

AN INVESTIGATION OF THE PROPERTIES
OF
SASKATCHEWAN VOLCANIC ASH

A Thesis

Submitted to

THE FACULTY OF GRADUATE STUDIES

In Partial Fulfillment of

The Requirements for

The Degree of

MASTER OF SCIENCE

in Chemical Engineering

in the

Department of Chemistry

University of Saskatchewan

by

Lloyd William Crawford

Written Under the Supervision of

Dr. A. B. Van Cleave

107959

Saskatoon, Saskatchewan

September 1951

ACKNOWLEDGMENTS

I wish to express my sincere thanks to Dr. A. B. Van Cleave for direction of my work and assistance in the preparation of this thesis.

I am indebted to the Ceramics Department for the use of grinding apparatus.

My thanks are due to G. Rennie for providing the data on calcination of ashes.

I am deeply grateful to the Saskatchewan Research Council, which provided me with financial assistance for this research.

I wish to thank Dr. S. D. Cavers for assistance in the preparation of the figures in this thesis.

TABLE OF CONTENTS

INTRODUCTION.....	1
Purpose.....	1
Definitions.....	1
Volcanic Ash in Saskatchewan.....	3
Uses of Volcanic Ash.....	6
POZZOLANS.....	
Introduction.....	9
Definition of Pozzolans.....	10
Pozzolanic Activity.....	11
Classification of Pozzolans.....	12
Properties of Portland-Pozzolan Concretes.....	13
Methods for Determining Pozzolanic Activity.....	20
Calcination of Pozzolanic Materials.....	22
PARTICLE SIZE AND SURFACE AREA.....	25
ADSORPTION OF GASES AND VAPORS BY SOLIDS	
Definitions.....	29
The Data of Adsorption.....	30
Experimental Methods of Determining Adsorption Data.....	32
Types of Adsorption Isotherms.....	34
Theories of Adsorption.....	35
EXPERIMENTAL	
Grinding.....	54
Clay Analyses.....	54
Reactivity Test.....	57
Calcination of Samples 3726 and 4021.....	75
Description of the Adsorption Apparatus.....	80
The Operation of the Apparatus.....	83

TABLE OF CONTENTS (continued)

Calculation of the Volume of Gas Adsorbed.....86

Specific Surfaces of Saskatchewan
Volcanic Ashes.....87

Comparison of Specific Surfaces with the
Results of the Reactivity Test.....91

SUMMARY.....92

SUGGESTIONS FOR FURTHER WORK.....93

BIBLIOGRAPHY.....96

APPENDIX.....100

LIST OF TABLES AND FIGURES

TEXT

TABLE I.....Saskatchewan Volcanic Ashes.....4

TABLE II.....Sieve Analysis of Volcanic Ashes.....5

TABLE III.....Saskatchewan Volcanic Ash Analyses.....55

TABLE IV.....Saskatchewan Volcanic Ash Analyses
on the basis of samples dried at 105 deg..56

TABLE V.....Reactivity Test with 0.5N Sodium
Hydroxide on Saskatchewan Volcanic Ashes..60

TABLE VI.....Reactivity Test on Saskatchewan Volcanic
Ashes varying the Normality of Sodium
Hydroxide.....71~~70~~^c

TABLE VII.....Reactivity Test on Volcanic Ashes 3726
and 4021.....76~~77~~^c

TABLE VIII...Calibration of Gas Buret..... 80b

TABLE LX.....Specific Surfaces of Saskatchewan Volcanic
Ashes.....90b

APPENDIX

TABLE ICalibration of Mercury Cutoff.....100

TABLE II.....Vapor^{Pressure} of Nitrogen and Oxygen as a
function of temperature.....100

TABLE III....Measurement of the Volume of Tubing
Joining the Buret and the Cutoff.....102

TABLE IV.....Measurement of the Volume of Tubing
between Stopcocks G and H.....102

Table V.....Primary Adsorption Data.....103

TABLE VI.....Adsorption Data Calculated for Figures
11 to 15.....107

LIST OF FIGURES

FIGURE 1....	Reduction in Alkalinity vs. Time for Saskatchewan Volcanic Ashes.....	68
FIGURE 2....	Silica Release vs. Time for Saskatchewan Volcanic Ashes.....	69
FIGURE 3....	Reduction in Alkalinity and Silica Release vs. Time for Calcined Sample 3726.....	78b
FIGURE 4....	Reduction in Alkalinity and Silica Release vs. Time for Calcined Sample 4021.....	78c
FIGURE 5....	Reduction in Alkalinity in 24 Hours vs. Calcination Temperature.....	78d
FIGURE 6....	Silica Release at 24 Hours vs. Calcination Temperature.....	78e
FIGURE 7....	Adsorption Apparatus.....	80c
FIGURE 8....	The Adsorption Bulb.....	80d
FIGURE 9....	Vapor Pressures of Nitrogen Corresponding to Vapor Pressures of Oxygen at the same Temperature.....	88b
FIGURE 10....	Nitrogen Adsorption Isotherms of Saskatchewan Volcanic Ashes.....	88c
FIGURE 11....	B.E.T. Plot of Adsorption Data.....	90c
FIGURE 12....	Huttig Plot of Adsorption Data.....	90d
FIGURE 13....	Harkins and Jura Plot of Adsorption Data.....	90e
FIGURE 14....	Harkins and Jura Plot of Adsorption Data.....	90f
FIGURE 15....	Harkins and Jura Plot of Adsorption Data.....	90g

AN INVESTIGATION OF THE PROPERTIES

OF

SASKATCHEWAN VOLCANIC ASH

INTRODUCTION

Purpose

The purpose of this investigation was to study the adsorptive and reactive properties of Saskatchewan volcanic ashes. As an indication of the chemical reactivity of the ashes, a test showing the reduction in alkalinity of a sodium hydroxide solution in contact with the ashes and the release of silica at the same time was performed on the ashes. Similar tests were carried out on calcined samples of two of the ashes. In addition, surface area measurements were made on the ashes by the nitrogen adsorption method, since the surface area is an important factor in the reactivity, adsorptive properties, and catalytic activity of substances.

Definitions

As has been noted many times before, the term "volcanic ash" is not a good one to apply to the material under investigation, since an ash is "the solid residue left when combustible material is thoroughly burned at not too high a temperature", (1), whereas volcanic ash is defined by Ladoo (2) as follows:

"Volcanic ash or pumicite is a more or less finely divided powder or dust made up of small, sharp, angular grains of volcanic glass of about the same composition as pumice. It is formed by the violent and explosive eruption of volcanoes, which throw out dust in great clouds. Ultimately,

the dust settles, often many hundreds or thousands of miles from its original source, and forms beds of pumicite."

There are many different definitions of volcanic ash, but authorities agree that it is material thrown from a volcano, and not of organic origin. For this reason, a more accurate term would be "volcanic dust", as defined by Eardley-Wilmot(3):

"Volcanic dust is a natural glass or silicate, atomized by volcanic explosions and thrown into the air in great clouds which ultimately settle, forming beds of varying thickness, in many cases hundreds or even thousands of miles from its original source. In many instances the dust has been washed down from higher levels and redeposited by the agency of waters, in which case the beds are stratified and often mixed with foreign substances."

Johannsen (4) calls the finest material thrown out by the explosive eruption of a volcano "volcanic sand, ashes, or dust."

It is thought by some authorities that volcanic ashes, under the proper weathering conditions, are converted to bentonites. Spence(5) described bentonite as a "transported, stratified clay, formed by the alteration of volcanic ash shortly after deposition." Ries(6) pointed out that the alteration must involve hydration, devitrification, and leaching of alkalis. Since bentonites occur over much of the continent, it appears that no special geological environment is required, unless the process is started by eruption.

According to J. Alexander(7) bentonites consist of

a group or series of clay-like materials characterized by an alkaline earth and alkaline content of 5-10 percent, fine grain size, high adsorptive properties and usually very strong colloidal properties.

Volcanic Ash in Saskatchewan

Worcester(8) in a report on volcanic ash in Saskatchewan described the location of the deposits as follows:

"While volcanic ash is not known to be widely or uniformly distributed over the province, it has been found to occur in a limited number of places, more especially in the south-central areas, at points near Waldeck, Duncairn, southwest of Neidpath, at St. Victor, west of Rockglen, and near Pickthall. It has also been reported as occurring near the lower end of Big Muddy Lake. It may be mentioned that the Waldeck deposit in the past has generally been known as the Swift Current deposit, while that now reported near Duncairn was formerly referred to as the Beverly or Webb deposit.

"While the known deposits are confined within an area bounded by R.28 west of 2 in the east and R.15 west of 3 to the west, and by T.2 on the south and T.16 on the north, an area of approximately 8000 square miles, it should not be assumed that the ash is continuous over such a large area. In fact, much of the territory within the above bounds has been deeply glaciated since the deposition of the volcanic ash; hence though the ash may originally have been uniformly distributed, large areas were denuded by the ice sheets so that at the present insofar as known, only isolated undisturbed areas remain. It is, however, fairly safe to assume that other areas and deposits than those known do exist, though possibly in other parts of Southern Saskatchewan. Though, at present, sufficiently large quantities near transportation are available for development that further search for new deposits does not appear to be very promising."

Table 1, on page 4, gives details of the samples of volcanic ash and bentonite collected by W.G. Worcester and G.S. Crawford in September of 1948. These details include location, thickness of bed, and approximate overburden and distance to rail.

TABLE I
SASKATCHEWAN VOLCANIC ASHES

Sample No. :	Location :	Thickness of Bed :	Over-burden :	Distance to Rail :
3726 :	Rockglen : N.W.-S.11-T. 3-R. 1-W.3 :	4ft-6in. :	1-20 ft :	3/4 mile :
4005 :	Same :	2ft-6in. :	Same :	Same :
4007 :	St. Victor : -S. 2-T. 6-R.29-W.2 :	5 ft. :	8-20 ft :	8 miles :
4008 :	Same :	8 ft. :	0-20 ft :	8 miles :
4015) :	Neidpath :	6 ft. :	4-10 ft :	6-8 miles :
4016) :	-S.13-T.14-R.11-W.3 :			
4017 :	Same :	4 ft. :	2-8 ft :	Same :
4021 :	Dun Cairn : S.E.-S.19-T.13-R.15-W.3 :	1ft-2in. :	10-20ft :	5 miles by road :
4023 :	Same :	6 ft. :	8-10 ft :	Same :
4024 :	Waldeck : -S.17-T.16-R.12-W.3 :	8 ft. : Exposed :	10-30ft :	1 1/2 miles :
4009 ^a :	Pickthall : -S.34-T. 5-R.30-W.3 :	4 ft. :	0-40 ft :	1 mile :

a Bentonite

The nature of the ash varies from district to district and there is even variation between beds in a particular deposit. That this is true was shown by Worcester(8), who studied the

properties of the above ashes, as summerized in the following four paragraphs.

A study of color was made, with respect to whiteness or freedom from color as judged by the eye. Samples 4023, 4005, and 4021 were ranked highest, with 3726 next. Samples 4015, 4016 and 4017 were medium grey in color, due to dark particles. Samples 4007 and 4008 were quite yellowish, while 4024 was light cream.

As an indication of fineness, the percent of sample passing a 200 mesh sieve was determined. Table II, following, gives these results.

TABLE II
SIEVE ANALYSIS of VOLCANIC ASHES

Sample No.	Percent passing 200 mesh
4005	98.94
4021	96.09
3726	95.71
4023 ;	93.14
4024	88.24
4007	79.05
4008	60.14
4016	15.64
4015	14.98
4017	14.27

Photomicrographs were taken, to find the shapes of the particles making up the volcanic ashes. Samples 3726, 4007

and 4008 were found to be made up mostly of plate-like particles. Samples 4015 and 4023 were seen to contain both plate-like and angular grains, and samples 4016 and 4017 were made up mostly of conglomerations of angular grains. Samples 4005 and 4024 were mostly made up of plate-like particles, with some extremely small particles agglomerated into loosely cemented masses.

A study of burning characteristics at 1922 deg. F. showed all ashes to burn to a red or buff color, and all were more or less vitrified.

Uses of Volcanic Ash

G. S. Crawford(9) wrote a thesis on the industrial uses of volcanic ash in 1948. He studied a large number of references on the uses of volcanic ash up to that time. In this section some of his conclusions will be reported, in addition to some other references.

Pumicite (the American name for volcanic ash) is used a great deal in making cleansing compounds, such as Old Dutch cleanser, which are chiefly pumicite with small amounts of soap powder, soda ash or other ingredients. The Van-Kel Cleansers, Ltd., of Swift Current, Saskatchewan, for a time manufactured cleansers from the volcanic ash found in the deposits now termed as "Waldeck" and "Duncairn". The company ceased to function, although apparently not because of any defects of the material.

Ceramic uses of volcanic ash are limited at the present time.

time. In general, as mentioned before, the Saskatchewan ashes burn to a red or buff color, and this precludes their use in any case where white-burning qualities are required. However, where color is not important, volcanic ashes can sometimes be used as a substitute for feldspar in a number of ceramic products.

Use has been made of volcanic ash as a constituent of glass in Europe, but not in the United States. In colored glasses where the iron content does not matter, volcanic ash can be used as one of the constituents of a very low cost glass.

Volcanic ash has been used to make bricks, but was found to have undesirable properties. However, when used with other substances, it was found possible to produce a satisfactory product, superior in some cases to bricks made from ordinary material, and lower in cost.

Burwell(10) of the Oklahoma Geological Survey studied the use of Oklahoma volcanic ash in the manufacture of a cellular product by heating the ash above 1300 deg. C. Above this temperature are formed tiny cells of gas which improve the insulating properties and render the ash light weight. Reagan(11), at the Ceramic Department, University of Saskatchewan, studied the use of samples 3726 and 4023 in making a light weight structural product. Bentonite was used as bonding agent and a combustible material added in small percentages. The materials were fired to cones 01,

05 and 1. Under certain conditions a satisfactory product was obtained.

Recently, volcanic ash and pumicites have been used as pozzolans. This will be discussed in the section on pozzolans.

Bentonites have been used in the clarification of petroleum. Burroughs(12), Billings(13) and Draper(14) at the University of Saskatchewan did work on the adsorptive powers and decolorizing properties of certain of the ashes as compared to a commercial bentonite, "Filtrol". Pretreatment of the ash included the attack of sulphuric acid at 100 deg. for a few hours, ^{a treatment} approximately equivalent to the industrial activation of bentonite. With only this activation, the decolorization by the ash was not nearly as complete as with the Filtrol, but other treatment might yet be discovered which could improve the ash.

There are numerous other uses to which volcanic ashes have been put, some of which are: in mineral wool(insulation), enamels, fertilizers, as a source of aluminum, as a constituent of asphalt, as an ingredient of acoustic tile, in sweeping compounds, as a paint filler, as an adsorptive packing material, and in the purification of lard and tallow.

In addition to the uses of volcanic ash, mention should be made of the uses of bentonite, which apparently is related to volcanic ash, and which is found in Saskatchewan. It may be used as an adsorptive clay in the petroleum industry, in cement, ceramics, asphalts, fertilizers, paints, printer's

inks, putty, stove polish, soaps, detergents and water softeners. In addition there is a large use in drilling muds, where the thixotropic property of bentonite is important(15). Also, activated bentonite has been used as a cracking catalyst in the petroleum industry(16).

POZZOLANS

Introduction

Before the discovery of natural cements less than two centuries ago, the only hydraulic cements were those composed of a mixture of pozzolan and lime. Such cements date back to ancient Roman and Greek times, when they were employed in the masonry construction of aqueducts, arch bridges, retaining walls, and buildings.

One of the materials used with lime was a consolidated volcanic ash found near Pozzuoli, Italy. This came to be designated as Pozzuolana, a general term covering similar materials of volcanic origin found in other deposits in Italy, Spain and France. Later in Europe, a material showing similar properties was so designated. According to Davis(17), technical men in the United States prefer the spelling "pozzolan".

In Europe, pozzolans have been used extensively as an ingredient of portland-cement concrete, particularly in marine and hydraulic structures. In the United States, the use has not been so extensive, although, as far back as 1912,

600,000 bbl. of portland and pozzolan cement were used in the construction of the Los Angeles aqueduct. Some other structures in which extensive amounts of pozzolans have been or are being used are in the Bonneville Dam(1935), Friant Dam(1942), Davis Dam on the Colorado River, and the Hungry Horse Dam in Montana.

Former practice was to use portland-pozzolan cement produced by intergrinding pozzolan with the cement clinker. However, according to Davis(17), the most recent trend, except in small work, has been to add the pozzolan as a separate material at the mixer, not only as an economical measure but also because different proportions of pozzolan may be desired for different types of concrete.

Definition of Pozzolans

Lea(18), one of the foremost cement chemists, presented the following discussion on the definition of pozzolans:

"The term 'pozzolana' was originally applied to the Italian materials of volcanic origin, but in later times its use has spread to cover other materials which, though different in type, exhibit similar properties, and no useful purpose would now be served by attempting to restrict the term to the natural volcanic earths. The definition suggested is as follows:

"Pozzolanas are siliceous materials which though not cementitious in themselves, contain constituents which at ordinary temperatures will combine with lime in the presence of water to form compounds which have a low solubility and possess cementing properties. It seems desirable to limit the term 'pozzolana' to materials in which silica plays an essential part and not to extend it indefinitely to include any substances showing similar properties, as, for example, arsenious oxide. This limitation is admittedly arbitrary, but once the restriction 'siliceous' is removed, no further limit can be placed on the extension of the term and it becomes entirely independent of chemical composition.

Blast-furnace slag is not considered to be a pozzolana within the terms of this definition, for there is considerable evidence that it is a latent hydraulic cement and that its cementing action does not depend primarily on combination with additional lime."

This definition, or slight variations of it, is accepted generally by investigators working with pozzolans.

Pozzolanic Activity

As portland cement hydrates, calcium hydroxide is liberated. This compound contributes nothing to the strength of concrete, and may be leached out by water. Pozzolans can combine with this lime, and for this reason improve the qualities of concrete.

The nature of the reaction with lime is not at this time clearly understood, but some researchers consider the principal product is a hydrous calcium silicate, perhaps monocalcium silicate. In addition, since most pozzolans contain substantial amounts of materials other than silica, probably other more complex compounds involving alumina, iron, and the alkalis are formed. According to Lea(18), base exchange probably plays little part in the reaction with lime, and even if it did, it is unlikely the action would be cementitious, since normal zeolites show no such cementing properties. The alternative is that direct chemical combination occurs with the formation of compounds mentioned above.

Not all silicious materials are pozzolans. Davis(17) differentiates between pozzolans and non-pozzolans by the

form in which the silica exists. According to him, silica in the amorphous forms reacts with calcium hydroxide much more rapidly than does silica in the crystalline forms, and for a given fineness, the larger the crystals the less rapid the rate of reaction. Thus, in a general way, pozzolans are silicious materials in which at least a substantial portion of the silica is of amorphous structure, while the silica of non-pozzolans is mostly crystalline.

Classification of Pozzolans

Lea (18) classifies pozzolans into five groups:

1. Volcanic tuffs.
2. Diatomaceous earths.
3. Other highly silicious rocks.
4. Burnt clays and shales.
5. By-product hydrated silica.

Blanks (19) enumerates the following types:

1. Clays and shales of Kaolinite or Montmorillonite type.
2. Opaline materials such as diatomaceous earth or opaline cherts and shales.
3. Volcanic tuffs and pumicites.
4. Industrial byproducts such as fly ash or byproduct silica from bauxite purification.

Davis (17) separates pozzolans into two main groups of natural and artificial. Natural pozzolans are subdivided into

two principal classes: (1) those derived from volcanic rocks in which the amorphous constituent is a glass produced by fusion and (2) those derived from rocks or earth for which the silica constituent contains opal, either from precipitation of silica from solution or from the remains of organisms.

In the first class are pumicites, pumice, obsidian, scoria and tuffs. In the second class are diatomites and cherts, shales and clays containing substantial quantities of opaline silica.

Artificial pozzolans are those mentioned by Blanks.

Mielenz et al. (20) over a period of many years carried out experiments on calcination of pozzolans. They classified natural pozzolans, and those substances in which pozzolanic qualities can be induced by calcination, into five main "activity types": volcanic glass, opal, clays, zeolites and hydrated oxides of aluminum. Calcination will be discussed later.

Properties of Portland-Pozzolan Concretes

When comparing properties of portland-pozzolan cements and concretes with portland cement and concrete made from it, the pozzolan may be considered either as an "addition" or a "replacement".

When concretes containing pozzolans are compared with those which do not, the basis may be on equal weights of portland cement alone, in which case the pozzolan is considered

an "addition". If the basis be on equal weights of cementing material, i.e. portland cement plus pozzolan, the pozzolan is considered to be a "replacement."

In practice, "additions" refer to small amounts relative to portland cement, when the amount used is not sufficient to affect weathering resistance or strength, but changes other properties. An example of this is the use of diatomites (approximately 3 percent) to improve workability and prevent segregation.

Usually, pozzolans are used in much larger quantities to improve one or more of the properties of hardened concrete. When larger amounts are used, almost always the quantity of portland cement is less than would be the case if no pozzolan were employed. Thus, it is more convenient to compare test results on the basis of portland cement plus pozzolan, either on a weight basis or a volume basis. Since in general the specific gravities of cement and pozzolans differ, it is usual to compare results on equal weights of cementitious material.

The amount of pozzolan added as replacement depends on a number of factors, such as (17):

1. The properties of fresh and hardened concrete it is desired to enhance.
2. The character and fineness of the pozzolan.
3. The composition of the portland cement.
4. The richness of the mix.
5. The grading of the aggregate.

The optimum amount can be determined only by experiment and may range from as low as five or six percent to as high as

forty or fifty percent replacement.

In general, the amount of calcium hydroxide released by a cement depends on the portion of tricalcium silicate present, so that types of cement high in this substance would be expected to allow higher replacements by pozzolans than those which have a low percentage of tricalcium silicate.

