

THE CONCENTRATION OF GERMANIUM IN COAL
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by

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TABLE OF CONTENTS

	Page
I. INTRODUCTION	1
II. LITERATURE REVIEW	3
History and Discovery of Germanium	3
Occurrence of Germanium	4
Metallurgy of Germanium	5
Properties of Germanium	5
Germanium in Coal	7
Methods of Coal Fractionation	8
Uses of Germanium	9
Outlook for Germanium	10
III. EXPERIMENTAL	11
Purpose of Investigation	11
Investigation Procedure	11
Materials	12
Equipment	15
Coal Used	16
Sizing of Coal	17
Specific Gravity Separations	20
Solvent Extraction of Coal	22
Flotation Tests	22

	Page
IV. DISCUSSION	24
Results	24
Size Analyses	24
Specific Gravity Separations	27
Solvent Extractions	31
Flotation Tests	36
Ash Analyses	49
Volatile Matter Analyses	52
Fixed Carbon Analyses	52
Germanium Analyses	52
Washability Curves	56
Juniper Theory	61
Analytical Difficulties	62
Preparation of Phenylfluorone	64
Ashing Temperatures	65
Ash Colors	68
Character of Coke Buttons	71
V. CONCLUSIONS	73
VI. SUMMARY	75
VII. SUGGESTIONS FOR FUTURE WORK	76
VIII. ACKNOWLEDGMENTS	78

	Page
IX. BIBLIOGRAPHY	80
X. VITA	100
APPENDIX	101
Sample Calculations	102
Germanium Analyses	102
Composites	104
Sampling and Analyses	109
Ash Analyses	110
Volatile Matter Analyses	110
Fixed Carbon Analyses	111
Germanium Analyses	111
Data	115

LIST OF FIGURES

	Page
Figure 1. Size Distribution of Coal Received	19
Figure 2. Germanium in Ash-free Coal vs. Size of Coal	25
Figure 3. Germanium in Ash vs. Size of Coal	26
Figure 4. Germanium in Ash-free Coal of Specific Gravity Fractions vs. Size of Coal	29
Figure 5. Germanium in Ash of Specific Gravity Fractions vs. Size of Coal	30
Figure 6. Percentage of Germanium Extracted by Hexane vs. Time of Run	34
Figure 7. Ash Content of Specific Gravity Fractions vs. Size of Coal	50
Figure 8. Germanium Content vs. Ash Content	51
Figure 9. Volatile Matter of Ash-free Coal of Specific Gravity Separations vs. Size of Coal	53
Figure 10. Fixed Carbon Content of Ash-free Coal of Specific Gravity Fractions vs. Size of Coal	54
Figure 11. Ratio of Concentration Obtained by Ashing Specific Gravity Fractions vs. Size of Coal	55
Figure 12. Analyses of Oversize Products vs. Size	57
Figure 13. Analyses of Undersize Products vs. Size	

	Page
Figure 14. Analyses of Float Products vs. Specific Gravity	59
Figure 15. Analyses of Sink Products vs. Specific Gravity	60
Figure 16. Germanium Recovered vs. Ashing Temperature	67
Figure 17. Calibration Curve Showing Germanium Content in Micrograms	103
Figure 18. Sketch of Analytical Distillation Setup	114

LIST OF TABLES

	Page
Table 1. Analyses of the Head Sample	18
Table 2. Results of Flotation Test 1	38
Table 3. Results of Flotation Test 2	39
Table 4. Results of Flotation Test 3	40
Table 5. Results of Flotation Test 4	41
Table 6. Size Distribution of Products of Flotation Test 4	43
Table 7. Ash Analyses of Sized Products of Flotation Test 4	44
Table 8. Germanium Content of Sized Products of Flotation Test 4	45
Table 9. Results of Separating the Sized Tailing Fractions of Flotation Test 4 by a Specific Gravity of 1.90 by Weight Per Cent	46
Table 10. Ash Per Cent of the Sink-Float and Sized Fractions of the Tailings from Flotation Test 4	47
Table 11. Germanium Content of the Sink-Float and Sized Fractions of the Tailings from Flotation Test 4 in Parts Per Million	48
Table 12. Germanium Recovery at Various Temperatures	66
Table 13. Ash Color of Petrographic Constituents	69

	Page
Table 14. Ash Color of the Products of the Specific Gravity Separations and of the Head Sample	70
Table 15. Character of Coke Buttons for Various Specific Gravity Fractions	72
Table 16. Germanium in Parts Per Million in the Ash-free Coal of the Sized Products of Flotation Test 4	116
Table 17. Germanium in Parts Per Million in the Ash of the Sized Products of Flotation Test 4	117
Table 18. Germanium in Parts Per Million of the Ash-free Coal of the Sink-Float and Sized Fractions of the Tailings from Flotation Test 4	118
Table 19. Germanium in Parts Per Million in the Ash of the Sink-Float and Sized Fractions of the Tailings from Flotation Test 4	119
Table 20. Weight Per Cent of Products of Sink-Float and Size Separations	120
Table 21. Ash Per Cent of Products of Sink-Float and Size Separations	121
Table 22. Volatile Matter Per Cent of Products of Sink-Float and Size Separations	122
Table 23. Fixed Carbon Per Cent of Products of Sink-Float and Size Separations	123
Table 24. Germanium in Parts Per Million of Products of Sink-Float and Size Separations	124

	Page
Table 25. Volatile Matter Per Cent of Ash-free Products of Sink-Float and Size Separations	125
Table 26. Fixed Carbon Per Cent of Ash-free Products of Sink-Float and Size Separations	126
Table 27. Germanium in Parts Per Million of Ash-free Products of Sink-Float and Size Separations	127
Table 28. Germanium in Parts Per Million in Ash of Products of Sink-Float and Size Separations	128
Table 29. Ratio of Concentration Obtained by Ashing Products of Sink-Float and Size Separations	129
Table 30. Weight Per Cent of Products of 1.50 Specific Gravity Separation of the Sized Fractions	130
Table 31. Ash Per Cent of Products of 1.50 Specific Gravity Separation of the Sized Fractions	131
Table 32. Volatile Matter Per Cent of Products of 1.50 Specific Gravity Separation of the Sized Fractions	132
Table 33. Fixed Carbon Per Cent of Products of 1.50 Specific Gravity Separation of the Sized Fractions	133
Table 34. Germanium in Parts Per Million of Products of 1.50 Specific Gravity Separation of the Sized Fractions	134
Table 35. Volatile Matter Per Cent of Ash-free Products of 1.50 Specific Gravity Separation of the Sized Fractions	135

	Page
Table 36. Fixed Carbon Per Cent of the Ash-free Products of 1.50 Specific Gravity Separation of the Sized Fractions	136
Table 37. Germanium in Parts Per Million of Ash-free Products of 1.50 Specific Gravity Separation of the Sized Fractions	137
Table 38. Germanium in Parts Per Million in Ash of Products of 1.50 Specific Gravity Separation of the Sized Fractions	138
Table 39. Ratio of Concentration Obtained by Ashing of Products of 1.50 Specific Gravity Separation of the Sized Fractions	139

I. INTRODUCTION

The possibility of extracting germanium from coal and recovering the coal for use as saleable fuel is quite attractive from a commercial standpoint, although doubt has been expressed as to this⁽¹⁴⁰⁾. The value of the germanium in the coal used in this investigation is \$22.80 per ton, based on the present price of \$295 per pound for unrefined germanium. At the present time, gold ores assaying \$10 per ton or even less are being worked at a profit, using complex metallurgical processes.

Selective mining to separate the germanium-enriched part of coal seams would include processes that are already common in mechanized mining of coal. Undercutting the face before shooting down the coal is accomplished by means of a cutting machine. This cutting machine removes the bottom three inches of coal by cutting a kerf in the coal. The coal removed, known as bug dust, is thus separated before the bulk of the low germanium coal is shot. Since the bug dust contains the highest concentration of germanium, it would be the logical product to treat for germanium extraction.

At the present time the most promising commercial source of germanium from coal is the fly ash of large coal burning plants. One of the main reasons for this is the concentration

effected by ashing of the coal. In many cases the germanium content of the ash is ten times greater than that of the coal from which the ash was derived.

The purpose of this investigation was to find a method or methods of concentrating the germanium in coal prior to extraction.

In this investigation the work was divided into two major phases. The first being to determine that component of coal that is most enriched in germanium and in the second phase to investigate possible means of concentrating the germanium-enriched component.

To determine that component most enriched in germanium, size and specific gravity fractionations were carried out on the coal sample received. Means of concentration investigated were sizing, washing the coal by means of specific gravity separations, solvent extraction with organic solvents, and froth flotation.

The combination of these methods of concentration, together with the orthodox metallurgy of germanium, could lead to a profitable means of extracting germanium from coal.

II. LITERATURE REVIEW

History and Discovery of Germanium

The first mention of germanium to be found in the literature was the statement in 1864 by J. A. R. Newlands, an English chemist, when he mentioned "that silicon and tin formed the extremities of a triad, the middle member of which is at present wanting"⁽¹⁰⁶⁾.

Mendeleef also recognized this, and in his periodic chart of 1871 he predicted many of the properties of the element, which he designated as eka-silicon⁽⁹³⁾.

The discovery of germanium in 1886 by the German chemist Clemens Winkler was a strong point in the support of Mendeleef's theory, which the chemists of that day were reluctant to accept.

Winkler was a professor of chemistry at the Freiburg School of Mines. He had been a practical mining man for 14 years before coming to Freiburg in 1873⁽¹¹¹⁾. In the summer of 1885 one of his associates, Albin Weisbach, professor of mineralogy, had discovered a new type of silver ore which he named argyrodite, and had asked Winkler to make a chemical analysis of the mineral. Winkler was unable to account for two per cent of the ore and by further work he was able to isolate the new element, which he named "germanium" in honor of his native land⁽¹⁶⁹⁾.

Germanium is in many ways a paradox. It is at the so-called "cross-roads" of the periodic chart⁽⁷²⁾ and is thus neither metal nor nonmetal and neither conductor nor nonconductor. It is more appropriately called a metalloid semi-conductor. In chemical reactions it acts much like silicon and is found associated with nearly all silicate rocks. The appearance of the element is decidedly metallic, and the element has a very high mechanical Q, that is, an undamped bar will ring for many seconds when struck⁽⁷⁶⁾.

Occurrence of Germanium

Germanium has never been found free in nature. It may occur in the form of germanates, similar to silicates, but the most common occurrence is as an associated sulfide with deposits of the metal sulfides of tin, lead, zinc, copper, and mercury. Germanium is widely distributed. Its concentration in the earth's crust is low, averaging 7 ppm, and the element ranks 41st in abundance^(31,32,91,152). It is so finely disseminated that it has never been petrographically identified⁽⁷⁷⁾. Traces of germanium have been found in meteorites, topaz, granite, limestones, vichy water, plants, and coals^(7,41,50,100,114,124,129).

At present germanium is being produced commercially as a by-product from zinc refining in the United States and from the treatment of flue dusts in Great Britain. Potentially, an important additional source will be the germanite ores of South Africa (5,33,40,85,87,97,101,120,122,146,156,162,167,168).

Metallurgy of Germanium

In the extraction processes, the germanium-bearing material is made water-soluble using basic fluxes. The soluble germanium is then converted to the volatile tetrachloride, with subsequent purification by distillation. The pure germanium tetrachloride is hydrolyzed to the dioxide, which is converted to the metal in an atmosphere of hydrogen. Because the germanium absorbs hydrogen this leaves the element in the form of a porous sponge. Solid ingots of germanium are obtained by melting the sponge in a vacuum furnace (21,40,53,66,76,77,97,98,99,120,122).

Properties of Germanium

The metal is extremely brittle and will shatter when Brinell hardness testers are used. The hardness is about 6.25 on Mohs scale. Germanium is very resistant to attack by all ordinary acids and alkalis at room temperature, and

has been used to make tarnish-proof mirrors because of its optical reflectivity and stability at ordinary temperatures. However, a three per cent solution of hydrogen peroxide will completely dissolve germanium⁽¹¹⁷⁾.

A few of the pertinent facts are^(27,52,53);

Atomic weight	72.60
Atomic number	32
Density	5.35 g/cc
Valence	-4,+4,+2
Lattice form	Diamond
Ductility	Frangible
Melting point	958°C
Boiling point	volatile at 2700°C
Appearance	Bright metallic
Atomic radius	1.22 Å
Optical reflectivity	Approximately 50 per cent
Specific heat	0.072 cal/gm °C

Germanium is transparent to infra-red light.

Germanium in Coal

The occurrence of germanium in coal was first noted in 1930 by Goldschmidt^(47,48). Since that date, investigators have noted the occurrence of germanium in the coals of all continents^(5,12,34,44,56,57,58,62,63,95,96,97,108,117,131,141,143,145,146,170,171). The most marked concentrations in coal seams generally occur where the coal is adjacent to rock formations. The highest isolated concentrations of the element have been found in cauldron vitrains and fossil stumps^(5,142). The concentration varies considerably in both vertical and lateral extent. Sections of some seams may run as high as fifty parts per million (ppm), while others will contain no appreciable germanium^(5,108).

The nature and origin of the germanium in coal is not known, but most investigators feel that it is part of the coal substance and not connected with the extraneous ash or rock in the coal bed⁽⁶²⁾. The nature of the germanium has been suggested to be either as a sulfide or tied up as a complex tannin-like substance. Some investigations consider the origin to have been from the original plants that formed the coal, while others favor the idea of the germanium being adsorbed from solutions that passed through the coal^(47,62).

Methods of Coal Fractionation

Coals have been conveniently classified by means of their petrographic constituents, these constituents having definite relationships to the original type of plant substance from which the coal was formed (10,15,38,62,70,84,103,115,116,128,130,136,137,147,157,158,159,163).

The petrographic constituents differ in their physical properties. Friability, the tendency for breaking down, has been employed in effecting concentrations of the constituents by sizing. Vitrain, the glassy looking component, usually reports in the finest size fractions (15,86,94). Vitrain has been shown to contain most of the germanium (62).

Specific gravity separations have been applied to coal to reduce their ash content by removing the rock and shale from the coal (94).

Solvent extraction of coal by means of organic solvents has been investigated for many years in hopes of shedding light on the nature of coking, and for studies on the chemical nature of coals (9,11,24,25,49,61,78,79,86,112,113).

Froth flotation is readily adaptable to fine sizes of coal and is a highly selective separating process when done under controlled conditions (1,18,19,60,94,135,150,151).

Uses of Germanium

Until relatively recent, the uses of germanium were minor. It had been used to treat anemia; it made possible a gold alloy that was well suited for dental work; it was used in place of silicon to make glasses with special optical properties; and it was an interesting laboratory curiosity^(66,67).

In 1941, researchers at Purdue University showed that germanium made an excellent semi-conducting material for use in diodes to rectify alternating currents. These germanium diodes quickly replaced vacuum tube rectifiers in low power applications and present developments have made possible germanium power rectifiers that handle 2000 watts with an efficiency of 98 to 99 per cent^(27,28,104). These investigations led to methods whereby germanium was obtained that had less than one part of impurity per ten billion parts of germanium. This high purity germanium is selling for \$565 per pound.

Further work on germanium led to the development of the transistor by the Bell Telephone Laboratories in 1948⁽⁶⁾. These transistors can do all the jobs that a conventional vacuum tube triode can do plus a few extra; also, it takes 1/60 the space, requires 1/20,000 as much power to do the same job, and the life expectancy has not yet been

determined^(88,110). These and future developments¹ will undoubtedly cause a large demand for germanium. The price for unrefined germanium is now \$295 per pound.

There are many excellent reviews on the compounds of germanium and on the methods for its analysis^(2,4,8,16,20,37,44,45,46,59,65,71,72,73,82,92,105,107,133,138,139,154).

Outlook for Germanium

Since coal is the largest ultimate source of germanium, and because continued developments in the field of electronics will create a growing demand for germanium, future needs for germanium will probably be met by recovery from coals⁽¹³²⁾.

¹ A new type of transistor that will outperform the vacuum tube tetrode has been announced by the Bell laboratories.

III. EXPERIMENTAL

Purpose of Investigation

The purpose of the investigation was to determine a method or methods for concentrating the germanium in coal prior to extraction.

Investigation Procedure

A washability study was carried out to determine the effect of sizing and specific gravity separations on the concentration of germanium. In addition to this, a series of tests was made to correlate germanium content with volatile matter, fixed carbon, and/or ash.

The concentration of the germanium by means of solvent extraction was included as a promising method with attractive possibilities.

An alternate method investigated for concentrating the germanium in the coal was froth flotation.

Materials

The following materials were used in this investigation:

Acacia, Gum Arabic. White powder, U. S. P., Code No 1212, Lot No K187. Obtained from Baker and Adamson. Used as colloidal suspensoid.

Acetone. Practical. Obtained from Eastman Kodak Company. Used as organic solvent.

Aerofroth 80 Frother. Obtained from American Cyanamid Company. Used as flotation agent.

Aerosol OS. Wetting agent. Obtained from American Cyanamid Company. Used as flotation agent.

Anthracene Salts. Sample No 54478, May 26, 1954. Obtained from Ironton Plant, Barrett Division, Allied Chemical and Dye Corporation. Used as organic solvent.

Barrett-634. Coal tar creosote. Obtained from Barrett Division, Allied Chemical and Dye Corporation. Used as flotation reagent.

