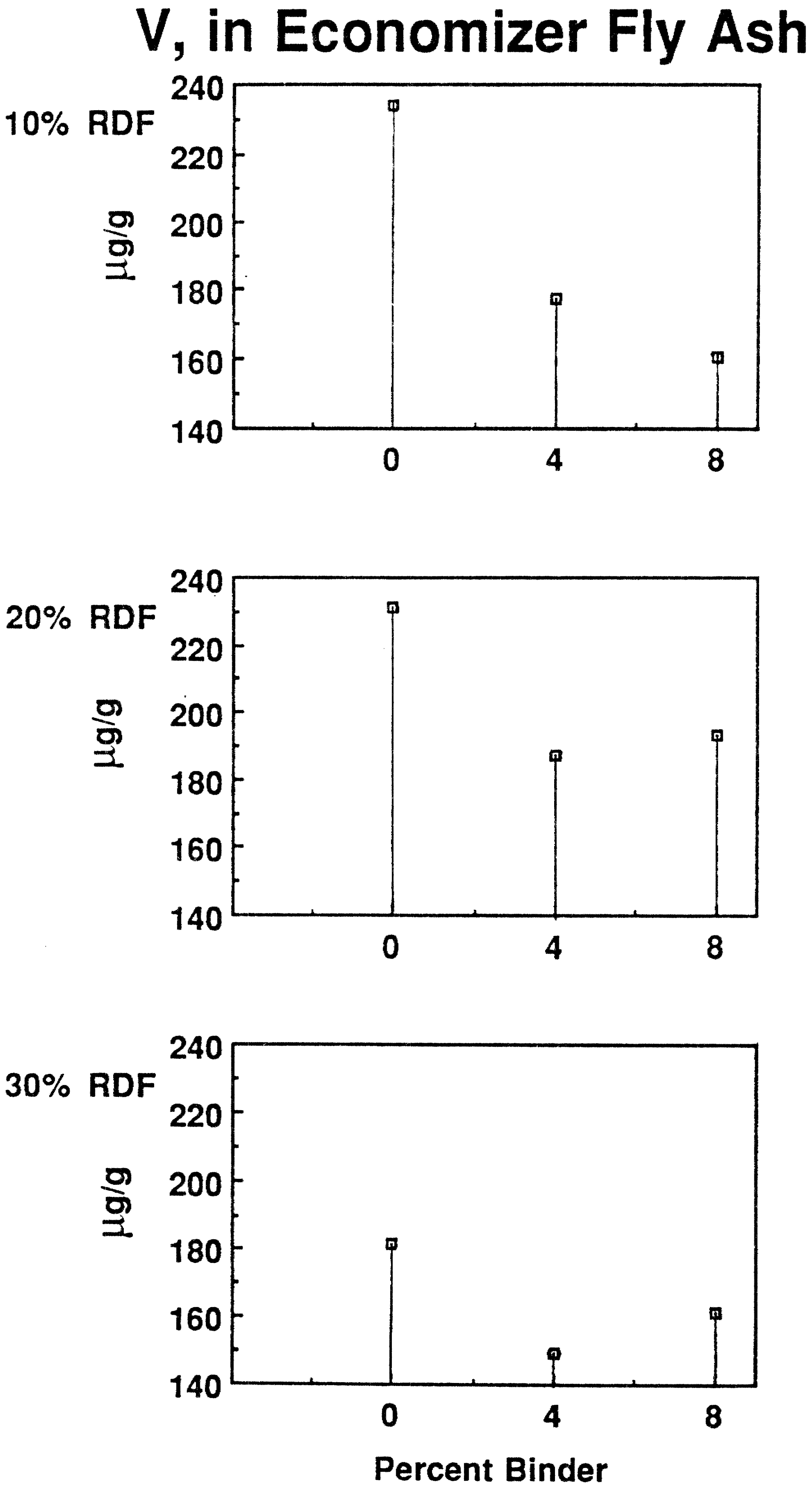

V, in Economizer Fly Ash
10% RDF
20% RDF
30% RDF
µg/g
240
220
200
180
160
140
0
4
8
Percent Binder

Figure 65.

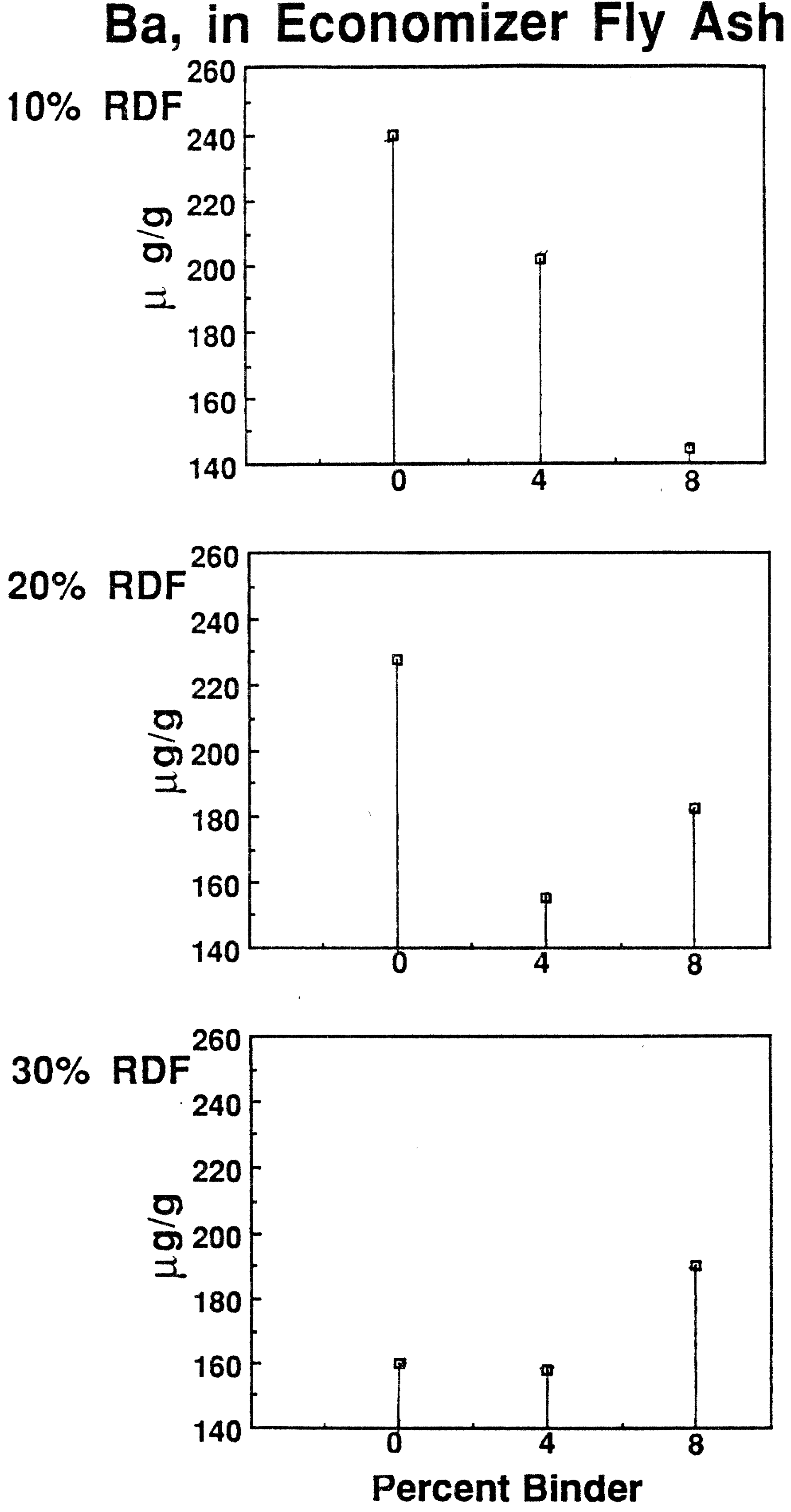

Ba, in Economizer Fly Ash
10% RDF
20% RDF
30% RDF
µ g/g
µg/g
µg/g
260
240
220
200
180
160
140
0
4
8
Percent Binder

Figure 66.