Characteristically, pozzolans used as cement replacements increase the plasticity and decrease the tendency towards bleeding and segregation of mortar and concrete mixes. These advantages are especially pronounced in lean mixes, although the character and fineness of the pozzolan greatly affects the degree of improvement. Most effective are finely ground diatomites, opaline shales, and calcined clays. Less effective are volcanic glasses and water-quenched boiler slags. Finer fly ashes contribute substantially to workability and also decrease bleeding.

For a given slump or flow, in general pozzolans increase the water requirement of mortars and concretes. Some of the very fine fly ashes of low carbon content are exceptions. Increase in water requirement over portland cement without replacement is likely to be greater for opaline substances and calcined clays than for volcanic glasses.

For constant remolding effort as determined by the use of the Powers remolding apparatus, the difference in water requirement for a concrete with replacement and a

concrete containing straight portland cement may be less than the corresponding difference in water requirement based on a given slump or flow. Water-reducing agents seem to be more effective in cutting water requirement of concrete containing some of the pozzolans than when portland-cement concrete is used.

In very lean and harsh mixes, the water requirement for pozzolan-replaced concrete may indeed be less than for straight portland cement concrete, even in cases where, for rich mixes, the water requirement is increased by pozzolan replacement. Many properties of hardened concretes and mortars may be changed by pozzolan replacement.

Davis(17) lists such properties and describes effects of pozzolan replacement. The properties listed are strength of mortars, compressive strength of concretes, elasticity and creep, volume changes, weathering resistance, resistance to aggressive waters, heat of hydration, permeability, alkali-aggregate reaction. Blanks(19) discusses nearly all the same properties with particular pozzolans used in the Friant and Altus Dams.

The tensile strength of mortars generally appears to be greater for mortar containing pozzolans than for mortars not containing pozzolans, if continuous moist curing is used. However, when drying conditions are used, the tensile strength is decreased for opaline pozzolans, and, for glassy pozzolans, is increased. Compressive

strength shows similar tendencies to tensile strength.

Compressive strength of concretes is generally less at early ages if pozzolan replacements are used. However, in lean mixes, such as are usually used in mass concrete, pozzolans generally contribute almost as much to strength as the replaced portland cement, except when water requirement is excessive.

The modulus of elasticity is but slightly affected by pozzolan replacements, although it is lower.

Plastic flow or creep is also greater when pozzolan replacements are used.

Expansion in mortars and concretes under continuously wet conditions generally exceeds slightly that of mortars and concretes containing straight portland cement. Shrinkage under continuously dry conditions generally considerably exceeds that of samples containing only portland cement, particularly for opaline replacements. However, crack-resistance under laboratory conditions does not seem to be affected greatly. However, the relatively large shrinkage suggests that large pozzolan replacements should not be used in mortars and thin concrete sections subjected to continuously drying conditions.

Weathering resistance, as determined by freezing-and-thawing tests on concretes without purposely entrained air, usually is observed to be less for pozzolan concretes.

However, if air entraining agents are added, weathering resistance may be greater than for corresponding air-entrained concrete containing straight portland cement.

Resistance to sulfate waters is improved by opaline and glassy pozzolans, ~~more so~~ by opaline. This is true especially for cements high in tricalcium silicate. In addition, resistance to waters of low pH is increased by some pozzolans.

Weight for weight, heat of hydration for straight portland cement is always greater than for a mixture of portland cement and any known pozzolan. However, pozzolanic reaction does contribute to heat, and for a number of pozzolans at very early ages, rate of hydration may be greater in portland cement-pozzolan mixtures than for portland cement itself. This is desirable in mass concrete construction, as more heat may be dissipated from a lift of concrete before it is covered with the succeeding lift.

"Perhaps one of the most important properties of pozzolans, when used as replacements for a portion of the portland cement, is their ability greatly to reduce the permeability of concrete in lean mixes"(17). Opaline pozzolans are more effective than glassy ones, in fact at early ages concretes using pumicite or fly ash as 50 percent replacement may have permeability several times as large as concrete containing portland cement only. However, at later ages under moist conditions, this same 50 percent replacement

may produce a concrete with a permeability coefficient $1/6$ to $1/15$ that for concrete with straight portland cement. For lean mixes, particularly, a fine pozzolan used as a replacement in moderate to high percentages will lead to a degree of watertightness not otherwise obtainable.

In some regions aggregates have been found which react with the portland cement used in the concrete. This reaction, known as the "alkali-aggregate reaction", causes expansion of the concrete over a period of time, with resultant cracking of the structure involved. According to Lerch(21), the alkali-aggregate reaction is considered to be due to formation of alkali-silicate gels which, when localized in the concrete, exert high osmotic pressures, causing expansion and cracking. There is a minimum alkali content of cement below which the reaction will not occur, and this is because a certain concentration of alkali is necessary to decrease the solubility of calcium hydroxide, in the "free water" in hardened concrete. If the solubility of calcium hydroxide is not repressed, calcium silicates of low solubility and osmotic pressure are formed. Certain pozzolans decrease this alkali-aggregate reaction. Highly reactive opaline pozzolans are more effective in preventing excessive expansion than are glassy pozzolans, and may be used in smaller amounts. Stanton(22) suggests that the effectiveness of pozzolans may be explained by the assumption that the reactive silica of the pozzolan can distribute the alkali-silicate gel throughout the concrete so that localized osmotic pressure cannot become excessive.

Methods for Determining Pozzolanic Activity

Davis(23) says "although there are a number of short-time tests for evaluating the activity of a pozzolan with calcium hydroxide, its effect upon the properties of hardened concrete can be determined with certainty only by long-time tests".

However, Moran and Gilliland(24) have summarized a number of tests. Some of these tests have been originated or adapted at the Bureau of Reclamation in Denver, Colorado, where Moran and Gilliland are employed. In addition, they have included tests from papers previously presented by Feret(25,26), Stanton(27) and Lea(18,28).

They separate the tests into three main groups: tests on pozzolans alone, tests on pozzolan-lime mixtures, and tests on pozzolan-portland cement blends.

Under "tests on pozzolans alone" are considered the chemical composition, solubility studies, lime absorption, optical methods (petrographic analysis) and X-ray analysis.

Chemical composition seems to have no significance in the activity of pozzolans, although silica and alumina are the active constituents. The physical state of the active constituents is of more significance.

Solubility studies include tests to determine solubility in acids or alkalis. Lea(18) came to the conclusion that solubility tests for silica have some value for comparing similar materials, but are of little significance

in indicating the quality of the pozzolan.

The Bureau of Reclamation has specified a test for the calcined shale being used at Davis Dam. The test involves determination of the reduction in alkalinity of a 1N NaOH solution in contact for 24 hours with a finely divided silicious material. It is not claimed that this test is indicative of pozzolanic activity, but when the reduction in alkalinity is compared with the amount of silica dissolved, there seems to be a certain amount of significance with regard to preventing the alkali-aggregate reaction. However, the test has not proven completely satisfactory, and the Bureau of Reclamation in 1949 was working on a test using 0.5N NaOH and varying amounts of ash. The significance of these tests has not yet been published.

Petrographic Analysis of pozzolans, in the hands of a skilled operator, is useful in that the mineralogic composition, petrographic identity and particle size of a proposed pozzolan may be established. By examination of particle size, need for further grinding may be indicated. By means of the microscope, glassy and amorphous substances, indistinguishable by X-ray techniques, may be observed and identified.

X-ray powder analysis of the pozzolanic material may also aid in identification of the minerals present. By means of intensities, relative proportions of minerals present may be estimated, but in general, it is rather difficult to find out how much glassy or amorphous material is present.

Tests on Lime-Pozzolan mixtures include "time-of-set" test, compressive and tensile strength tests, determination of remaining uncombined lime, and insoluble residue tests. In general, these tests are not accurate, but indicate in a general way the activity of the pozzolan. A differentiation can be made between an active, a medium and an inactive pozzolan.

Tests on Pozzolan-Portland Cement blends include a compressive strength test, determination of insoluble residue and uncombined lime, resistance to leaching, lime solubility, resistance to sulfate solutions and reduction-in-expansion tests. The compressive strength results depend on many factors, such as richness of mix, condition of curing, age at test and quantity of admixture. If these variables are recognized and taken into account, pozzolanic action can be recognized. The significance of the results of the insoluble residue and uncombined lime, and the lime solubility tests has never been really proven. Resistance to leaching by distilled water is considered of great importance in Sweden, but resistance to sulfate solutions, according to T. Thorvaldson(29), is not a conclusive method of determining pozzolanic activity due to the large number of variables involved.

Calcination of Pozzolanic Materials

Throughout the references given on pozzolans are statements that pozzolans are frequently improved in activity

by calcination. In 1949 Mielenz, Witte and Glantz(20) of the Bureau of Reclamation published a summary of the results obtained from a study of the effects of calcination on 70 different pozzolans over a period of fifteen years. Tests made on most of the pozzolans included water requirement, setting time of lime-pozzolan paste, strength development of portland pozzolan mortar, and alkalinity reduction and silica release. In addition, some estimates of change in surface were made by means of the Lea-Nurse air permeability method or the Blaine method. As a result of the study, they concluded that natural pozzolans can be classified according to their essential active ingredient or ingredients. This classification was based on five "activity types", as follows:

Activity type	Essential active constituent
1	Volcanic glass
2	Opal
3a	Kaolinite-type clay
3b	Montmorillonite-type clay
3c	Illite-type clay
3d	Mixed clay with vermiculite
4	Zeolites
5	Hydrated oxides of aluminum
6	Nonpozzolan (inactive)

The general conclusion reached was that materials of type 3(a,b,c,d) required calcination to develop satisfactory

activity, and types 1,2 and 4 frequently can be improved. No materials of type 5 were included in the tests.

The conclusions reached by Mielenz et. al. are as follows: pozzolans of activity types 3a and 3b are most affected by calcination between 1000 and 1800 deg. F, due to the changes in composition and crystallographic structure. Pozzolans of activity types 1,2,3c,3d, and 4 (dependent on the zeolite), are not greatly affected up to about 1600 or 1800 deg. F, because the constituents are not affected to such a great extent. Water requirement, strength development of portland-pozzolan mortar and control of alkali-aggregate reaction are greatly improved by calcination of pozzolans of activity types 3a and 3b from 1000 to 1600 deg. F. For pozzolans of type 1, calcination frequently increases strength development of mortar, but alkali reactivity may decrease. Diatomites (type 2) are decreased in water requirements by calcination, but the requirement is still too large to allow large replacements of diatomites. However, more massive, less absorptive opaline pozzolans are affected slightly up to 1800 deg. F. Over 2000 deg., the original active ingredients of all types are destroyed, glasses form, and sometimes pozzolanic activity is induced in previously inactive substances.

W. C. Hanna(30), in commenting on this work, finished his discussion thus:

"We are naturally interested in the reactivity tests

reported in this paper. We think tests of this kind have value, but it is our opinion that before accepting any given pozzolan, thorough tests as to concrete quality should be carried out".

PARTICLE SIZE AND SURFACE AREA

The surface area is an important factor in many properties of a solid. In chemical reactions, the area exposed to reagents will influence the rate. Rate of solution is affected by the area accessible to solvents. Adsorption of liquids and gases depends both on the nature and on the surface area of the adsorbent.

The surface area of regular solids can be related to the particle size if the shape of the particle is known. In a mass of particles of various sizes, a statistical diameter must be ascribed to the particle. There are various types of statistical diameters used to correlate different properties. If one gram of a substance of density ρ has a surface area of S , and is made up of N particles, then

$$S = \frac{6}{\rho d} ,$$

where d is the harmonic mean diameter

$$\frac{1}{d} = \frac{1}{N} \sum \frac{n}{d_i}$$

where n is the number of particles of diameter d_i . These equations apply if the particles are spheres or parallelepipeds.

There are many methods of determining particle size distribution(31). For particles down to 325 mesh (44 microns) in size, sieve analysis is one of the simplest and most accurate methods for determination of particle size distribution.

Down to about 1 micron, a microscope may be used effectively, and below this size the ultramicroscope and electron microscope may be used. However, microscopic methods are tedious, and the small size of the sample used casts doubt on whether the sample is representative.

Sedimentation analyses have been performed by many different methods, and the size distribution is calculated from Stokes' law. Some of the experimental procedures used have been the Andreasen pipet method, as modified by Schweyer and Work(32), the hydrometer method for soils(33), a differential pressure method and a photographic method. In general, sedimentation analyses are valid down to a size of 1 or 2 microns.

For sizes below 1 micron, centrifugal analysis is a useful method of determining distribution of particle size. The ordinary centrifuge(34), the supercentrifuge(36) and the ultracentrifuge(35) have been used for determination of particle size distribution and for fractionation of substances.

Air and liquid elutriation, based on the same theory as sedimentation analysis, has been used to determine size distribution and to fractionate materials. However, the method suffers from the fact that the apparatus is expensive and the experimental procedure is time-consuming.

Turbidimetric methods are used for determining the

surface of portland cement. The Wagner method(37) was found by Schweyer and Work(32) not to apply for substances other than portland cement and ground silica, but due to certain peculiar properties of these substances, the simplifying assumptions used are valid.

Surface area is a more important property of substances in chemical reactions than the particle size. Adsorbents may have a much larger area than would be indicated from the particle size, due to porosity and submicroscopic fissures in the surface.

There are many different methods of determining surface areas, but some of these are so involved that they can not economically be used for a large number of determinations, but only as checks on more rapid methods.

As in determination of particle size, microscopic methods are useful in determining surface areas, but are valid only if there are no pores or cracks. Kenrick(38) suggested a microscopic method of finding surface areas, based on the assumption that the area of a number of particles is four times as large as the projected area on a plane, provided a random distribution of positions of the particles is obtained.

The rate of solution has been used to estimate the surface area of powders, but some known area must be used to calibrate the method. Palmer and Clark(39) calculated the surface area of silica powder, using quartz rods for calibration. However, this method is restricted to those

substances for which a suitable solvent and analytical method can be found.

The permeability method of Carmen(40,41) has been used for evaluation of surface areas. A liquid of known viscosity is allowed to flow through a bed of powder. The void space of the powder is determined from the volume of the bed and the true density of the powder. The rate of flow through a pressure gradient is measured, and from these data the surface can be evaluated from a semi-empirical equation. This method is generally valid for particle sizes down to 2 microns, and is useful for those substances that are too large for adsorption measurements.

Some types of adsorption measurements are adsorption of dyes and radioactive indicators from solution, and adsorption of gases and vapors at temperatures above and below the critical temperature.

Radioactive indicators and dyes suffer from the limitation that the adsorption appears to be a chemical process and does not allow evaluation of the total surface of heterogeneous substances. Indeed, there is uncertainty in the results even for pure chemical compounds.

The adsorption method of Brunauer, Emmett and Teller(42) and others using nitrogen as an adsorbate at liquid nitrogen temperature has been established over a period of years to be a method valid for fine particles. Brunauer(43) states that a conservative estimate of accuracy for the method is 20

percent, and that the method is universal. The adsorption of inert gases like argon and nitrogen generally does not affect surface, and the experimental procedure is quite simple. In a few particular cases, even nitrogen is too large a molecule to penetrate the finest pores, and helium or hydrogen at their boiling points should be used. Because of these advantages, it was considered that the gas adsorption method would be the most satisfactory one to use for evaluation of the surface areas of the volcanic ashes. Discussion of the apparatus, experimental procedure and theories of adsorption are presented in the next section, and in the appendix.

ADSORPTION OF GASES AND VAPORS BY SOLIDS

Definitions(43)

When gas or a vapor is brought into contact with an evacuated solid a part of it is taken up by the solid. The molecules taken up by the solid may either enter the inside of the solid or remain on the outside, attached to the surface. The former phenomenon is called absorption, the latter, adsorption. If these two processes occur simultaneously, the uptake of gas is designated by the term sorption.

The solid taking up the gas or vapor is called the adsorbent, and the gas or vapor attached to the surface is called the adsorbate.

Actually the definition of adsorption given above may cause confusion when applied to porous substances, in which the surface of the adsorbent accessible to molecules may greatly exceed the external surface, that surface which may be observed by a microscope. However, as long as the gas does not penetrate into the field of force between the atoms, ions or molecules inside the solid, it is considered to be on the "outside".

Absorbed gases may merely form a solid solution or may combine chemically with the solid to form a different compound. Likewise, adsorbed substances may interact with solids by one of two processes, either by a weak interaction between solid and gas, similar to condensation, or by a strong interaction, similar to chemical reactions. The former is called "physical adsorption" or "van der Waals adsorption", and the latter is called "chemical adsorption", "chemisorption", or "activated adsorption". The name "van der Waals' adsorption" implies that the same forces active in condensation are also active in physical adsorption. The name "activated adsorption" ^{implies that the process} requires a large activation energy, as chemical reactions do.

Since data from physical adsorption are used in surface area determinations almost to the exclusion of chemical adsorption, the latter will not be further discussed.

The Data of Adsorption

Adsorption data may be separated into two broad groups,

rate data and equilibrium data. Since rate data is of interest in surface area measurements only insofar as equilibrium must be reached or very closely approached in order that surface areas may be calculated, rate of adsorption will not be discussed here.

The amount of gas or vapor adsorbed when equilibrium is established at a given temperature and pressure is a function of the nature of the adsorbent and adsorbate. Equilibrium data are generally arranged in one of three ways.

1. If temperature is kept constant for a given solid adsorbing a given gas, the plot of amounts adsorbed at different pressures against the pressure is called the adsorption isotherm.

2. When temperature is varied while pressure is kept constant, the plot of amount adsorbed at a given temperature against the temperature is called the adsorption isobar.

3. If a plot is made, for a given gas and a given solid, of the temperature against the pressure for a definite amount of gas adsorbed, the plot is called an adsorption isostere.

Since a series of adsorption isotherms at different temperatures can be replotted to give adsorption isosteres or isobars, a theory which gives a complete account of the adsorption isotherm accounts for the isostere and isobar as well.

The amount of gas adsorbed is generally expressed either as the volume of gas adsorbed at S.T.P. taken up per gram of adsorbent, or as the weight of gas adsorbed per gram of adsorbent.

Besides the relationships between amount of gas adsorbed, temperature, and pressure, the energy changes involved in adsorption may be studied. The heat of adsorption may be either measured by direct calorimetric means or evaluated by the use of certain thermodynamic functions on the adsorption data.

Experimental Methods of Determining Adsorption Data

In general, adsorption measurements are divided into two groups, determination of amount adsorbed, and determination of the heat of adsorption.

The amount of adsorption may be determined either directly or indirectly. Direct methods are used to measure either the volume or the weight of adsorbed material, whereas indirect methods make use of some other physical properties which are known to be related to the amount adsorbed.

Before measurements of any sort are made, the surface of the adsorbent must be purified. However, Emmett(44) says that for routine surface area measurements, small amounts of chemically adsorbed gases don't make much difference in the final result, although all adsorbed moisture must be removed.

The volumetric method, by which the volume of gas adsorbed is determined, is the oldest and probably the most

widely used method for obtaining adsorption data. The fundamental parts of the apparatus are a bulb containing the sample, a manometer for measuring pressures, a gas buret for measuring amounts of gas, and a system for evacuating the adsorbent. Many modifications of this basic design have been made. Some experimenters prefer to use no stopcocks, but mercury cutoffs instead. Others include different manometers for different pressure ranges.

Emmett(44) describes a simple apparatus for adsorption determinations, as do Bugge and Kerlogue(45), who used a similar apparatus. Harkins and Jura(46) use a somewhat modified apparatus which, they claim, permits more precise measurements. The apparatus used in the present investigation was built according to Harkins and Jura's model and will be described in the section on experimental results.

In general, the method used with a volumetric apparatus involves evacuation of the sample, followed by admitting a known amount of gas into the adsorption bulb, which is surrounded by a constant temperature bath. After equilibrium has been reached, the final pressure of the system is measured. In order to calculate the amount of gas adsorbed, it is necessary to determine the "dead space", that space in the adsorption bulb not occupied by the sample. This space includes any pores or cracks in the sample, and must be measured by a gas which is not adsorbed at the temperature of measurement. Helium is usually used for this purpose, since even at low temperatures such as the boiling point of liquid nitrogen, its

adsorption is so much less than the adsorption of other gases, it may be assumed that no adsorption occurs.

The volume of gas adsorbed may be calculated from the following equation,

$$v = v_1 - v_r - v_h(1 + \alpha),$$

where v is the adsorbed volume, v_1 is the total volume of gas in the buret before adsorption, v_r is the volume remaining in the buret after adsorption, v_h is the volume of helium necessary to fill the dead space at the equilibrium pressure and temperature, and α is a correction factor taking into account the deviation of the gas in the dead space from the ideal gas law.

The gravimetric method is used to determine the weight of gas adsorbed from the increase in weight of adsorbent in contact with the gas at a given pressure. McBain and Baker⁽⁴⁷⁾ developed the sorption balance. This consists of a helical spring of fused silica, to the upper end of which is hooked a glass supporting sphere, and to the lower end of which is attached a bucket which holds the adsorbent. The spring is calibrated, and the weight of vapor taken up at various pressures can be estimated from the stretching of the spring. A buoyancy correction must be made with this apparatus. The sorption balance is particularly useful at high pressures, considerably greater than one atmosphere.

Types of Adsorption Isotherms

It has been found by Brunauer⁽⁴³⁾ that the shape of any isotherm corresponds to one of five basic types. Type I curves represent unimolecular adsorption, and are generally

called Langmuir isotherms. They are concave to the pressure axis at all pressures up to the saturation pressure. Type II isotherms are concave to the pressure axis at low pressures, linear in the intermediate pressure region, and convex to the pressure axis at higher pressures. This type of isotherm is called the S-shaped or sigmoid isotherm. Type III isotherms are convex to the pressure axis through the whole range of pressures from zero to saturation pressure. Type IV isotherms are similar to type II isotherms, except that a portion of the isotherm near saturation becomes concave to the pressure axis. Similarly, type V isotherms resemble type III isotherms except that near the saturation pressure the isotherm becomes concave to the pressure axis.