Benzaldehyde. Chlorine free. Obtained from Eastman Kodak Company. Used in synthesis of phenylfluorone.

Benzene. Practical. Obtained from Eastman Kodak Company. Used as organic solvent.

Dowfroth 250. A propylene glycol ether. Obtained from Dow Chemical Company. Used as flotation reagent.

Germanium Dioxide. Lot No 1-971-802, Batch No RP-2. Obtained from Eagle-Picher Company. Used as analytical standard.

Hexane, Petroleum Ether. Obtained from Eastman Kodak Company. Used as organic solvent.

Hydrochloric Acid. Reagent, C. P., Sp. Gr. 1.18. Obtained from Baker and Adamson. Used as analytical reagent.

Methanol. Absolute, Reagent, A. C. S., Code No 1212, Lot No K187. Obtained from Baker and Adamson. Used as a solvent for the phenylfluorone.

Naphthalene. Manufactured by Koppers Company. Used as organic solvent.

1,2,4-Phenyl Triacetate, Triacetylhydroxyhydroquinone. Obtained from Eastman Kodak Company. Used in preparation of phenylfluorone.

Phenylfluorone. Obtained from Jasonols Chemical Corporation. Used as a specific reagent for germanium.

Pyridine. Practical. Obtained from Eastman Kodak Company. Used as organic solvent.

Quinoline. Technical. Obtained from Eastman Kodak Company. Used as organic solvent.

Sodium Carbonate. Anhydrous powder, reagent, A. C. S., Code No 2248, Lot No H015. Obtained from Baker and Adamson. Used as analytical reagent.

Sodium Hydroxide. Pellets, reagent, A. C. S., Code No 2255, Lot No J197. Obtained from Baker and Adamson. Used as analytical reagent.

Sulfuric Acid. Reagent, C. P., Code No 1180, Lot No E712021. Obtained from Baker and Adamson. Used as analytical reagent.

Tallso. Tall oil skimmings, "Black Liquor." Obtained from Industrial Chemical Sales Division, West Virginia Pulp and Paper Company. Used as flotation agent.

Tetrahydronaphthalene, Tetralin. Practical. Obtained from Eastman Kodak Company. Used as organic solvent.

Equipment

The following equipment was used in this investigation:

Assayers Mill. Hand-operated. Manufactured by Wilson Brothers. Obtained from Fisher Scientific Company.

Ball Mill. Abbe, porcelain, 4 quart. Obtained from Burrell Corporation.

Beckman pH Meter. Serial No 30883M, battery-powered, industrial model. Obtained from Fisher Scientific Company.

Centrifuge. International Clinical, Model No CL, No 1718A. Obtained from Fisher Scientific Company.

Colorimeter. Klett-Summerson photoelectric, Serial No 3366, equipped with filter No 54. Loaned from Chemistry Department, Virginia Polytechnic Institute.

Drying Oven. Serial No 16005. Manufactured by Burrell Corporation.

Flotation Machine. Fagergren, laboratory, Serial No 5114101. Manufactured by Western Machinery Company.

Furnace. Electric, ashing, type MPLA, Serial No 1894. Manufactured by Cooley Electric Company.

Screens. Round-hole, punch-plate. Manufactured by Hendrick Manufacturing Company, Carbondale, Pennsylvania.

Screens. Tyler standard series. Manufactured by W. S. Tyler Company.

Soxhlet Micro Extraction Apparatus. Pyrex, with 3 joints. Obtained from Fisher Scientific Company.

Volatile Matter Furnace. Hoskins, type FA120, Serial No 21677. Obtained from Fisher Scientific Company.

Coal Used

The coal used in these investigations was obtained from Mr. Leslie Larsen, who stated in his letter of December 15, 1953 to C. T. Holland, that the coal was hand picked from the bottom three inches of the seam. The seam was the Lower Bakerstown seam of the Conemaugh formation.

The coal was delivered to Blacksburg by rail and arrived in three double-strength burlap feed sacks. The total weight of coal received was 459.3 pounds. The coal was divided by means of ASTM recommended procedures and 231.4 pounds were put aside for future use while the remaining 227.4 pounds were taken for a head sample. It was noticed that the coal was very friable and that gentle handling was required to minimize the formation of excessive dusts and fines. The head sample was prepared by coning, quartering, crushing, and splitting methods as recommended in the ASTM

standards. A sample was sent to Dr. A. J. W. Headlee, Chief Chemist, West Virginia Geological Survey for his analysis of the germanium content and a sample was retained for analysis in the mining laboratories. The analysis of the head sample is shown in Table 1.

Sizing of Coal

After the head sample had been taken the remainder of the 227.4 pounds was screened. The sizes used were 1-1/2", 3/4", 3/8"; 4, 8, 14, 28, 48, 100, and 200-mesh. The three larger sizes were round-hole punch-plate screens, and the seven smaller sizes were Tyler Standard Series screens. The coal was screened by hand and as the smaller screens were used it became possible to split the amount of sample in the undersize, thus reducing the amount of work, but not affecting the validity of the results. The guide used in making these splits was the sampling chart prepared by Battelle Memorial Institute from data collected by Taggart^(94,155). All products were weighed and the distribution of sizes is presented in Figure 1. The eleven sized products were then put into bags and saved for the specific gravity separations.

Table 1

Analyses of the Head Sample

Moisture	0.74 %
Dry Basis:	
Ash	15.6 %
Volatile Matter	28.9 %
Fixed Carbon	<u>55.5 %</u>
	100.0
Sulfur	1.06 %
Germanium:	
In Mining Laboratories	35 ppm
U.S.B.M.	37 ppm
Headlee	57 ppm

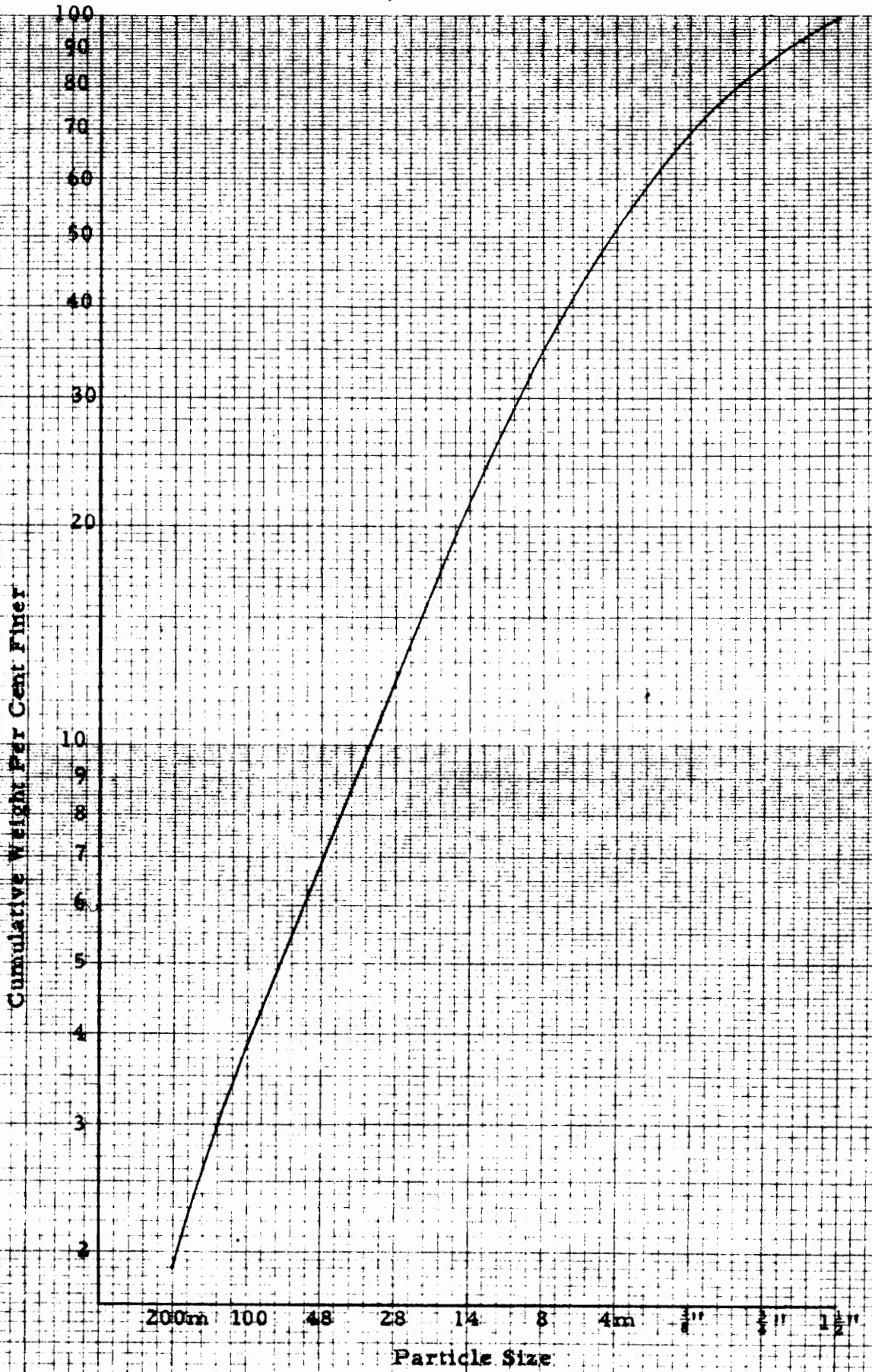


Figure 1 Size Distribution of Coal Received

Specific Gravity Separations

The sized fractions of the coal were further separated by making specific gravity separations of all sizes. The specific gravities used were 1.25, 1.30, 1.35, and 1.50. These gravities were obtained by using calcium chloride solutions for the first three gravities, and zinc chloride solutions for the 1.50 specific gravity solution. The separations were carried out in large jars, separatory funnels, and centrifuge tubes, depending on the size of the coal. In the larger sizes down to -4+8 mesh the separations were carried out by placing the coal in a jar containing the 1.35 specific gravity solution and allowing the particles to sink or float depending on their density. The material that floated was then transferred to the jar containing the 1.30 specific gravity solution and the same process repeated, with the float material being transferred to the 1.25 jar. In this manner four products were obtained, Sink 1.35, Float 1.35-Sink 1.30, Float 1.30-Sink 1.25, and Float 1.25 specific gravity fractions. The solutions were checked for specific gravity at frequent intervals with a hydrometer and adjusted by adding water or salts, so that the specific gravity was maintained within ± 0.005 specific gravity.

In the sizes from -8+14 mesh down to -28+48 mesh, the separatory funnels were used. About one-third of the funnel was filled with coal and the specific gravity solutions were poured in until the funnel was about three-fourths full. The contents were then well shaken and allowed to come to equilibrium. When equilibrium had been attained the sink material was drawn off at the bottom and the process repeated until the entire size had been separated.

The two smaller sizes, -48+100 mesh and -100+200 mesh, were separated into gravity fractions by the use of a centrifuge. The centrifuge tubes were made of Lusteroid, a clear plastic, and when the tubes were taken out of the centrifuge it was possible to pinch the tubes closed at the point where one could see the near-gravity material, thus sealing the sink material and allowing the float material to be poured off.

The minus 200 mesh size was not separated into gravity fractions due to the impracticability of obtaining good separations; the viscosity of the gravity solutions, and the small size of the particles caused an undifferentiated suspension to be formed. In all separations other than those done in the jars the products from each separation were washed free of chlorides, as determined by taste, and dried in a steam-heated oven at 90°C before separation at the next lower gravity.

Solvent Extraction of Coal

The use of organic solvents to extract the germanium from coal was investigated by using micro-Soxhlet extraction apparatus. The solvents used were benzene, naphthalene, anthracene, pyridine, quinoline, hexane, chloroform, tetralin, gasoline, alcohol, water, hydrochloric acid, ammonium hydroxide, acetone, and carbon tetrachloride. Extraction runs for 16 hours were made with each of the solvents; the residues were then analyzed for germanium. It was thus possible to eliminate many solvents as being unsatisfactory for further investigation. The best results of the tests were obtained with hexane which extracted 48 per cent of the germanium while only removing 0.2 per cent of the coal substance. As a result of this preliminary study, an investigation was made to determine the effect of time on the degree of extraction.

Flotation Tests

Flotation tests were run to see if a germanium concentrate could be made. The coal used was the minus 8 mesh fraction set aside during preparation of the head sample. This coal was used directly in the first test, but all other tests were run on the coal fraction screened to remove the + 28 mesh material. In each test, 250 grams of coal were used; this gave a pulp density

of approximately 10 to 12 per cent. The flotation tests were carried out in a 500-gram laboratory Fagergren flotation machine with a glass cell in order that changes in pulp appearance could be observed during tests.

Four flotation tests were run. In the first test, Dowfroth 250 was used and the froth collected was called the concentrate; Tallso was then added and all material that floated was called the middlings, and the underflow was called tailings.

In the second test, no reagents were added and the first froth collected was designated concentrate; AC 80 was then added, this second froth was designated middlings, and the underflow was called tailings.

In the third test, Aerosol OS, AC 80, and Barrett-634 were used in that order. Time of collection was a variable factor in this test, in which five products were obtained.

In the fourth and last test, Barrett-634 was used in two stages, giving a concentrate, middlings, and tailings. Each of these last three products was screened into three size fractions for closer determination of germanium distribution.

The tailings from the fourth test apparently required further fractionation and these sized fractions were further separated at a specific gravity of 1.90. All flotation test products and fractions thereof were analyzed for ash and germanium.

IV. DISCUSSION

Results

Size Analyses. The germanium content of the size fractions based on the ash-free coal and in the ash varied with the size of the coal (see Figures 2 and 3), both values reaching a peak in the -8+14 mesh coal. At this size the ash-free coal and the ash assayed, respectively, 55 and 428 ppm germanium. The corresponding values for the head sample were, respectively, 41 and 224 ppm germanium.

Other investigators⁽¹¹⁶⁾ on the Bakerstown coal have shown that the petrographic composition of the coal will vary with the size of the particles examined. In the reference mentioned the bright attrital coal which is equivalent to the clarain dropped from 70 to 40 per cent in going from 10 to 325 mesh while the anthraxylon, which is equivalent to the vitrain, rose from 5 to 55 per cent in the same range; the dull attrital coal, equivalent to the durain, dropped from 25 to 5 per cent in the range mentioned. As previously stated, the anthraxylon tends to concentrate in the fine sizes, while the attrital coal tends to concentrate in the coarser sizes; the rock and shale of most coals is also known to be concentrated in the largest sizes. Since the