Be, in Economizer Fly Ash

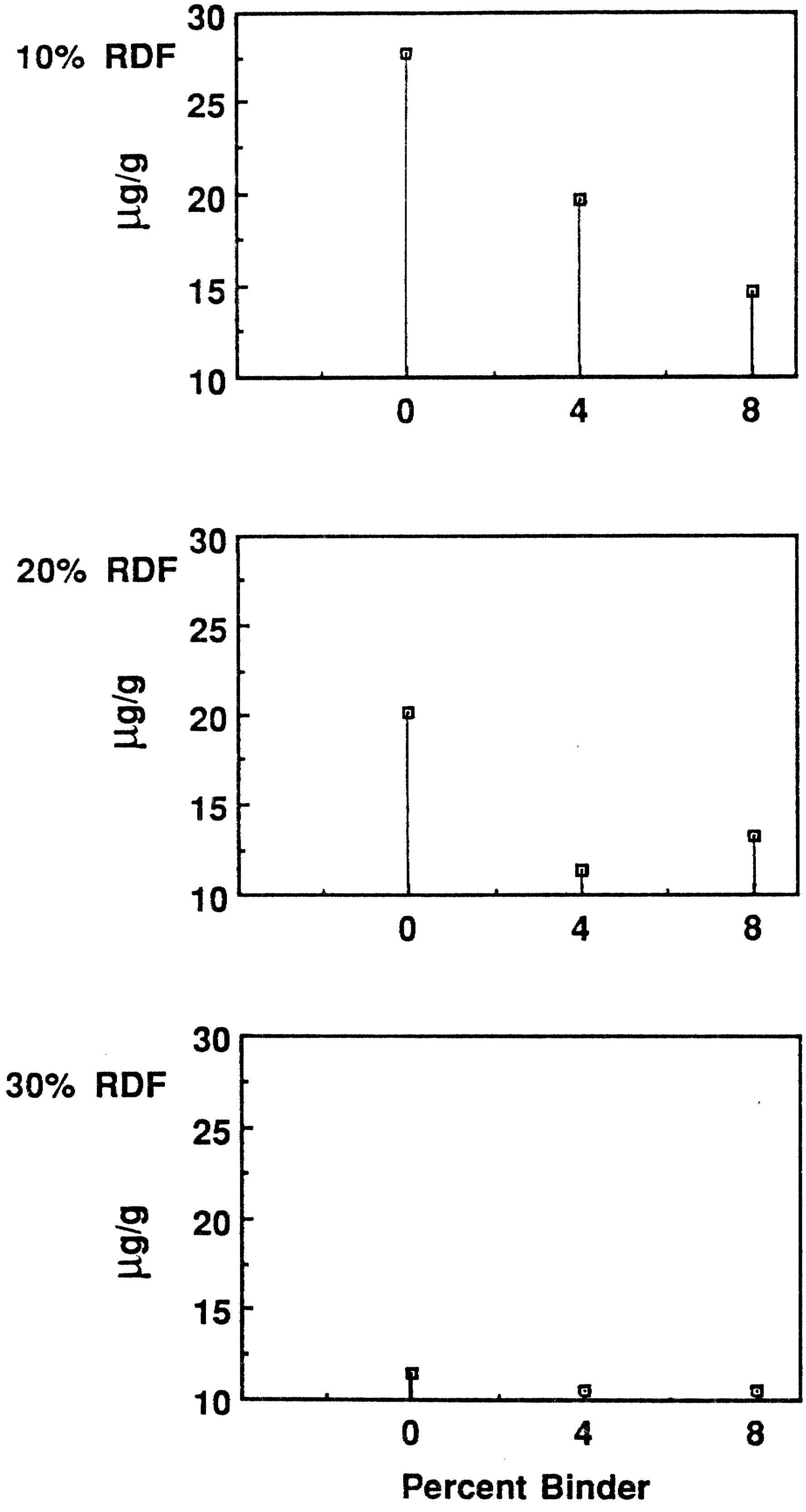


Figure 67.

Zn, in Economizer Fly Ash

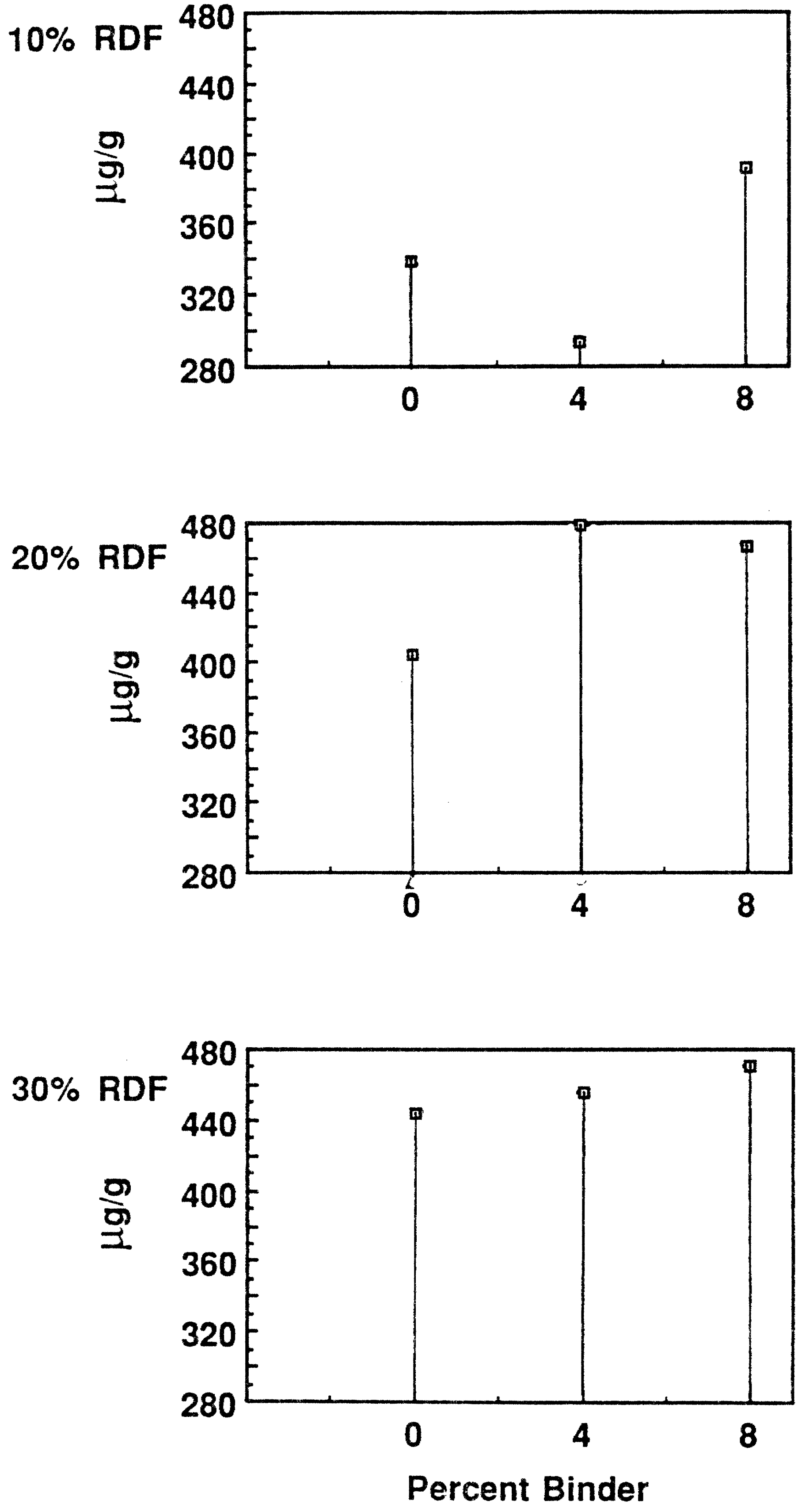


Figure 68.