Theories of Adsorption

At the present time the most widely used theories of adsorption for estimation of surface areas are the Brunauer, Emmett and Teller theory, the Harkins and Jura theory, and the Hüttig theory. In this section these three theories will be discussed, along with the Langmuir theory, which is the basis for the B.E.T. and Hüttig theories.

In 1915, Langmuir(48) proposed a theory to explain adsorption. The Langmuir equation is considered by Brunauer(43) to be the most important single equation in the field of adsorption. It is necessary to understand this theory before attempting to understand the B.E.T. and Hüttig theories.

The Langmuir equation has been derived in three ways, from kinetic principles, from thermodynamic principles, and from statistical principles.

According to the original Langmuir kinetic derivation, adsorption arises when a collision of a gas molecule with a solid surface results in inelastic collision, thus allowing the molecule to remain on the surface for a finite length of time. After a while, the molecule can return to the gas phase. In some cases the molecule may be elastically reflected, particularly when high temperatures are involved.

When the rate at which molecules strike the surface is μ and the rate of evaporation is ν , the net rate of adsorption is,

$$1 \quad \frac{ds}{dt} = \alpha\mu - \nu$$

where s is the surface concentration (gas molecules adsorbed per cm^2 of surface), and α is the condensation coefficient (ratio of number of molecules condensing on the surface to the number striking the surface). Since, except at high temperatures, most collisions are inelastic, α is close to unity.

When equilibrium is reached, the rate of adsorption is zero. Therefore,

$$2 \quad \alpha\mu = \nu$$

From the kinetic theory of gases,

3
$$\mu = \frac{P}{(2\pi m kT)^{1/2}}$$
 where m is the mass of the molecule of gas and k is Boltzmann's constant.

The value of ν depends on the strength of binding between the solid and adsorbed molecule. If q is the heat of adsorption for one molecule, then only those molecules can escape which have an energy equal to or greater than q . Therefore,

$$\nu = k_0 \exp(-q/kT)$$

where k_0 is a constant.

Forces active in adsorption have a short range of action. Valence forces decrease exponentially with distance between an adsorbed molecule and an atom of the surface, and van der Waals' forces decrease with the seventh power of the distance. Therefore it appears unlikely that surface forces will affect molecules beyond those in the first layer. However, there are attractive forces between adsorbed molecules in the first layer and molecules in the gaseous phase. If these are strong enough, it is possible a second layer may be formed. Since the rate of evaporation varies exponentially as the heat of adsorption, a small difference in q between first and second layers would affect ν greatly. Langmuir considered the difference large enough to prevent a second layer from forming, but present theories consider the possibility of multilayer formation.

Langmuir derived his equation on the assumption that only unimolecular adsorption occurred. Put in other words, he assumed that every molecule coming from the gas phase and striking a molecule already adsorbed is elastically reflected, and only those molecules striking bare surface are adsorbed. This

is expressed by,

5

$$\alpha\mu = \alpha_0(1-\theta)\mu$$

where α_0 is the condensation coefficient on the bare surface, and θ is the fraction of surface covered. He also assumed that the probability of evaporation of a molecule from the surface is the same whether neighboring positions on the surface are occupied by other gas molecules or not. This is equivalent to assuming the adsorbed molecules have no effect on one another.

6

$$v = v_1\theta$$

is the equation expressing this assumption, if v_1 is the rate of evaporation from a completely covered surface. This equation also implies that the heat of adsorption q is everywhere the same.

Substituting in the equation $\alpha\mu = v_1\theta$,

7

$$\alpha_0(1-\theta)\mu = v_1\theta$$

or

8

$$\theta = \frac{\frac{\alpha_0}{v_1}\theta}{1 + \frac{\alpha_0}{v_1}\theta}$$

This equation is often written

9

$$\theta = \frac{bp}{1+bp}$$

where

10

$$b = \frac{\alpha_0 \exp(q/kT)}{k_0(2\pi mkT)^{1/2}}$$

If v is the amount adsorbed at a given pressure p , and V_m is the amount adsorbed when a complete layer is formed,

11

$$\theta = \frac{v}{V_m}$$

and 12 $\frac{V_m bp}{1+bp} = v$

The Langmuir equation may be tested by putting the last equation in the form

13

$$\frac{p}{v} = \frac{1}{V_m b} + \frac{p}{V_m}$$

and plotting f vs p . It is found for quite a large number of isotherms that this equation gives a linear plot over a fairly large pressure range. However, this in itself is not sufficient to establish the validity of any equation. From the slope and the intercept of the line, V_m and b can be evaluated, and unless these values are reasonable, the straight lines obtained must be considered fortuitous. It is usually found that V_m values obtained from different gases at the same temperature or from the same gas at different temperatures are not consistent with one another. In addition, a check on V_m values found on mica sheets of known geometrical area showed that the values found were from 3 percent to 86 percent of the true area, even assuming no cracks or capillaries. This work was done at very low pressures. In order to explain the discrepancies, Langmuir suggested that the surfaces may not have been homogeneous, in which case the V_m values would not have been constant over the whole surface. Thus, the volume adsorbed

$$\underline{14} \quad V = \sum \frac{v_i b_i p}{1 + b_i p}$$

where $\sum v_i = V_m$ and the b_i correspond to various different heats of adsorption. Thus he claimed that different gases may be attracted to various parts of the heterogeneous surfaces, explaining inconsistencies in V_m values.

If multilayer adsorption occurs, Langmuir's equation should not apply, since his method of derivation assumes a

unimolecular layer. However, when high pressures do not produce multilayer adsorption, it is found that V_m values become more consistent. Deviations from the straight line plot still occur at lower pressures, presumably due to the heterogeneity of the surface, perhaps containing a relatively small number of active sites of adsorption.

An extension of Langmuir's equation to include multilayer adsorption is the equation first proposed by Brunauer, Emmett and Teller(42), usually referred to as the B. E. T. equation.

In deriving this equation, Brunauer, Emmett and Teller started with Langmuir's concept that the rate of evaporation is equal to the rate of condensation, when equilibrium is reached,

$$2 \quad a_0(1-\theta)\mu = v_1\theta$$

In B.E.T. symbols, the fundamental equation is expressed as,

$$15 \quad a_1 p s_0 = b_1 s_1 \exp(-E_1/RT)$$

where p is the pressure, S_0 is the area covered by zero layers of molecules, s_1 is the area covered by one layer of molecules,

E_1 is the heat of adsorption in the first layer, and a_1 and b_1 are constants. Similarly, if the subscripts 2,.....,i,..... refer to the 2nd,.....ith layer of molecules,

$$16 \quad \begin{aligned} a_2 p s_1 &= b_2 s_2 \exp(-E_2/RT) \\ a_3 p s_2 &= b_3 s_3 \exp(-E_3/RT) \\ &\vdots \\ a_i p s_{i-1} &= b_i s_i \exp(-E_i/RT) \end{aligned}$$

These equalities are considered true from the principle of microscopic reversibility(49).

The total surface of the adsorbent is given by

$$\underline{17} \quad A = \sum_{i=0}^{\infty} S_i$$

and the total volume adsorbed is

$$\underline{18} \quad V = V_0 \sum_{i=0}^{\infty} i S_i$$

where V_0 is the volume adsorbed per cm^2 of surface when it is covered with a complete unimolecular layer. It follows that,

$$\underline{19} \quad \frac{V}{AV_0} = \frac{V}{V_m} = \frac{\sum i S_i}{\sum S_i}$$

where V_m is the volume of gas adsorbed when the entire adsorbent surface is covered with a complete unimolecular layer.

At this point, the simplifying assumptions of the B.E.T. equation are introduced. Brunauer, Emmett and Teller assumed that the molecules in the second and higher layers have evaporation-condensation properties similar to those of the liquid state. This seems reasonable, since the molecules in the second and higher layers are not in contact with the adsorbent, but only with one another. The assumption may be expressed as,

$$\underline{20} \quad E_2 = E_3 = \dots = E_i = \dots = E_L$$

where E_L is the heat of liquifaction, and

$$\underline{21} \quad \frac{b_2}{a_2} = \frac{b_3}{a_3} = \dots = \frac{b_i}{a_i} = \dots = g$$

where g is an appropriate constant.

From 15 we find

$$\underline{22} \quad S_i = y S_0, \quad \text{where } y = \frac{p}{g} \exp(E_i/RT)$$

Similarly,

$$\begin{aligned} \underline{23} \quad S_2 &= x S_1, \quad \text{where } x = \frac{p}{p_0} \exp(E_L/RT) \\ S_3 &= x S_2 = x^2 S_1 \\ S_i &= x S_{i-1} = x^{i-1} S_1 = C x^i S_0 \\ \text{where } C &= \frac{V}{x} \end{aligned}$$

24

We now can substitute in the summations and find that

$$\underline{25} \quad V = \frac{V_m C S_0 \sum (x^i)}{S_0 (1 + C \sum x^i)}$$

To evaluate the summations, we can recall that

$$\underline{26} \quad \sum x^i = \frac{x}{1-x} \quad \text{if } x < 1$$

and that

$$\underline{27} \quad \sum i x^i = \frac{x}{(1-x)^2}, \quad \text{if } x < 1$$

Substituting for the summations, and simplifying,

$$\underline{28} \quad \frac{V}{V_m} = \frac{C x}{(1-x)(1-x+Cx)}$$

Now when $p = p_0$, liquifaction should occur and V approaches infinity. Therefore, from the final equation, when $p > p_0$,

$$\underline{29} \quad x > 1 \quad \text{and since } x = \frac{p}{p_0} \exp\left(\frac{E_L}{RT}\right), \quad 1 = \frac{p_0}{p} \exp\left(\frac{E_L}{RT}\right) \quad \text{and}$$

$$x = \frac{p}{p_0}$$

The B.E.T. equation can be put in the form

$$\underline{30} \quad \frac{p}{V(p_0 - p)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \frac{p}{p_0}$$

for the purposes of testing, and if the equation is valid, a

plot of $\frac{p}{V(p_0 - p)}$ against $\frac{p}{p_0}$ should give a straight line. The intercept is $\frac{1}{V_m C}$ and the slope, $\frac{C-1}{V_m C}$. In order to establish the correctness of the theory, the constants V_m and C must also have reasonable and consistent values.

There are other forms of the B.E.T. equation to apply to cases where the number of layers is restricted i.e. if there are capillaries. In this case the summations cannot be carried

to infinity, but to a finite number of layers, the number being n . In this case,

$$31 \quad \sum_{x=1}^n X_i = X \frac{(1-X^n)}{1-X}$$

and

$$32 \quad \sum_{x=1}^n i X_i = \frac{x(1-x^n)}{(1-x)^2} - \frac{nx^{n+1}}{(1-x)^2}$$

which results in the modified equation

$$33 \quad \frac{V}{V_m} = \frac{cX}{1-X} \frac{(1-(n+1)X^n + nX^{n+1})}{1 + (c-1)X - cX^{n+1}}$$

When $n=\infty$, this equation reduces to equation 30, and when $n=1$ (unimolecular adsorption), the equation reduces to

$$34 \quad \frac{V}{V_m} = \frac{\frac{c}{P_0} P}{1 + \frac{c}{P_0} P}$$

which is Langmuir's equation if $b = \frac{c}{P_0}$.

Brunauer, Emmett and Teller(42), and Brunauer, Deming, Deming and Teller(50) have derived more accurate equations to be applied in the case of capillary condensation, but the constant V_m , which is of interest in surface area determinations, is not generally derived from these equations but from equation 30

The B.E.T. equations can account qualitatively for the five different shapes of isotherm. Type I isotherms can be accounted for by the Langmuir equation or the B.E.T. equation for $n=1$. Type II and type III isotherms are accounted for by the B.E.T. equation for $n=\infty$. If $E_1 > E_2$, a type II isotherm is obtained, whereas if $E_1 < E_2$, a type III isotherm is obtained. Type IV and type V isotherms are obtained when the more complicated equations of B.E.T. and Brunauer, Deming, Deming and Teller are used.

In order to find the surface area from the equation, use is made of V_m , the volume corresponding to a complete unimolecular layer. The area per molecule is found by assuming that the adsorbed molecules have the same packing on the surface as the molecules of the solidified gas have in their plane of closest packing. Brunauer ⁴³ gives this as

$$35 \quad \text{Area} = 4(0.866) \left(\frac{M}{4\sqrt{2} N \delta_s} \right)^{\frac{2}{3}} \text{ cm}^2$$

where M is the molecular weight of the gas, δ_s is the density of the solid adsorbate and N is Avogadro's number. If the packing of the molecules on the surface approximates that of the liquified gas, δ_l , the density of the liquid adsorbate is substituted in the above equation. Then the surface area of the substance corresponding to V_m may be calculated by obtaining the number of molecules from V_h .

The validity of the B.E.T. equation for finding surface areas has been checked by many investigators by many different methods, Brunauer(43) and Emmett(44) cite a number of instances in which the areas calculated from nitrogen adsorption are compared with areas found by other methods, and in which particle sizes estimated from nitrogen adsorption are compared with sizes estimated by other methods. One of the best checks for the B.E.T. theory is the fact that it gives areas which agree quite well with areas found by the Harkins and Jura method, discussed later.

The most direct method of determining surface areas is by microscopic examination, using the method of Kenrick(38).

Barrett, Birnie and Cohen(51), using Kenrick's method, estimated the surface area of finely powdered silica(230-270 mesh) to be 558 cm^2/gm . Using adsorption of water vapor and the B.E.T. plot, an area of 576 cm^2/gm was found.

Another check of surface area measurements is on sized glass beads of small diameter. Emmett(52) performed a surface area determination with nitrogen, and by assuming the beads were spherical, found the average diameter to be 4.5 μ . A microscopic determination showed the average diameter to be 7 μ . The difference was accounted for by a roughening of the surface, increasing the area, due to treatment by cleaning solution. Another treatment by cleaning solution increased the area another 40 percent. Microscopic examination can not take into account roughness of surface on a molecular scale, whereas nitrogen adsorption can.

Comparison of surface areas as found by the gas adsorption method and the permeability method of Carmen(40,41) show good agreement, if the substance examined is smooth and not too small. The two methods checked well on Zinc Oxide pigments, which are known to be smooth, since ultramicroscopic values also agree well.

Although the B.E.T. theory gives surface area values which check well with values obtained by independent methods, it is considered by many theorists that the assumptions on which the theory is built are "crude and unrealistic".(53)

The B.E.T. isotherm, when fitted to the experimental points in the region where equation 30 is linear, does not predict the correct isotherm outside this region. From the linear plot, V_m and C can be evaluated, and then values of V , the volume adsorbed, against p , the pressure, can be calculated. When this is done it is found that the B.E.T. isotherm is generally below the experimental isotherm at low relative pressures (0-0.1), and above the experimental isotherm at high relative pressures (above 0.3). This is true even when there are no complications from capillary condensation (type II isotherm). According to McMillan and Teller(53), the discrepancy at low relative pressures is usually ascribed to heterogeneity of the adsorbent surface, as was also assumed to explain deviations from the Langmuir isotherm. McMillan(54) examined the case of two different types of surface on the same adsorbent, with different heats of adsorption. He managed to obtain a better fit with experimental data, but concluded that even the additional complication of two types of surface did not completely describe the isotherm at low pressures. Walker and Zettlemyer(55) applied a two surface B.E.T. theory to account for non linearity of the B.E.T. equation over any range at all for activated magnesia. A value for V_m could be obtained by drawing a straight line among the points, but by their dual-surface theory they obtained higher V_m values in every case.

McMillan and Teller have summarized the assumptions, limitations, and attempted corrections of the B.E.T. theory and other adsorption theory. It is recognized that the two main troubles with the B.E.T. theory are that no account is taken of horizontal interactions between adsorbed molecules, and that the heat of adsorption in the second and higher layers is likely to be greater than the heat of liquifaction. However, if one, but not both, of these corrections is taken into account, the isotherm is seriously overcorrected. The two corrections so balance one another that in spite of its shaky foundation, the B.E.T. theory gives results which are close to the correct ones, over a relative pressure range from about 0.1 to 0.3.

Another theory which has been advanced to account for S-shaped isotherms, and which is provoking a great deal of discussion at present, is the Hüttig theory. Hüttig assumes multimolecular adsorption, but challenges a basic assumption of the B.E.T. theory. Rosa(56) has presented the Hüttig theory in B.E.T. terminology.

He assumes that there are $n_1, n_2, n_3, \dots, n_i, \dots$ molecules in the 1st, 2nd, 3rd,ith....layers of adsorbed molecules; n_0 is the number of molecules adsorbed if a complete monomolecular layer is formed. Then, Hüttig says that the rate of evaporation is equal to the rate of condensation at equilibrium, but expresses it as,

36

$$a_1 p (n_0 - n_1) = b_1 n_1 \exp(-E_1/RT)$$

$$a_2 p (n_1 - n_2) = b_2 n_2 \exp(-E_2/RT)$$

$$\vdots$$

$$a_i p (n_{i-1} - n_i) = b_i n_i \exp(-E_i/RT)$$

In other words, he assumes that condensation can occur only on exposed surface, but evaporation can occur by all the molecules, those which are covered as well as those which are exposed. Other assumptions are the same as the B.E.T. assumptions. Then,

37

$$n_0 - n_1 = \frac{n_1}{y}, \text{ where } y = \frac{a_1 p}{b_1} \exp(E_1/RT)$$

38

$$n_1 - n_2 = \frac{n_2}{x}, \text{ where } x = \frac{a_2 p}{b_2} \exp(E_2/RT)$$

$$n_{i-1} - n_i = \frac{n_i}{x}$$

Then,

39

$$(n_0 - n_1) + (n_1 - n_2) + \dots = n_0 = \frac{n_1}{y} + \frac{1}{x} (n_2 + n_3 + \dots)$$

and the total number of molecules adsorbed

40

$$n = n_1 + n_2 + n_3 + \dots$$

Now from 3741

$$n_1 = \frac{y}{1+y} n_0$$

and from 3942

$$n_2 + n_3 + \dots = x(n_0 - \frac{n_1}{y})$$

Therefore,

43

$$\frac{n}{n_0} = \frac{n_1 + x(n_0 - \frac{n_1}{y})}{n_0} = \frac{(1+x)y}{1+y}$$

But $\frac{n}{n_0} = \frac{v}{v_m}$, the ratio of the volume adsorbed to the volume of a unimolecular layer. In addition $y = cx$, whence

44

$$\frac{v}{v_m} = \frac{(1+y)cx}{1+cx}$$

If the assumption is made that $x = \frac{p}{p_0}$, as is true for the B.E.T. theory,

$$45 \quad \frac{V}{V_m} = \frac{(1 + \frac{p}{p_0}) c p}{p_0 + c p}$$

which can be put in the form

$$46 \quad \frac{p}{V} (1 + \frac{p}{p_0}) = \frac{p_0}{V_m c} + \frac{p}{V_m}$$

for the purposes of testing. According to Ross(56) the equation gives straight lines over a longer range than does the B.E.T. equation. The constant V_m as determined from the slope is generally slightly smaller than that obtained from the B.E.T. theory.

According to Corrin(57) the equation does not give straight lines over so large a range nor does it give as consistent values for V_m and c as does the B.E.T. equation. He used data of four different gases on ten different substances a total of 40 isotherms.

Hill(58) argues that the Hüttig equation is contrary to the principle of microscopic reversibility, besides which he had also previously shown by a statistical argument(59) that the B.E.T. equation was the only one possible under the assumed conditions.

Harkins and Jura have proposed an isotherm equation based on an entirely different principle from the B.E.T. equation.

By considering the adsorbed film on the adsorbent as a condensed film, they derived the equation,

$$47 \quad \log \frac{p}{p_0} = B - \frac{A}{V^2}$$

where A and B are constants. They also determined the surface

area of a substance (TiO_2) by what they believed was an absolute method. By means of measuring the heat of immersion in liquid adsorbate of that solid when covered with a film of adsorbate, the true or absolute surface of titanium dioxide was measured. It was then found by using different amounts of titanium dioxide that the surface area was proportional to the root of the slope in the above equation, or

$$\underline{48} \quad \Sigma = k A^{\frac{1}{2}}$$

where Σ is the surface area per gram and k is a constant. In this way Σ was evaluated for various adsorbates at various temperatures. When the areas from the different gases are compared to one another, Harkins and Jura found that their equation gives more consistent results than does the B.E.T. equation.

As was mentioned above, Harkins and Jura started from the assumption that the adsorbed film represented a condensed phase on the adsorbent. The condensed phase here is analogous to the condensed phase of the films on liquids. An empirical equation for the condensed phase is

$$\underline{49} \quad \pi = b - a\sigma$$

where π is the decrease of free surface energy, σ is the area per molecule and a and b are suitable constants for each condensed phase. Harkins and Jura plotted π against σ for a number of adsorbents on titanium dioxide. π is found by integration of the Gibb's equation

$$\underline{50} \quad T' = -\frac{a}{RT} \left(\frac{\partial \gamma}{\partial a} \right)_T$$

where Γ is the surface excess of adsorbate in moles/cm², γ is the free surface energy and a is the activity of the adsorbate. Then, at constant temperature,

$$51 \quad d\gamma = -\Gamma RT \frac{da}{a}$$

Now $\Gamma = \frac{v}{V\Sigma}$, where v is volume adsorbed at N.T.P., V is the molar volume at S.T.P. and Σ is the surface area. In addition, for low pressures p is proportional to a , so that

$$52 \quad d\gamma = -\frac{v}{V\Sigma} RT \frac{dp}{p}$$

Then

$$53 \quad \pi = -\int_{\gamma_s}^{\gamma_{sf}} d\gamma = \gamma_s - \gamma_{sf} = \frac{RT}{V\Sigma} \int_0^p \frac{v}{p} dp$$

where γ_s is the free surface energy of the clean surface and γ_{sf} is the surface energy of the surface with an adsorbed film at pressure p . π may be evaluated by graphical integration of this equation. Similarly, if σ is the area per molecule,

$$54 \quad \sigma = \frac{\Sigma v}{Nv}$$

where N is Avogadro's number. A plot of π vs σ for N_2 and H_2O (60) indicates that over a range of pressures, π is proportional to σ . Harkins and Jura then derived their equation from a consideration of Gibb's equation

$$55 \quad d\pi = \frac{v}{V\Sigma} RT \frac{dp}{p}$$

and by putting $\pi = b - a\sigma$, where

$$54 \quad \sigma = \frac{\Sigma v}{vN}$$

Then

$$56 \quad d\pi = \frac{a\Sigma v}{nv^2} dv$$

and therefore,

$$57 \quad \frac{a\Sigma^2 v^2}{NRT} \frac{dv}{v^3} = \frac{dp}{p}$$

By integration from the limits p to p_0 , the saturation vapor pressure,

$$\ln \frac{p}{p_0} = \frac{1}{2} \frac{a \Sigma^2 V^2}{NRT} \left(\frac{1}{V_0^2} - \frac{1}{V^2} \right)$$

where V_0 is the volume adsorbed at $p = p_0$.