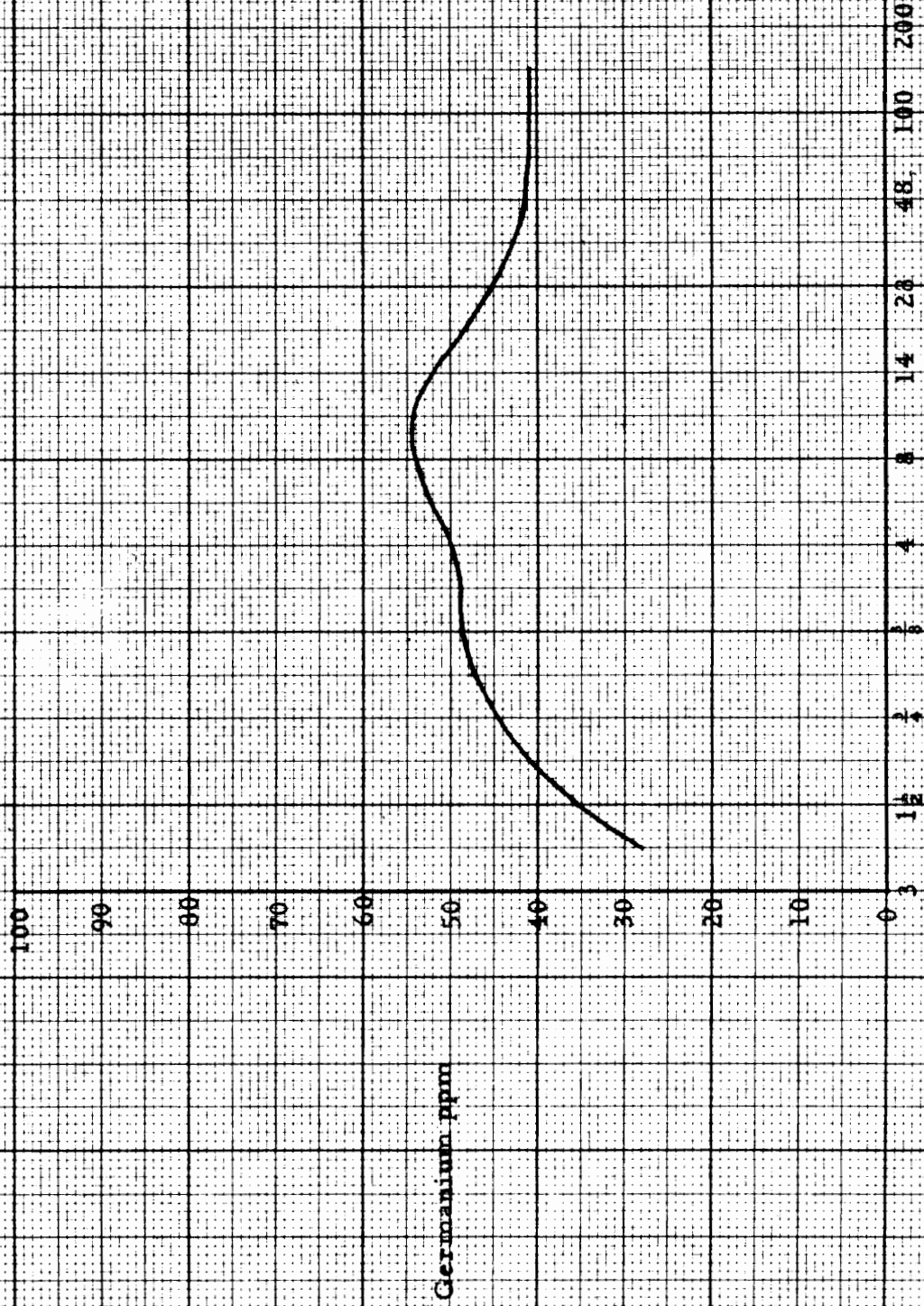


Figure 2 Germanium in Ash-Free Coal vs. Size of Coal

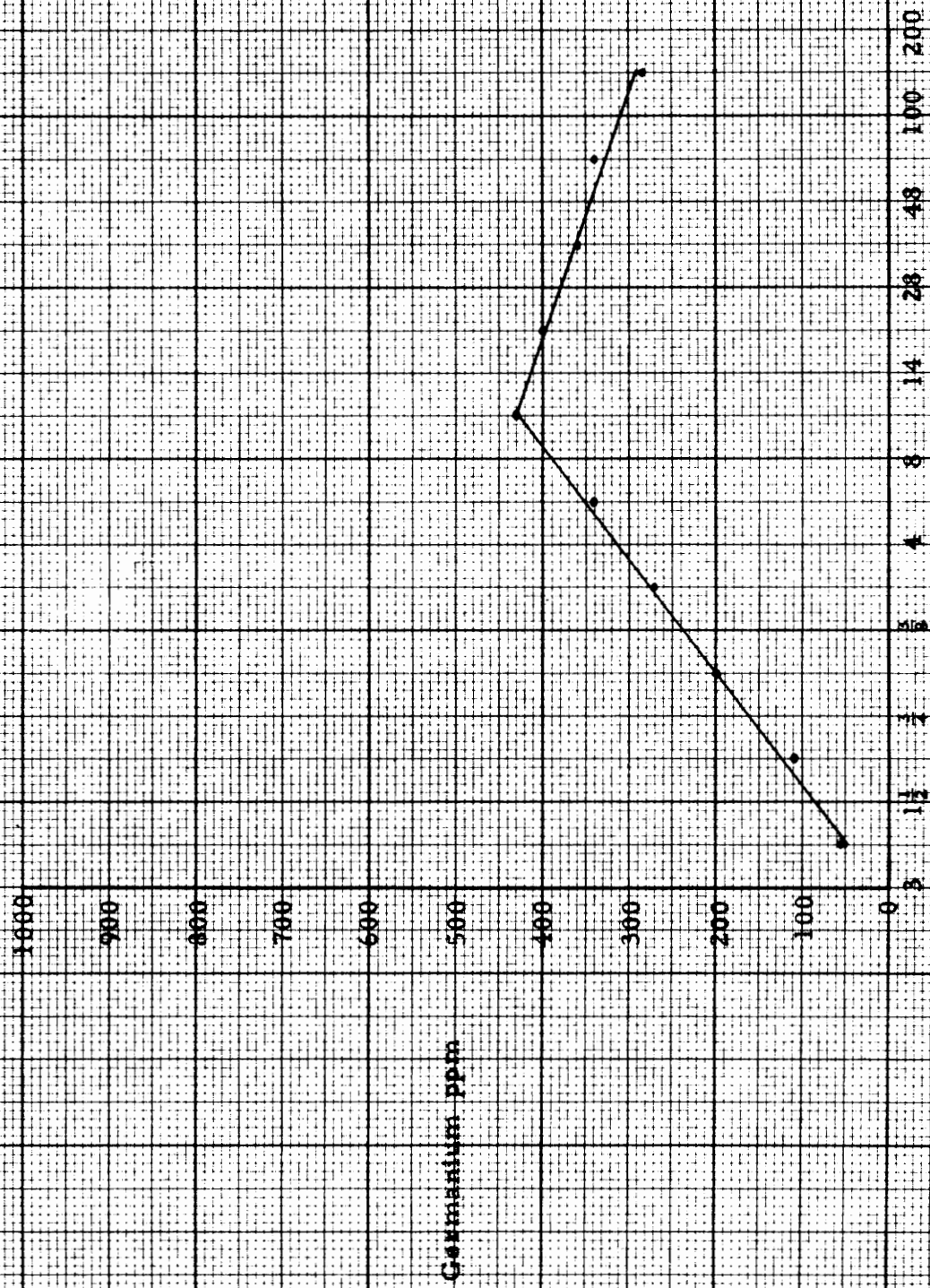


Figure 3 Germanium in Ash vs. Size of Coal

concentration of germanium reaches a maximum in the middle of the size range, it is difficult to deduce which petrographic component is responsible for the germanium. The germanium concentration may come about as an interaction between several of the components. Apparently, the germanium is chiefly associated with the anthraxylon since the concentration is slightly higher in the small sizes than it is in the large sizes. Sizing the coal to obtain high concentrations of germanium is inadvisable by itself, since too much of the germanium is lost, and the ratio of concentration is less than two.

As explained later in the discussion of flotation test 4, it may be that the germanium is contained in a component of the coal that is only incidentally associated with the common petrographic constituents of the coal. This would explain the higher concentrations in the finer sizes because of the more complete liberation of the petrographic constituents in the finer sizes. This subject warrants further investigations.

Specific Gravity Separations. In making specific gravity separations it was noted that there was very little material in the Float 1.25 fraction. The material reporting in this fraction was mostly extraneous material such as grain (from the burlap feed sacks), paper, and bits of wood and trash. Most of this material was removed by drying the coal and then making

a separation at specific gravity of 1.00 by using water. Since the amount of Float 1.25 was so small, this fraction has been composited with the Float 1.30 fraction in presenting the data.

On the two larger sizes, separations were carried out at gravities of 1.40, 1.50, and 1.60 as well, but the results indicated that no significant advantage was gained thereby. For example, in the two larger sizes the germanium contents of both the Sink 1.35 and the Sink 1.50 are 15 ppm. A specific gravity separation was made at 1.275 on the -4+8 fraction to see if any concentration of germanium could be obtained in this manner. There was no notable increase in the germanium content based on the ash-free coal, but, when examined on the basis of germanium in the ash, the concentration was increased almost five times. A separation was made on the eight smaller sizes at a specific gravity of 1.50 in order to determine concentration of germanium with increased recovery. A separation at 1.50 specific gravity recovered almost 98 per cent of the germanium in less than 90 per cent of the feed and the ash content was reduced from sixteen to six per cent, thus increasing the concentration of germanium in the ash from 224 to 723 ppm.

Examination of Figures 4 and 5 and Table 27 points out that the highest concentration of germanium in the coal was in the Sink 1.30-Float 1.35 specific gravity fraction with the

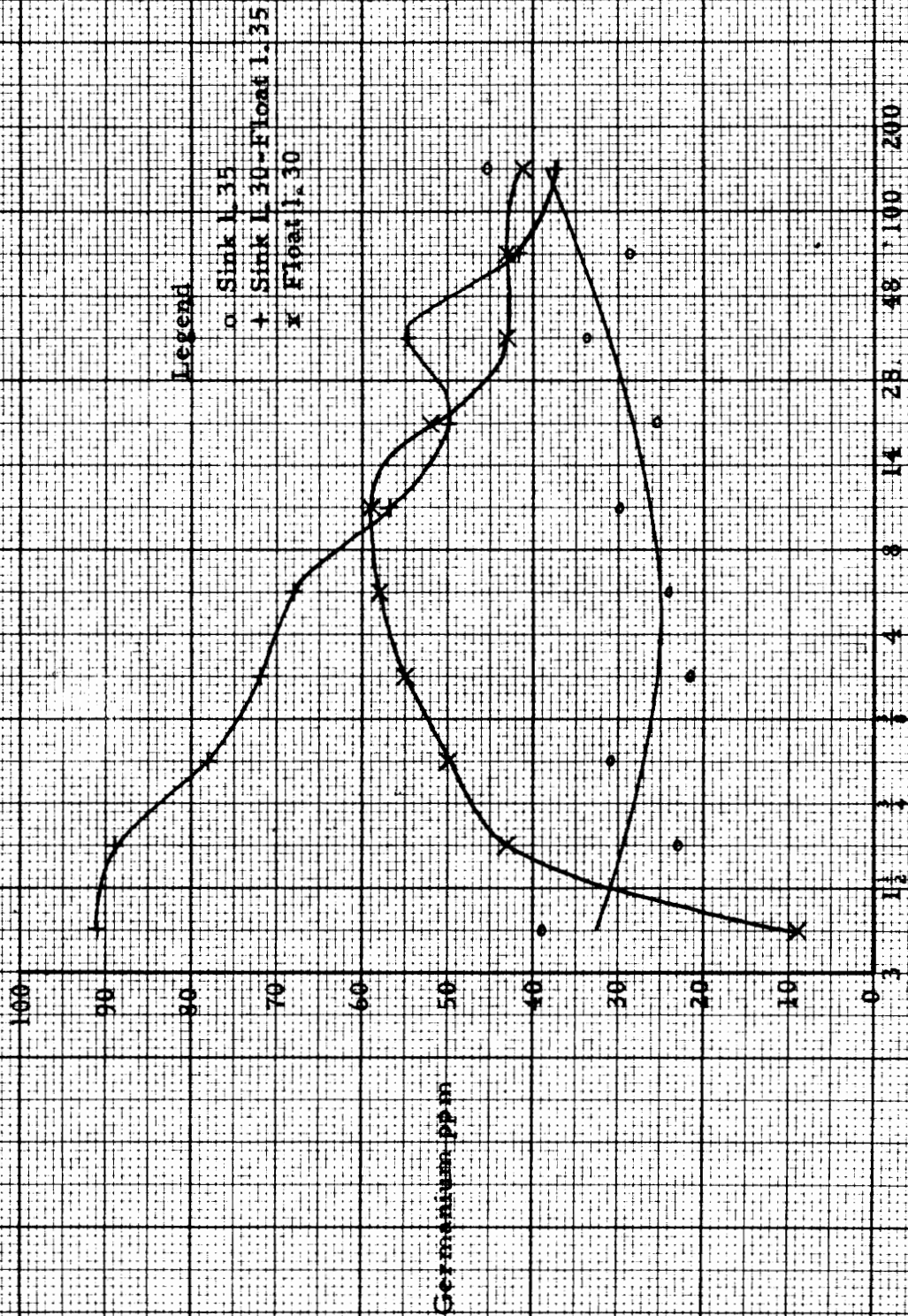


Figure 4 Germanium in Ash-Free Coal of Specific Gravity Fractions vs. Size of Coal



Figure 5 Germanium in Ash of Specific Gravity Fractions vs. Size of Coal

highest value being 91 ppm in the ash-free coal. The average for this gravity fraction was 55 ppm on the same basis. On the other hand, the concentration of germanium in the ash was greatest in the Float 1.30 fraction with the highest value being 2000 ppm and the average being 1190 ppm (see Figures 4 and 5). The concentrations of germanium in the head sample, based on ash-free coal and on ash, were 41 and 224 ppm, respectively. Thus, specific gravity separation can increase the concentration of germanium in ash-free coal, and it can increase the concentration of germanium in the ash. The germanium content of the sink products was inversely proportional to the separating gravity; this holds true for both the germanium in the ash-free coal and the germanium in the ash.

Interestingly enough, the highest value based on germanium in coal was obtained in the coarsest size, while the highest content of germanium in the ash was obtained in the -100+200 range.

Solvent Extractions. The use of organic solvents to extract the germanium from coal was investigated by using micro-Soxhlet extraction apparatus. The principle of the Soxhlet apparatus is the continuous refluxing of fresh solvent, and for this reason only volatile solvents can be used effectively. In operation, the material to be extracted is placed

in a fat-free paper thimble which is inserted in the extractor between the refluxing condenser and the flask containing the solvent. The three parts are then connected and heat is applied to the flask, while cooling water is circulated through the condenser. The vapors travel from the flask, through the extractor, and into the refluxing condenser where it is condensed, drips into the extractor, and forms a vapor trap. This continues until the liquid level in the extractor is above the level in the siphon tube, at which time the contents of the extractor empty into the flask and the operation begins again. This cycle of renewing the solvent to the sample is one of the most effective extraction processes known.

In the investigations on the solvation of coal, all solvents that were known to be effective in coal extraction were tried. The solvents used were benzene, naphthalene, anthracene, pyridine, quinoline, hexane, chloroform, tetralin, gasoline, alcohol, water, hydrochloric acid, ammonium hydroxide, acetone, and carbon tetrachloride. These solvents were each used for a period of sixteen hours and the residues were then analyzed for germanium. By this method it was possible to eliminate many solvents as being unsatisfactory for further investigation; benzene, chloroform, gasoline, alcohol, water, hydrochloric acid, ammonium hydroxide, acetone, and carbon tetrachloride extracted little or none of the

germanium. Some solvents were good from the standpoint of germanium removed, but they were unselective and extracted too much coal, without effecting any great concentration. Naphthalene, anthracene, pyridine, quinoline, and tetralin merely ripped the coal apart without selective extraction of the germanium. The best results of the tests were obtained with hexane which extracted 48 per cent of the germanium while only removing 0.2 per cent of the coal substance thus giving a concentration of 250.

As a result of this preliminary study, an investigation was made to determine the effect of time of extraction on the degree of extraction. These were run for periods of 2, 4, 8, and 16 hours using hexane on a coal fraction that was richer in germanium than the sample used in the preliminary 16-hour tests. Coal extracted during each run was, respectively, 1.5, 2.1, 3.2, and 2.1 per cent. The values obtained for the 2, 4, and 16-hour tests show an extraction of germanium of 3.5, 7.0, and 32.0 per cent (see Figure 6). The amount of coal extracted is insignificant and seems to bear no relation to the germanium extracted. The amount of germanium extracted by the hexane is almost linear with time in the range investigated. The maximum ratio of concentration obtained was about 16:1. The main disadvantage to this phase of the investigations was the lack

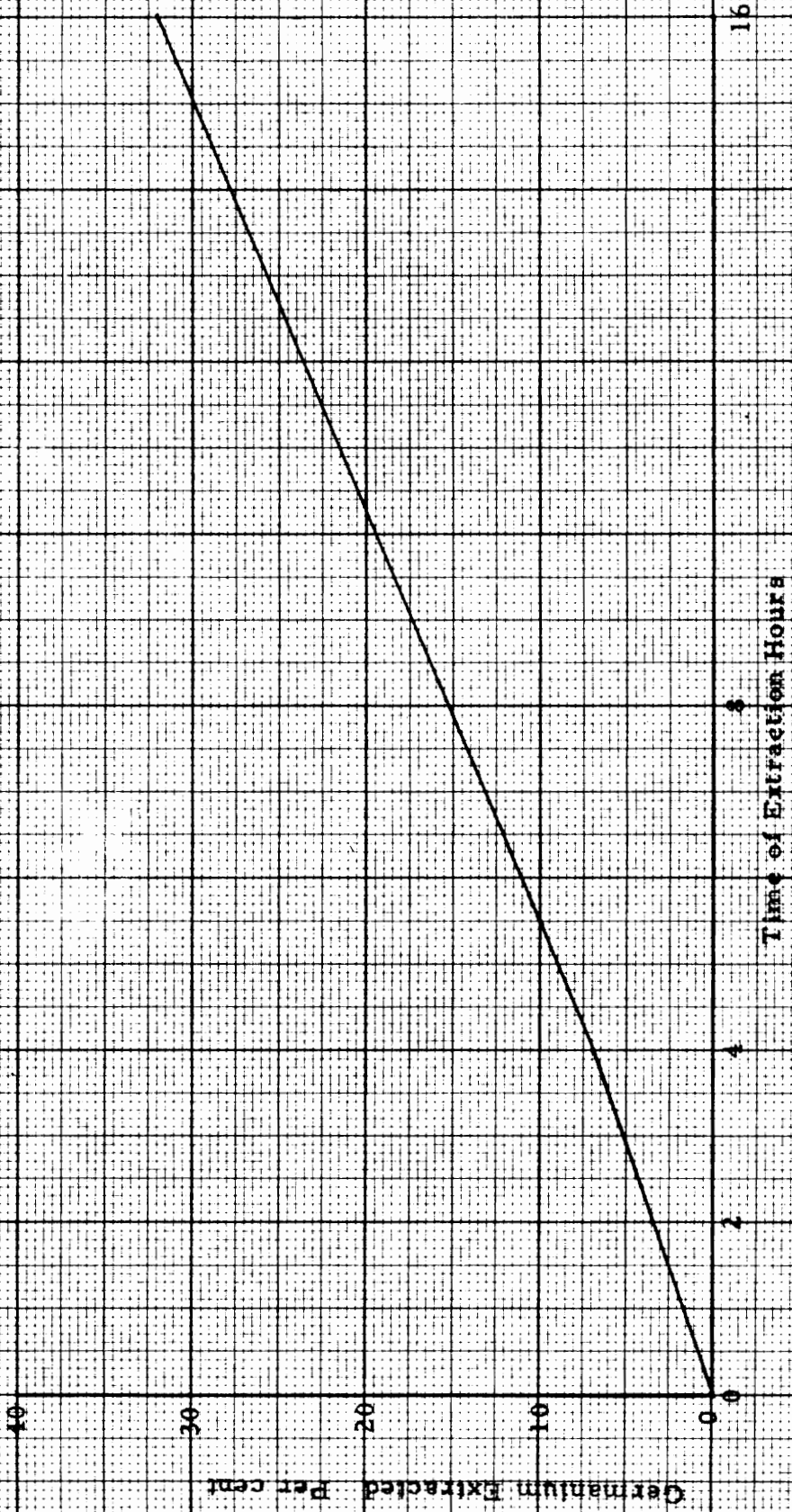


Figure 6 Percentage of Germanium Extracted by Hexane vs. Time of Run

of a material balance, since the extracts could not be satisfactorily analyzed. In using the Soxhlet apparatus it was found helpful to add a few grains of pure sand to the flask to prevent undue bumping. For those high boiling point organic solvents that absorb water it was found necessary to preboil in order to prevent explosions within the apparatus. When using solvents that are ordinarily solids care must be taken to keep the condenser from becoming plugged, causing pressure to build up and blow the apparatus apart.