Cu, in Economizer Fly Ash

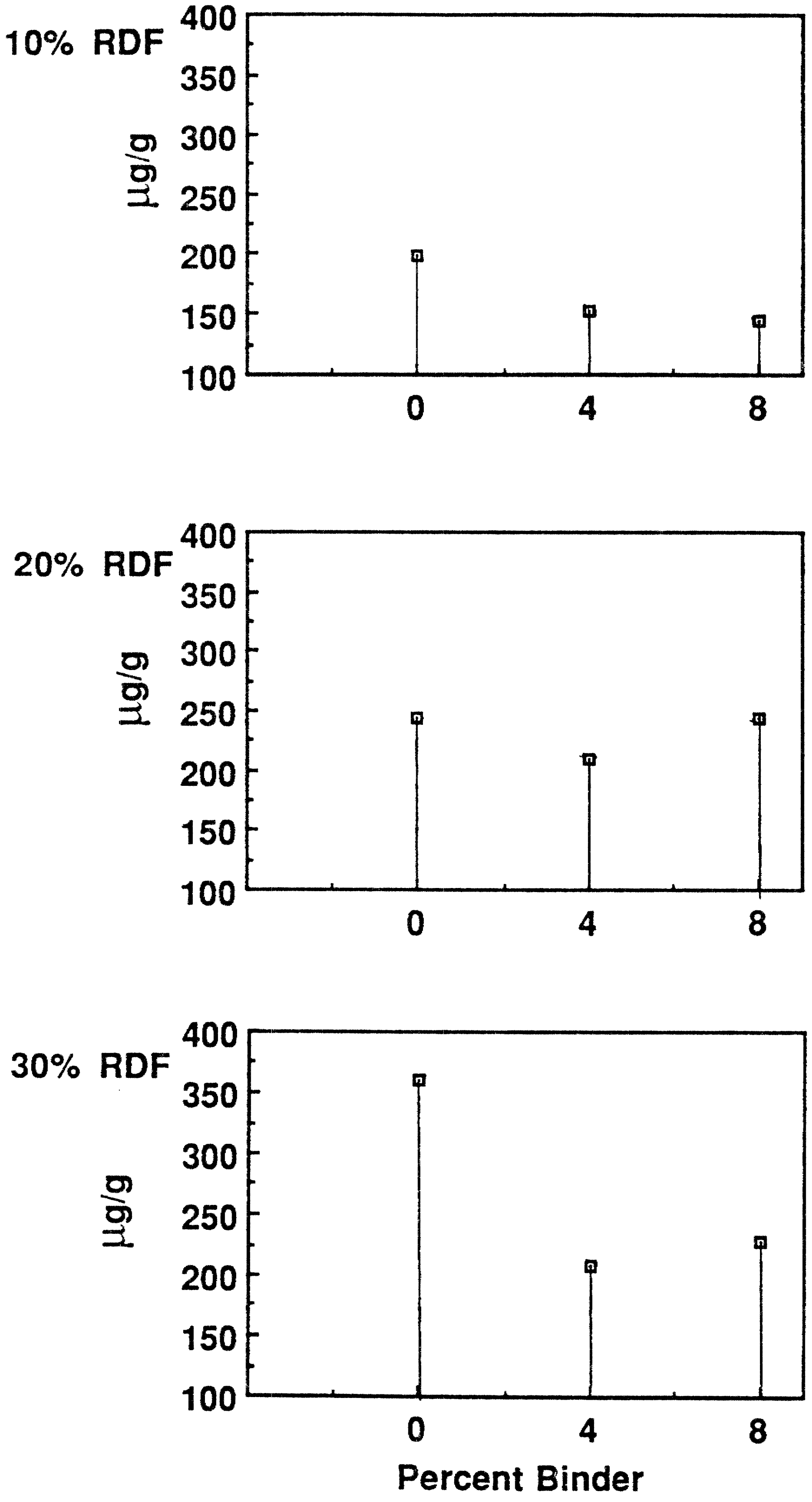
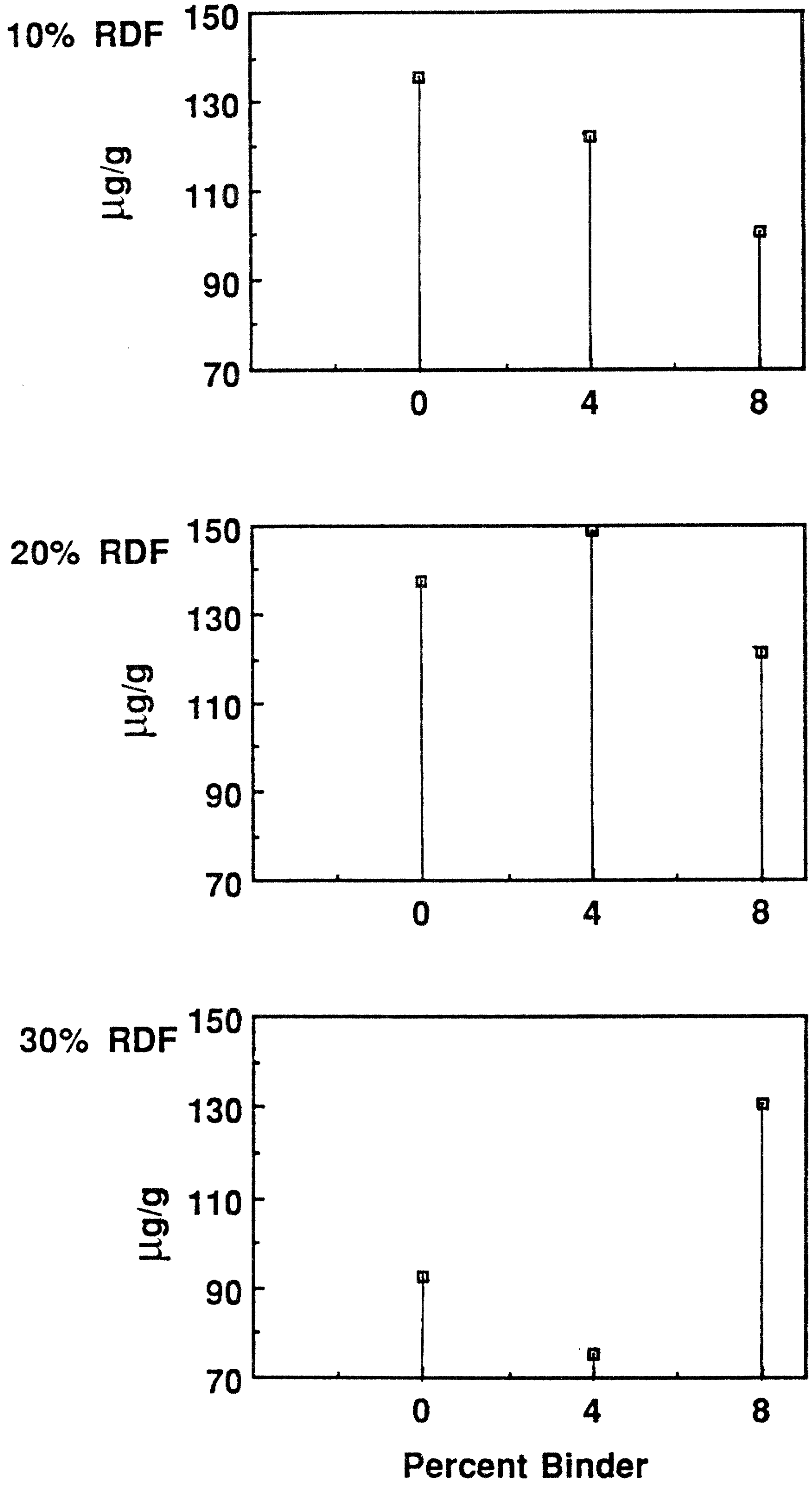


Figure 69.

Ni, in Economizer Fly Ash



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APPENDIX A

TABLE XXXIV

Btu ANALYSIS OF dRDF WITH ZERO PERCENT BINDER

Percent of Btu by Weight

Trial Number	FF1[a]	FF 4,5	R1[b]	R 4	R 5	R
13						
1	6910	7310	6824	6043	7216	6592
2	7129	7058	5766	6042	5953	6068
3	6727	6272	6896	6876	6527	6336
4	8880	6862	6685	6924	6714	6587
5	7310	6595	6482	6570	7023	6670
6	10,675			6288	6350	6585
7	9071			6231	6935	6770
8	8930					
Average	8204	6820	6530	6425	6674	6515

a = Future Fuel pellets
b = Reuter pellets

TABLE XXXIV

ASH ANALYSIS OF dRDF WITH ZERO PERCENT BINDER

Percent of Ash by Weight							
Trial Number	FF1[a]	FF 4,5	R1[b]	R 4	R 5	R 13	R14
1	5.86	6.19	8.24	9.54	9.60	7.97	8.20
2	6.41	6.00	8.42	9.90	8.36	7.65	7.51
3	7.10	6.67	8.68	9.19	8.92	7.72	7.28
4	6.40	5.13	8.59	8.10	7.49	9.24	7.67
5	6.48	5.81	8.59	8.79	9.44	8.06	7.67
Average	6.45	5.96	8.50	9.10	8.76	7.85	7.67

a = Future Fuel pellets
b = Reuter pellets

APPENDIX B

Table XXXVI : Standard Deviation of the Elements Analyzed Using ICP.

	Run #1	Run #2	Run #3	Run #4
As	0.123	0.508	0.001	0.284
Hg	0.064	0.046	0.060	0.263
Se	0.000	0.287	0.244	0.076
Cr	0.005	0.013	0.115	0.009
Sb	0.000	0.189	0.176	0.211
Be	0.000	0.000	0.000	0.000
Cu	0.000	0.027	0.009	0.003
Tl	0.060	0.288	0.177	0.832
Zn	0.005	0.010	0.012	0.010
Cd	0.000	0.011	0.005	0.009
Pb	0.206	0.710	0.094	0.138
Ni	0.048	0.640	0.080	0.089
Ba	0.005	0.004	0.000	0.000

Table XXXVI ......continue...

Element	Run #5	Run #6	Run #7	Run #8
As	0.117	0.017	0.000	0.625
Hg	0.042	0.057	0.084	0.000
Se	0.171	0.272	0.000	0.077
Cr	0.010	0.033	0.044	0.006
Sb	0.041	0.000	0.000	0.080
Be	0.003	0.000	0.000	0.000
Cu	0.017	0.012	0.041	0.003
Tl	0.431	0.180	0.038	0.291
Zn	0.006	0.005	0.004	0.006
Cd	0.001	0.003	0.004	0.000
Pb	0.341	0.068	0.119	0.389
Ni	0.790	0.342	0.218	0.080
Ba	0.000	0.000	0.004	0.009

Table XXXVI ....continue...

Element	Run #9	Run #10	Run #11	Run #12
As	0.433	0.000	0.337	0.040
Hg	0.039	0.123	0.062	0.206
Se	0.000	0.000	0.024	0.010
Cr	0.005	0.020	0.009	0.028
Sb	0.000	0.031	0.000	0.099
Be	0.000	0.000	0.000	0.000
Cu	0.050	0.006	0.004	0.009
Tl	0.454	0.444	0.440	0.959
Zn	0.003	0.003	0.004	0.007
Cd	0.000	0.014	0.001	0.036
Pb	0.142	0.037	0.107	0.163
Ni	0.026	0.224	0.067	0.327
Ba	0.004	0.004	0.003	0.009