Then, if

$$A = \frac{1}{2} \frac{a \Sigma^2 V^2}{NRT} \quad \text{and} \quad B = \frac{A}{V_0^2}$$

$$\ln \frac{p}{p_0} = B - \frac{A}{V^2}$$

Since $A \propto \Sigma^2$, then there is a theoretical justification for the relation

$$\Sigma = k A^{\frac{1}{2}}$$

However, this implies that the constant "a" is indeed a constant for all surfaces. If it is, then according to Harkins, the only way to correlate areas found by this method and areas found from the B.E.T. method is to assume a variation in the area covered per molecule in the first layer, as calculated by the B.E.T. method. This apparent variation is from 13 to 20 \AA^2 per molecule, with peaks at 14.05, 15.2 and 16.15 \AA^2 . Harkins mentions experimental evidence for the variation in area. Thus, comparison of B.E.T. and Harkins-Jura values of areas on a silica-alumina gel gave a molecular area for nitrogen of 14.1 \AA^2 . The surface was coated with a carbonaceous deposit, and although the surface area was decreased, the area per molecule was increased to 16.2 \AA^2 . Removal of the carbonaceous deposit returned the surface area to its original value, but the molecular area was 14.2 \AA^2 .

H.K.Livingston(61) discusses the relationship between

the Harkins and Jura and the B.E.T. equations. According to the B.E.T. theory, $v = \frac{c V_m P P_0}{(P_0 - P)(P_0 - P + cP)}$

This may be substituted into the equations for d and σ , giving

$$k_1 \pi = \log \frac{P_0 - P + cP}{P_0 - P}$$

$$k_2 \sigma = \frac{(P_0 - P)(P_0 - P + cP)}{c P P_0}$$

where $k_1 = \frac{V \Sigma}{RT V_m \ln 10}$, $k_2 = \frac{N V_m}{V \Sigma}$

By plotting $k_1 \pi$ vs $k_2 \sigma$ for various values of c , a check may be made on the validity of Harkins and Jura's assumption, equation 49. It is found that for c values from 25 to 250, (the usual range), $k_1 \pi$ vs $k_2 \sigma$ plots are linear over a fairly wide range of $\frac{P}{P_0}$ values. Thus, it would be expected that both B.E.T. and Harkins and Jura equations would give straight plots if $\pi = b - a\sigma$.

It was found by Emmett(62) that if surface areas are calculated from the Harkins-Jura equation, ~~it is found that~~ the area per molecule of nitrogen varies with the B.E.T. constant. It is not yet possible to say whether this variation is true, or whether the constant "a" of Harkins and Jura may vary from one surface to another.

EXPERIMENTAL

Grinding

The Saskatchewan volcanic ash samples tested were those collected by Worcester and Crawford in September, 1948 (see Table I). These ashes have been stored in stoppered glass bottles since received. Representative samples of approximately 1000 gm. were taken by quartering the contents of the bottle twice. The ashes were passed through a jaw crusher to decrease size to $\frac{1}{4}$ inch and smaller, and then were put through a coffee mill grinder. Most of the ashes passed through the grinder with no difficulty, but samples 4009, 4023 and 4024 contained so much moisture that it was necessary to air-dry them before grinding.

Representative samples, weighing approximately 50 gm., were taken of all ashes after grinding, and placed in 4 oz. bottles with tight rubber stoppers. These were then delivered to the Analytical Department for clay analyses.

In order to obtain comparable results in experimental work, representative portions of the ashes were ground until the whole portion passed a 200 mesh sieve (U.S. Standard). Grinding was done by hand using an agate mortar and pestle.

Clay Analyses

Clay analyses were performed on the ground ashes by Mr. E. Bailey of the Analytical Department, University of Saskatchewan. The results obtained are reported in table III. In table IV the analyses are recalculated on the basis of the sample dried at 105 deg. C.

TABLE III
SASKATCHEWAN VOLCANIC ASH
ANALYSES

Sample Number	3726	4005	4007	4008	4015 4016	4017	4021	4023	4024	4009	4801	Y
Moisture at 105°C	5.43	5.65	3.71	2.71	3.68	3.16	2.19	3.32	10.03	13.47	2.64	
Ignition loss 950°C	6.16	5.72	4.38	4.23	3.95	3.93	5.47	5.48	5.08	5.31	12.99	
SiO ₂	61.93	62.57	66.76	68.51	67.39	67.76	68.90	67.88	59.36	53.21	52.18	
Fe ₂ O ₃	4.18	3.91	2.98	2.44	2.65	2.57	2.28	2.44	4.05	5.36	4.27	
TiO ₂	0.51	0.48	0.26	0.25	0.35	0.26	0.10	0.14	0.44	0.41	0.41	
Al ₂ O ₃	12.53	13.03	14.32	14.00	13.44	13.28	12.54	12.39	12.55	15.93	8.81	
CaO	2.16	1.15	0.94	1.03	1.53	1.44	0.50	0.78	1.38	1.71	12.06	
MgO	2.06	2.30	1.00	0.91	1.64	1.32	0.83	0.91	1.63	2.26	1.51	
Na ₂ O	1.70	1.50	2.65	2.64	2.14	2.35	3.00	2.90	2.46	1.35	1.47	
K ₂ O	3.12	2.94	2.45	2.45	2.57	2.87	3.63	3.70	2.12	0.48	2.73	
Total	99.78	99.25	99.45	99.17	99.34	98.94	99.44	99.94	99.10	99.49	99.07	

TABLE IV

SASKATCHEWAN VOLCANIC ASHANALYSES

On the Basis of the Sample Dried
at 105 deg. C.

Sample Number	3726	4005	4007	4008	4015 4016	4017	4021	4023	4024	4009	4801
Ignition Loss 950C	6.51	6.07	4.55	4.35	4.10	4.06	5.59	5.69	5.65	6.14	13.34
SiO ₂	65.49	66.35	69.35	70.43	69.98	70.00	70.45	70.21	66.04	61.54	53.61
Fe ₂ O ₃	4.42	4.15	3.10	2.51	2.75	2.65	2.33	2.52	4.51	6.20	4.37
Ti O ₂	0.54	0.51	0.27	0.25	0.36	0.27	0.10	0.14	0.49	0.47	0.42
Al ₂ O ₃	13.25	13.83	14.87	14.39	13.96	13.96	12.82	12.82	13.96	18.42	9.05
CaO	2.28	1.22	0.98	1.06	1.59	1.49	0.51	0.81	1.54	1.98	12.39
MgO	2.18	2.44	1.04	0.94	1.70	1.36	0.85	0.94	1.81	2.61	1.55
Na ₂ O	1.80	1.59	2.75	2.71	2.22	2.43	3.07	3.00	2.74	1.56	1.51
K ₂ O	3.30	3.12	2.54	2.52	2.67	2.96	3.71	3.83	2.36	0.56	2.88
Total	99.77	99.28	99.45	99.16	99.33	98.94	99.43	99.96	99.10	99.48	99.06

There is no wide variation from one ash to another in the percentages of the major constituents, silica and alumina. The bentonite, sample 4009 is considerably lower in silica and higher in alumina than are the ashes. The alkalis are considerably lower in the bentonite.

Samples from different beds of the same deposit correspond quite closely in the proportions of all analyzed constituents.

Reactivity Test

As an indication of the chemical reactivity of the ashes, samples were shaken with 0.5 N sodium hydroxide for certain lengths of time, after which an aliquot of the solution was removed and analyzed for alkali content and dissolved silica. According to Moran and Gilliland(24), this test is not an absolute one for pozzolanic activity, but within a class of materials, it indicates which substances are active and which are not active as pozzolans. Non-pozzolanic material, such as powdered quartz, cause a very low reduction in alkalinity of the solutions and only a small amount of silica is released.

The procedure used for the reactivity test was as follows:

A 10.00 gm. sample of ash was weighed out on a piece of glazed paper. The weighed ash was poured into a 100 ml. Pyrex centrifuge tube and stoppered tightly. When all the needed samples had been weighed out, the rubber stoppers were removed and 25 ml of sodium hydroxide of the desired concentration were introduced into each centrifuge tube by

means of a volumetric pipette. The stoppers were replaced and each tube was shaken vigorously to ensure wetting of all parts of the ash. The tubes were then placed in a rotary shaker in the Chemistry Sub-basement, where the temperature could be kept quite constant at about 25 deg. C. After a certain period of time (4 hours, 1 day or 1 week) the tubes were removed from the shaker and centrifuged for 10 minutes or longer if required. When the solid had settled, an aliquot was removed from the solution by means of a pipette. If possible, a 10 ml. aliquot was removed, but swelling of certain samples required that only 5 ml. or even 2 ml. could be taken. The aliquot was placed in an Erlenmeyer flask of appropriate size and titrated with standard hydrochloric acid to the phenolphthalein and modified methyl orange end-points. After neutralization, the solution was placed in a 150 ml. beaker. Impure silica was determined by the perchloric acid method, using 10 ml. of acid. This was less acid than usually recommended for silica analyses, but the amount of silica to be determined was much smaller than the amount usually found in analyses of siliceous materials. A blank determination was made by placing 25 ml. of sodium hydroxide solution in an empty centrifuge tube, and performing the same operations on it as on the ash samples.

As it was virtually impossible to prevent atmospheric carbon dioxide from entering the sodium hydroxide solution, the following reasoning was used to arrive at reduction in alkalinity. Suppose there were A moles of sodium hydroxide

in the solution added to the ash. In this solution there were B moles of carbonate ion. Suppose in the solution after shaking there were C moles of sodium hydroxide and D moles of carbonate ion. If E moles of sodium hydroxide were taken up by the ash, a material balance of sodium hydroxide shows that $A = C + E + 2(D-B)$, where (D-B) moles of carbon dioxide had entered the solution. Therefore, $E = (A + 2B) - (C + 2D)$. The quantity, (A + 2B) is proportional to the amount of acid required to titrate an aliquote of original solution to the modified methyl orange end-point, at which pH both hydroxyl and carbonate ions are neutralized. If no water were taken up by the ash, (C + 2D) would be proportional to the volume of acid required to titrate an aliquote of the solution from the ash sample. Since water was taken by some ashes, the results were reported as "reduction in alkalinity", rather than "sodium hydroxide uptake".

In accordance with accepted practice(24) the results were calculated as reduction in alkalinity per liter of solution for 10 gm. of ash. The formula used was,

$$\text{Reduction in alkalinity} = (V_1 - V_2)N \times 100,$$

where V_1 was the volume of acid required to neutralize 10 ml. of the blank solution, V_2 was the volume of acid required to neutralize 10 ml. of solution from the ash sample, N was the normality of the acid and 100 is a conversion factor from 10 ml. to 1000ml. If an aliquot different from 10 ml. was used, the conversion factor was changed accordingly.

The silica release was also calculated to a basis of millimoles per liter of solution for 10 gm. of sample, from the formula

$$\text{Silica Release} = \frac{W \times 100}{60}$$

where W was the weight in mg. of silica released in 10 ml. of solution (weight of silica in the crucible less weight of the blank solution), 60 is the formula weight of silica, and 100 is the conversion factor from 10 ml. to 1000ml.

Table V gives the experimental data on 10gm. samples of the ashes and also gives the results calculated from the data. Column 1 gives the time of agitation of the samples; column 2 gives the size of aliquot taken; column 3 gives the difference in titration between the blank solution and the aliquot taken from the sample; column 4 gives the weight of silica released; columns 5 and 6 give the calculated results. Figure 1 shows the reduction in alkalinity as plotted from the results in column 5. Figure 2 shows the silica release as plotted from the results in column 6. In both these figures, all results at a single time were averaged.

The Chicago Fly Ash and Butte, Montana, Pumicite were kindly supplied by Professor H. Douglas of the Department of Civil Engineering. The Fly Ash is being used by the United States Bureau of Reclamation in one of their dams as a partial replacement for portland cement. The Butte, Montana, Pumicite has also been approved by the Bureau of Reclamation for use as a pozzolan.

TABLE V

REACTIVITY TEST WITH 0.5N

SODIUM HYDROXIDE ON SASKATCHEWAN

VOLCANIC ASHES

Volcanic Ash 3726

Normality of acid 0.200

Normality of base 0.487

Time hrs.	Aliquot ml.	Difference in titration ml.	Weight of Silica mg.	Reduction in Alkalinity millimoles per liter	Silica Release per 10 gm.
4	10	6.60	12.1	132	20.1
4	10	6.64	12.4	133	20.7
24	10	7.10	22.8	142	38.0
24	10	7.02	22.3	140	37.2
120	10	7.53	41.6	151	69.3
120	10	7.45	41.0	149	68.3

TABLE V (ctd.)

Volcanic Ash 4005

Normality of acid .200

Normality of base .462

Time hrs.	Aliquot ml.	Difference in titration ml.	Weight of Silica mg.	Reduction in Alkalinity millimoles per liter	Silica Release per 10 gm.
4	10	7.52	11.2	150	18.7
4	10	7.65	11.4	153	18.9
24	10	7.83	22.8	157	38.0
24	10	7.85	23.5	157	39.2
168	10	7.95	41.2	159	68.6
168	10	8.15	41.4	163	69.0

TABLE V (ctd.)

Volcanic Ash 4007^a

Normality of acid 0.201

Normality of base 0.462

Time	Aliquot	Difference in titration	Weight of Silica	Reduction in Alkalinity	Silica Release
hrs.	ml.	ml.	mg.	millimoles per liter per 10 gm.	
4	5	1.44	2.6	58.0	8.7
4	5	1.35	2.3	54.0	7.5
68	2	-0.20	11.0	-20	92.0
68	2	-0.25	11.9	-25	99.0
264	2	-0.58	19.2	-58	150
264	2	-0.68	18.8	-68	157

TABLE V (ctd.)

Volcanic Ash 4008 a

Normality of acid 0.215 Normality of base 0.445

Time	Aliquot	Difference in titration	Weight of Silica	Reduction in Alkalinity	Silica Release
hrs.	ml.	ml.	mg.	millimoles per liter	per 10 gm.
4	10	2.56	4.9	56.0	8.3
4	10	2.20	5.3	47.4	8.8
24	5	0.95	12.0	41.0	40
24	5	1.02	12.0	45.4	40

Bentonite 4009 ^b

Normality of acid 0.215 Normality of base 0.445

24	2	0.85	0.9	91	7.5
24	2	0.77	1.0	83	8.3
24	2	0.89	1.0	96	8.3
24	2	0.97	1.1	104	9.1

TABLE V (ctd)

Volcanic Ash 4017

Normality of acid 0.201 Normality of base 0.462

Time	Aliquot	Difference in titration	Weight of Silica	Reduction in Alkalinity	Silica Release
hrs.	ml.	ml.	mg.	millimoles per liter	per 10 gm.
½	10	4.21	7.1	84.2	11.8
4	10	4.14	7.3	82.8	12.2
70	10	4.07	20.1	81.4	33.4
168	10	3.90	23.4	78.0	39.0
168	10	4.05	23.9	81.0	39.8

Volcanic Ash 4021

Normality of acid 0.200 Normality of base 0.487

½	10	2.09	---	41.8	---
4	10	2.69	13.0	53.8	21.7
24	10	2.76	17.8	55.2	29.7
24	10	2.76	18.2	55.2	30.3
240	10	3.46	31.2	69.2	52.0

TABLE V (ctd.)

Volcanic Ash 4024

Normality of acid 0.190 Normality of base 0.445

Time	Aliquot	Difference in titration	Weight of Silica	Reduction in Alkalinity	Silica Release
Hrs.	ml.	ml.	mg.	Millimoles per liter	per 10 gm.
4	10	6.00	18.8	114.0	25.6
24	10	6.24	25.6	118.3	36.1
168	2	1.23	9.4	117.3	78.0

Butte, Montana, Pumicite^c

Normality of acid 0.215 Normality of base 0.445

4	10	6.29	13.8	135	23.0
4	10	5.89	13.5	126	22.5
24	10	7.17	25.5	154	42.5
24	10	7.17	25.2	154	42.0

TABLE V (ctd.)

Chicago Fly Ash ^d

Normality of acid 0.215

Normality of base 0.445

Time	Aliquot	Difference in titration	Weight of Silica	Reduction in Alkalinity	Silica Release
Hrs.	ml.	ml.	mg.	Millimoles per liter	per 10 gm.
4	10	3.40	7.4	73.0	12.3
4	10	3.57	7.0	76.8	11.7
24	10	5.07	11.1	109.0	18.5
24	10	4.87	10.7	105.0	17.8

Footnotes to table V

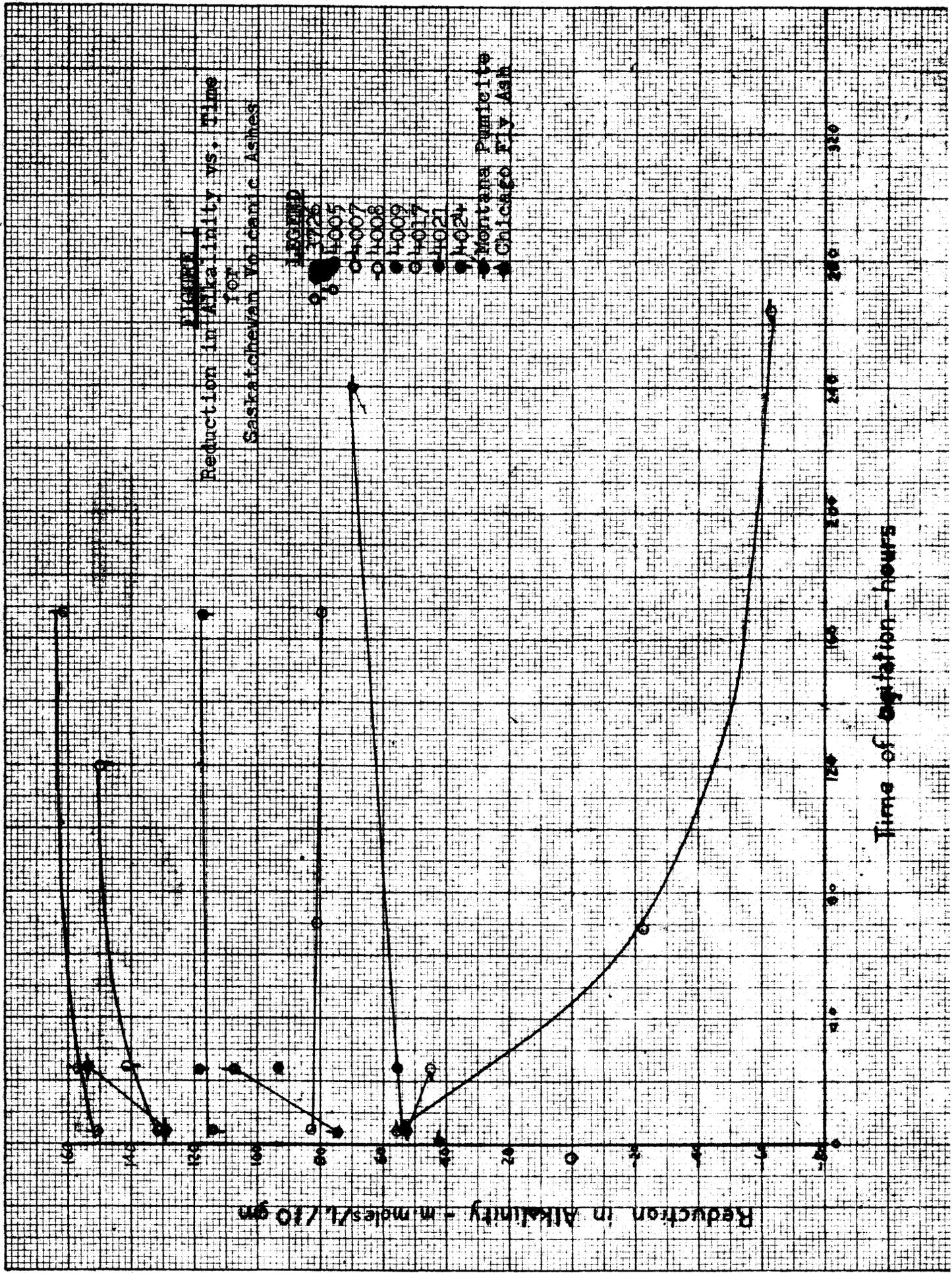
a Sample 4008 swelled up so much that it was impossible to do a determination for a one week period.

b Sample 4009 swelled up so much that it was impossible to do a determination at all with 25 ml. of solution. These results were obtained using 50 ml. of solution.

c The pumicite apparently formed a colloidal solution when agitated with the solution for one week. A portion of the ash remained suspended in the solution in spite of all attempts to centrifuge it.

d The Fly Ash when agitated with the solution for one week, was also impossible to centrifuge.