The ground glass joints were found to be mating too well and a few roughening strokes with emery cloth made it possible to take the apparatus apart without breakage.

In all cases, approximately one gram of sample (accurately weighed) was placed in the thimble and the top pinched closed. When the thimble was placed in the extractor, care was taken to prevent the condensate from dripping directly into the thimble. This reduced the possibility of material being splashed out or being displaced by the heavier organic liquids. At the end of the predetermined period of extraction, the thimble was removed and the residual solvent in the thimble was driven off by placing the thimble in a conventional drying oven until the thimbles no longer gave a smell of the solvent. The dry thimbles were weighed and the loss in weight was attributed to the coal extracted by the solvent. The thimbles were then ashed in the

same manner as the coal samples. When the ash per cent was calculated on the basis of the original coal in the thimble prior to extraction, the ash per cent was the same as that of the original coal, indicating little or no removal of the ash-forming substances by the solvents. After ashing, the material was analyzed for germanium in the same manner as the coal samples.

The treatment of the extract is described under the heading "Analytical Difficulties."

Flotation Tests. Blacksburg tap water was used in all flotations. The water has a pH of 7.4. The hardness varies from 200 to 500 ppm. A 250 gram sample of coal was mixed with 2.3 liters of water in the flotation cell before each test was begun. In all cases, the air was turned off while the reagents were being added. The reagent consumption is reported in terms of pounds per ton (lbs./ton), which is standard in flotation practice.

Unless specified, reagent additions after the first increment were made when the froth became virtually barren, that is, when the froth contained very little coal.

Test One. The pulp was treated with 0.05 lb./ton Dowfroth 250 and the froth collected, then 1.5 lbs./ton of Tallso were added and the second froth collected.

Test Two. No reagents were added and the first froth was collected. The pulp was next treated with 0.05 lb./ton

American Cyanamid Aerofroth 80 (AC 80) and the froth collected once more.

Test Three. An addition of 0.05 lb./ton American Cyanamid Aerosol OS was made and the froth removed for one minute. To the remaining pulp 0.02 lb./ton AC 80 was added and this froth was skimmed off for one minute. An additional 0.01 lb./ton AC 80 was added and the froth scraped off once more. A last aliquot of 0.02 lb./ton AC 80 was added to obtain a fourth product. Finally, two drops (approximately 0.42 lb./ton) of Barrett-634 (a coal tar creosote) were introduced. This produced the last froth collected. These froths were numbered 1, 2, 3, 4, 5, and the underflow was designated as 6.

Test Four. Four drops (0.85 lb./ton) of Barrett-634 and 0.1 lb./ton AC 80 were added in stages to obtain the first froth. Two drops (0.24 lb./ton) of Barrett-634 and an additional 0.1 lb./ton AC 80 were added to effect the last separation.

In tests one, two, and four, the first froth was designated Concentrate, the second froth was designated Middlings, and the remaining underflow was the Tailings product.

The results of these tests are shown in Tables 2, 3, 4, and 5.

Table 2

Results of Flotation Test 1

Product	Weight %	Ash %	Germanium ppm
Concentrate	24.0	7.1	46
Middlings	33.4	14.5	36
Tailings	42.6	26.4	18
Composite	100.0	17.8	31

Table 3

Results of Flotation Test 2

Product	Weight	Ash	Germanium
	%	%	ppm
Concentrate	26.2	7.5	46
Middlings	19.8	10.5	36
Tailings	54.0	20.8	38
Composite	100.0	15.3	40

Table 4

Results of Flotation Test 3

Product	Weight %	Ash %	Germanium ppm
1	5.2	6.4	42
2	5.7	7.5	47
3,4	15.6	8.6	34
5	29.2	7.6	48
6	44.3	18.9	42
Composite	100.0	12.7	43

Table 5

Results of Flotation Test 4

Product	Weight	Ash	Germanium
	%	%	ppm
Concentrate	37.1	6.5	46
Middlings	59.3	14.3	39
Tailings	3.6	85.6	17
Composite	100.0	13.7	41

The three products of test four were divided into three size groups (+48, -48+100, and -100 mesh), each of which was analyzed for ash and germanium content. This was done to note the size-germanium distribution of the products as tabulated in Tables 6, 7, and 8.

The sized tailings were further fractionated by specific gravity separation at 1.90. This 1.90 specific gravity liquid was a mixture of carbon tetrachloride, white gasoline, bromoform, and acetylene tetrabromide. The results of this separation are shown in Table 9. The analyses of this fractionation and composites calculated therefrom are shown in Tables 10 and 11.

Flotation tests can effect a concentration of germanium, but the ratio of concentration is close to unity. The ratios of concentration between feed and concentrate for each of the four flotation tests were 1.5, 1.2, 1.1, and 1.1 in that order.

Germanium was concentrated in the smaller sizes by means of froth flotation, which means froth flotation would concentrate the germanium in the finer sizes that are not amenable to specific gravity separations. Since the tailings were approximately one-half the total weight, but contained less than one-half of the germanium, the amount of material to be handled was reduced, but most of the germanium was retained.

Table 6

Size Distribution of Products
of Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Total %
Concentrate	6.2	20.6	73.2	100.0
Middlings	45.4	31.7	22.9	100.0
Tailings	46.7	29.9	23.4	100.0
Composite	31.0	27.6	41.4	100.0

Table 7

Ash Analyses of Sized Products
of Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Concentrate	3.9	4.2	7.4	6.5
Middlings	10.9	13.6	22.2	14.3
Tailings	79.5	89.9	92.4	85.6
Composite	13.7	13.6	13.8	13.7

Table 8

Germanium Content of Sized Products
of Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Concentrate	33	55	45	46
Middlings	43	38	33	39
Tailings	16	18	18	17
Composite	41	42	40	41

Table 9

Results of Separating the Sized Tailings Fractions
of Flotation Test 4 by a Specific Gravity
of 1.90 by Weight Per Cent

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Fleat 1.90	10.0	1.0	3.3	5.8
Sink 1.90	90.0	99.0	96.7	94.2
Total	100.0	100.0	100.0	100.0

Table 10

Ash Per Cent of the Sink-Float and Sized Fractions
of the Tailings from Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Float 1.90	40.6	23.8	67.5	43.4
Sink 1.90	88.8	92.4	95.5	91.3
Composite	84.6	91.7	94.2	88.0

Table 11

Germanium Content of the Sink-Float and Sized
Fractions of the Tailings from Flotation
Test 4 in Parts Per Million

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Float 1.90	18	198	74	35
Sink 1.90	18	23	14	17
Composite	18	24	16	20

The size analysis of the last test showed that size alone had little or no effect on the ash and germanium analyses.

The analyses of the fractions made from the tailings of test four led to interesting conclusions about the distribution of germanium in coal, but the weights of the samples available were too small to justify any major assumptions. The germanium content of the coal in the tailings was 118 ppm. When further fractionated by sizing, the finest size was found to contain 236 ppm of germanium in the ash-free coal. This indicates the germanium-enriched component is less floatable, and shows the more effective liberation of this component in the finer sizes. The germanium content of the two froths would thus be attributed to unfreed particles of the germanium-enriched component locked up with the more floatable coal. In the minus 100 mesh fraction of the tailings the concentration of germanium in the ash-free coal is five times greater than the germanium in the feed to flotation.

Ash Analyses. As would be expected, variations in the ash content was less for finer sized coal and the ash of the Sink-Float products varied directly as the separating gravity (see Figure 7). The relationship between germanium content and ash is presented as a scatter diagram in Figure 8. The general trend shows the germanium content to vary inversely with the ash.



Figure 7 Ash Content of Specific Gravity Fractions (vs. Size of Coal)

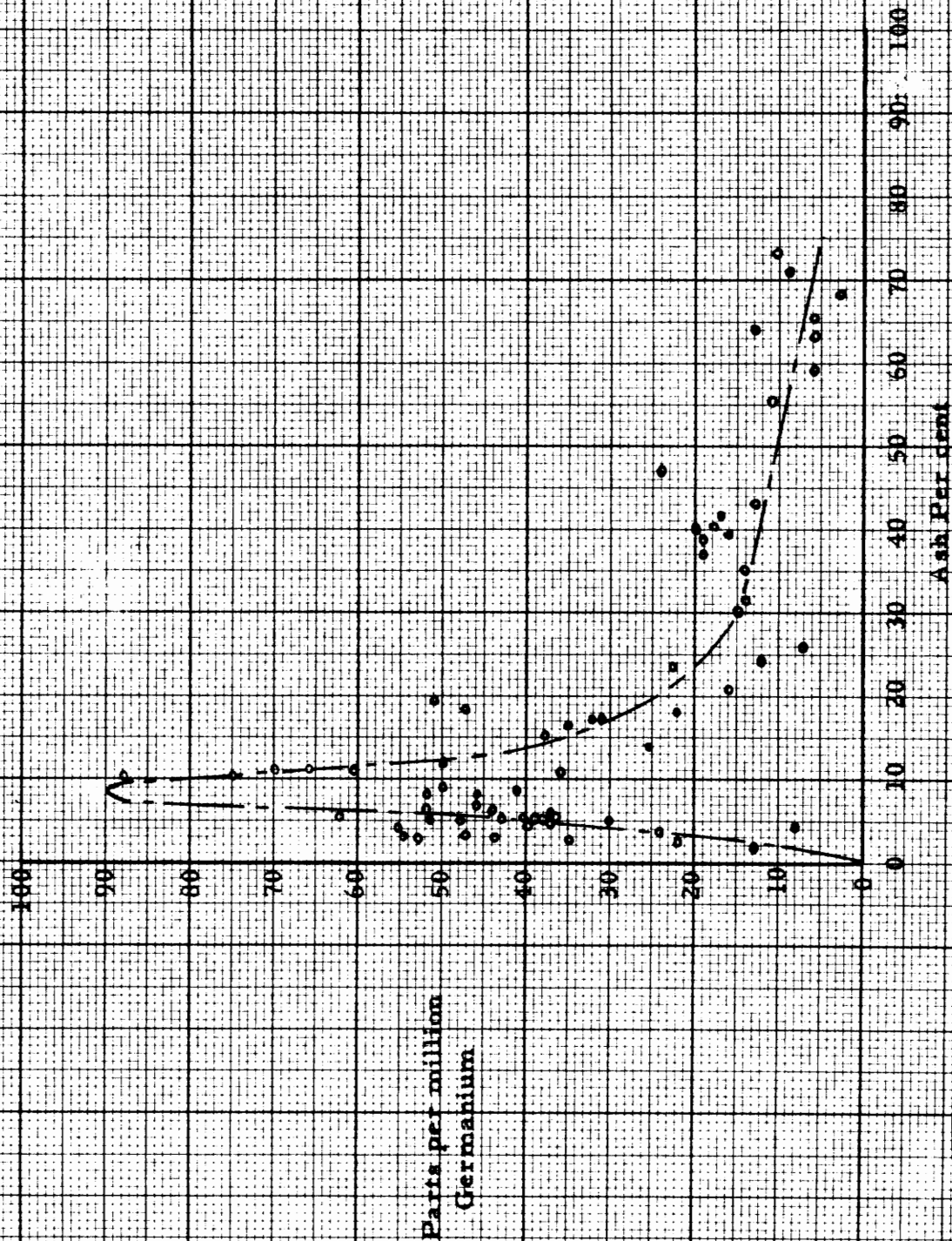


Figure 3 Germanium Content vs. Ash Content

Volatile Matter Analyses. The volatile matter content of the samples on the ash-free basis was fairly constant (see Figure 9) and no correlation was drawn between germanium and volatile matter in coal.

Fixed Carbon Analyses. Since the variations in the volatile matter were small and were not correlated with the germanium content, the fixed carbon and germanium were also left uncorrelated (see Figure 10).

Germanium Analyses. The germanium analyses have been compared with the other factors of coal in the preceding sections, and a general summary will reveal that the higher concentrations of germanium tend to occur in the lighter gravity fractions, while the sink products are low in germanium content.

The germanium in the ash is naturally greater than the germanium in the coal sample, and in all cases the germanium can be concentrated merely by ashing the coal. The highest ratio of concentration was found in the -100+200 size and Float 1.30 fraction, where the ratio of concentration was 50. The lowest value, also obtained at -100+200, but for the Sink 1.35 product, was 2.1. The ratio of concentration obtained by ashing the head sample was 6.4. The ratios of concentration are presented in Figure 11 for the specific gravity fractions at each size.

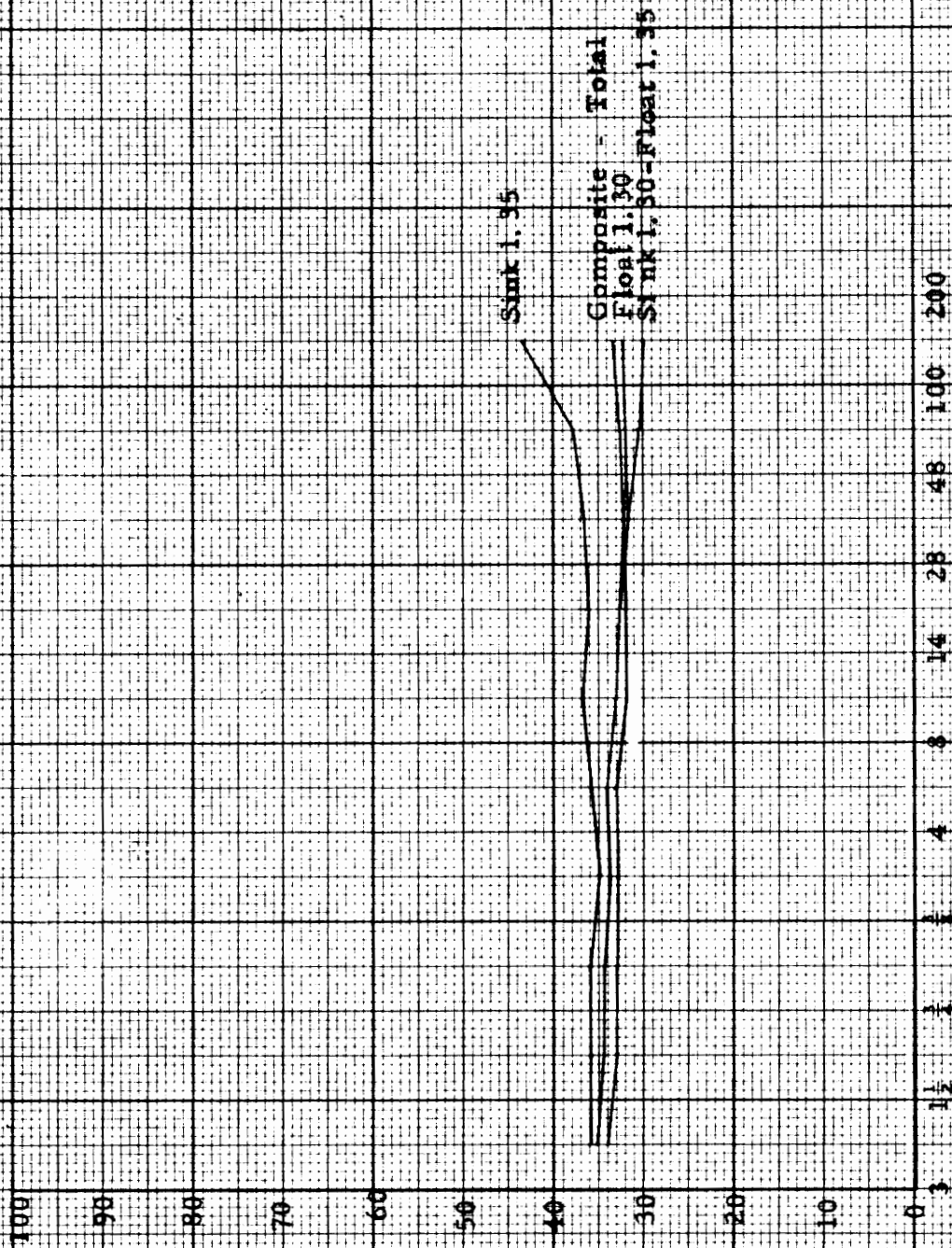


Figure 9 Volatile Matter of Ash-Free Coal of Specific Gravity Separations vs. Size of Coal