APPENDIX C

```
SEMI-QUANTITATIVE ANALYSIS: 1 20/4%6/23/87 200X
EL    NORM. K-RATIO

AL-K 0.15441 +- 0.00148
SI-K 0.27200 +- 0.00188
S -K 0.05806 +- 0.00091
K -K 0.04661 +- 0.00090
CA-K 0.18459 +- 0.00185
TI-K 0.01397 +- 0.00059
FE-K 0.25361 +- 0.00327
CU-K 0.01671 +- 0.00110

ZAF CORRECTION       20.00 KV       45.00 Degs

No. of Iterations  3
----      K       [Z]     [A]     [F]    [ZAF]   ATOM.%   WT.%
AL-K   0.154   0.998   1.511   0.984   1.484   22.14   17.47   *
SI-K   0.272   0.965   1.598   0.995   1.536   38.94   31.86   *
S -K   0.058   0.973   1.524   0.993   1.474    6.98    6.53   *
K -K   0.046   1.009   1.180   0.974   1.161    3.62    4.13
CA-K   0.184   0.986   1.143   0.991   1.118   13.46   15.74
TI-K   0.013   1.082   1.117   0.981   1.187    0.90    1.26
FE-K   0.253   1.083   1.030   0.997   1.114   13.16   21.54
CU-K   0.016   1.124   1.030   1.000   1.158    0.79    1.48
 * - High Absorbance

SSQ:
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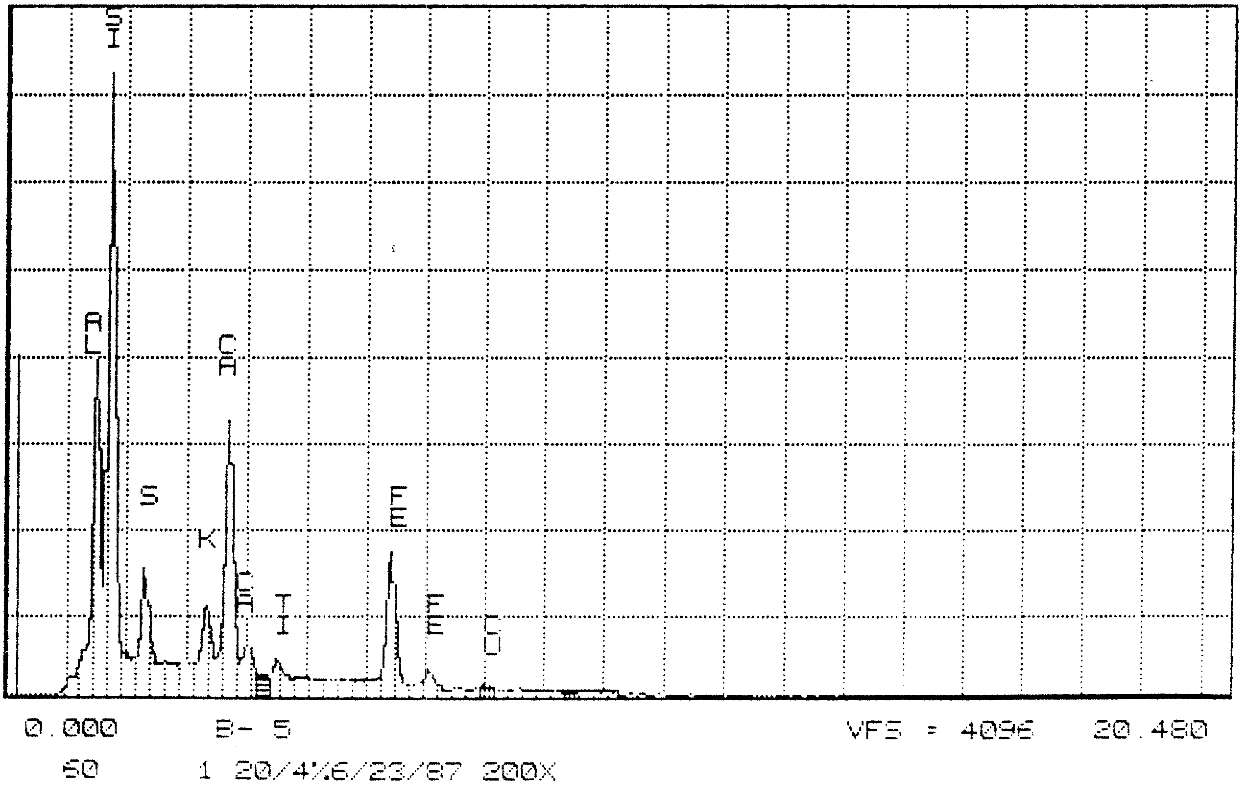

```
SEMI-QUANTITATIVE ANALYSIS: 2 20/4%6/23/87 150X
EL     NORM. K-RATIO

AL-K 0.15370 +- 0.00140
SI-K 0.26009 +- 0.00174
S -K 0.05318 +- 0.00083
K -K 0.03992 +- 0.00079
CA-K 0.15254 +- 0.00159
TI-K 0.02494 +- 0.00074
FE-K 0.29584 +- 0.00335
CU-K 0.01448 +- 0.00097
MG-K 0.00527 +- 0.00027

ZAF CORRECTION         20.00 KV        45.00 Degs

No. of Iterations  3
----      K       [Z]      [A]      [F]    [ZAF]    ATOM.%   WT.%
AL-K   0.153   0.995   1.561   0.985   1.530   22.75   17.81   *
SI-K   0.260   0.962   1.637   0.996   1.570   38.08   30.91   *
S -K   0.053   0.970   1.533   0.994   1.479    6.42    5.95   *
K -K   0.039   1.006   1.181   0.976   1.160    3.10    3.51
CA-K   0.152   0.983   1.140   0.989   1.109   11.05   12.81
TI-K   0.024   1.079   1.105   0.978   1.167    1.58    2.20
FE-K   0.295   1.080   1.027   0.998   1.108   15.28   24.81
CU-K   0.014   1.120   1.033   1.000   1.157    0.68    1.27
MG-K   0.005   0.952   1.950   0.987   1.834    1.05    0.73   *
 * - High Absorbance

SSQ:
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```
CMC, SEM/XEDS Analysis                         THU 08-MAR-90   08:13
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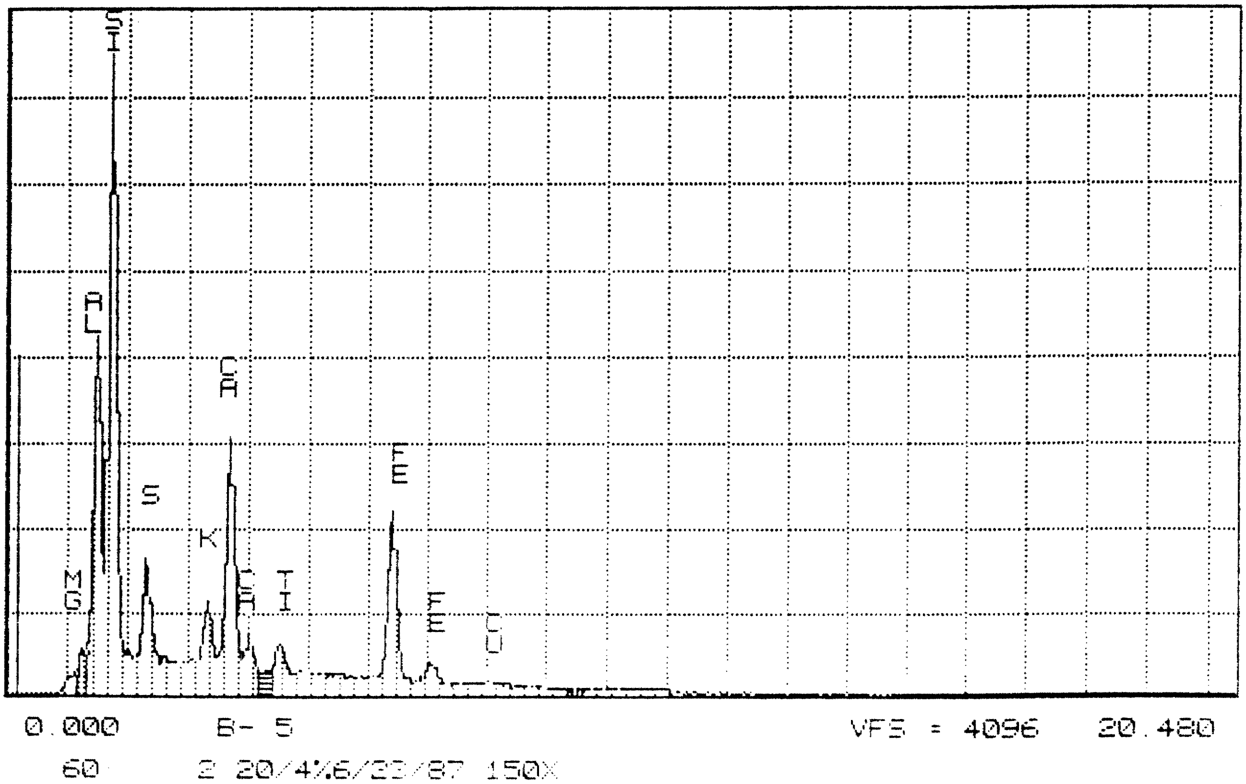

```
SEMI-QUANTITATIVE ANALYSIS: 3 20/4%6/23/87 75X
EL     NORM. K-RATIO

AL-K 0.18247 +- 0.00156
SI-K 0.29420 +- 0.00190
S -K 0.04769 +- 0.00080
K -K 0.04391 +- 0.00085
CA-K 0.11391 +- 0.00141
TI-K 0.02016 +- 0.00068
FE-K 0.27861 +- 0.00333
CU-K 0.00936 +- 0.00080
MG-K 0.00966 +- 0.00037

ZAF CORRECTION          20.00 KV        45.00 Degs

No. of Iterations  3
----      K       [Z]      [A]      [F]     [ZAF]   ATOM.%   WT.%
AL-K   0.182    0.997    1.510    0.984    1.483    24.86    20.07  *
SI-K   0.294    0.965    1.644    0.996    1.582    41.23    34.51  *
S -K   0.047    0.973    1.571    0.995    1.522     5.62     5.38  *
K -K   0.043    1.009    1.190    0.981    1.180     3.29     3.84
CA-K   0.113    0.986    1.148    0.990    1.123     7.93     9.48
TI-K   0.020    1.082    1.099    0.978    1.165     1.21     1.74
FE-K   0.278    1.084    1.025    0.998    1.110    13.69    22.93
CU-K   0.009    1.124    1.029    1.000    1.158     0.42     0.80
MG-K   0.009    0.955    1.839    0.985    1.732     1.73     1.24  *
 * - High Absorbance

SSQ:
```