FIGURE I
Reduction in Alkalinity vs. Time
for
Saskatchewan Volcanic Ashes

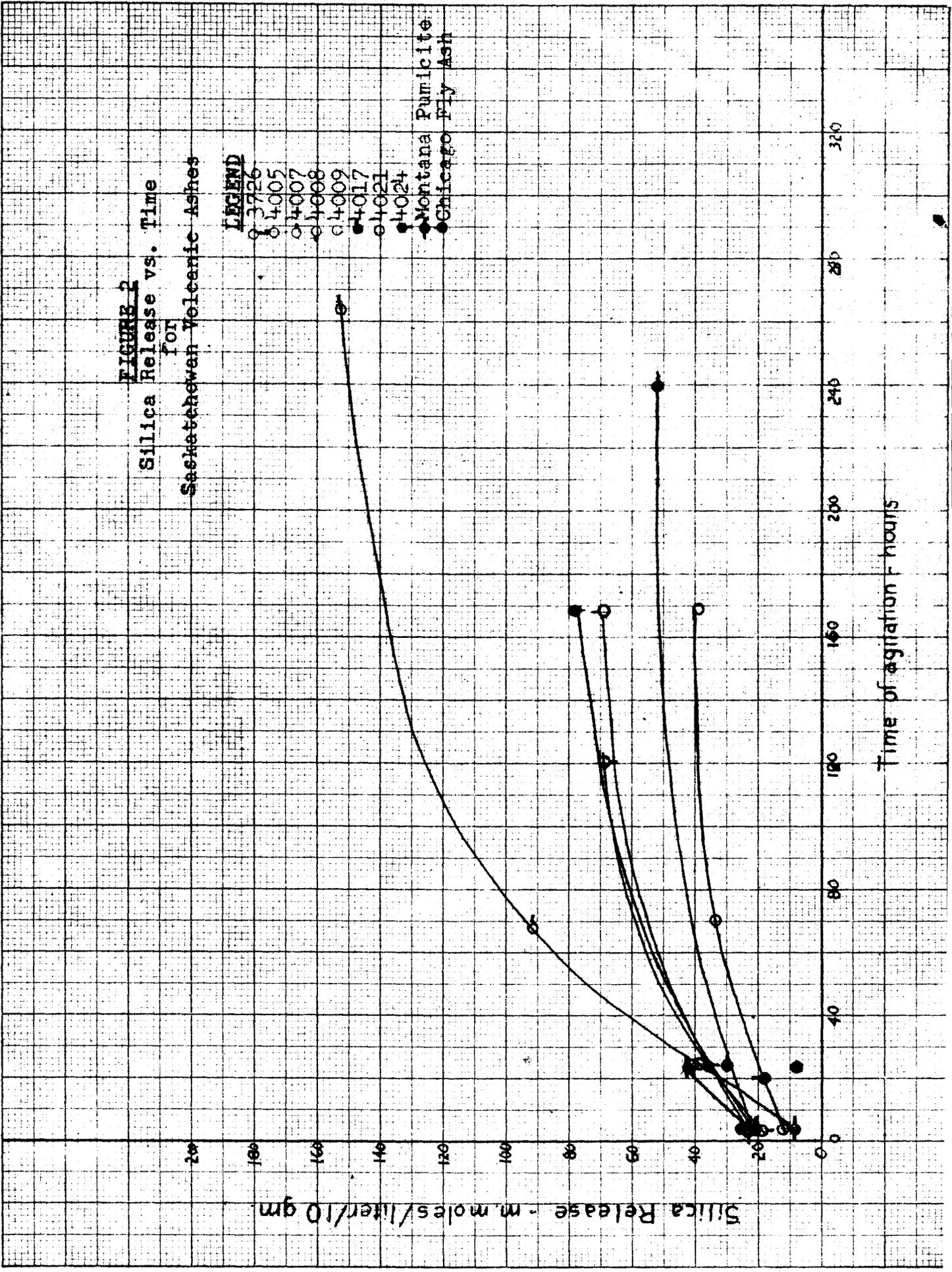


Reduction in Alkalinity - mmoles/l/10 gm

Time of agitation - hours

FIGURE 2
Silica Release vs. Time
for
Saskatchewan Volcanic Ashes

- LEGEND
- 3726
 - 4005
 - 4007
 - 4008
 - 4009
 - 4017
 - 4021
 - 4024
 - Montana Pumicite
 - Chicago Fly Ash



W. L. G. S. A.

From Figure 1 it can be seen that there was considerable variation between the ashes in the reduction in alkalinity. Two pairs of the samples were from the same district. Samples 3726 and 4005 (Rockglen) showed reductions in alkalinity which were quite close to one another. In addition, for the times tested, samples 4007 and 4008 (St. Victor) showed similar reductions in alkalinity. Samples 3726, 4005 and 4021 had slight increases in reduction in alkalinity as the time increased. With increased time, samples 4024 and 4017 had practically constant reductions in alkalinity. Samples 4007 and 4008 showed distinct decreases in reduction in alkalinity with increases in time.

A reactivity test with sample 4021 was done for 15 minutes. Even for this short time, the reduction in alkalinity was close to the reduction in alkalinity for longer times. For this reason, it was considered that the largest portion of the uptake of sodium hydroxide occurred in a short time.

It was observed that samples 4007, 4008 and 4009 (bentonite) swelled up after contact with the solution. Swelling in water is characteristic of bentonite. According to Worcester(65) samples 4007 and 4008 were partially converted to bentonite, and according to Cowie(66) the St. Victor ash was greatly contaminated with bentonite. Therefore it would be expected that samples 4007 and 4008 would swell.

It was observed that samples 4007 had a negative sodium hydroxide uptake at 68 hours. If relatively more water than sodium hydroxide was taken up by the ash, the sodium hydroxide solution would be more concentrated than it was originally. If the uptake of water was slower than the uptake of sodium hydroxide, the reduction in alkalinity would decrease as time of agitation increased. For this reason, it was considered that for those ashes which swelled when agitated with sodium hydroxide solution, the reduction in alkalinity did not give a true indication of the reactivity of the ashes.

The reduction in alkalinity for the pumicite and fly ash showed a rapid increase with time, for the times tested. Samples 3726, 4005 and 4024 had similar reductions in alkalinity to the pumicite.

From Figure 2 and Table V it can be seen that the silica release for samples 4024, 3726 and 4005 were smaller than for the pumicite. Samples 4007 and 4008 have higher releases than the other ashes. This may have been caused by concentration of the dissolved silica in the small amount of water which was not taken up by the ashes, since the silica release was not significantly larger than for the other ashes up to 24 hours of agitation.

A few of the ashes were tested using a sodium hydroxide solution of a concentration different from 0.5. These results are summarized in Table VI.

From Table VI it can be seen that the silica release for all three ashes increased with the concentration of sodium hydroxide. However, the reduction in alkalinity did not vary in a consistent manner with concentration. For sample 4005, the reduction in alkalinity was larger at a normality of 0.5 than at 0.2N or 0.9N. For sample 4017, the reduction in alkalinity was slightly higher for 0.5N sodium hydroxide than for the other two normalities. For sample 4007, the reduction in alkalinity was lower at a normality of 0.5, in fact the reduction in alkalinity was negative at 0.5N, whereas for 0.2N and 0.9N solutions, the reductions in alkalinity were small but positive.

Without further investigation, it is not possible to suggest a reason for the fluctuations. However, it must be remembered in any explanation that the three ashes were from different localities and reacted differently from one another when time of agitation was varied.

The results of Table VI emphasize the necessity of performing the reactivity test using sodium hydroxide of the same normality at all times, if the results are to be compared with one another.

The mechanism of the reaction of volcanic ashes with sodium hydroxide solutions was not elucidated from the results obtained in this investigation. It was found that for sample 4021, the reduction in alkalinity for a time of agitation of 15 minutes was close to what it was at longer times. This suggested that the reduction in alkalinity was

TABLE VI
REACTIVITY TEST
for
SASKATCHEWAN VOLCANIC ASHES

Varying the Normality of Sodium Hydroxide
Volcanic Ash 4005

Time 24 Hours

Normality of acid 0.200

Normality of base	Aliquot ml.	Difference in titration ml.	Weight of Silica mg.	Reduction in Alkalinity Millimoles per liter	Silica Release per 10 gm.
0.169	10	6.12	11.3	132	18.8
0.462	10	7.84	23.1	157	38.6
0.920	10	4.86	42.7	97.2	71.2

TABLE VI (ctd.)

Volcanic Ash 4007

Time 68 Hours

Normality of acid 0.201

Normality of base	Aliquot ml.	Difference in titration ml.	Weight of Silica mg.	Reduction in Alkalinity Millimoles per liter per 10 gm.	Silica Release
0.181	2	0.25	6.3	25	52.5
0.462	2	-0.225	11.5	-22.6	95.0
0.920	5	1.02	35.0	20.4	117.0

Volcanic Ash 4017

Time 70 Hours

Normality of acid 0.201

0.179	10	3.78	7.9	75.6	13.2
0.462	10	4.07	20.1	81.4	33.4
0.92	10	3.66	34.6	73.2	57.6
0.92	10	3.82	35.2	76.4	58.6

caused mainly by adsorption of the alkali from solution, perhaps followed by a slower absorption of alkali. The silica release was not equivalent to the reduction in alkalinity, and the amount of silica released always increased with time of agitation. However, except for samples 4007 and 4008, the silica release at 4 hours was generally at least half the silica release for 24 hours. This would be expected if the smallest particles of ash were dissolved in a relatively short time of agitation. If this happened, only the larger particles of ash would be reacting with the sodium hydroxide after the smaller ones were dissolved, so that the rate of solution of silica would be smaller.

The reactivity test is not an absolute test for pozzolanic or chemical activity (24), but is particularly useful as a short-term control test on substances which have been approved for commercial use. If there are no complications from swelling of the sample, the test gives an indication of the chemical and pozzolanic activity of the substance tested, within a class of materials.

Calcination of Samples 3726 and 4021.

It has been found that calcination sometimes improves the properties of pozzolans. (20). Calcination of ashes 3726 and 4021 was carried out at 100 deg. intervals between 320 deg. and 1065 deg. C.

The ash was first crushed to a size of one quarter inch and smaller with a jaw crusher. The crushed samples were calcined in porcelain evaporating dishes for one hour. After cooling, the samples were ground in a high speed, rotary hammer mill at the Ceramics Department. If a portion of the ash did not pass through a 200 mesh sieve after this treatment, it was ground down to the required size by hand. The samples calcined at 980 deg. and 1065 deg. were ground entirely by hand.

The reactivity test for reduction in alkalinity and silica release was applied to these ashes for periods of 4 hrs., 1 day, and 1 week.

Table VII gives the results from these determinations. Figures 3 and 4 are plotted from this table. These figures give the reduction in alkalinity and silica release of the calcined ashes as a function of time of agitation.

The reduction in alkalinity and silica release are plotted against the temperature of calcination in figures 5 and 6. The values for 24 hrs. are the only ones plotted. The tests were performed by G. Rennie.

From Table VII and Figures 3,4,5,and 6, the effect of calcination on samples 3726 and 4021 can be seen. The reduction in alkalinity for sample 3726 remained practically equal to that of the uncalcined ash up to a calcination temperature of 520 deg., then decreased rapidly, becoming negative at a calcination temperature of 980 deg..

TABLE VII
REACTIVITY TEST ON CALCINED ASHES

Volcanic Ash 3726

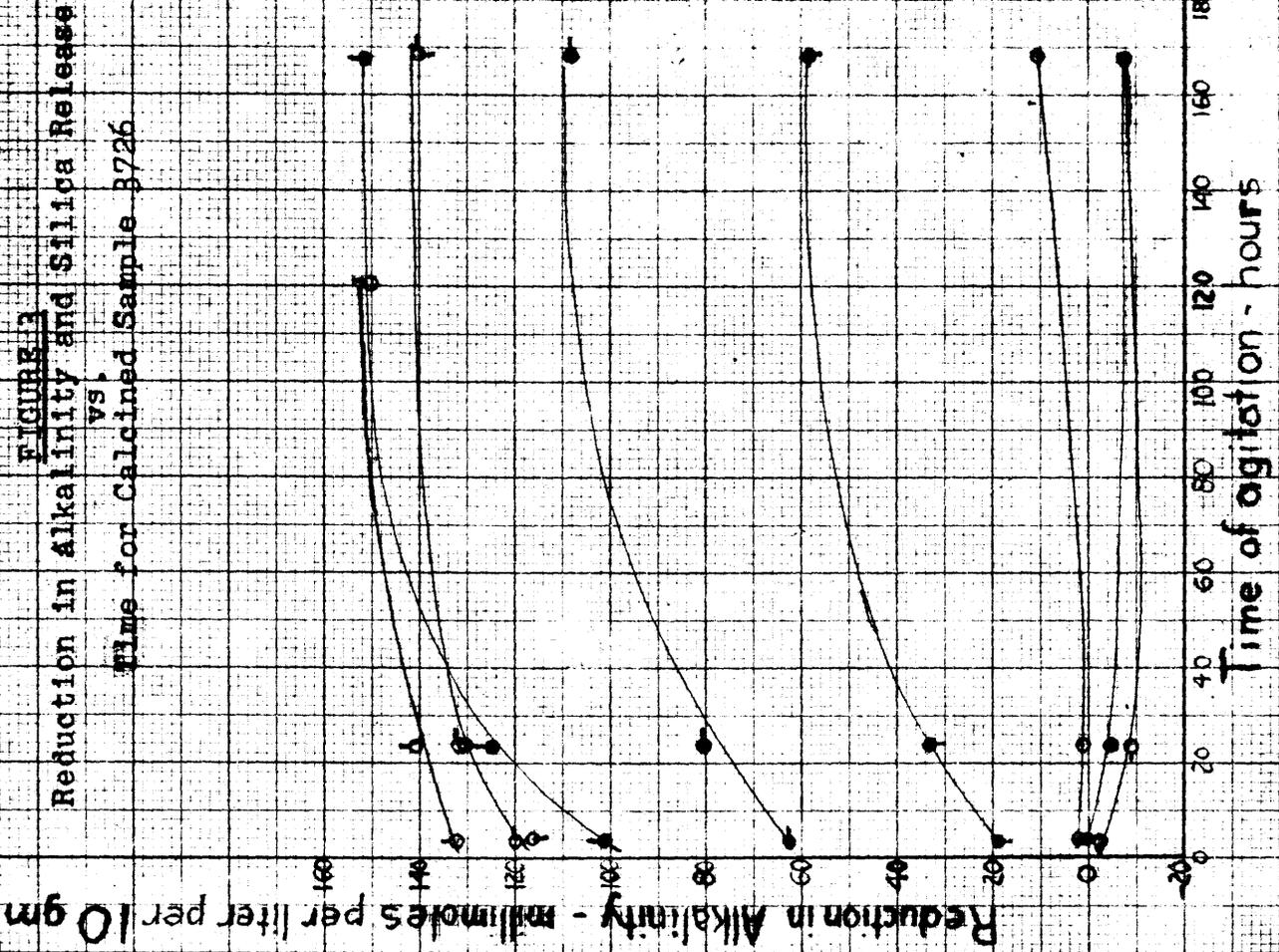
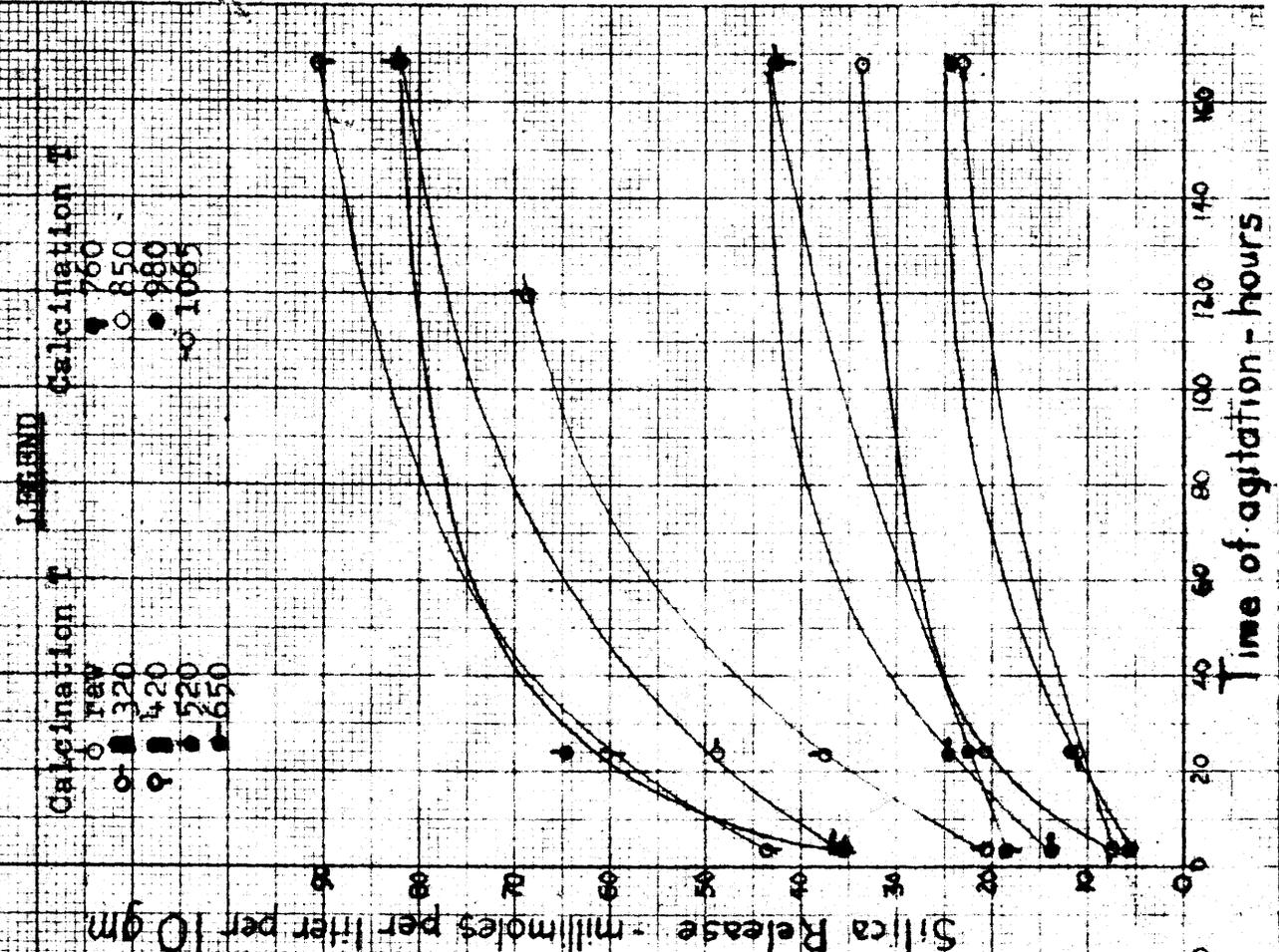
Temperature of Calcination deg. C	Percent Loss in Weight On Calcination	Reduction in Alkalinity Millimoles per liter			Silica Release per 10 gm.		
		4 hrs.	24 hrs.	168 hrs.	4 hrs.	24 hrs.	168 hrs.
raw ash	0.00	132.0	141.0	150.0	20.5	37.6	68.8
320	7.07	120.0	132.2	140.8	36.5	48.3	82.4
420	---	116.2	130.4	140.7	43.3	60.1	90.8
520	8.87	101.1	125.0	151.9	35.6	64.4	82.1
650	10.23	62.8	80.5	108.3	13.7	24.3	42.3
760	10.67	19.4	33.2	58.1	18.5	22.4	42.9
850	10.71	2.5	1.7	10.3	7.3	20.8	33.5
980	10.96	00.6	-4.9	-8.0	5.2	11.7	24.3
1065	10.93	-2.3	-8.9	-7.8	7.0	11.2	23.0

TABLE VII(ctd.)