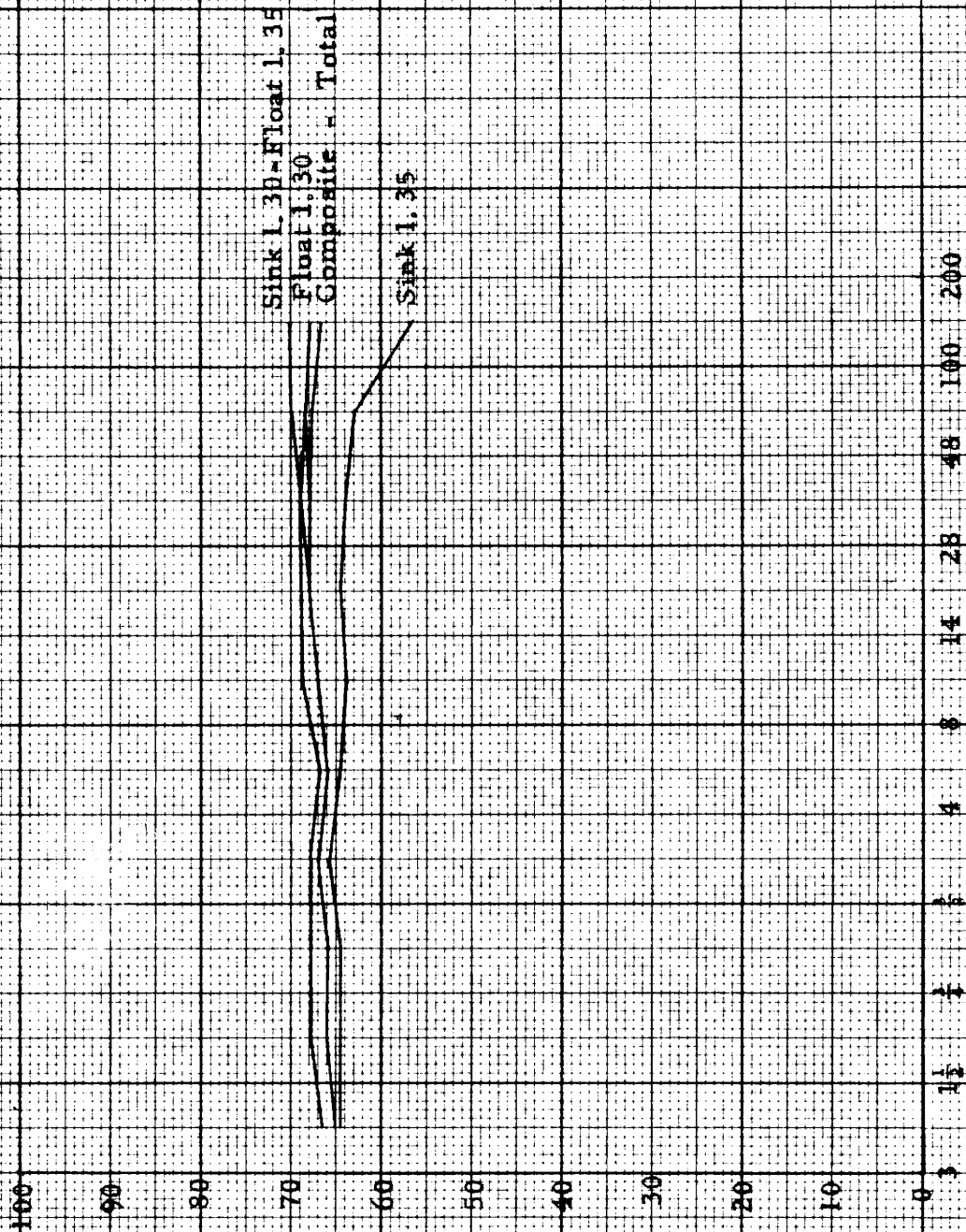


Figure 10 Fixed Carbon Content of Ash-Free Coal of Specific Gravity Fractions vs. Size of Coal

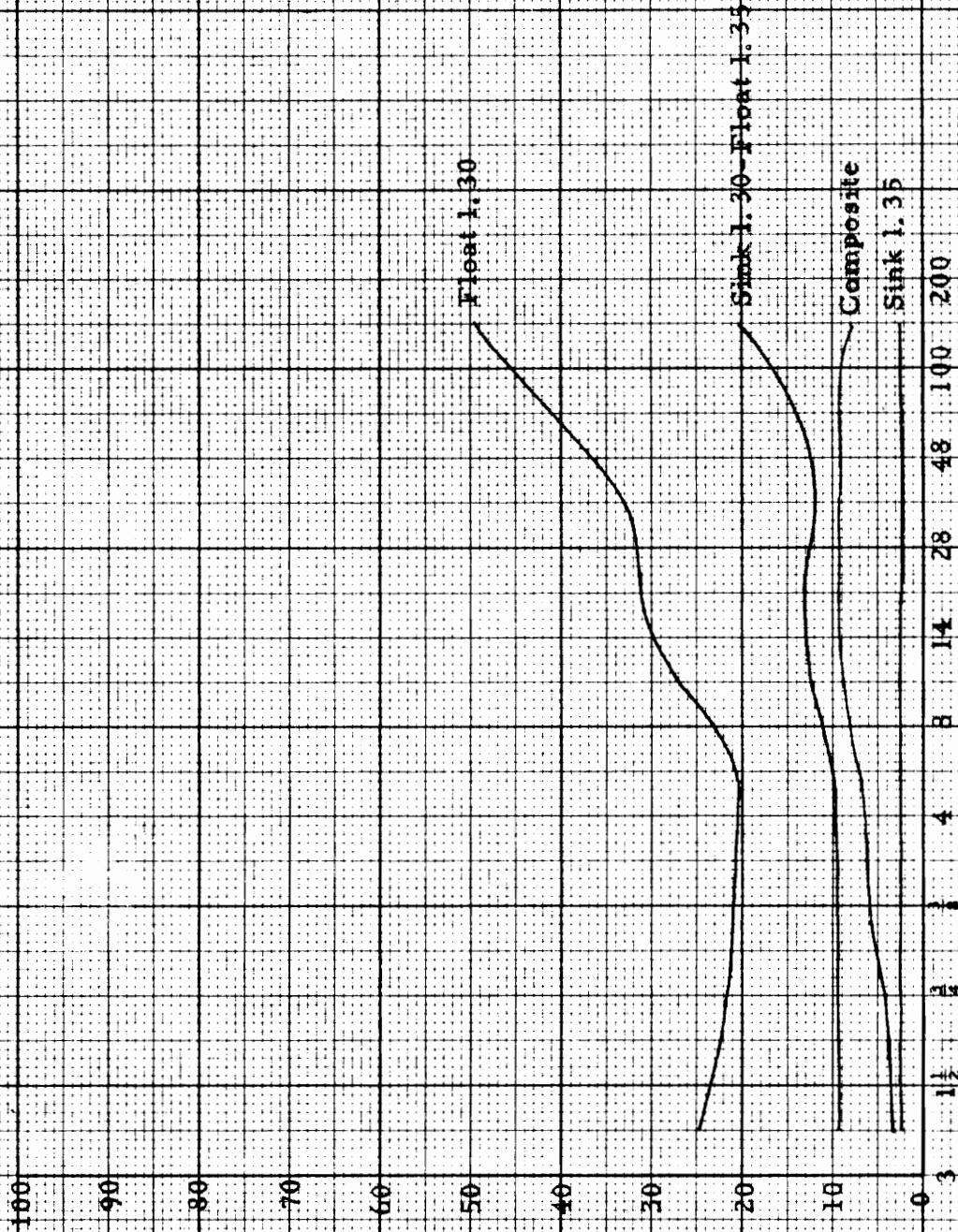


Figure 11 Ratio of Concentration Obtained by Ashing Specific Gravity Fractions vs. Size of Coal

Washability Curves. Figures 12, 13, 14, and 15 are graphs of the analyses obtained by compositing the various size and gravity separations. From these graphs it is possible to determine the analyses of the products that would be formed by making a separation at a single size or specific gravity. The data plotted are: the germanium content in parts per million of the ash and of the ash-free coal, the per cent ash, the per cent volatile matter on the ash-free basis, and the weight per cent of the product. The values of germanium in the ash should be multiplied by ten in order to get the results in parts per million. For example, if a separation were made at a specific gravity of 1.35 the float material would contain five per cent ash, 33 per cent volatile matter, 55 ppm germanium in the coal, 1000 ppm germanium in the ash, and would comprise 68 per cent of the feed to the separation. The other graphs are read in a similar manner.