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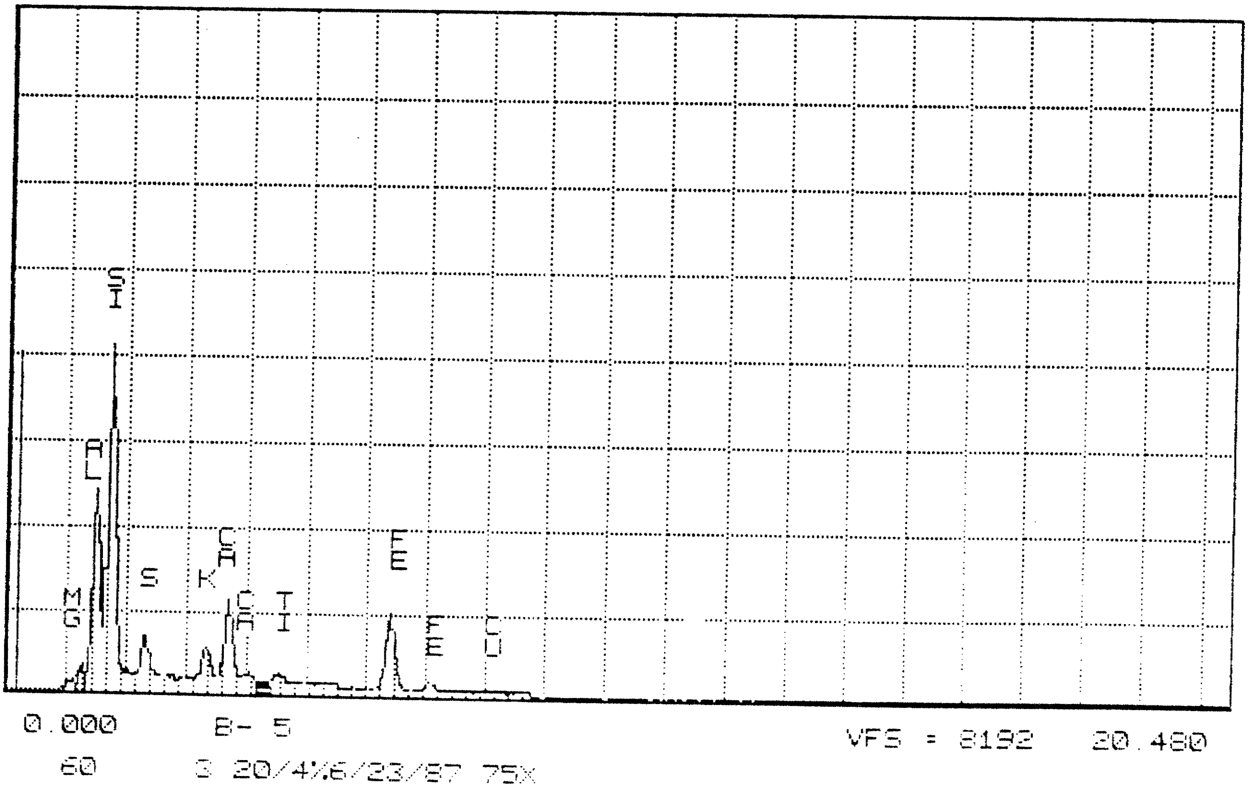

```
SEMI-QUANTITATIVE ANALYSIS: 4 20/4%6/23/87 75X
EL     NORM. K-RATIO

AL-K 0.18826 +- 0.00178
SI-K 0.31146 +- 0.00218
S -K 0.03829 +- 0.00080
K -K 0.04625 +- 0.00097
CA-K 0.07817 +- 0.00131
TI-K 0.03276 +- 0.00098
FE-K 0.30478 +- 0.00390

ZAF CORRECTION        20.00 KV       45.00 Degs

No. of Iterations  3
-----     K       [Z]     [A]     [F]    [ZAF]  ATOM.%  WT.%
AL-K   0.188   0.995   1.494   0.983   1.463   25.51   20.51   *
SI-K   0.311   0.963   1.641   0.997   1.577   43.86   36.57   *
S -K   0.038   0.971   1.589   0.995   1.537    4.60    4.38   *
K -K   0.046   1.007   1.192   0.984   1.182    3.51    4.07
CA-K   0.078   0.984   1.151   0.988   1.120    5.48    6.52
TI-K   0.032   1.080   1.091   0.976   1.151    1.97    2.81
FE-K   0.304   1.081   1.023   1.000   1.107   15.07   25.13
 * - High Absorbance

SSQ:
```

```
CMC, SEM/XEDS Analysis                         THU 08-MAR-90  08:32
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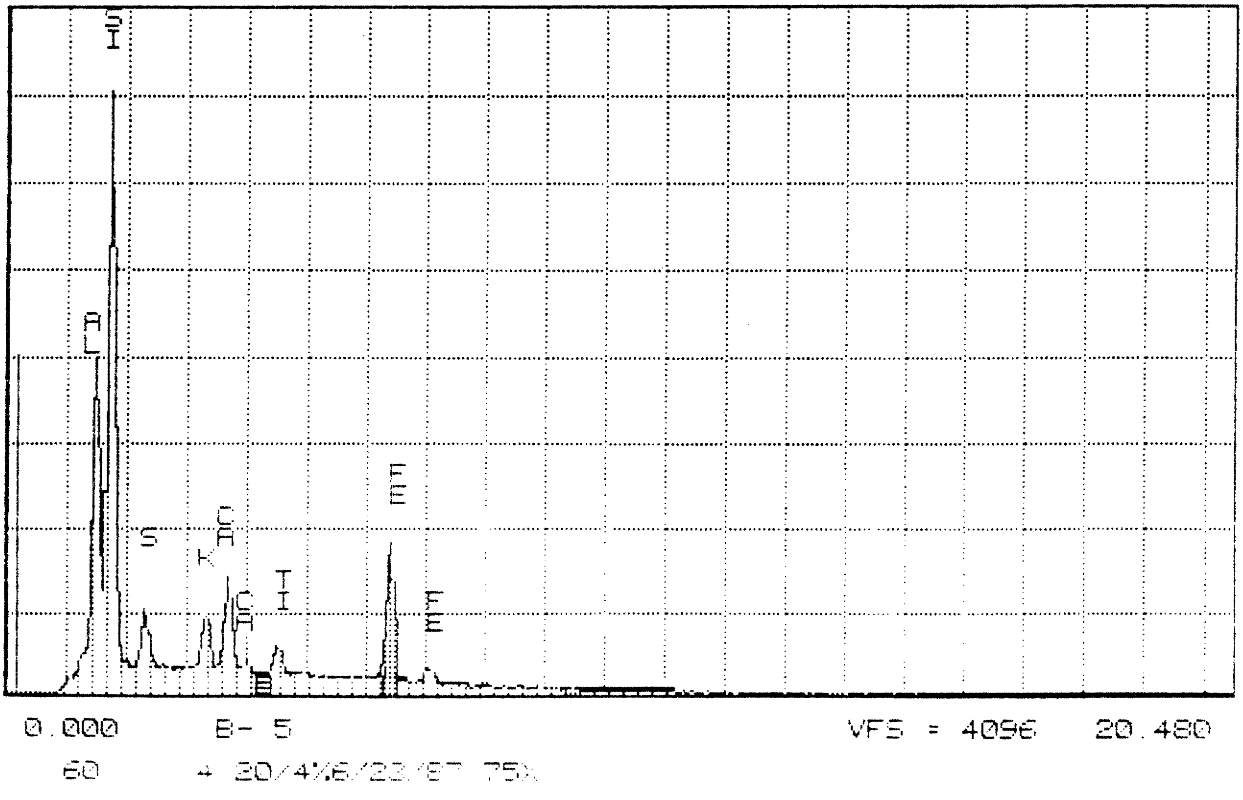

```
SEMI-QUANTITATIVE ANALYSIS: 5 20/4%6/23/87 50X
EL    NORM. K-RATIO

AL-K 0.20930 +- 0.00206
SI-K 0.36270 +- 0.00259
S -K 0.04956 +- 0.00101
K -K 0.06250 +- 0.00125
CA-K 0.05776 +- 0.00124
TI-K 0.03134 +- 0.00105
FE-K 0.22681 +- 0.00370

ZAF CORRECTION        20.00 KV        45.00 Degs

No. of Iterations  3
----      K       [Z]     [A]     [F]    [ZAF]   ATOM.%  WT.%
AL-K   0.209   1.001   1.394   0.980   1.368   25.41   21.20
SI-K   0.362   0.969   1.587   0.996   1.533   47.54   41.13   *
S -K   0.049   0.977   1.609   0.995   1.566    5.81    5.75   *
K -K   0.062   1.013   1.204   0.988   1.206    4.63    5.58
CA-K   0.057   0.990   1.167   0.990   1.145    3.96    4.89
TI-K   0.031   1.087   1.095   0.982   1.170    1.83    2.71
FE-K   0.226   1.089   1.024   1.000   1.116   10.83   18.74
 * - High Absorbance