Volcanic Ash 4021

Temperature of Calcination deg.C	Percent Loss in Weight on Calcination	Reduction in Alkalinity Millimoles per liter per 10 gm.			Silica Release		
		4 hrs.	24hrs.	168 hrs.	4 hrs.	24 hrs.	168hrs.
RAW ASH	0.00	53.8	55.2	62.0	21.7	30.0	51.0
320	6.86	38.7	47.1	52.7	29.8	32.5	54.9
420	7.40	37.0	51.6	56.0	30.0	40.8	55.9
520	7.87	29.4	44.4	62.2	25.0	38.3	58.8
650	8.18	16.7	25.4	42.1	19.8	28.1	41.5
760	8.12	0.8	1.7	14.2	17.8	24.8	31.8
850	8.29	- 4.9	-7.6	-6.3	6.7	17.3	28.6
980	8.38	-3.0	-11.8	-5.3	9.8	22.0	33.0
10.65	9.07	-4.9	-12.0	-8.9	15.6	23.8	33.3

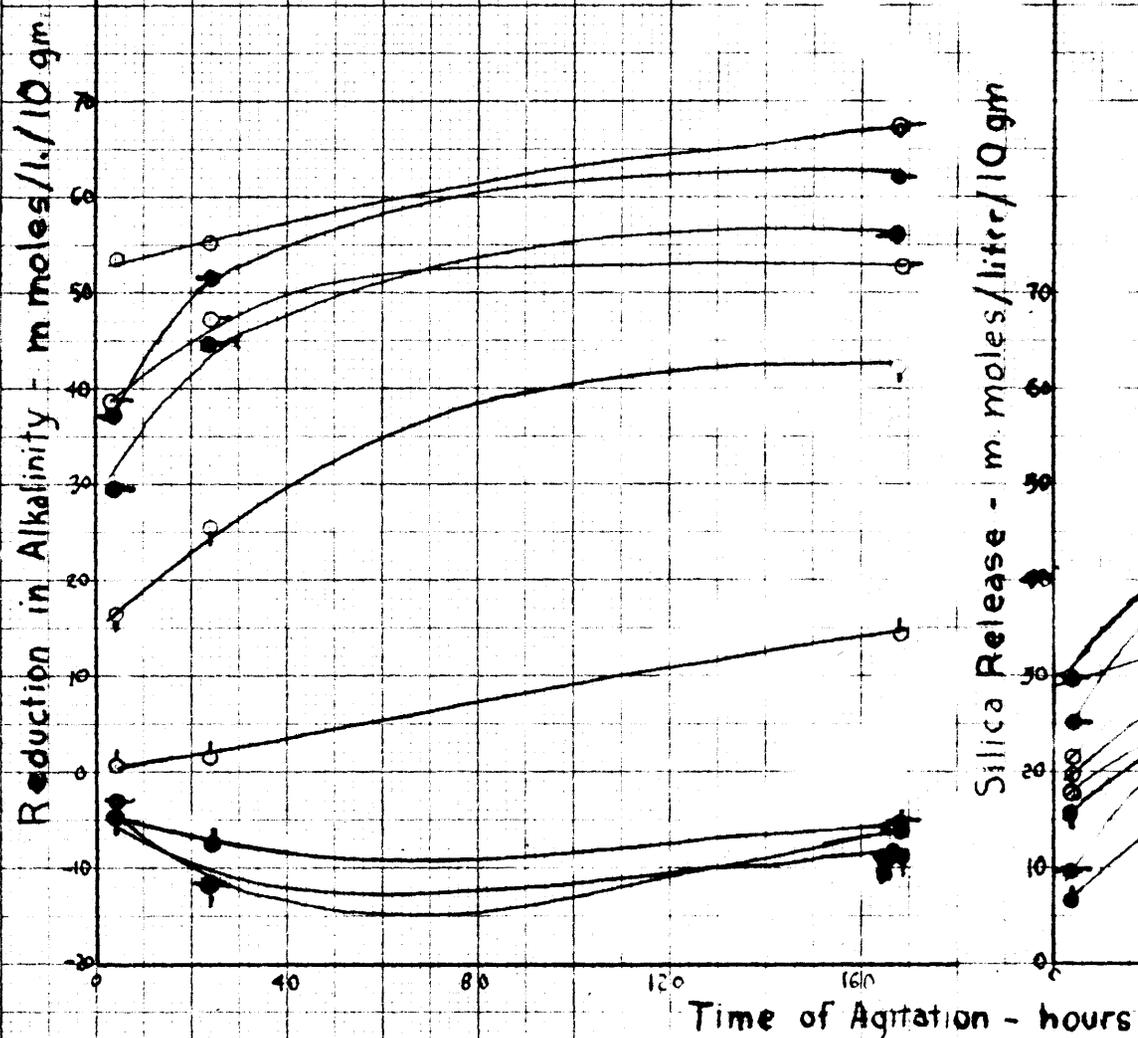
FIGURE 1
 Reduction in Alkalinity and Silica Release
 vs.
 Time for Calcined Sample 3726



Time of agitation - hours

Time of agitation - hours

FIGURE 4
 Reduction in Alkalinity and Silica Release
 vs.
 Time for Calcined Sample 4021



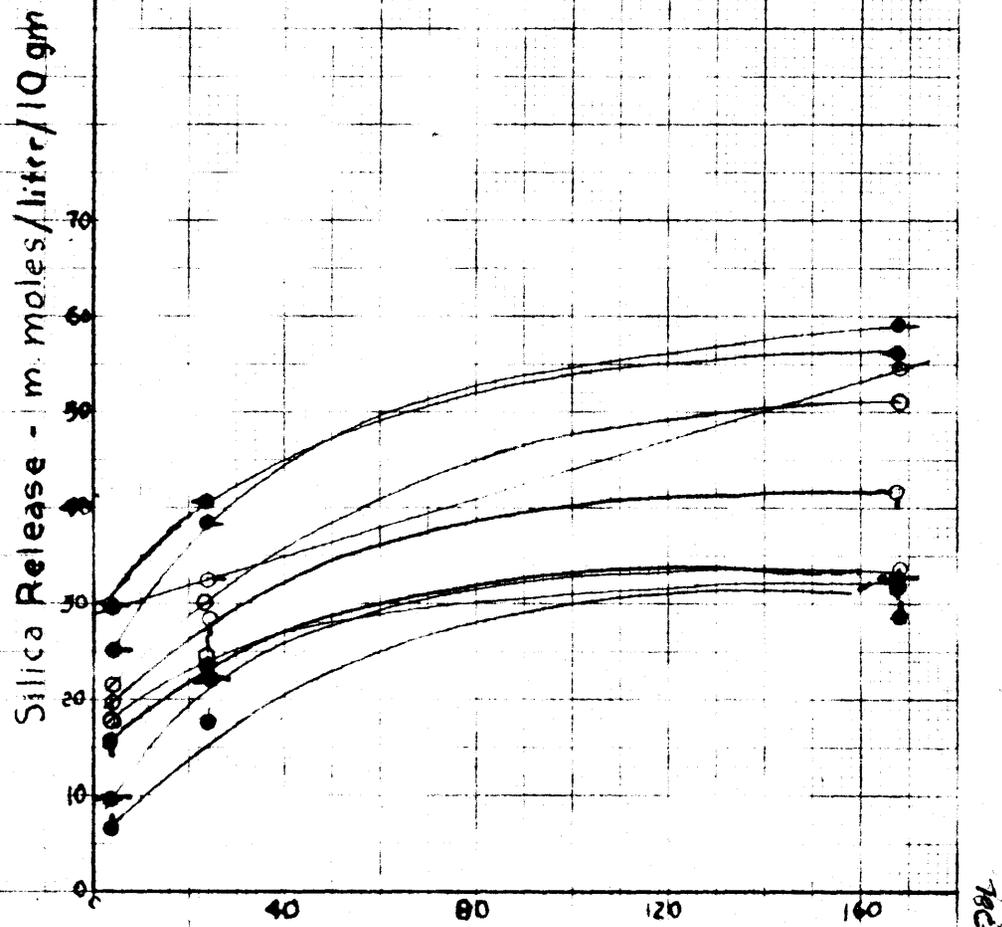
LEGEND

Calcination T

- raw
- △ 260
- 420
- 520
- 650

Calcination T

- ▲ 760
- ◆ 850
- 980
- 1065



782

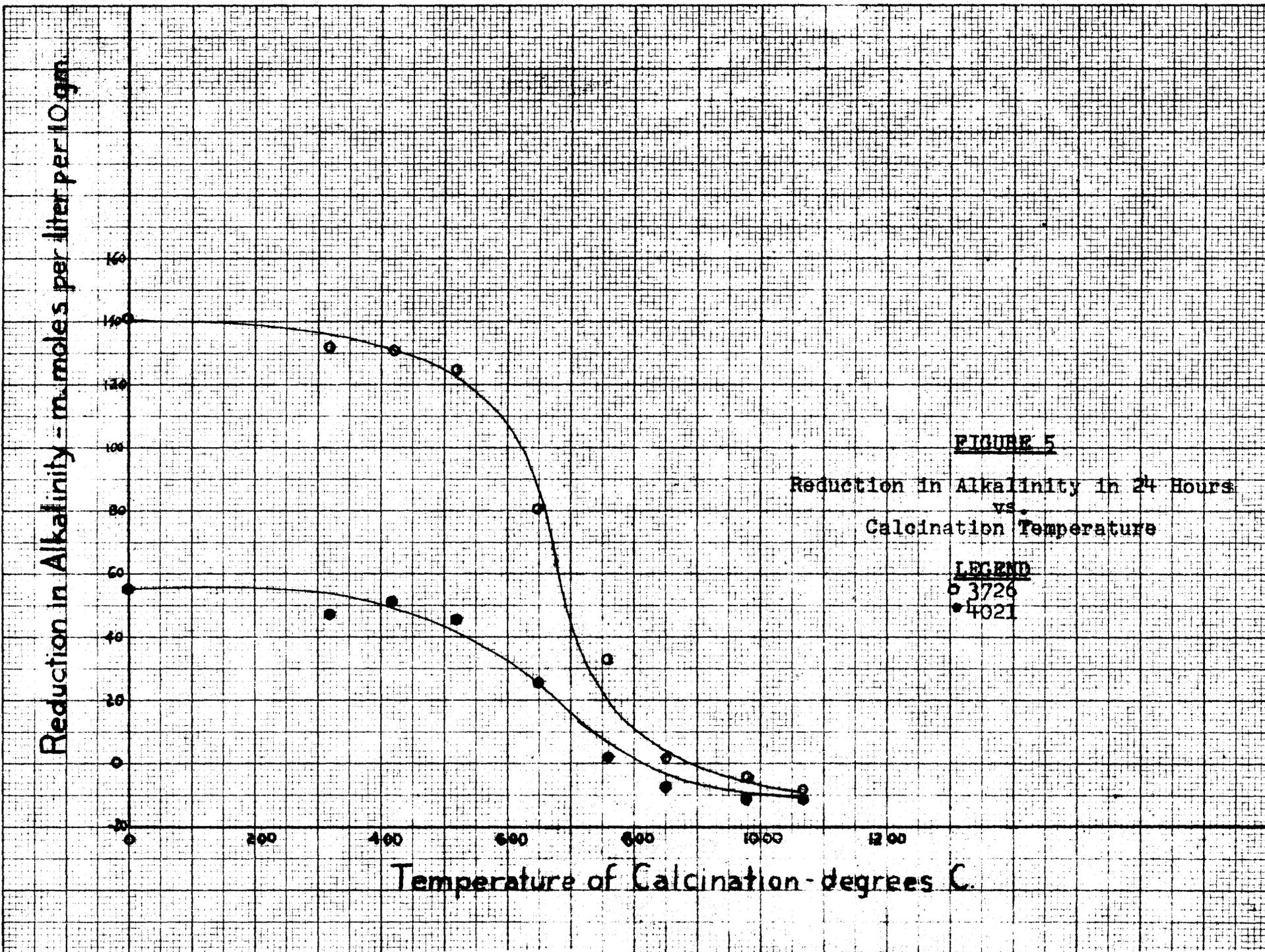
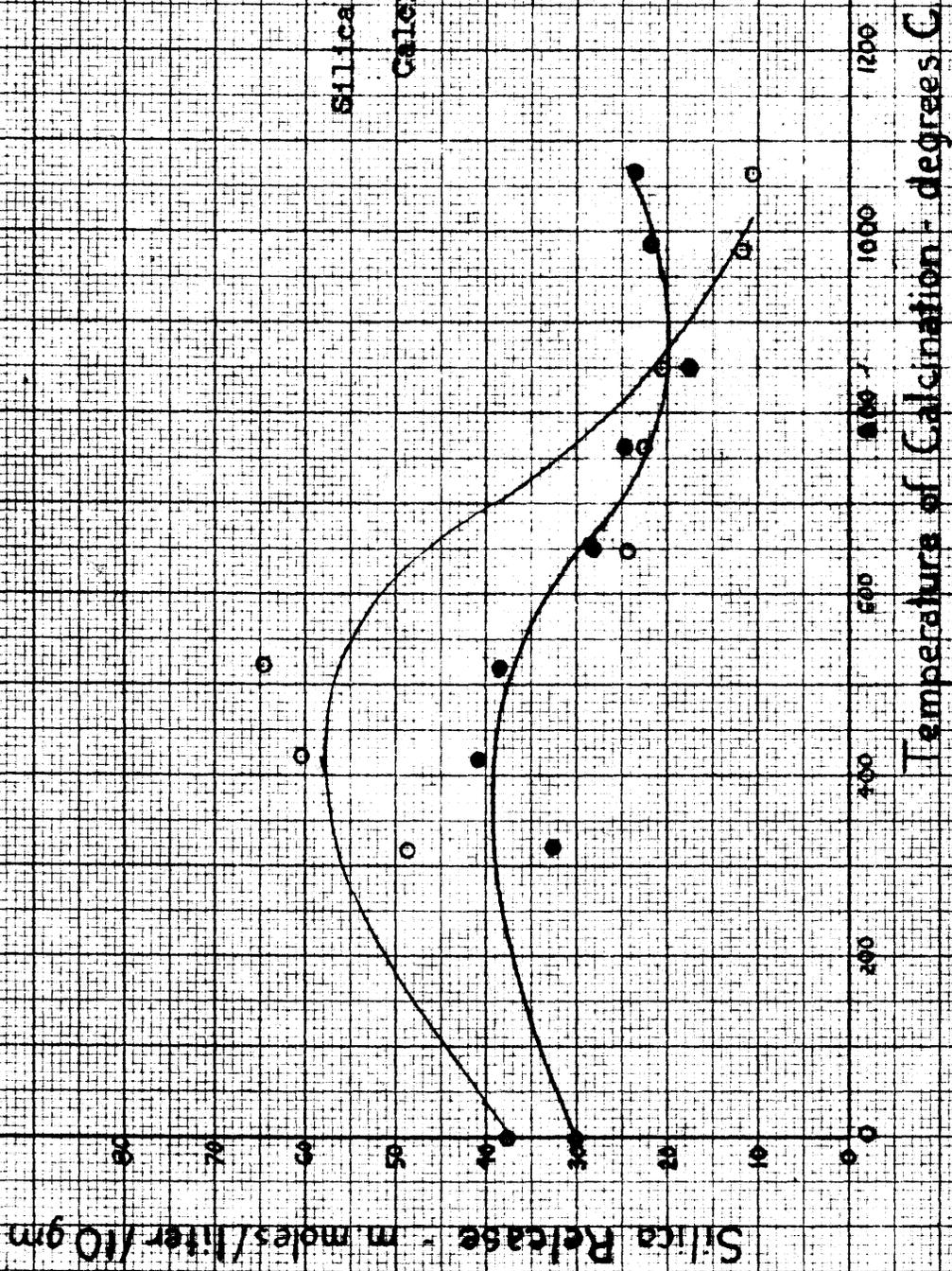


FIGURE 6

Silica Release at 24 Hours
vs.
Calcination Temperature

LEGEND
○ 3720
● 4021



For sample 4021, although the reduction in alkalinity was smaller than for sample 3726, a similar variation in reduction in alkalinity was observed.

The silica release for sample 3726 was increased by calcination, reaching a maximum between calcination temperatures of 420 deg. and 520 deg. For samples calcined at higher temperatures the silica release decreased as the temperature of calcination increased. For sample 4021, the release was smaller for the uncalcined sample than for sample 3726, and the change in silica release caused by calcination was less pronounced. Even so, calcination up to 520 deg. C increased the silica release over that of the uncalcined ash.

There are two possible reasons for variation in the reactivity of the calcined ashes. Either the nature of the silica in the ash may be changed, or the specific surface may be affected by calcination.

It has been shown (20) that pozzolans owing their activity to montmorillonite may be improved by calcination from 1000 to 1600 deg. F. (550 to 900 deg. C).

By means of X-ray diffraction, G.A. Rennie (private communication) showed that montmorillonite is present in both these ashes, and that its characteristic lines became negligible when the ash calcined at 650 deg. C (1200 deg. F.) was examined. Therefore, the increased activity of the ashes when calcined to 520 deg. has been partly due to the activation

of montmorillonite, and the decreased activity of the samples calcined at higher temperatures could have been caused by the destruction of the montmorillonite lattice.

The effect of specific surface on the reactivity will be discussed in a later section.

Description of the Adsorption Apparatus.

Surface areas of the ashes were determined by the nitrogen adsorption method at liquid nitrogen temperatures. The apparatus used was patterned after that of Harkins and Jura⁽⁴⁶⁾, the fundamental parts of which were the adsorption bulb(A), the gas buret(B), the manometer(D), the mercury cutoff(C) and the vapor pressure thermometer(E), as illustrated in figure 7.

The adsorption bulb(A) was patterned after that of Mackower et al.⁽⁶⁴⁾. A larger diagram of the bulb is seen in figure 8. The bulb was calibrated with mercury in order to determine the volume up to each graduation mark on the sidearm(K). The sample was introduced through the sidearm, which was then sealed off at one of the graduations. The bulb was attached to the apparatus through a ground glass joint(J).

The gas buret(B) consisted of five bulbs connected by capillary tubing. The volume of each bulb was calibrated with mercury before assembly of the apparatus. Table VI¹¹ gives the volume of each bulb, (Bulb 1 is the bottom bulb.)

TABLE VIII

CALIBRATION OF GAS BURET

Temperature 25.5 deg. C.

Bulb No.	Wt. of Mercury gm.	Volume of Bulb ml.
1	419.4	30.99
2	306.9	22.68
3	162.1	11.98
4	87.93	6.498
5	35.20	2.601

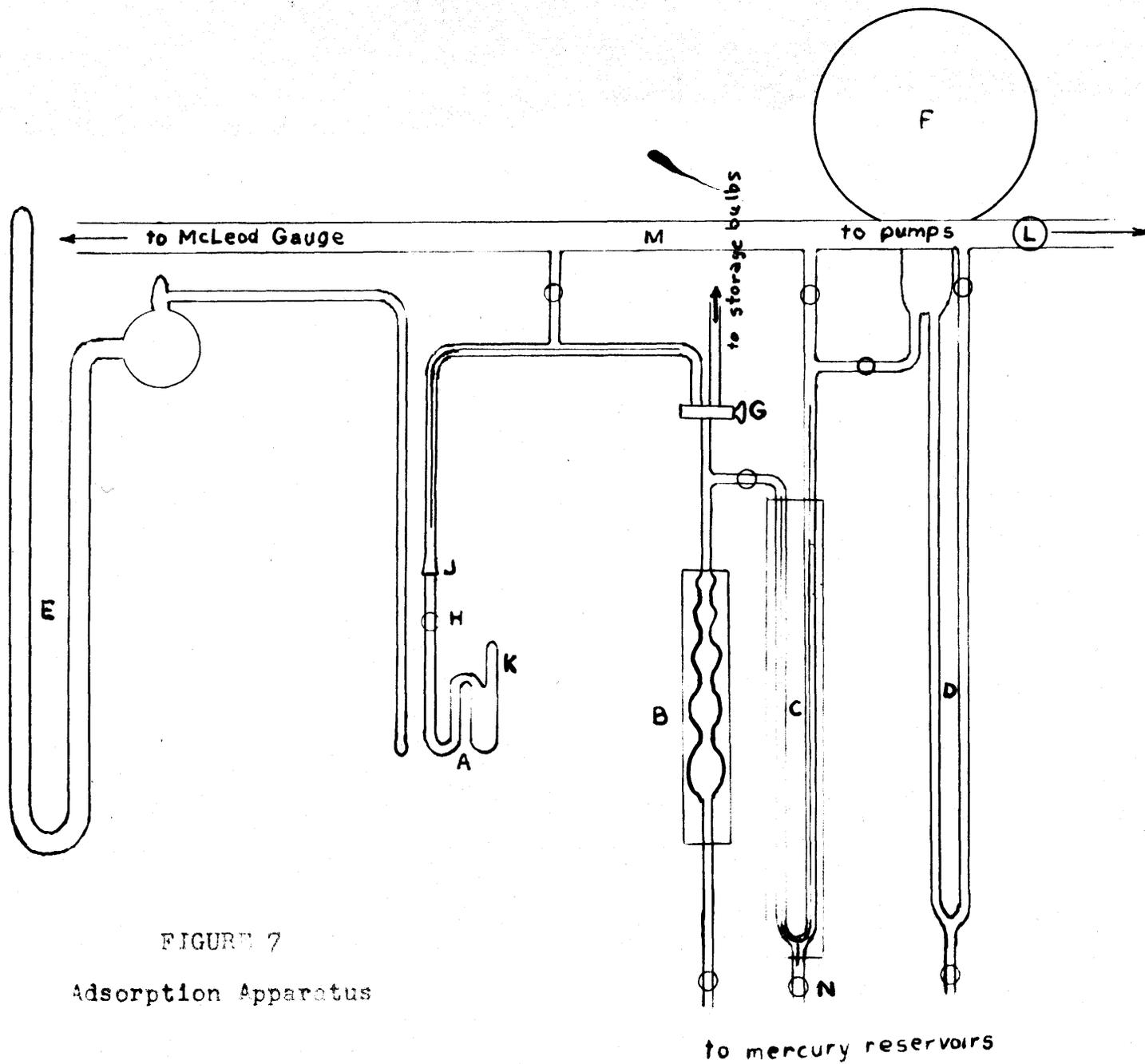


FIGURE 7
 Adsorption Apparatus

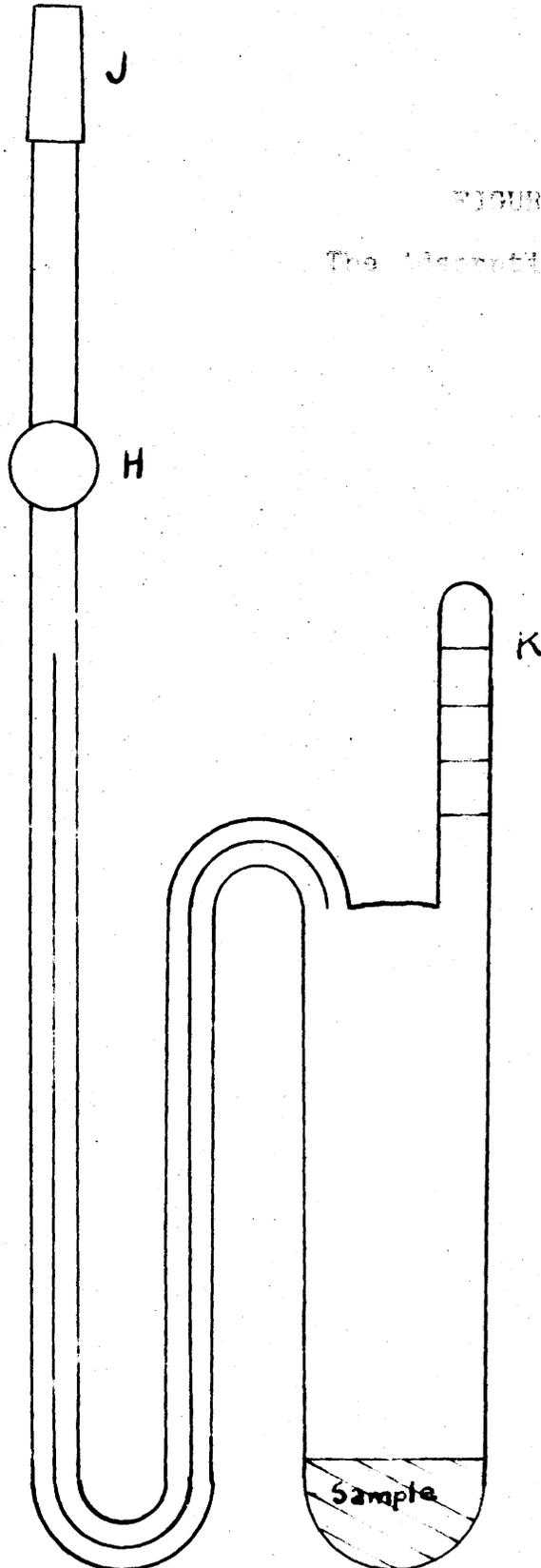


FIGURE 8
The Microtiter Bell

The mercury cutoff(C), of 3 mm capillary tubing, was advocated by Harkins and Jura(46) because use of it cut down the volume of dead space. Also, it allowed greater precision in the pressure measurements. The left hand side of the cutoff was calibrated for volume at a number of graduation marks, approximately at every centimeter of length. These volumes are reported in table 1 in the Appendix. When the apparatus was assembled, graduation mark 1 was just hidden by the rubber stopper, so mark 2 is the first one seen.