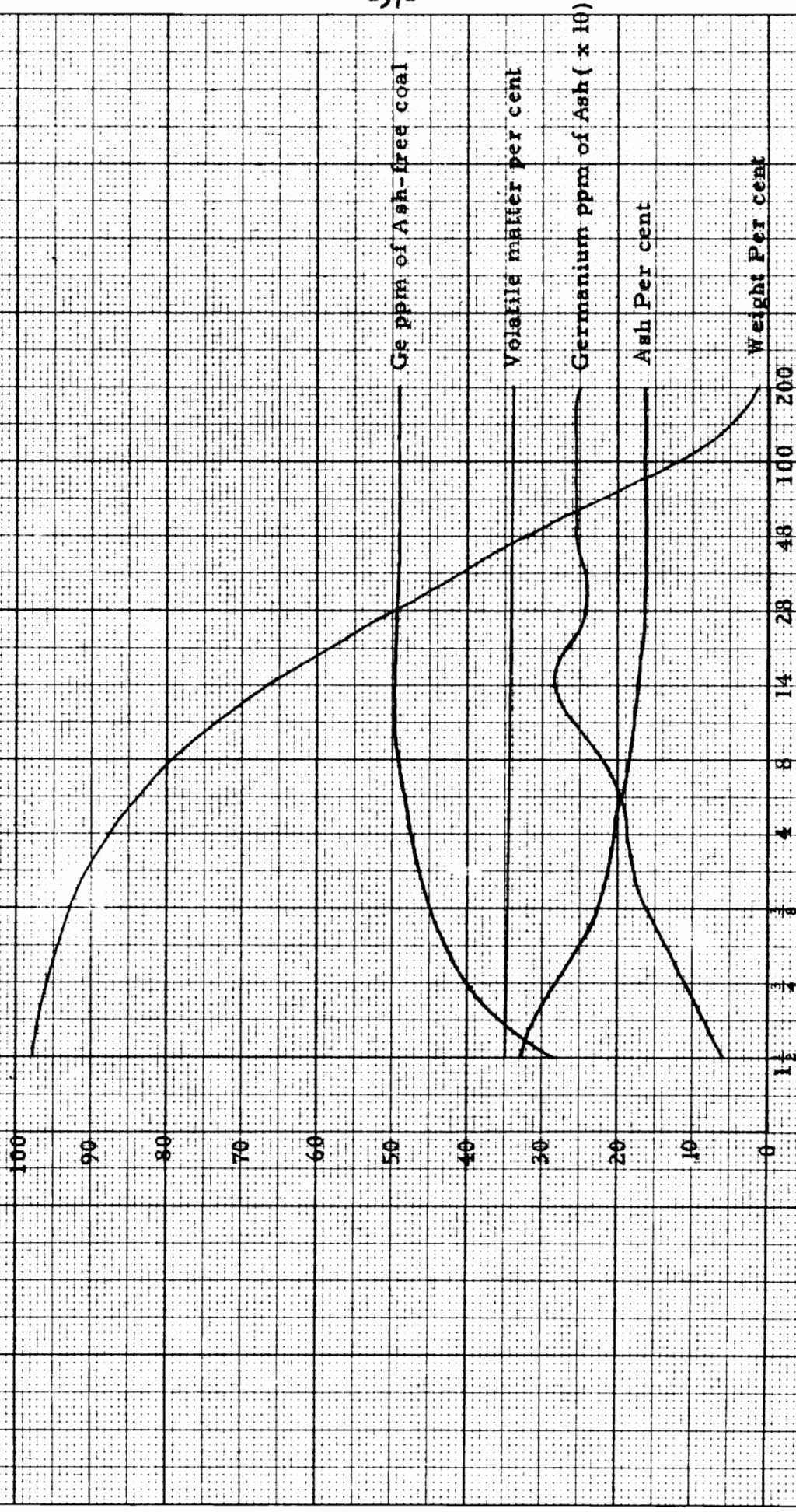


Figure 12 Analysis of Oversize Products vs. Size

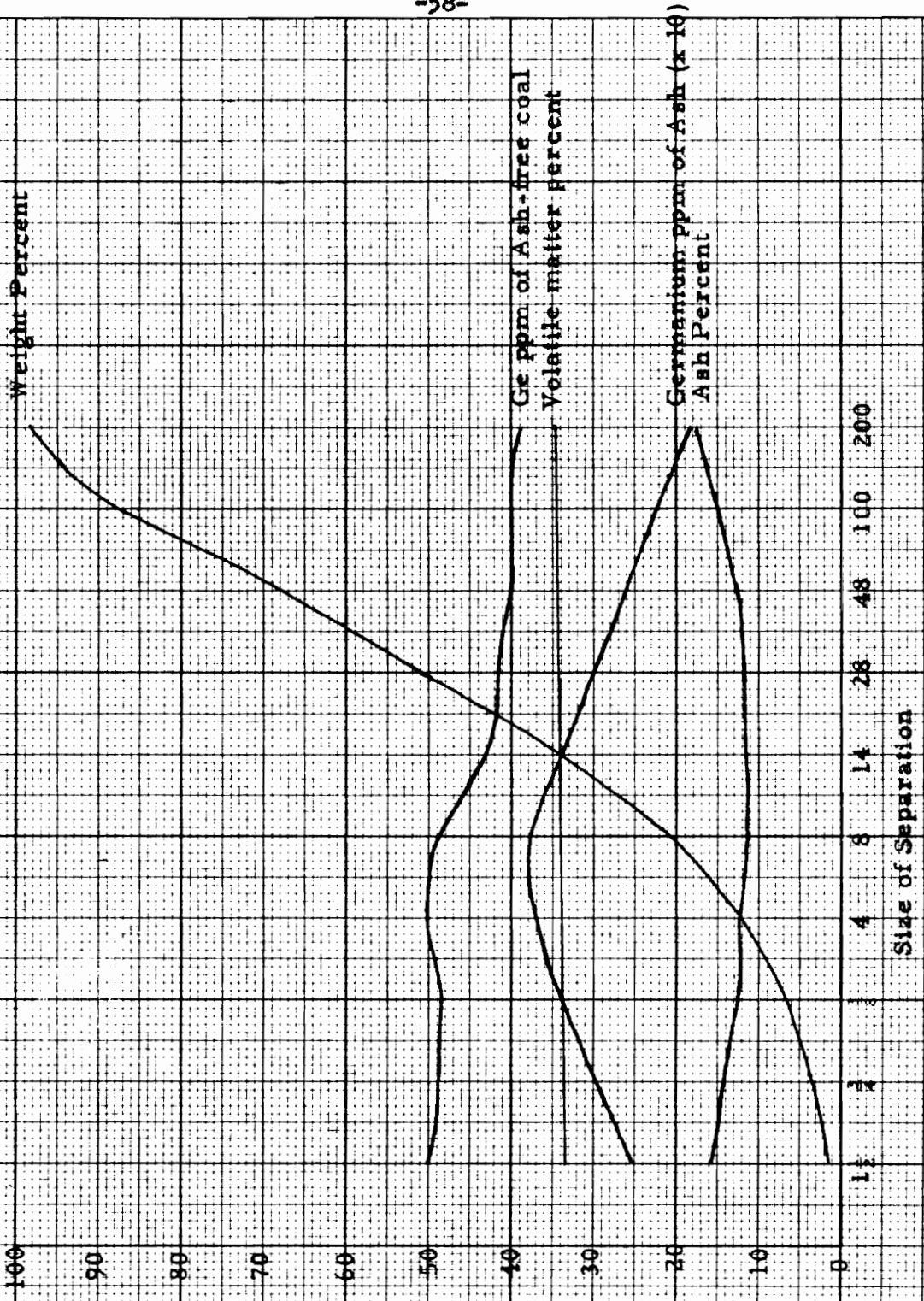


Figure 13 Analysis of Undersize Product vs. Size

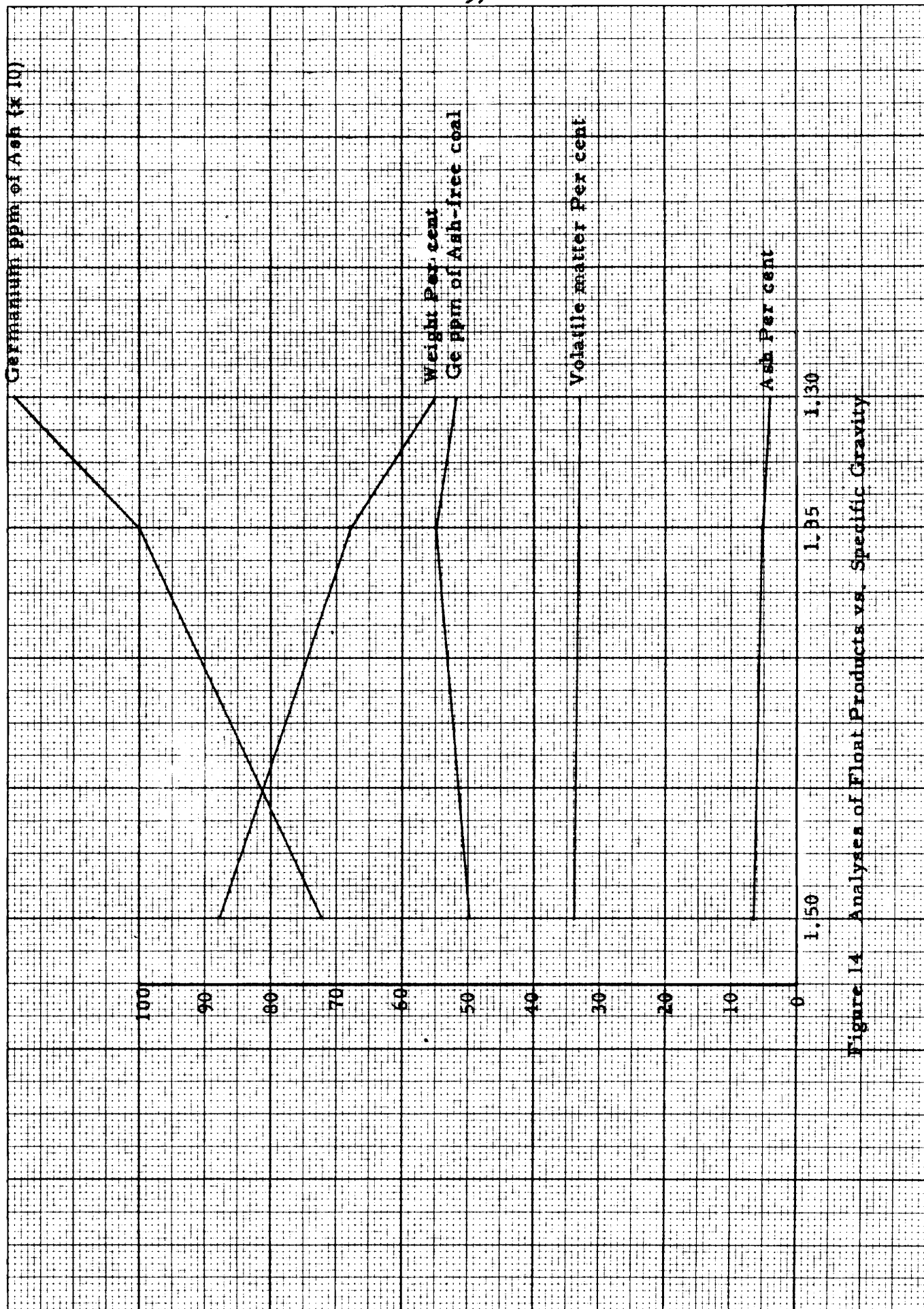


Figure 14 Analysis of Float Products vs. Specific Gravity

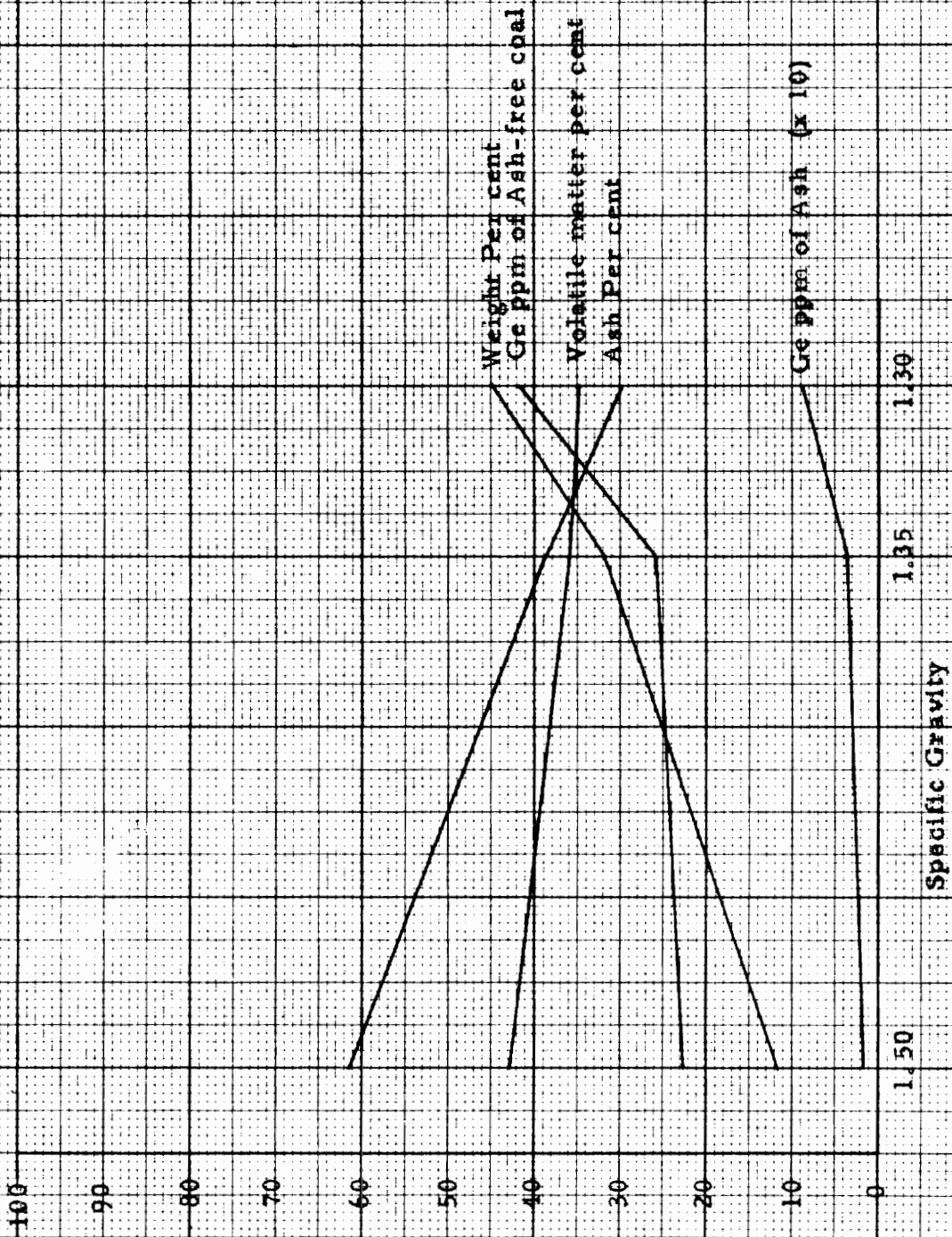


Figure 15 Analyses of Sink Products vs. Specific Gravity

Juniper Theory

This theory is proposed to explain the distribution of germanium in coal seams. Germanium is found to occur concentrated in the bottom of most seams, with a lesser concentration being found in the top layers and adjacent to partings in the seams⁽⁵⁸⁾.

The fossil lignites found by Stadnichenko in the District of Columbia were the ancestors of the present day arbor vitae and juniper^(80,81,142).

These species are known to flourish in areas that are near swamps, but they will tend to die out either on high dry land or when their main trunks become inundated. This fact has been noted in present day investigations by Brauchli⁽¹²⁴⁾.

Therefore, these plants that have exceptional ability to concentrate the germanium would be expected to grow along the shore of the great coal forming swamps; as the swamps subsided⁽¹²⁸⁾ the germanium-rich plants would die and be replaced by plants with lower germanium concentrating abilities and thus the bottom layers would be composed of germanium-rich plant remains and the succeeding layers would be formed of relatively germanium-barren plant matter. If there were hummocks in this swamp, one would expect the germanium-rich plants to grow there before submergence of the hummocks. If, when the coal laid down is covered by the

rock materials that form the top of the coal seam, these plants would be growing along the shore, and they would thus be among the last plants to be laid down.

Analytical Difficulties

The best method for the analysis seemed to be the phenyl-fluorone colorimetric method described by Gillis et al.⁽⁴⁵⁾ and used by Almond⁽²⁾ and Cluley⁽²⁰⁾. Because of its apparent simplicity and the recommended use of the less expensive nickel crucibles, the method of Almond was the first tried. It proved to be unsatisfactory for quantitative work and was later found to be only a semi-quantitative method used for rapid survey methods⁽¹⁴¹⁾.

Cluley's method was next explored using the nickel crucibles in place of the recommended platinum crucibles. The nickel crucibles proved to be entirely unsatisfactory, since they were shown to absorb the germanium and after three or four runs they disintegrated. Metallographic examination of a specimen of one of the ruined nickel crucibles showed intergranular corrosion with an unidentified precipitate along the grain boundaries. The use of platinum crucibles was then adopted.

Analyses made in one of the platinum crucibles were consistently and abnormally high. Checking of the records showed that the crucible had been used to fuse one gram of germanium in preparing a standard. Attempts to remove the germanium from the platinum crucible were completely unsuccessful. Methods tried were alkali fusions, boiling in hydrochloric, nitric, and aqua regia acids, scouring, and high temperatures. The standard prepared and the contaminated crucible were not used in subsequent work.

In spite of all care, the results were inconsistent and no reliance could be placed on the analyses.

The writer was then fortunate in being invited to the Bureau of Mines in Pittsburgh where he was shown the correct technique as developed there. The major changes made when he returned to Blacksburg were those of technique and the change from the long slanting condenser to a short vertical one. These changes made possible consistent analyses and the work of analyzing the washability products was then begun.

In analyzing the products of the solvent extraction, the residues were ashed in the same manner as the coal samples, but the determination of the germanium in the extract has thus far been an unsolved problem. Methods tried included soaking the extract in sodium carbonate with evaporation and subsequent

fusion. All samples handled in this manner showed no germanium. Micro-combustion techniques were then tried, and much time was spent in trying to get a technique that would permit analysis, but no positive results were obtained. The use of wet combustion methods seems to be the most promising line of attack^(154,164), but its use was not tried until late in the project, thus the technique has not been mastered. Distillation has also been suggested as a means of separating the germanium compound from the solvent. One of the major difficulties in an analysis of this kind is that the nature of the germanium compound is not known, so that several experiments would have to be run on products containing very small amounts of germanium. It is likely that for different solvents one might have to use different techniques. Time did not permit thorough investigation of these possibilities. Thus, no material balances are available for the solvent extraction experiments.

Preparation of Phenylfluorone. The first four batches of phenylfluorone were synthesized in the mining laboratories using the method given by Cluley⁽²⁰⁾. Indifferent results were obtained in the syntheses, with variable quality and yield of product. The total yield was two grams of phenylfluorone.

It was then thought best to obtain the reagent from Jasonols Chemical Corporation and enough phenylfluorone was obtained to

ensure freedom from variance in the quality and strength, and to also obviate the necessity for the syntheses.

Ashing Temperatures

Waring and Tucker⁽¹⁶⁵⁾ have stated that lignites containing germanium can be ashed at temperatures up to 1000°C without losing any germanium by volatilization.

Most investigators recommend the use of low-ashing temperatures to prevent loss of germanium through volatilization^(20,142).

A series of tests were made on the head sample at various temperatures to determine the effect of ashing temperature on the germanium recovery.

Temperatures of ashing used were 450, 600, 750, 850, and 900°C, the time of ashing being eight hours in each case.

The germanium found by analysis for the various ashing temperatures is presented in Table 12 and shown in Figure 16.

The lower values obtained at the lower temperatures are probably due to the insufficient time of ashing so that the samples were not oxidized completely. The low values obtained at the high temperatures are attributed to the volatilization of the germanium compounds. It was thought best to ash the coals at a low temperature to minimize the loss of germanium.

Table 12

Germanium Recovery at Various Temperatures

Temperature	Germanium
°C	ppm
450	15
600	23
750	37
850	10
900	7

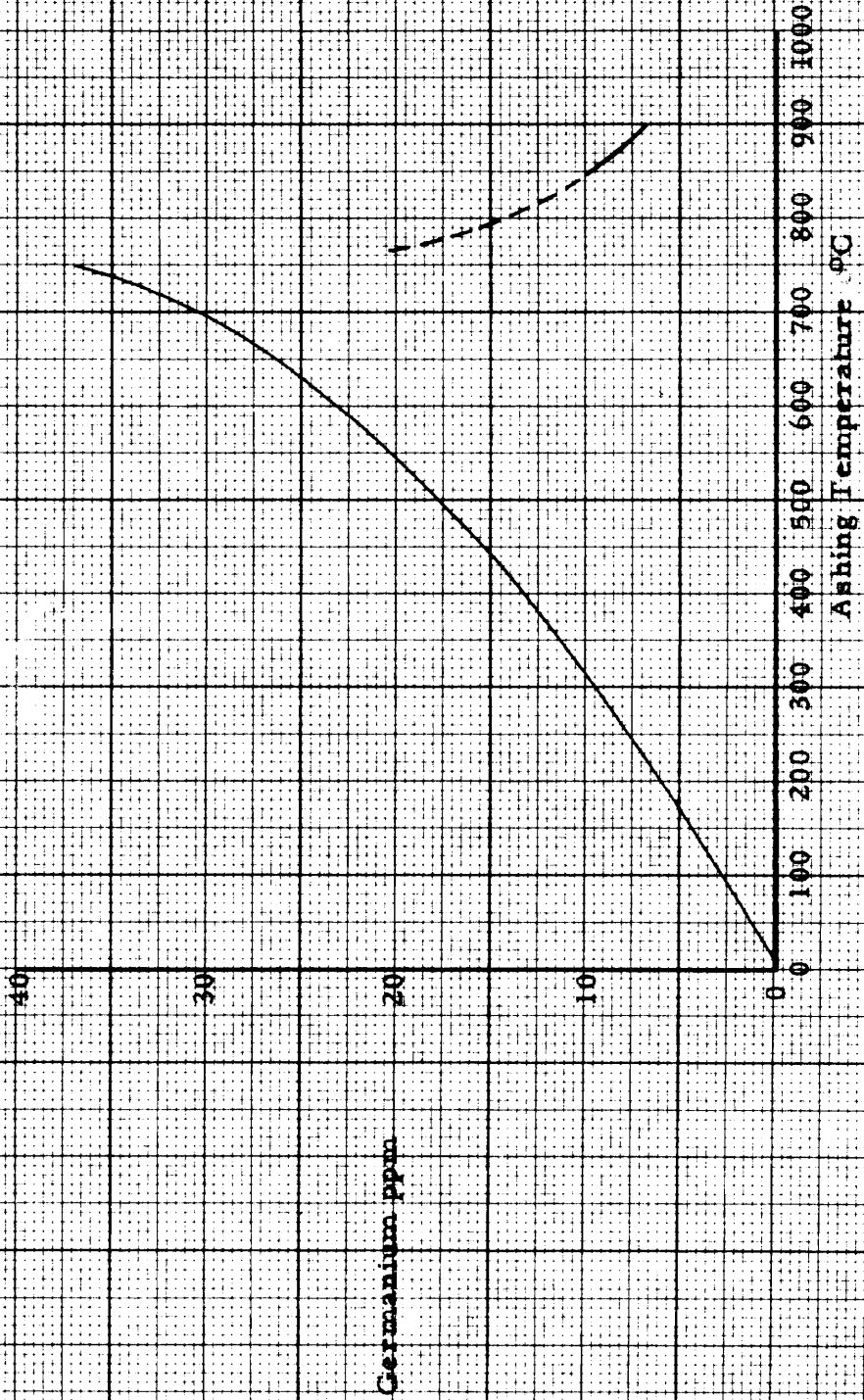


Figure 16 Germanium Recovered vs. Ashing Temperature

By using the lowest temperature (450°C) for a longer period of time (16 hours) it was possible to obtain a consistent value of 36 ppm germanium in the head sample.

Ash Colors

A variation in the color of the ash from various products was noted and the possibility of a connection between ash color and germanium was investigated. In 1920, Lessing⁽⁸⁴⁾ noted that the petrographic varieties of coal gave ashes of different colors. The petrographic varieties and the colors noted by Lessing are shown in Table 13.

The iron in coals can often be estimated by the color of the ash, with a high iron content giving a deep red coloration to the ash. In comparing the ashes from the washability study, it was noted in all cases that the ash became redder as the size decreased. The minus 200 mesh material was definitely red. The color of the products is shown in Table 14.

The only conclusions to be drawn from the ash colors are:

- (1) the iron concentration increases as the size becomes smaller,
- and (2) the mixture of petrographic constituents in the products does not permit petrographic identification of any particular fraction on the basis of its ash color.

Table 13

Ash Color of Petrographic Constituents

Fusain	Dark brown, gray
Durain	Pure pale gray, no brown
Clarain	Reddish brown, biscuit colored
Vitrain	Pale biscuit color

Table 14

Ash Color of the Products of the
Specific Gravity Separations
and of the Head Sample

Product	Color
Float 1.30	Pale gray
Float 1.35-Sink 1.30	Dark gray
Float 1.40-Sink 1.35	Light gray
Float 1.50-Sink 1.40	Buff
Float 1.60-Sink 1.50	Light buff
Sink 1.60	Pale buff
Float 1.50	Dark gray
Sink 1.50	Reddish gray
Float 1.25	Dark gray
Head Sample	Reddish buff

Character of Coke Buttons

The coke buttons from the volatile matter analyses were compared to see if there were any connection between the character of the coke and the germanium content. As the specific gravity of the coal fractions increased the coke buttons ranged from weak bloated coke to good strong coke to fused sinter and finally to pulverulent cake (see Table 15). The effect of size was slight, with smaller sizes giving slightly poorer cokes.