SSQ:
```

```
CMC, SEM/XEDS Analysis                          THU 08-MAR-90   08:41
Cursor: 0.000keV = 0        ROI     (0) 4.180: 4.380=0/sec
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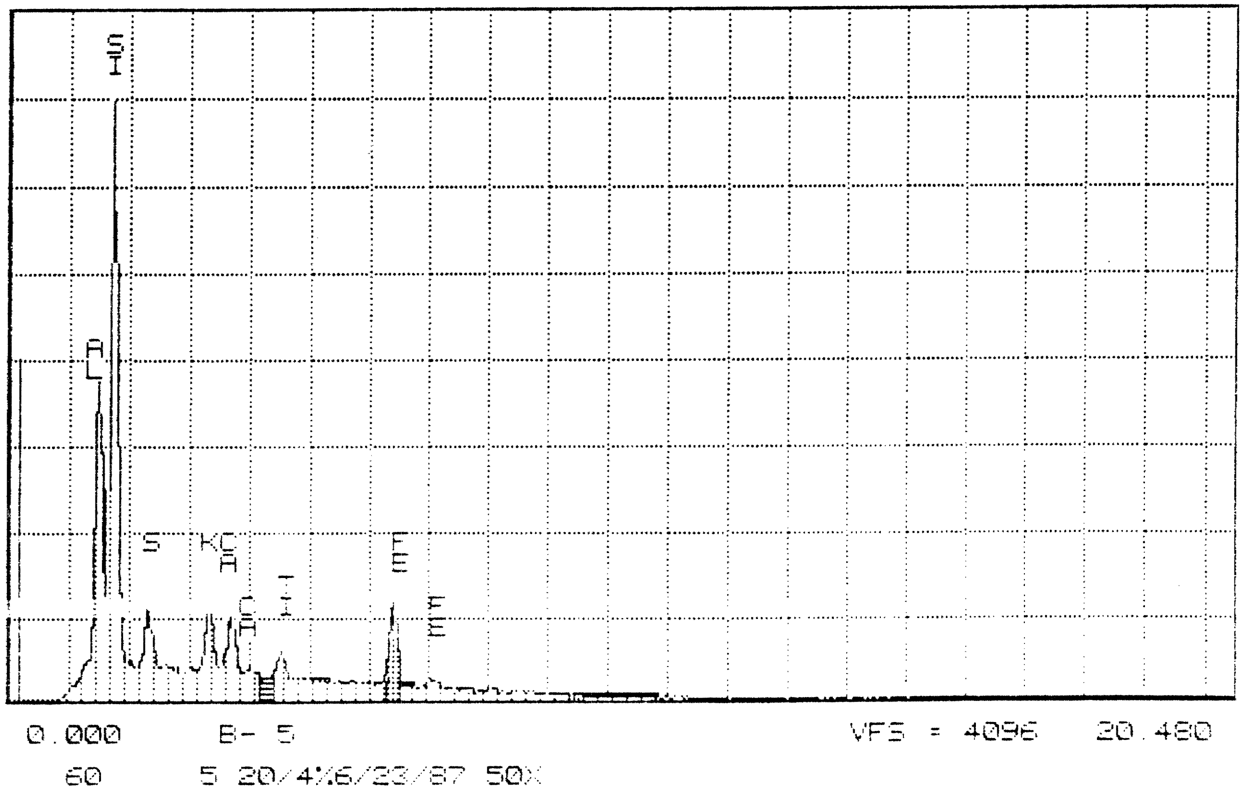

```
SEMI-QUANTITATIVE ANALYSIS: 6 20/4%6/23/87 50X
EL    NORM. K-RATIO

AL-K 0.20367 +- 0.00196
SI-K 0.36350 +- 0.00250
S -K 0.04906 +- 0.00096
K -K 0.06331 +- 0.00121
CA-K 0.04824 +- 0.00109
TI-K 0.02909 +- 0.00098
FE-K 0.24310 +- 0.00369

ZAF CORRECTION        20.00 KV       45.00 Degs

No. of Iterations  3
----     K       [Z]     [A]     [F]    [ZAF]   ATOM.%  WT.%
AL-K  0.203  1.000  1.408  0.980  1.381  25.04  20.81  *
SI-K  0.363  0.968  1.589  0.997  1.535  47.85  41.23  *
S -K  0.049  0.976  1.611  0.996  1.567   5.77   5.69  *
K -K  0.063  1.012  1.205  0.989  1.207   4.71   5.65
CA-K  0.048  0.989  1.167  0.990  1.144   3.32   4.08
TI-K  0.029  1.086  1.093  0.981  1.165   1.70   2.51
FE-K  0.243  1.088  1.023  1.000  1.114  11.62  20.03
 * - High Absorbance

SSQ:
```

```
CMC, SEM/XEDS Analysis                      THU 08-MAR-90  08:49
Cursor: 0.000keV = 0         ROI     (0) 4.180: 4.380=0/sec
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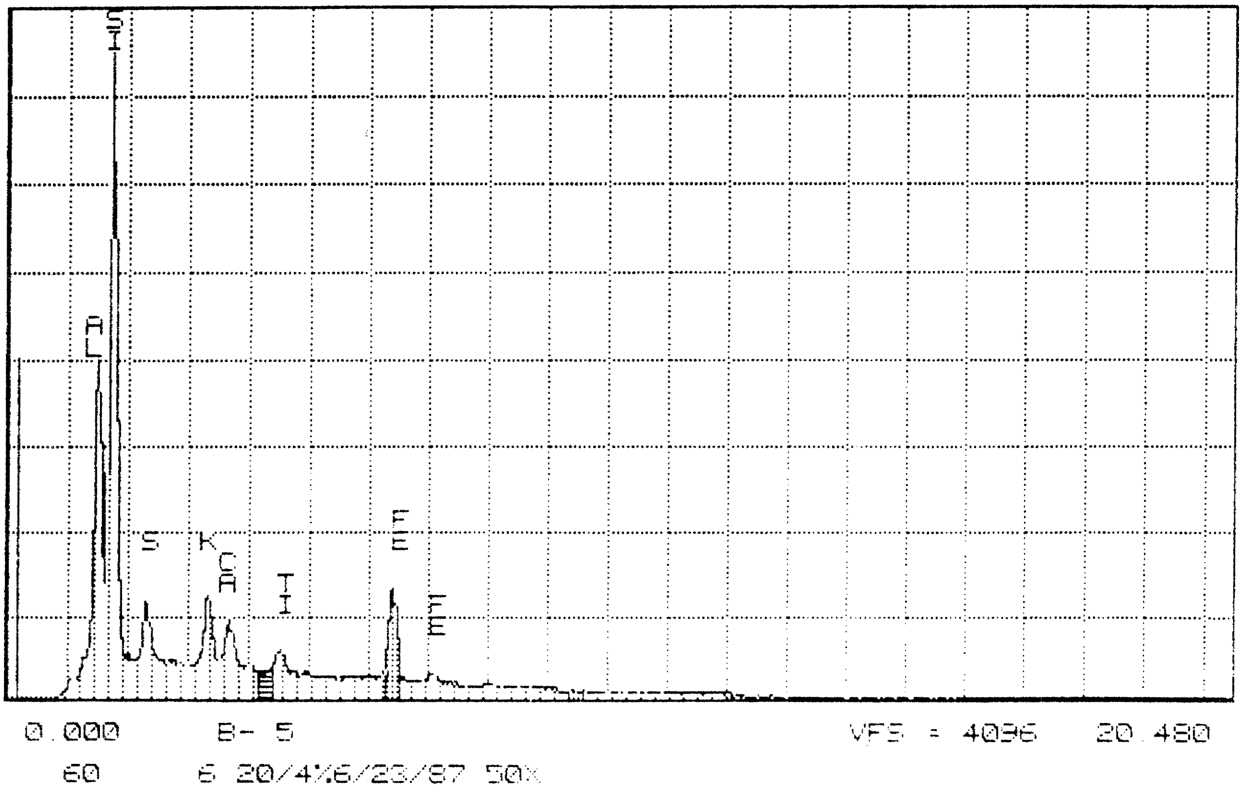

```
SEMI-QUANTITATIVE ANALYSIS: 7 20/4%6/23/87 35X
EL    NORM. K-RATIO

AL-K 0.14159 +- 0.00213
SI-K 0.25593 +- 0.00274
S -K 0.16103 +- 0.00229
K -K 0.04655 +- 0.00135
CA-K 0.07641 +- 0.00179
TI-K 0.03629 +- 0.00143
FE-K 0.23733 +- 0.00476
CU-K 0.04484 +- 0.00272

ZAF CORRECTION       20.00 KV       45.00 Degs

No. of Iterations  2
----     K       [Z]      [A]      [F]     [ZAF]   ATOM.%  WT.%
AL-K   0.141   0.996   1.519   0.983   1.489   20.10   15.87  *
SI-K   0.255   0.964   1.577   0.993   1.510   35.51   29.06  *
S -K   0.161   0.972   1.488   0.995   1.440   18.65   17.44  *
K -K   0.046   1.008   1.218   0.986   1.210    3.72    4.24
CA-K   0.076   0.985   1.170   0.990   1.142    5.62    6.57
TI-K   0.036   1.080   1.102   0.981   1.169    2.28    3.19
FE-K   0.237   1.082   1.028   0.993   1.105   12.05   19.73
CU-K   0.044   1.122   1.027   1.000   1.153    2.08    3.89
 * - High Absorbance