The gas buret(B) and mercury cutoff(C) were surrounded by water jackets through which water from a constant temperature bath (not shown in figure 6) was circulated. The constant temperature bath was adjusted so that the water in the jacket was kept about 25.0 deg. C. When gas was introduced into the system, the volume at jacket temperature was the sum of the volumes of the buret bulbs filled with gas and the volume of the mercury cutoff filled with gas.

When adsorption data were determined, the adsorption bulb(A) was surrounded by a bath of liquid nitrogen, the temperature of which was measured by an oxygen vapor pressure thermometer. The thermometer(E), (Figure 7) was assembled according to the model described by Farkas and Melville(63). Pure oxygen for the thermometer was prepared by evacuating potassium permanganate, and heating it gently to evolve oxygen. The oxygen was further purified by fractionally distilling twice, each time discarding the first and last fractions.

The pressure of the oxygen was measured with a cathetometer. From the oxygen pressure, the temperature of the liquid nitrogen bath was found from the equation

$$\log p_{\text{O}_2}(\text{mm}) = -\frac{419.30}{T} + 8.1173 - .00648T.$$

The vapor pressure of nitrogen at this temperature was calculated from the equation

$$\log p_{\text{N}_2}(\text{mm}) = -\frac{334.64}{T} + 7.5778 - .00476 T.$$

These two empirical equations were taken from a paper by Kerlogue and Bugge(45).

To facilitate the evaluation of the vapor pressures of nitrogen from oxygen pressures, pressures of oxygen and nitrogen were calculated for a series of temperatures from 77.0 to 78.0 deg. K. These calculations are summarized in Table 11 in the Appendix. A plot of pressure of nitrogen against the pressure of oxygen is drawn up in Figure 9.

Nitrogen and helium were stored in large bulbs connected to the gas buret (Figure 7). The nitrogen was purified by passing tank nitrogen through a glass tube at 600 deg. C, packed with copper turnings, to remove oxygen. The gas was next passed through a tube packed with phosphorus pentoxide and finally through a liquid nitrogen trap, before flowing into the storage bulb. Helium, for calibration, was obtained from a small tank, and was passed through a liquid nitrogen trap to remove condensable impurities.

To obtain low pressures of the order of 10^{-5} mm of mercury, an oil pump and mercury diffusion pump were used in series. The pressure was measured with a McLeod gauge assembled and calibrated by Dr. W. Graham. If the gauge was

used on the quadratic scale, the pressure in cm. of mercury was obtained by multiplying the square of the reading (in cm.) by the conversion factor 1.07×10^{-5} .

The Operation of the Apparatus.

The adsorption bulb(A) was cleaned and dried by washing with soap and water, or cleaning solution if required, followed by alcohol and ether rinsings. The ether vapor was swept out by drawing dry air through the bulb with an aspirator.

The bulb was weighed to three decimal places ^{in gms.} and ash was carefully introduced through the sidearm with a semimicro spatula. The bulb was then weighed again, the difference in weights giving the weight of ash added.

The sidearm on the bulb was sealed off, and the bulb was attached to the apparatus through the ground glass joint (J) (Figure 8). The adsorption bulb was then evacuated. In evacuation of the sample, care had to be taken not to subject it to sudden pressure drops, which resulted in violent escape of entrained air, thus driving a portion of the sample out of the adsorption bulb. This difficulty was overcome by connecting the bulb(A) through the manifold(M) to the manometer system(D,F), all at atmospheric pressure. Then the stopcock(L) was opened slightly to allow the pump to evacuate the system gradually.

It was found that every sample investigated gave off water vapor. Even when the system had been pumped on for eight hours, water vapor was shown to be present by the behavior

of the McLeod gauge. Heating the ashes overnight in an oven at 105 deg. C. did not remove all the water vapor. To get rid of the vapor, water in a large beaker was placed around the adsorption bulb and heated to the boiling point. While the water was heating, a few centimeters pressure of nitrogen were maintained over the sample, and after the water started to boil, the system was evacuated. When the water had boiled for a half an hour the beaker was removed, When the bulb had cooled, a pressure of 10^{-5} mm could be attained. This treatment was adequate for all ashes investigated.

The buret(B) and mercury cutoff(C) were evacuated to a pressure of 10 mm, and mercury was allowed to rise in the cutoff until it reached a graduation mark somewhere around the twenty-fifth. When the mercury level was exactly at one of the marks, the stopcock(N) was turned off. Thus a fixed weight of mercury was in the mercury cutoff. A reading was made with a cathetometer on the mercury levels in both the left and right tubes of the cutoff. In general, due to capillarity, these readings were not equal. Whenever the mercury level was returned to the graduation mark, the pressure on both sides of the cutoff was the same.

After the quantity of mercury in the cutoff was fixed, the gas to be used (nitrogen or helium) was admitted to the buret from a storage bulb. (see Figure 7) This caused the mercury level in the cutoff to change. Nitrogen was admitted to the manometer system (D,F) until the mercury level in the cutoff in the left tube of the cutoff was raised to the same

graduation mark as before, so the pressure in the buret and the manometer was the same.

The manometer and the upper end of the cutoff were struck sharply several times with a rubber stopper on a rod to ensure that no sticking of the mercury occurred. In practice, therefore, it was difficult to bring the mercury level exactly to the graduation mark. Hence, a small correction was added to or subtracted from the uncorrected pressure. This correction was found by reading the heights of the mercury columns in the cutoff with the cathetometer and comparing these heights to the readings made when the system had been evacuated. The uncorrected pressure was measured with the cathetometer. By using this correction, it was possible to reproduce pressure readings to 0.1 mm.

When adsorption studies were made using liquid nitrogen, the nitrogen had to be allowed to come to equilibrium with the adsorbent. This was done by leaving the gas in contact with the adsorbent for about twenty-five minutes, while the adsorption bulb was surrounded by liquid nitrogen. After twenty-five minutes, two consecutive readings of the pressure were made. If these agreed to within 0.1 mm it was considered that equilibrium had been reached. If the second reading was lower than the first, more pressure readings were made until the pressure became constant.

Calculation of the Volume of Gas Absorbed.

In order to calculate the volume of gas adsorbed at any pressure, it was necessary to calculate the volume of gas not adsorbed, and subtract that volume from the volume of gas added to the system. The following is a sample calculation. All volumes were calculated to an equivalent volume at S.T.P. The ash considered is sample 3726, calcined at 760 deg. C. The weight of the sample was 2.048 gm. When the pressures were equal in the manometer and the buret, the mercury level in the cutoff was at graduation mark 23. From Table 1 in the Appendix the volume of gas in the cutoff at jacket temperature is $1.57 - 0.06 = 1.51$ cc. The portion of tubing joining the buret and the cutoff was calculated to be 5.0 CC (see Table III, Appendix). This volume of tubing was at room temperature. Helium was admitted to the buret through stopcock(G). All five buret bulbs were filled with helium so the total volume at jacket temperature was $1.51 + 74.75$ (Table 8) = 76.26 CC. The pressure of helium was 26.22 cm., room temperature was 25.5 deg. C., and jacket temperature was 25.2 deg. C. By the ideal gas law, the total volume of helium converted to S.T.P. in the buret, tubing, and cutoff was

$$\left(\frac{76.26}{298.4} + \frac{5.0}{298.7} \right) 26.22 \times \frac{273.2}{76.00} = 25.67 \text{ CC.}$$

After the pressure reading was made, the two-way stopcock(G) was opened so the helium could flow into the adsorption bulb(A). A Dewar flask full of liquid nitrogen

was placed around the adsorption bulb up to the stopcock(H). The volume of tubing between the stopcocks(G) and (H) was determined previously with nitrogen to be 10.20 CC. (Table VIII, Appendix).

Mercury was raised in the gas buret(B) until only the top buret bulb contained helium. After equilibrium was reached, the helium pressure was 11.73 and room temperature had dropped to 25.1 deg.c. The volume of tubing at room temperature was $5.0 + 10.20$ CC., and the volume of apparatus at jacket temperature was $1.51 + 2.60 = 4.11$ cc. The volume of helium not in the adsorption bulb was $\left(\frac{4.11}{298.4} + \frac{10.20 + 5.0}{298.3} \right)$

$11.73 \times \frac{273.2}{76.00} = 2.73$ CC. at S.T.P. Then the volume of helium in the adsorption bulb was $25.67 - 2.73 = 22.94$ CC at S.T.P. This was the volume of dead space at 11.73 CM., and at unit pressure the equivalent volume of the dead space was $\frac{22.94}{11.73} = 1.956$ $\frac{\text{cc}}{\text{cm}}$.

The helium was pumped off and nitrogen admitted to the buret through stopcock(G). By a calculation similar to the first one, it was found that 23.05 cc. at S.T.P. had been admitted. Stopcock(G) was then opened to the adsorption bulb(A), and when equilibrium was reached, the pressure was 6.19 cm. Room temperature was 26.0 deg.C. The volume of nitrogen contained in the buret, tubing and cutoff was

$$\left(\frac{76.26}{298.4} + \frac{15.20}{299.2} \right) 6.19 \times \frac{273.2}{76.00} = 6.69 \text{ cm}^3 \text{ at S.T.P.}$$

The volume of the dead space in the adsorption bulb had to be corrected for imperfection of nitrogen at its boiling point.

The correction amounted to 5% at 76 cm., and was assumed to vary as the pressure (44). At 6.19 cm. the correction factor was $\left(1 + \frac{5}{100} \times \frac{6.19}{76}\right) = 1.004$. The volume of nitrogen in the dead space was $1.956 \frac{\text{cc}}{\text{cm}} \times 6.19 \text{ cm} \times 1.004 = 12.28 \text{ cc}$ at S.T.P. Therefore, the volume of gas not adsorbed is $6.69 + 12.28 = 18.92 \text{ cc}$. Hence, the volume adsorbed at 6.19 cm, is equivalent to $23.05 - 18.92 = 4.13 \text{ cc}$ at S.T.P. This was converted to a basis of one gm. of adsorbent. The volume adsorbed at 6.19 cm. was equivalent to $\frac{4.13}{2.048} = 2.02 \frac{\text{cc}}{\text{gm}}$ at S.T.P. When the data were used for the B.E.T. plot, it was necessary to find p_0 , the saturation pressure of nitrogen. The oxygen pressure in the thermometer (E) was measured, and the corresponding nitrogen pressure found from Figure 9.

Specific Surfaces of Saskatchewan Volcanic Ashes.

The specific surface of a substance is its surface area per gram. The specific surface is generally reported either as cm^2 per gm. or as meters² per gm.

The adsorption isotherms were determined for a number of the volcanic ashes and calcined samples of samples 3726.

The data from which the adsorbed volumes were calculated are given in Table V in the Appendix. Figure 10 shows the variation of v , the volume of nitrogen adsorbed per gram of adsorbent, against p , the relative pressure.

Specific surfaces were estimated from the adsorption data by three different methods.

The first method used was that of Brunauer, Emmett and Teller (42). According to their theory,

30

$$\frac{p}{v(p_0 - p)} = \frac{1}{V_{mL}} + \frac{p}{p_0} \frac{(C-1)}{V_{mL}}$$

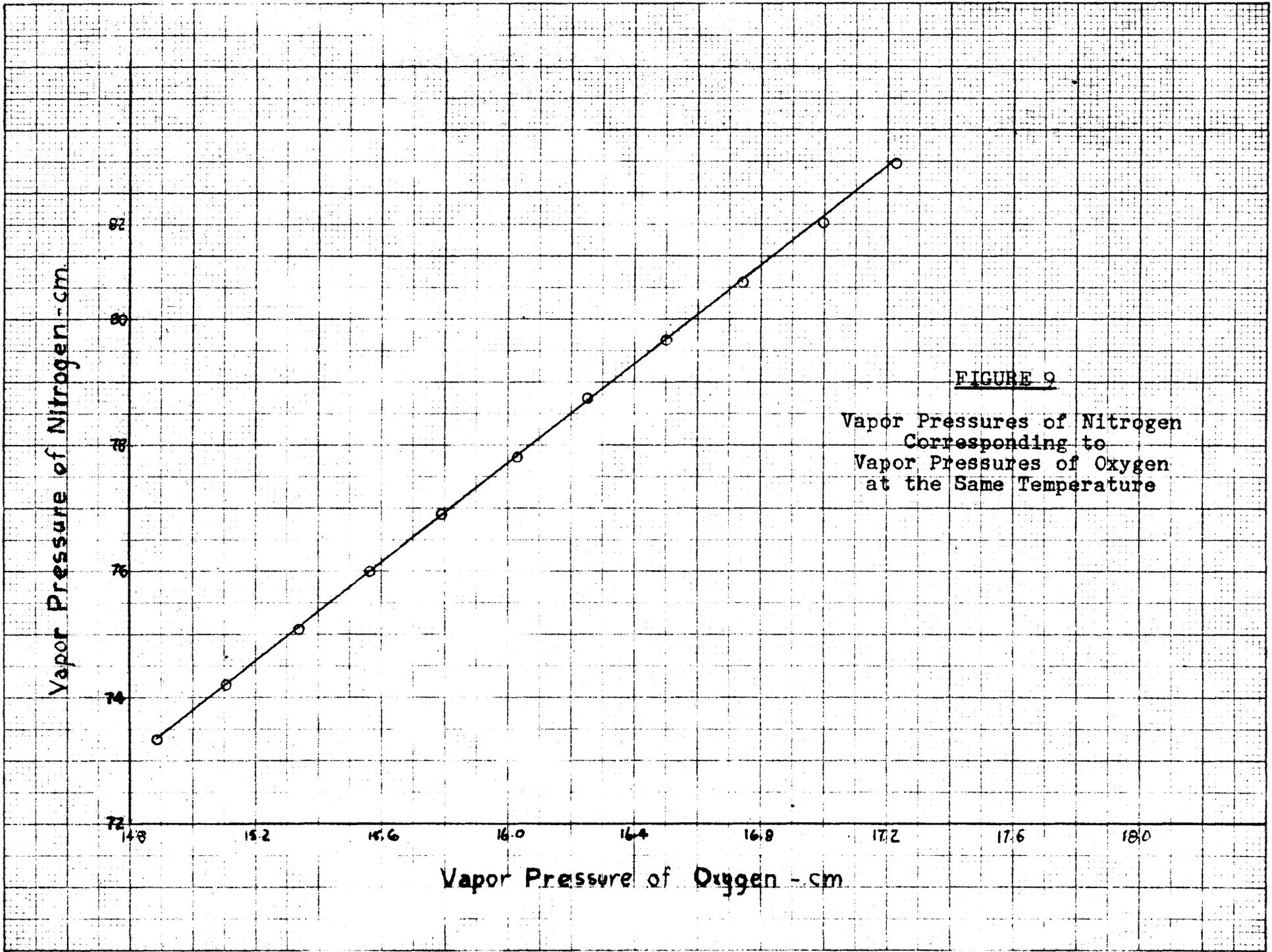


FIGURE 9

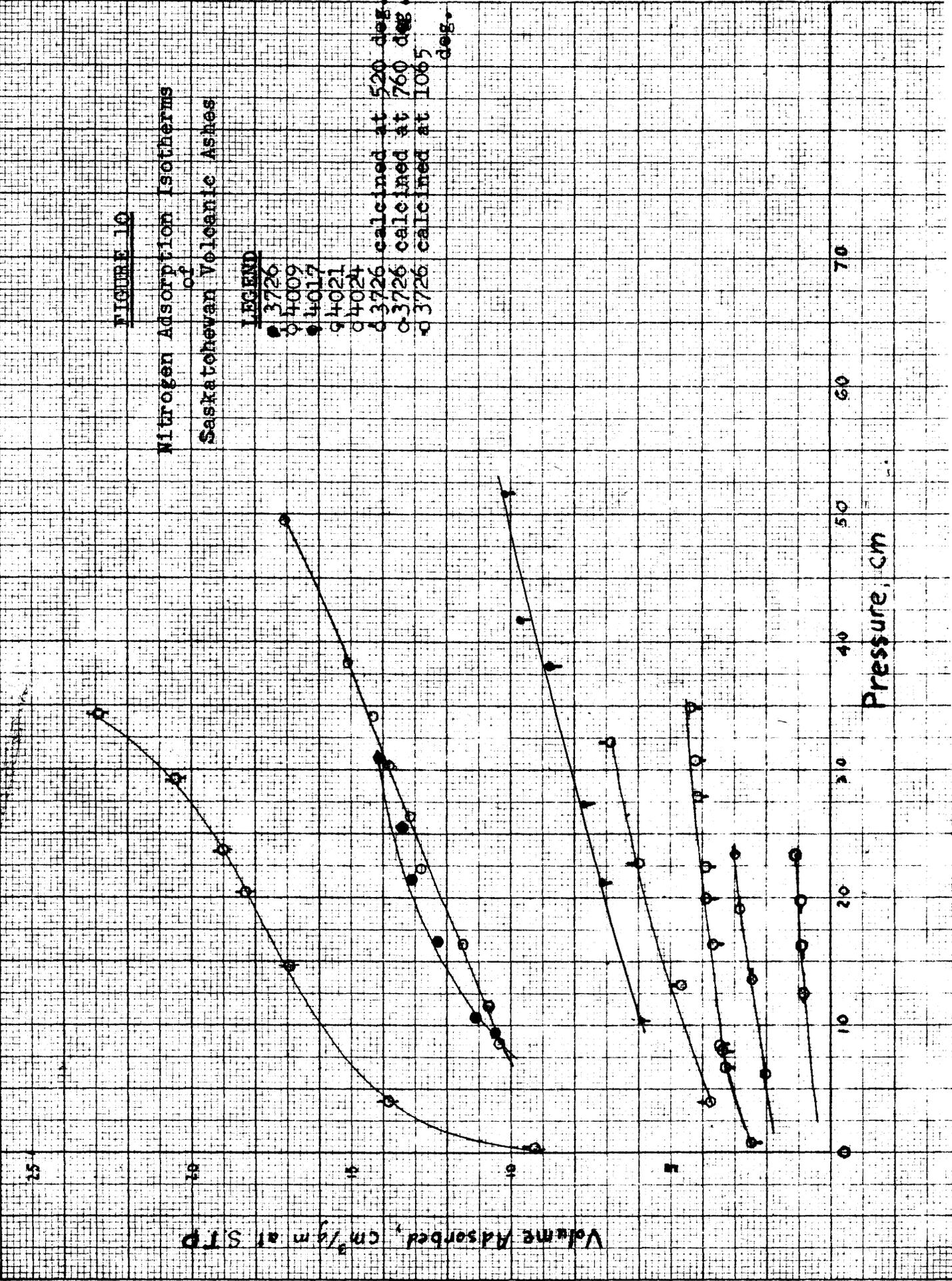
Vapor Pressures of Nitrogen
 Corresponding to
 Vapor Pressures of Oxygen
 at the Same Temperature

FIGURE 10

Nitrogen Adsorption Isotherms
of
Saskatchewan Volcanic Ashes

LEGEND

- 3726 calcined at 520 deg.
- 4009 calcined at 760 deg.
- 4017 calcined at 1065 deg.
- 4021 calcined at 520 deg.
- 4024 calcined at 760 deg.
- △ 3726 calcined at 520 deg.
- 3726 calcined at 760 deg.
- 3726 calcined at 1065 deg.



A plot of $\frac{p}{v(p_0-p)}$ against $\frac{p}{p_0}$ is supposed to be linear, with a slope of $\frac{C-1}{v_{mc}}$ and an intercept of $\frac{1}{v_m}$. Generally, between the relative pressure limits of 0.05 and 0.35, the plot is linear (44). In addition, usually C is so large that the intercept is very small, and the slope is approximately equal to $\frac{1}{v_m}$.

The second method used was that of Hüttig(56).

According to his theory,

46 $\frac{p}{v} \left(1 + \frac{p}{p_0}\right) = \frac{p}{v_m} + \frac{p_0}{v_{mc}}$, so that a plot of $\frac{p}{v} \left(1 + \frac{p}{p_0}\right)$ against p should be linear for about the same relative pressure range as the B.E.T. equation. The slope of the line gives $\frac{1}{v_m}$ directly.

When the B.E.T. and Hüttig plots are used, the specific surface is determined from v_m values. According to Emmett(44), at -195.8 deg.C., one molecule of nitrogen covers 16.2 \AA^2 . Then, if Σ is the specific surface,

$$\Sigma = \frac{v_m}{22400} \times 16.2 \times 10^{-20} \times 6.02 \times 10^{23} = 4.36 v_m \text{ m}^2$$

since v_m is calculated at S.T.P.

The third method used was that of Harkins and Jura(60).

According to their theory,

47 $\log p = B - \frac{A}{v^2}$, and the plot of $\log p$ against $\frac{1}{v^2}$

should be linear, and is usually linear over a larger range than is the B.E.T. equation. According to the Harkins and Jura theory, the specific surface Σ is proportional to the square root of the constant A, $\Sigma = kA^{\frac{1}{2}}$ where k is 4.06 for nitrogen at -195.8 deg. C.