The connection between coking properties and germanium in the coal is very evident, with the poorer coking fractions being low in germanium and the best coking fractions being high in germanium content. It must be remembered that the quality of the coke was judged from the appearance of the coke buttons left from the volatile matter determinations, and was not based on standard coking tests. For this reason, no hard and fast rule can be made, but the results will justify the following generalization: The germanium tends to associate with the better-coking fractions.

Table 15

Character of Coke Buttons for Various
Specific Gravity Fractions

Product	Character of Coke Button
Float 1.50	Good strong coke
Sink 1.50	Sinter and pulverulent coke
Float 1.30	Weak bloated coke
Float 1.35-Sink 1.30	Good strong coke
Sink 1.35	Slightly coked sinter
Head Sample	Slightly bloated coke
Float 1.25	Bloated coke

V. CONCLUSIONS

The findings of this investigation can be briefly stated as follows:

1. Germanium can be concentrated in coal prior to extraction.

2. Methods of concentration are listed, in order of decreasing effectiveness, with maximum ratio of concentration obtained:

a. Solvent extraction	250
b. Ashing	50
c. Froth flotation	1.5
d. Specific gravity	1.3
e. Sizing	1.1

There is probably little significance in the difference shown for the last three methods. However, it can be expected that other germanium-bearing coals may conceivably have the germanium-bearing component occurring at such sizes as to permit concentration by flotation or other means.

3. Germanium is lost by ashing at high temperatures.

4. There is a relation between coking character and germanium content.

5. The germanium-bearing component of the coal is associated with that constituent (vitrain) that is considered to contain the major part of the inherent ash.

VI. SUMMARY

In this investigation, approximately 500 pounds of germaniferous coal was sampled and split into size and specific gravity fractions. The specific gravity fractions were analyzed for ash, volatile matter, fixed carbon, and germanium. Richer fractions of the coal were further treated by solvent extraction, and on the basis of these tests, extraction tests of varying time were conducted. In addition, a sample of the coal was tested by froth flotation and the effects of flotation on germanium concentration noted.

Size and specific gravity separations have given products that contain two to three times as much germanium as the feed. Solvent extraction with suitable solvents was able to give products that contained as high as 250 times the germanium content of the feed. Froth flotation produced concentrations of the germanium that were only one and a half times greater than obtained in feed. The greatest concentration made by burning the coal was 50 to 1 when comparing the germanium in the ash to the germanium in the sample.

VII. SUGGESTIONS FOR FUTURE WORK

Intensive investigations into the extraction of germanium with solvents such as hexane for long periods of time (measured in days) is well warranted from the preliminary data. The use of elevated pressures and temperatures in extraction seems to offer an attractive commercial possibility which should not be overlooked, since a higher yield in shorter time should be possible.

For future work it is suggested that the coal be studied petrographically to isolate the germanium-enriched component of coal. This suggestion is based on the results of the flotation test four. Also, recent confidential information indicates a relationship between petrographic analyses and the coking properties of coal. Apparently, there may be a similar relationship found between the germanium content and the petrographic composition.

Further work on selective froth flotation may help to isolate the germanium compounds as they occur in coal. Other germanium-bearing coals may have effective liberation of the germanium component at a coarser size than obtained for the coal studied in this investigation. In that event froth flotation studies may be of more than academic interest.

Finally, it is suggested that a study be made of the economics of germanium extraction from coal when "bug dust" mining is used in conjunction with specific gravity separation and froth flotation to remove the high-ash, low-germanium material, followed by solvent extraction, germanium recovery, and refining of germanium.

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X. VITA

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He graduated from Virginia Polytechnic Institute in June, 1953, with the Bachelor of Science degree in Mining Engineering. In the summers between school sessions he has found employment with coal mining companies and has had jobs from "shovel operator" to engineer in the coal mines.

His main hobby is electronics, and he was engaged in a number of extra-curricula activities during his undergraduate career.

In his graduate work he has tended to direct his activities along the lines of mineral dressing and especially coal preparation.

Herbert L. Schaaf, Jr.

APPENDIX

Sample Calculations

Germanium Analyses. The method of determining the germanium concentration in parts per million (ppm) in the sample, in the ash-free coal, and in the ash is described below.

The coal sample is ashed, e.g., the minus 200 mesh coal contains 17.36 per cent ash. In the germanium analysis, 0.1000 gram of this ash is used. A 25/50 aliquot is taken from the final distillate and the colorimetric procedure applied to the aliquot to determine the germanium present. The scale reading of the colorimeter is 47 which corresponds to a germanium content of 9 micrograms (μgms) of germanium, as read from a previously prepared calibration chart such as Figure 17. Since 9 μgms are present in one-half of the distillate, then the germanium in the total distillate is 18 μgms . This is all the germanium present in the 0.1000 gram sample of ash, thus, the germanium in 1.000 gram of ash is $18/0.1000 = 180$ μgms per gram of ash or 180 ppm germanium in the ash. One ppm is equivalent to 0.0001 per cent; thus, the germanium in the ash can also be expressed as 0.0180 per cent.

The germanium content of the minus 200 mesh sample is the germanium content of the ash multiplied by the ash per cent; thus, $180 \times 17.36\% = 31$ μgms per gram of sample, or 31 ppm.

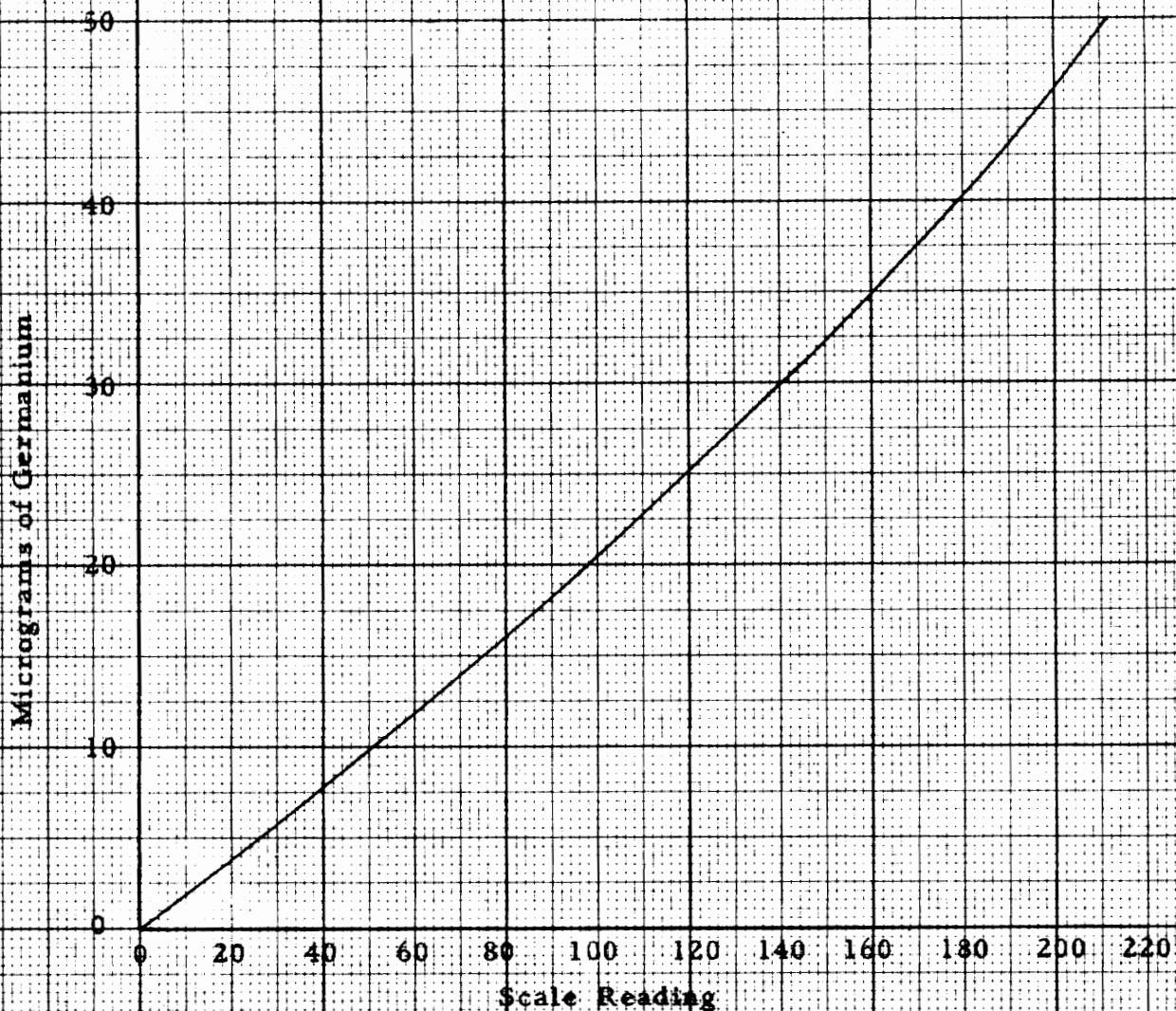


Figure 17 Calibration curve showing germanium content in micrograms.

Curve prepared using method of Cluley, phenylfluorone supplied by Jansons, Klett-Summerson photoelectric colorimeter number 3366 with filter number 54, and germanium standard supplied by Eagle-Picher.

The germanium content of the ash-free coal is the germanium content of the sample divided by the weight per cent of ash-free coal. The amount of ash-free coal is equal to 100.00 per cent minus the ash per cent. The per cent of ash-free coal is

$$100.00 - 17.36 = 82.64\%.$$

The germanium content on the ash-free basis is calculated to be:

$$31 \div 0.8264 = 38 \text{ ppm.}$$

The ratio of concentration obtained by ashing is the germanium in the ash divided by the germanium in the sample

$$180 \div 31 = 5.8.$$

Composites. By compositing is meant the grouping of data from many incremental observations into a whole or into larger increments. In compositing, the products to be combined are weighed in order to give the same results that would be obtained by actual combination of the products and analysis of the combination.

Example: A flotation test gives three products: concentrate, middlings, and tailings. The ash analysis of these products are 7.5, 10.5, and 20.8 per cent in that order. The weight per cents of the three products are 26.2, 19.8, and 54.0 per cent in the same order. If the ash per cent of each product is multiplied by the respective weight per cent, the product is expressed in terms of ash units.

The summation of the ash units divided by the summation of the weight per cent will give the composite ash per cent of the three products.

A form similar to the following will be found helpful.

Products	Weight %	Ash %	Ash Units
Concentrate	26.2	7.5	197
Middlings	19.8	10.5	208
Tailings	<u>54.0</u>	20.8	<u>1122</u>
Summation	100.0		1527

The ash per cent of the composite is then equal to sum of units divided by sum of weight per cents. This is equal to 1527 divided by 100 = 15.27 per cent, the ash content of the whole.

The same principles can be used for combining other products.

To combine the concentrate and middlings the set up would be:

Product	Weight %	Ash %	Ash Units
Concentrate	26.2	7.5	197
Middlings	<u>19.8</u>	10.5	<u>208</u>
Summation	46.0		405

The combined ash per cent of the concentrate and middlings is thus found to be $405 \div 46.0 = 8.8\%$ of ash.

To composite the middlings and the tailings:

Product	Weight %	Ash %	Ash Units
Middlings	19.8	10.5	208
Tailings	<u>54.0</u>	20.8	<u>1122</u>
Summation	73.8		1330

Ash % = $1330 \div 73.8 = 18.0\%$ in the combined middlings and tailings.

The same line of reasoning is used when compositing germanium, volatile matter, or any other quantitative measurement.

Example: In the same flotation test the germanium contents of the products were 46, 36, and 38 ppm in the same order as before.

Product	Weight %	Germanium ppm	Germanium units
Concentrate	26.2	46	1203
Middlings	19.8	36	712
Tailings	<u>54.0</u>	38	<u>2050</u>
Summation	100.0		3965

$$3965 \div 100 = 39.65 \text{ or } 40 \text{ ppm.}$$

The composite of the concentrate and middlings would be:

Product	Weight %	Germanium ppm	Germanium units
Concentrate	26.2	46	1203
Middlings	<u>19.8</u>	36	<u>712</u>
Summation	46.0		1915

$$1915 \div 46.0 = 41.6 \text{ or } 42 \text{ ppm.}$$

The composite germanium content of the middlings and tailings would be:

Product	Weight %	Germanium ppm	Germanium units
Middlings	19.8	36	712
Tailings	<u>54.0</u>	38	<u>2050</u>
Summation	73.8		2762

$$2762 \div 73.8 = 37.4 \text{ or } 37 \text{ ppm.}$$

Sampling and Analyses

The coal was sampled in accordance with the ASTM standards on coal and coke⁽³⁾. In this method the coal is sampled by systematic splitting and crushing until a representative sample of minus 60 mesh material and weighing approximately 50 grams is obtained. In all tests for volatile matter the prescribed ASTM method was followed. However, in the ash analysis the coal was ashed at 450°C for a period of sixteen hours, in lieu of the ASTM method of 750°C for a period of approximately four hours. The ashings were carried out at the lower temperature in order to prevent the loss of the volatile germanium compounds, which are said to be volatile at temperatures of 600 to 700°C. The fixed carbon was calculated from the ash and volatile matter analyses. All results are on the moisture-free basis. The samples from the washability studies were prepared for analysis by crushing down to minus 20 mesh in an assayers mill, and taking approximately 200 grams of the product and grinding it for thirty minutes in a pebble mill. Samples weighing less than 150 grams were crushed directly on the bucking board. All the samples were taken down to minus 60 mesh, as specified by the ASTM standards. Some samples, notably those from the flotation tests, were of such small weight that they were ground down in a small agate mortar.

Ash Analyses. Ash analyses were made by placing one gram of sample in a porcelain crucible which was then placed into a cool furnace. An electric muffle furnace was used and air was allowed free access to the samples by means of half-inch holes in the front and back of the furnace. The temperature in the furnace was gradually raised to 450°C over a period of four hours, and maintained at that temperature for sixteen hours. The sample was weighed again and the weight remaining was considered to be ash.

Volatile Matter Analyses. Volatile matter determinations were made in accordance with ASTM procedures to see if there were any relation between germanium content and volatile matter in coal. The sample of one gram of minus 60 mesh coal was weighed into the platinum crucible and the crucible was slowly lowered into a Hoskins volatile matter furnace which was kept at 950 ± 20°C and the sample allowed limited access to air by placing the lid on loosely. After the smoke and soot had stopped evolving the lid was tapped so as to form a snug fit. The time for most of the soot and smoke to evolve was about one minute. The total time of residence in the furnace was seven minutes as measured by a stop watch. The crucible and contents were weighed, but the lid and the deposit adhering to

the lid were not weighed. The loss in weight was considered to be volatile matter.

Fixed Carbon Analyses. Since the volatile matter and fixed carbon add up to 100 per cent on a dry, ash-free basis, the determination of fixed carbon merely consisted of calculating the difference between the volatile matter and 100 per cent.

Germanium Analyses. The analytical procedure finally adopted was an adaptation of the method suggested by Cluley⁽²⁰⁾. The coal to be analyzed was ashed in a porcelain crucible using about one gram of sample. The ashing was carried out at the low temperature of 450°C for a period of 16 hours. The temperature was gradually approached by raising the temperature from room temperature in increments of about 100°C each hour for the first four hours. The ash was weighed and a maximum of one-tenth of a gram of the ash was transferred to a platinum crucible. One-half gram of sodium carbonate was thoroughly mixed with the ash and this mixture was covered by an additional one-half gram of sodium carbonate. The platinum crucible was heated to redness in the flame of an ordinary Fisher burner. The heating was continued for 15 minutes, with the crucible contents being swirled every 5 minutes. The crucible was then allowed to cool naturally, which takes about 5 minutes. The cooled crucible was placed in a hot air bath and about 15 to 20 milliliters (ml.) of water

were added. This dissolves the fused melt in about one hour. If the water were added cold and no heat applied, the dissolution would take place in about six hours. The dissolved and loosened cake was washed and scraped into a 125-ml. distilling flask. About 4 ml. of 1:1 hydrochloric acid were added to the crucible to dissolve any last traces of the carbonate and the volume in the distilling flask adjusted so as to give 25 ml. when the acid was added. The level of 25 ml. was marked on the side of the flask with a ceramic-marking pencil. When the volume in the flask was more than 20 ml. prior to adding the 4 ml. of dilute acid, the contents were evaporated to give a volume of 20 ml.

Once the acid was added the following steps were carried out in rapid order. The volume was adjusted to approximately 25 ml. by adding distilled water when necessary. Twenty-five ml. of concentrated hydrochloric acid were added and the distilling flask quickly connected with the condenser by means of a glass tube and rubber stoppers. The glass tube was made with a bulb to prevent mechanical entrapment. The flask was heated so that approximately 2 ml. of condensate were collected each minute. This required a moderately vigorous flame. The condenser was vertical and water cooled. A short vertical

condenser was found better than a long slanting one. The condenser emptied into a graduate cylinder immersed in a crushed-ice bath. When 20 ml. had been collected, the cylinder was removed and the contents were poured into a 50 ml. volumetric flask. The cylinder was rinsed with water and the rinsings were added to the volumetric flask. The volume was brought up to the mark and the contents well mixed. Twenty-five ml. were then taken from the flask, leaving 25 ml. in the flask. To the 25 ml. remaining in the flask were added 5 ml. of fresh 0.5 per cent solution of gum arabic, 15 ml. of a 0.03 per cent solution of phenylfluorone, and enough distilled water to bring the volume to the mark. The flasks were kept at room temperature for 30 minutes, measured on the colorimeter, and compared with the calibration curve.