SSQ:
```

```
CMC, SEM/XEDS Analysis                      THU 08-MAR-90  09:04
Cursor: 0.000keV = 0        ROI     (0) 4.180: 4.380=0/sec
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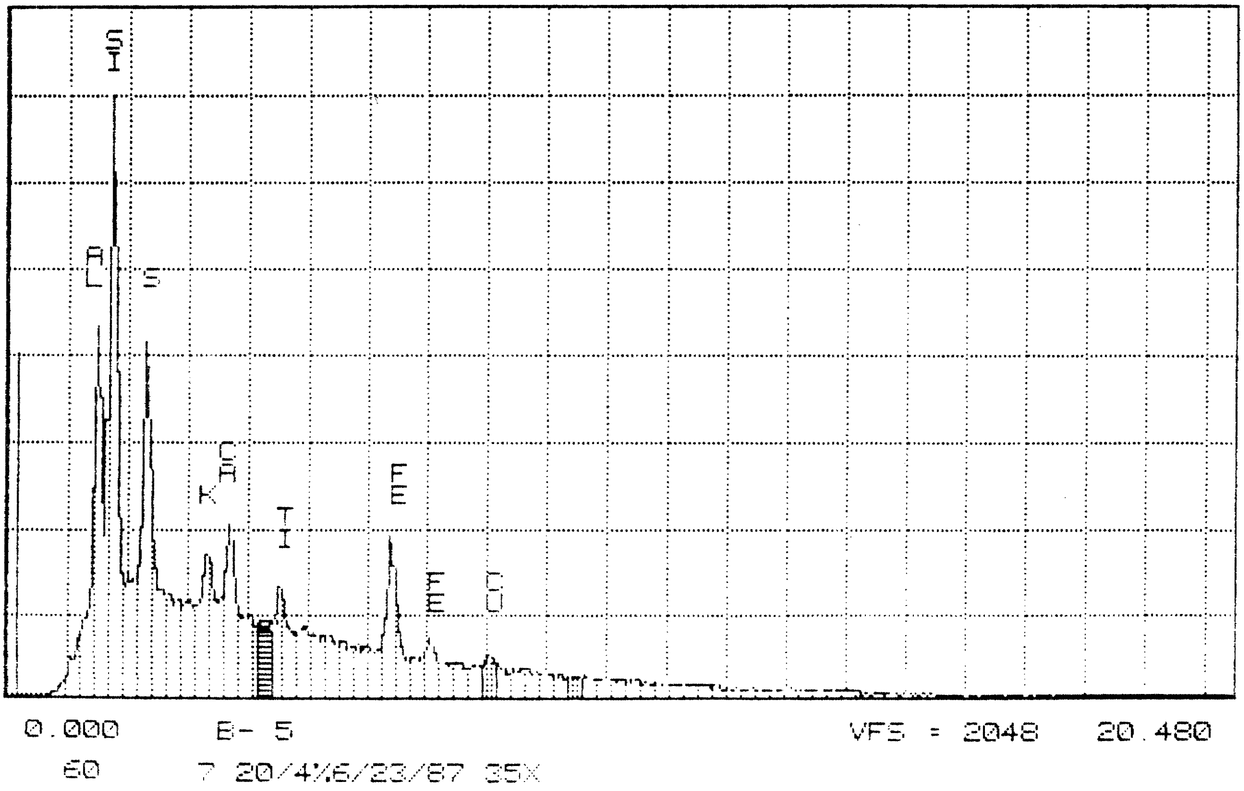

```
SEMI-QUANTITATIVE ANALYSIS: 8 20/4%6/23/87 35X
EL    NORM. K-RATIO

AL-K 0.16543 +- 0.00225
SI-K 0.21782 +- 0.00247
S -K 0.13415 +- 0.00204
K -K 0.02934 +- 0.00105
CA-K 0.06484 +- 0.00161
TI-K 0.03273 +- 0.00132
FE-K 0.30538 +- 0.00526
CU-K 0.05027 +- 0.00281

ZAF CORRECTION        20.00 KV       45.00 Degs

No. of Iterations  3
----      K      [Z]     [A]     [F]    [ZAF]   ATOM.%  WT.%
AL-K   0.165   0.991   1.589   0.986   1.554   24.77   19.21   *
SI-K   0.217   0.959   1.682   0.994   1.604   32.45   26.11   *
S -K   0.134   0.966   1.507   0.996   1.452   15.83   14.55   *
K -K   0.029   1.002   1.210   0.985   1.195    2.34    2.62
CA-K   0.064   0.979   1.157   0.988   1.121    4.73    5.43
TI-K   0.032   1.074   1.091   0.975   1.144    2.03    2.80
FE-K   0.305   1.075   1.023   0.993   1.094   15.51   24.96
CU-K   0.050   1.115   1.031   1.000   1.150    2.35    4.32
 * - High Absorbance

SSQ:
```

```
CMC, SEM/XEDS Analysis                  THU 08-MAR-90  09:13
Cursor: 0.000keV = 0        ROI    (0) 4.180: 4.380=0/sec
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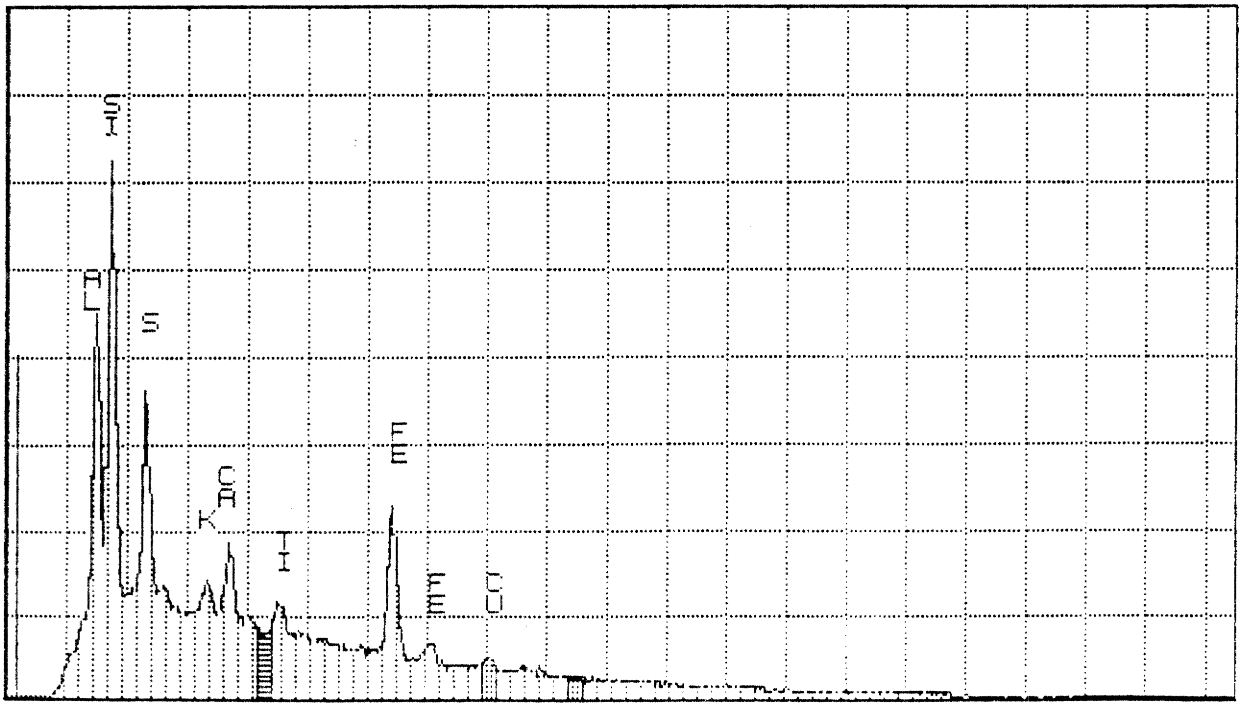
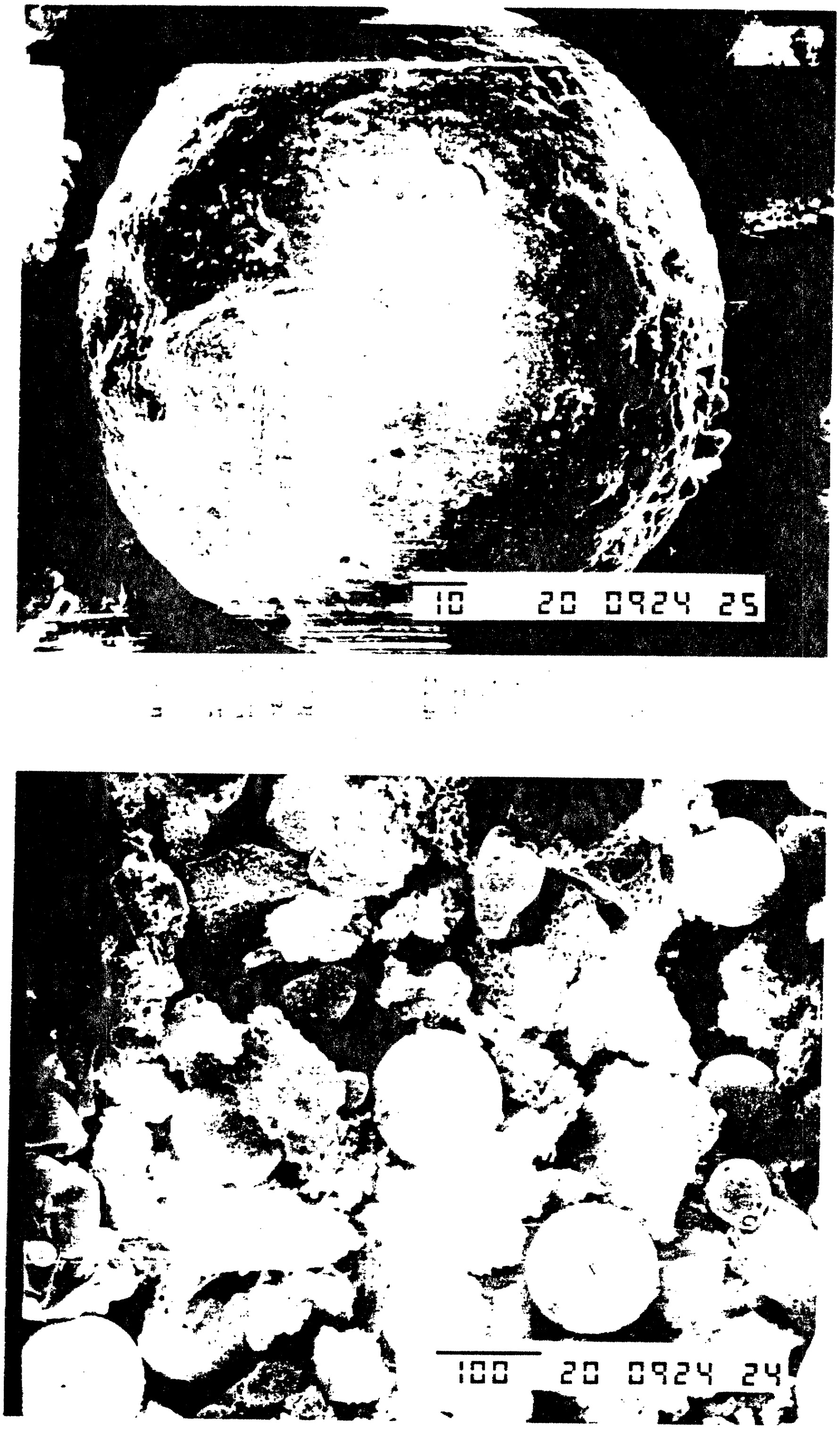
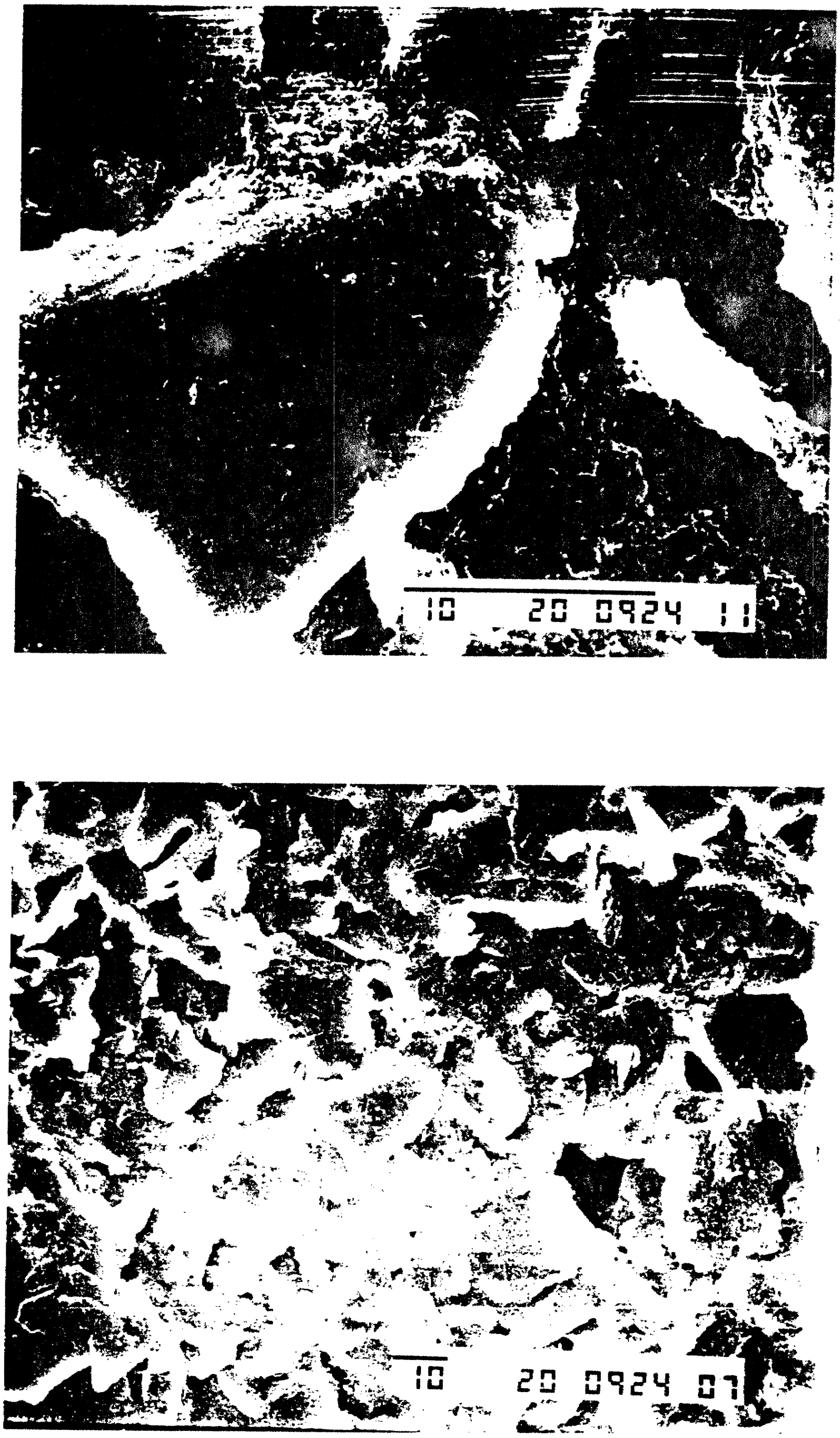


APPENDIX D



Run # 6 Economizer Fly Ash - 30% bdRDF/Coal, 4% Binder.



Run # 11 Economizer Fly Ash - 50% bdRDF/Coal, 4% Binder

APPENDIX E

Table XXXXIII: Detection Limits for ICP gas Samples Analyzed in mg/m^3

As	0.40
Hg	0.20
Se	0.40
Cr	0.04
Sb	0.20
Be	0.01
Cu	0.20
Tl	0.20
Zn	0.02
Cd	0.02
Pb	0.20
Ni	0.08
Ba	0.02

APPENDIX F

Statistical Analysis of Run # 2 and Run # 5 using the "Comparison of Two Experimental Means" Method:

$$X1 - X2 = \pm\sqrt{t\ S\ (N1 + N2) / (N1*N2)} \quad .....(1)$$

where

X1 = the mean of the first set of data

X2 = the mean of the second set of data

t = two sided statistical "t" value

S = standard deviation for both sets of data which can be calculated from

$$S = \sqrt{\{(N1-1)V1 + (N2-1)V2\} / \{(N1-1) + (N2-1)\}} \quad .....(2)$$

N1 = number of measurements of the first set of data

N2 = number of measurements of the second set of data

V1 = variance of the first set of data

V2 = variance of the second set of data

As

X1=1.03	V1=2.28	N1=4
X2=0.98	V2=1.52	N2=6

X1-X2= 0.05

at 95% confidence limit and 8 degrees of freedom t=2.31

S= 1.34 (from equation 2)

the right hand side of equation 1 equals ± 1.3

$X1 - X2 = 0.05 < \pm 1.3$

* so there is no difference between the two values at 95% confidence limit.

Hg

$X1=0.16$ $V1=0.04$

$X2=0.23$ $V2=0.07$

$X1 - X2 = -0.07$

** at 95% confidence limit and 8 degrees of freedom t=2.31.

S = 0.26 (from equation 2)

the right hand side of equation 1 equals ± 0.25.

$X1 - X2 = - 0.07 < \pm 0.25$

* so there is no difference between the two values at 95% confidence limit.

** at 90%, 80%, 68% confidence limit there is no difference between the two values.

** at 50% c.l. there is a difference between the two values.

Se

$X1 = 0.095$ $V1 = 0.036$

$X2 = 0.460$ $V2 = 0.396$

$X1 - X2 = -0.365$

S = 0.51 from eq. 2

**the right hand side of equation 1 equals ± 0.49 at 95% c.l. and 8 degrees of freedom

-0.365 < ± 0.49 so there is no difference at 95% c.l.

** at 80% c.l. the right hand side of eq. 1 equals ± 0.35

** so there is a difference at 80% c.l.

Cr

X1 = 0.798 V1 = 2.358

X2 = 0.087 V2 = 0.014

X1 - X2 = -0.711

S = 0.945 from eq. 2

**the right hand side of equation 1 equals ± 0.917 at 95% c.l. and 8 degrees of freedom

0.711 < ± 0.917 so there is no difference at 95% c.l.

** at 90% c.l. the right hand side of eq. 1 equals ± 0.65

** so there is a difference at 90% c.l.

Sb

X1 = 0.160 V1 = 0.102

X2 = 0.333 V2 = 0.277

X1 - X2 = -0.173

S = 0.460 from eq. 2

**the right hand side of equation 1 equals ± 0.446 at 95% c.l. and 8 degrees of freedom

-0.173 < ± 0.446 so there is no difference at 95% c.l.

** at 68% c.l. the right hand side of eq. 1 equals ± 0.173

** so there is a difference at 68% c.l.

Be

X1 = 0.0 V1 = 0.0

X2 = 0.002 V2 = 0.0

The values are very close to zero. It is hard to predict statistically but numerically the values are increased.

Cu

X1 = 1.28 V1 = 2.36

X2 = 0.60 V2 = 0.61

X1 - X2 = 0.68

S = 1.13 from eq. 2

**the right hand side of equation 1 equals ± 1.09 at 95% c.l. and 8 degrees of freedom

0.68 < ± 1.09 so there is no difference at 95% c.l.

** at 80% c.l. the right hand side of eq. 1 equals ± 0.61

** so there is a difference at 80% c.l.

Tl

X1 = 13.15 V1 = 1.455

X2 = 5.855 V2 = 4.684

X1 - X2 = 7.295

S = 3.0695 from eq. 2

**the right hand side of equation 1 equals ± 2.978 at 95% c.l. and 8 degrees of freedom

7.295 > ± 2.978 so there is a difference at 95% c.l.

Zn

X1 = 0.32 V1 = 0.20

X2 = 0.75 V2 = 2.14

X1 - X2 = - 0.43

S = 1.19 from eq. 2

**the right hand side of equation 1 equals ± 1.16 at 95% c.l. and 8 degrees of freedom

-0.43 < ± 1.16 so there is no difference at 95% c.l.

** at 68% c.l. the right hand side of eq. 1 equals ± 0.43

** so there is a difference at 68% c.l.

Cd

X1 = 0.008 V1 = 0.0002

X2 = 0.036 V2 = 0.0042

X1 - X2 = - 0.028

S = 0.052 from eq. 2

**the right hand side of equation 1 equals ± 0.051 at 95% c.l. and 8 degrees of freedom

$-0.028 < \pm 0.051$ so there is no difference at 95% c.l.

** at 80% c.l. the right hand side of eq. 1 equals ± 0.028

** so there is a difference at 80% c.l.

Pb

X1 = 0.569 V1 = 0.604

X2 = 0.938 V2 = 0.444

X1 - X2 = - 0.29

S = 0.71 from eq. 2

**the right hand side of equation 1 equals ± 0.689 at 95% c.l. and 8 degrees of freedom

$-0.29 < \pm 0.689$ so there is no difference at 95% c.l.

** at 68% c.l. the right hand side of eq. 1 equals ± 0.29

** so there is a difference at 68% c.l.

Ni

X1 = 1.85 V1 = 1.033

X2 = 1.22 V2 = 0.246

X1 - X2 = 0.63

S = 0.74 from eq. 2

**the right hand side of equation 1 equals ± 0.71 at 95% c.l. and 8 degrees of freedom

-0.63 < ± 0.71 so there is no difference at 95% c.l.

** at 90% c.l. the right hand side of eq. 1 equals ± 0.51

** so there is a difference at 90% c.l.

Ba

X1 = 0.005 V1 = 0.0001

X2 = 0.000 V2 = 0.0000

X1 - X2 = 0.005

S = 0.0061 from eq. 2

**the right hand side of equation 1 equals ± 0.0059 at 95% c.l. and 8 degrees of freedom

0.005 < ± 0.0059 so there is no difference at 95% c.l.

** at 90% c.l. the right hand side of eq. 1 equals ± 0.0040

** so there is a difference at 90% c.l.

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