The equipment setup is shown in Figure 18.

Note: Thirty minutes was adopted as the standard time allowed for color development. In the preparation of the calibration curve it was noted that the scale readings of the colorimeter approached nearly constant values at the end of 30 minutes.

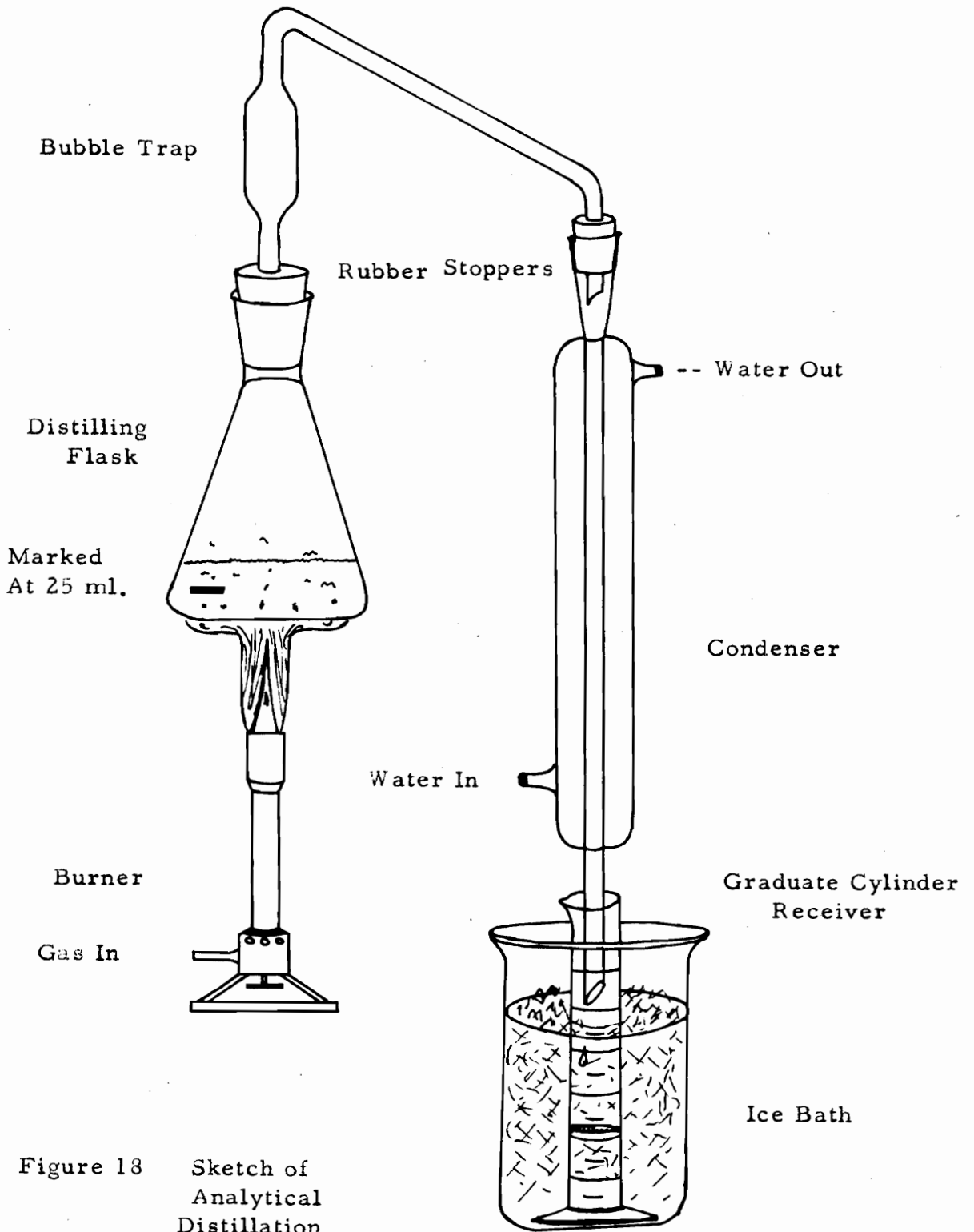


Figure 18 Sketch of Analytical Distillation Setup

DATA

Table 16

Germanium in Parts Per Million in the
Ash-free Coal of the Sized Products
of Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Concentrate	34	57	49	49
Middlings	48	44	43	45
Tailings	78	178	236	118
Composite	48	49	46	48

Table 17

Germanium in Parts Per Million in the
Ash of the Sized Products
of Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Concentrate	850	1310	600	710
Middlings	40	280	150	270
Tailings	20	20	20	20
Composite	300	310	290	300

Table 18

Germanium in Parts Per Million of the Ash-free
Coal of the Sink-Float and Sized Fractions
of the Tailings from Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Float 1.90	30	260	228	62
Sink 1.90	160	303	311	195
Composite	117	290	276	166

Table 19

Germanium in Parts Per Million in the Ash of the
Sink-Float and Sized Fractions of the
Tailings from Flotation Test 4

Product	+48 mesh	-48+100 mesh	-100 mesh	Composite
Float 1.90	44	830	110	81
Sink 1.90	20	25	15	19
Composite	21	26	17	23

Table 20

Weight Per Cent of Products of Sink-Float
and Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	0.245	0.078	1.015	1.339
- 1 1/2 + 3/4	3.139	1.374	6.117	10.630
- 3/4 + 3/8	9.606	2.583	8.435	20.622
- 3/8 + 4m	8.731	1.967	4.904	15.602
- 4 + 8	11.690	1.895	4.454	18.040
- 8 + 14	8.529	1.725	2.710	12.965
- 14 + 28	5.611	1.308	1.630	8.548
- 28 + 48	7.734	0.644	1.024	5.402
- 48 + 100	1.706	0.758	0.550	3.014
- 100 + 200	1.042	0.512	0.417	1.971
- 200	-	-	-	1.867
Composite	54.033	12.844	31.256	100.000

Table 21

Ash Per Cent of Products of Sink-Float
and Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	4.1	10.1	41.2	32.6
- 1 1/2 + 3/4	4.5	10.5	43.6	27.8
- 3/4 + 3/8	4.8	10.5	38.5	19.3
- 3/8 + 4m	4.8	10.3	35.8	15.2
- 4 + 8	4.9	10.0	37.1	13.4
- 8 + 14	3.6	8.3	37.3	11.3
- 14 + 28	3.2	7.8	39.6	10.8
- 28 + 48	3.0	8.4	40.8	10.8
- 48 + 100	2.4	7.1	40.9	10.6
- 100 + 200	2.0	4.9	48.3	12.5
- 200	-	-	-	17.4
Composite	4.2		39.2	16.0

Table 22

Volatile Matter Per Cent of Products of
Sink-Float and Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	32.7	30.5	21.0	23.7
- 1 1/2 + 3/4	31.5	30.8	20.3	25.0
- 3/4 + 3/8	32.6	30.8	22.0	28.0
- 3/8 + 4m	31.1	30.2	22.5	28.3
- 4 + 8	32.1	29.6	22.7	29.5
- 8 + 14	31.0	31.3	23.1	29.4
- 14 + 28	30.9	29.8	21.7	29.0
- 28 + 48	30.8	28.9	21.7	28.8
- 48 + 100	31.7	28.3	22.4	29.1
- 100 + 200	32.0	29.0	22.4	29.2
- 200	-	-	-	28.4
Composite	31.6	30.2	21.9	28.3

Table 23

Fixed Carbon Per Cent of Products of
Sink-Float and Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	63.2	59.4	37.8	43.4
- 1 1/2 + 3/4	64.0	58.7	36.1	47.2
- 3/4 + 3/8	62.6	58.7	39.5	52.7
- 3/8 + 4m	64.1	59.5	41.7	56.5
- 4 + 8	63.0	60.4	40.2	57.1
- 8 + 14	65.4	60.4	39.6	59.3
- 14 + 28	65.9	62.4	38.7	60.2
- 28 + 48	66.2	62.7	37.5	60.3
- 48 + 100	65.9	64.6	36.7	60.2
- 100 + 200	66.0	66.1	29.3	58.3
- 200	-	-	-	54.2
Composite	64.2	60.5	38.9	55.6

Table 24

Germanium in Parts Per Million of Products
of Sink-Float and Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	9	82	17	19
- 1 1/2 + 3/4	41	80	13	30
- 3/4 + 3/8	48	70	19	39
- 3/8 + 4m	52	65	14	42
- 4 + 8	55	62	15	46
- 8 + 14	57	52	19	48
- 14 + 28	50	46	16	43
- 28 + 48	42	50	20	39
- 48 + 100	42	39	17	37
- 100 + 200	40	36	24	36
- 200	-	-	-	32
Composite	50	60	16	41

Table 25

Volatile Matter Per Cent of Ash-free
Products of Sink-Float and
Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	34.1	33.9	35.8	35.2
- 1 1/2 + 3/4	33.0	34.4	36.0	34.6
- 3/4 + 3/8	34.2	34.4	35.8	34.7
- 3/8 + 4m	32.7	33.6	35.0	33.4
- 4 + 8	33.7	32.9	36.1	34.1
- 8 + 14	32.1	34.1	36.8	33.1
- 14 + 28	31.9	32.3	36.0	32.5
- 28 + 48	31.8	31.6	36.7	32.3
- 48 + 100	32.4	30.4	37.9	32.5
- 100 + 200	32.6	30.5	43.4	33.4
- 200	-	-	-	34.4
Composite	33.0	33.3	36.0	33.7

Table 26

Fixed Carbon Per Cent of Ash-free Products
of Sink-Float and Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	65.9	66.1	64.2	64.8
- 1 1/2 + 3/4	67.0	65.6	64.0	65.4
- 3/4 + 3/8	65.8	65.6	64.2	65.3
- 3/8 + 4m	67.3	66.4	65.0	66.6
- 4 + 8	66.3	67.1	63.9	65.9
- 8 + 14	67.9	65.9	63.2	66.9
- 14 + 28	68.1	67.7	64.0	67.5
- 28 + 48	68.2	68.4	63.3	67.7
- 48 + 100	67.6	69.6	62.1	67.5
- 100 + 200	67.4	69.5	56.6	66.6
- 200	-	-	-	65.6
Composite	67.0	66.7	64.0	66.3

Table 27

Germanium in Parts Per Million of Ash-free
Products of Sink-Float
and Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	9	91	29	28
- 1 1/2 + 3/4	43	89	23	41
- 3/4 + 3/8	50	78	31	48
- 3/8 + 4m	55	72	22	49
- 4 + 8	58	69	24	53
- 8 + 14	59	57	30	55
- 14 + 28	52	50	26	48
- 28 + 48	43	55	34	43
- 48 + 100	43	42	29	41
- 100 + 200	41	38	46	41
- 200	-	-	-	39
Composite	53	66	27	49

Table 28

Germanium in Parts Per Million in Ash of
Products of Sink-Float and
Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	219	812	41	59
- 1 1/2 + 3/4	911	762	30	112
- 3/4 + 3/8	1000	667	49	201
- 3/8 + 4m	1083	631	39	274
- 4 + 8	1122	620	40	342
- 8 + 14	1583	627	51	428
- 14 + 28	1563	590	40	397
- 28 + 48	1400	595	49	359
- 48 + 100	1750	549	42	345
- 100 + 200	2000	735	50	285
- 200	-	-	-	184
Composite	1200	646	42	256

Table 29

Ratio of Concentration Obtained by Ashing

Products of Sink-Float and

Size Separations

Size	Specific Gravity			
	Float 1.30	Sink 1.30 Float 1.35	Sink 1.35	Composite
+ 1 1/2"	24.4	9.9	2.4	3.1
- 1 1/2 + 3/4	22.2	9.6	2.3	3.7
- 3/4 + 3/8	20.8	9.5	2.6	5.2
- 3/8 + 4m	20.8	9.7	2.8	6.6
- 4 + 8	20.4	10.0	2.7	7.5
- 8 + 14	27.8	12.1	2.7	8.9
- 14 + 28	31.2	12.8	2.5	9.3
- 28 + 48	33.3	11.9	2.4	9.3
- 48 + 100	41.7	14.1	2.5	9.4
- 100 + 200	50.0	20.4	2.1	8.0
- 200	-	-	-	5.8
Composite	23.8	10.7	2.6	6.3

Table 30

Weight Per Cent of Products of 1.50 Specific Gravity Separation of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	19.05	3.00	22.05
- 4m + 8	20.41	2.47	22.88
- 8 + 14	17.95	1.73	19.68
- 14 + 28	13.69	1.28	14.97
- 28 + 48	7.85	0.82	8.67
- 48 + 100	5.08	0.60	5.68
- 100 + 200	2.26	0.31	2.57
- 200	-	-	3.50
Composite	86.29	10.21	100.00

Table 31

Ash Per Cent of Products of 1.50 Specific Gravity Separation of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	8.5	55.2	15.0
- 4m + 8	6.7	59.7	12.5
- 8 + 14	6.1	64.2	12.3
- 14 + 28	5.3	65.4	10.7
- 28 + 48	5.5	68.2	11.7
- 48 + 100	5.4	73.0	12.8
- 100 + 200	5.4	69.7	13.1
- 200	-	-	17.4
Composite	6.5	61.6	12.5

Table 32

Volatile Matter Per Cent of Products of
1.50 Specific Gravity Separation
of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	31.6	17.1	29.6
- 4m + 8	32.4	15.6	30.5
- 8 + 14	31.4	15.4	30.0
- 14 + 28	32.2	15.5	30.7
- 28 + 48	31.4	18.9	30.1
- 48 + 100	31.2	18.8	29.9
- 100 + 200	31.5	21.1	30.2
- 200	-	-	29.1
Composite	31.8	16.6	30.2

Table 33

Fixed Carbon Per Cent of Products of
1.50 Specific Gravity Separation
of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	59.9	27.7	55.4
- 4m + 8	60.9	24.7	56.9
- 8 + 14	62.5	20.4	58.7
- 14 + 28	62.5	19.1	58.6
- 28 + 48	63.1	12.9	58.1
- 48 + 100	63.4	8.2	57.3
- 100 + 200	63.1	9.2	56.6
- 200	-	-	53.5
Composite	61.7	21.8	57.3

Table 34

Germanium in Parts Per Million of Products
of 1.50 Specific Gravity Separation
of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	52	11	47
- 4m + 8	52	6	47
- 8 + 14	44	13	41
- 14 + 28	43	6	40
- 28 + 48	40	3	36
- 48 + 100	39	11	36
- 100 + 200	37	17	35
- 200	-	-	31
Composite	47	9	42

Table 35

Volatile Matter Per Cent of Ash-free Products
of 1.50 Specific Gravity Separation
of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	34.5	38.2	34.8
- 4m + 8	34.5	38.8	34.9
- 8 + 14	33.4	43.0	33.8
- 14 + 28	34.0	44.8	34.4
- 28 + 48	33.2	59.4	34.1
- 48 + 100	33.2	69.6	34.3
- 100 + 200	33.3	69.7	34.8
- 200	-	-	35.2
Composite	34.0	43.2	34.5

Table 36

Fixed Carbon Per Cent of the Ash-free Products of
1.50 Specific Gravity Separation
of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	65.5	61.8	65.2
- 4m + 8	66.5	61.2	65.1
- 8 + 14	66.6	57.0	66.2
- 14 + 28	66.0	55.2	65.6
- 28 + 48	66.8	40.6	65.9
- 48 + 100	66.8	30.4	65.7
- 100 + 200	66.7	30.3	65.2
- 200	-	-	64.8
Composite	66.0	56.8	65.5

Table 37

Germanium in Parts Per Million of Ash-free
Products of 1.50 Specific Gravity
Separation of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	57	25	55
- 4m + 8	56	15	54
- 8 + 14	47	36	46
- 14 + 28	45	17	45
- 28 + 48	42	9	41
- 48 + 100	41	41	41
- 100 + 200	39	56	40
- 200	-	-	38
Composite	51	23	48

Table 38

Germanium in Parts Per Million in Ash of
Products of 1.50 Specific Gravity
Separation of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4 μ m	612	20	314
- 4 μ m + 8	776	10	376
- 8 + 14	721	20	334
- 14 + 28	811	9	374
- 28 + 48	727	4	308
- 48 + 100	722	15	281
- 100 + 200	685	24	267
- 200	-	-	178
Composite	718	15	336

Table 39

Ratio of Concentration Obtained by Ashing
of Products of 1.50 Specific Gravity
Separation of the Sized Fractions

Size	Specific Gravity		
	Float 1.50	Sink 1.50	Composite
- 3/8" + 4m	11.8	1.8	6.7
- 4m + 8	14.9	1.7	8.0
- 8 + 14	16.4	1.5	8.1
- 14 + 28	18.8	1.5	9.4
- 28 + 48	18.2	1.3	8.6
- 48 + 100	18.5	1.4	7.8
- 100 + 200	18.5	1.4	7.6
- 200	-	-	5.8
Composite	15.3	1.7	8.0