The data required for plots by these three methods are recorded in Table VI in the Appendix and were calculated from the data in Table V in the Appendix. Figure 11 is a plot of $\frac{p}{v(p_0-p)}$ against $\frac{p}{p_0}$ the B.E.T. method. It is usual for the experimental points above a relative pressure of 0.35 to be above the straight line joining the points from a relative ^{pressure} of 0.05 to 0.35 (44). This was observed for those plots which were made.

Figure 12 is a plot of $\frac{p}{v} \left(1 + \frac{p}{p_0}\right)$ against p , the Hüttig method. Figures 13 to 15 are plots of $\log p$ against $\frac{1}{v^2}$, the Harkins and Jura method; three figures were necessary because of the large variation in $\frac{1}{v^2}$ from one sample to another.

Table IX gives the specific surfaces for the ashes investigated. In the first column is given the sample number. In the second, third and fourth columns are given the specific surfaces in meters²/gm as determined by the B.E.T., Hüttig and Harkins and Jura methods, respectively.

As can be seen from Table IX the specific surfaces found by the three methods were quite consistent.

The bentonite, 4009, had the largest specific surface of the samples examined. Since its particles are colloidal in size (67), bentonite would be expected to have a larger specific surface than volcanic ashes, from which it is thought to be formed (7).

TABLE IX

SPECIFIC SURFACES OF SASKATCHEWAN VOLCANIC ASHES

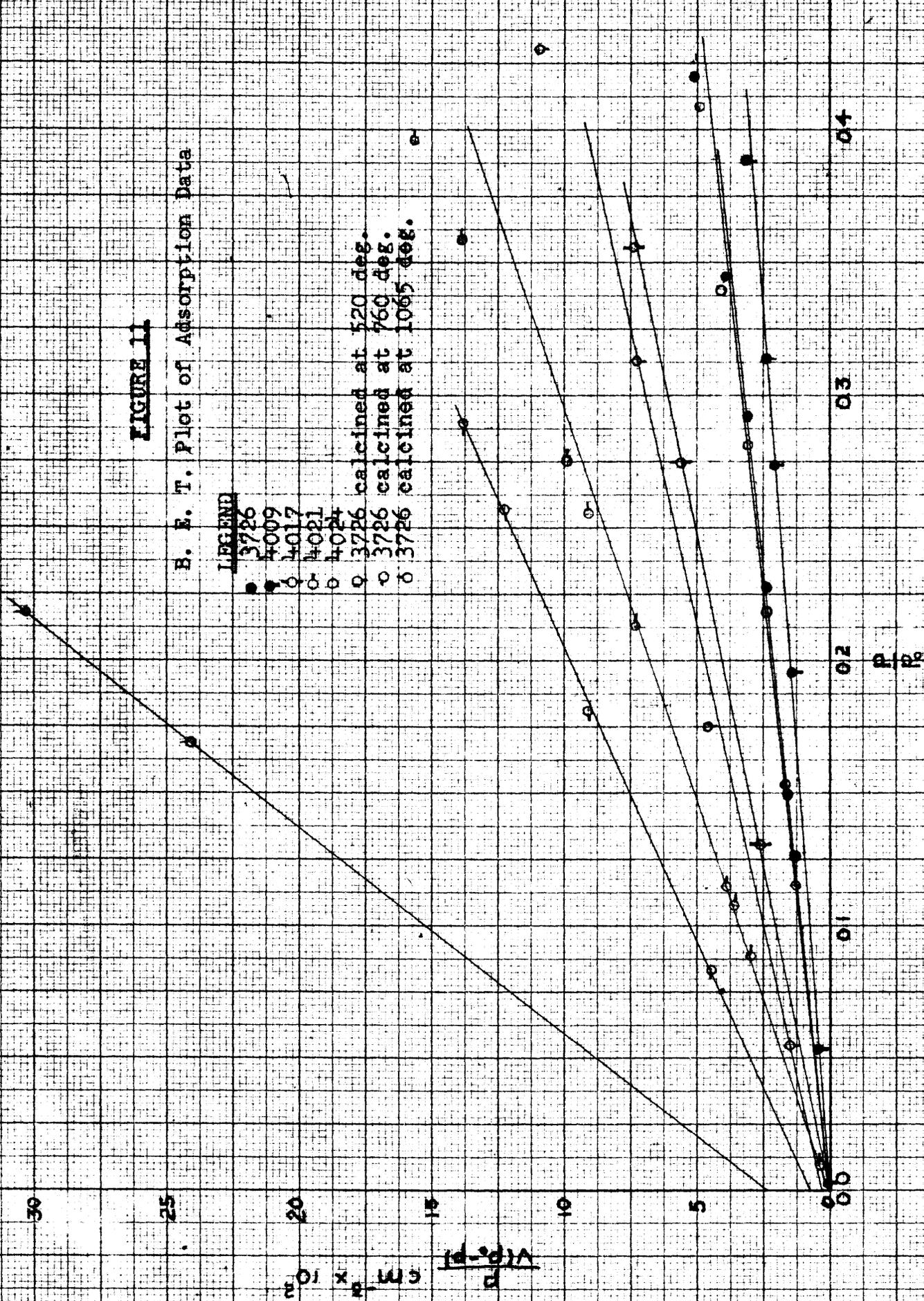
Sample No.	B.E.T.	Huttig	Harkins and Jura
	m^2/gm	m^2/gm	m^2/gm
3726 crawford	38.4	41.2	40.2
3726 calcined at 520 deg.	19.0	23.9	20.1
3726 calcined at 760 deg.	9.6	8.55	8.35
3726 calcined at 1065 deg.	1.14	1.22	0.95
4009	58.1	65.5	61.1
4017	21.4	25.6	19.8
4021	12.8	13.2	14.3
4024	37.3	41.2	39.8

FIGURE 11

B. E. T. Plot of Adsorption Data

LEGEND

- 3726
- 4009
- 4017
- 4021
- 4024
- 3726 calcined at 520 deg.
- 3726 calcined at 760 deg.
- 3726 calcined at 1065 deg.



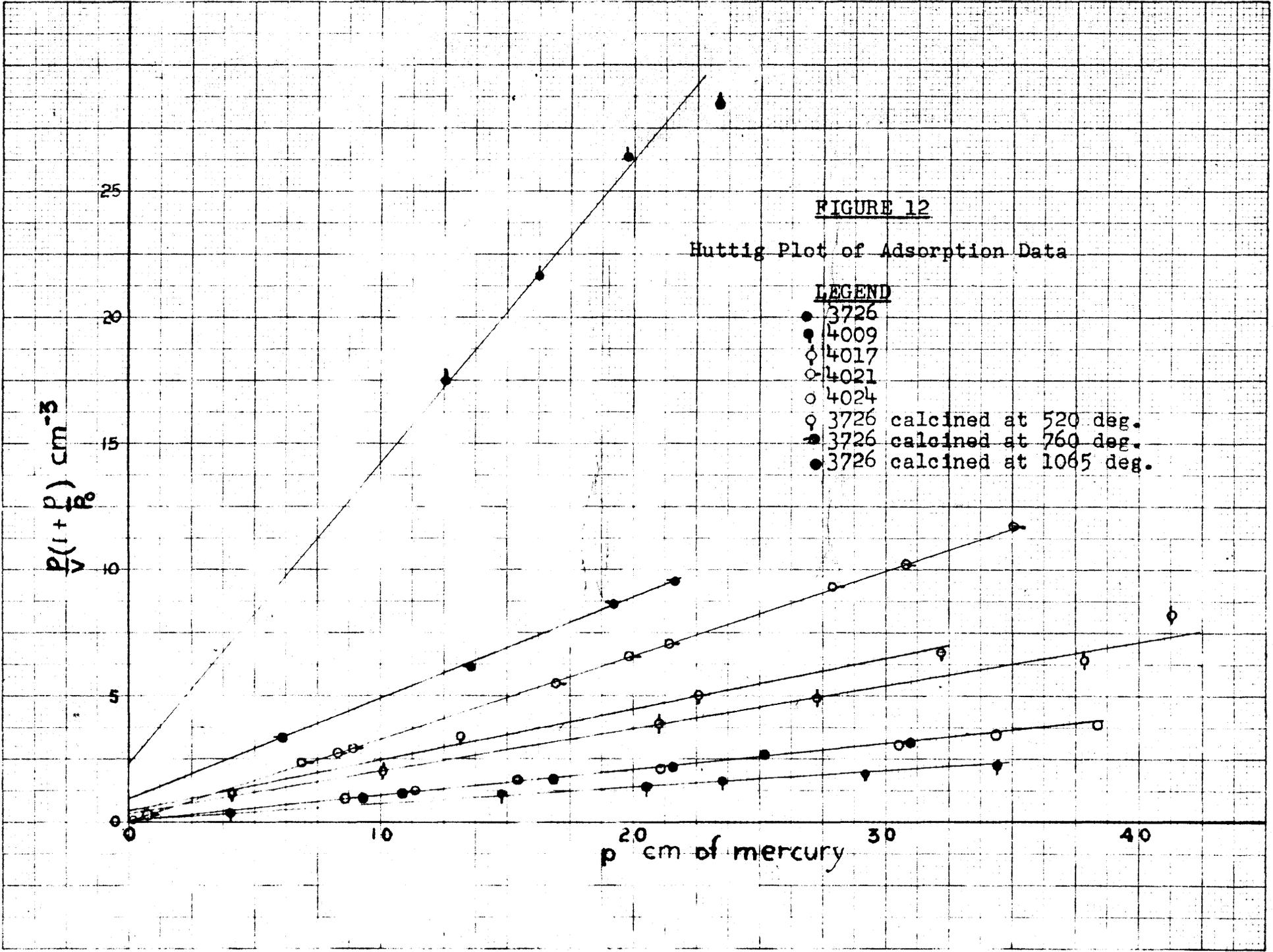


FIGURE 12

Huttig Plot of Adsorption Data

LEGEND

- 3726
- ▲ 4009
- ◇ 4017
- 4021
- 4024
- ◇ 3726 calcined at 520 deg.
- ▲ 3726 calcined at 760 deg.
- 3726 calcined at 1065 deg.

FIGURE 13
Harkins and Jura Plot
of
Adsorption Data

LEGEND

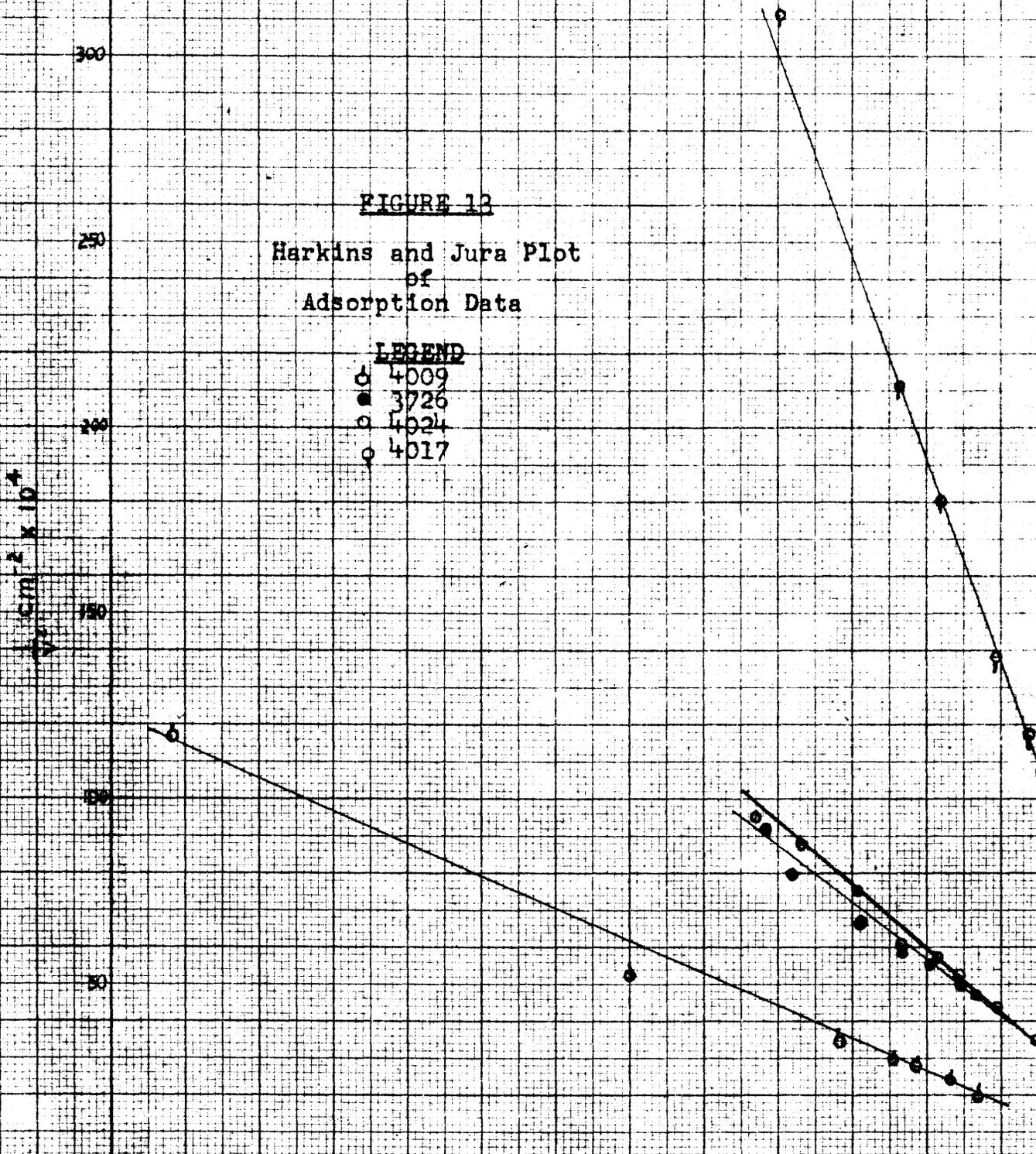
- 4009
- 3726
- 4024
- 4017

$V_{ads} \times 10^4$

300
250
200
150
100
50
0

log p

12 1.6 0.0 0.4 0.8 1.2 1.6



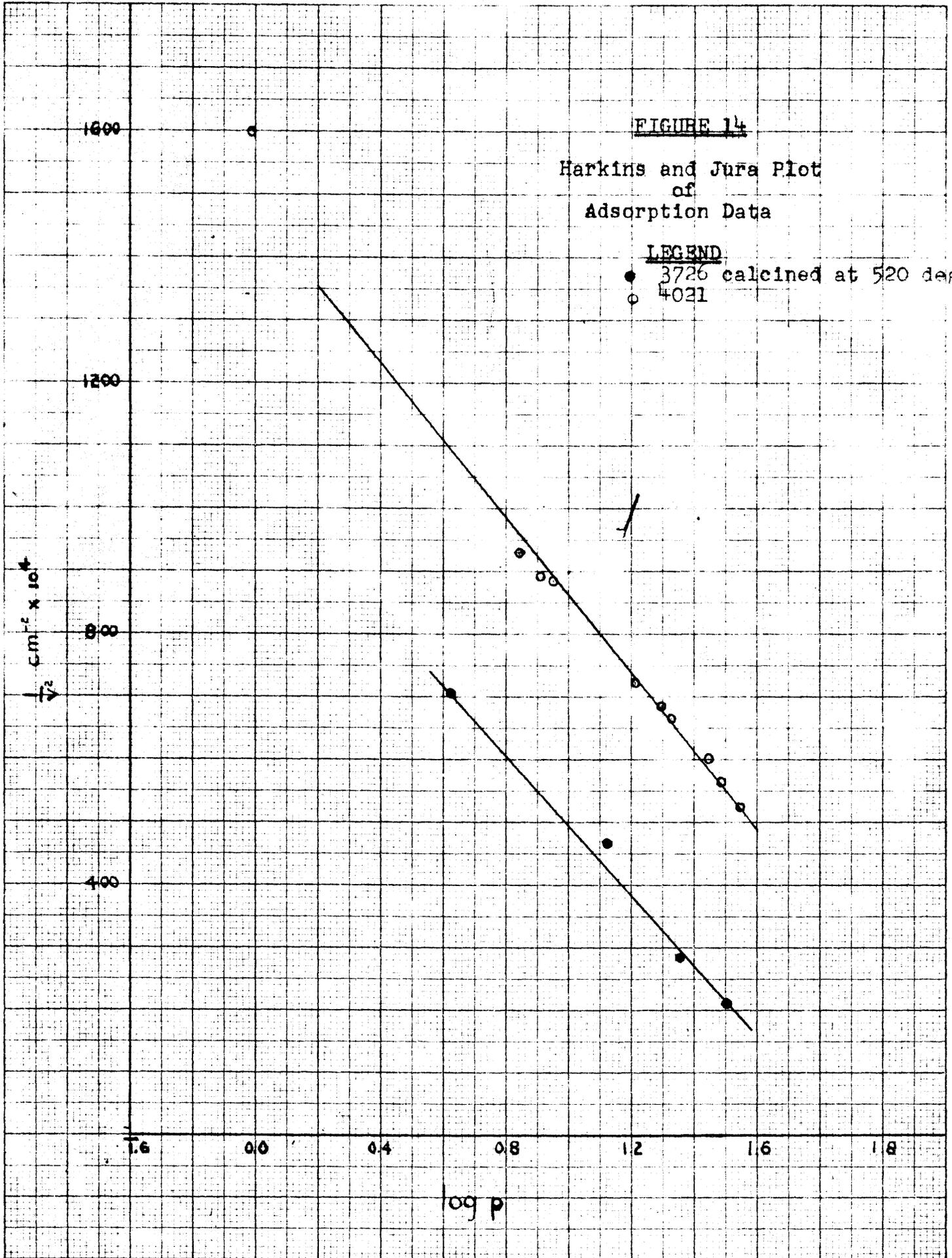
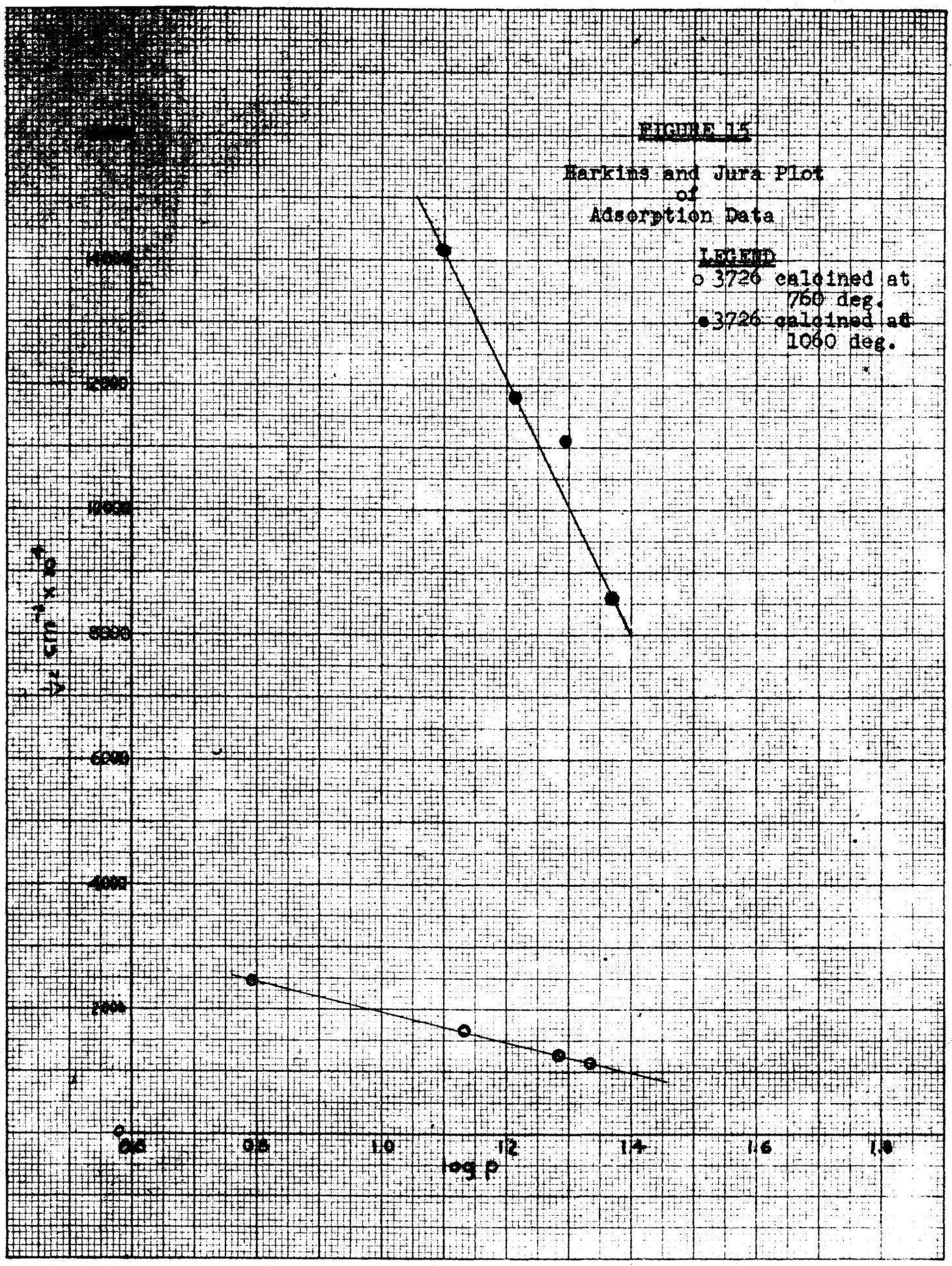


FIGURE 15

Harkins and Jura Plot
of
Adsorption Data

LEGEND

- 3726 calined at 760 deg.
- 3726 calined at 1060 deg.



Comparison of Specific Surface with the Results of the
Reactivity Test.

Samples 3726 and 4024 had almost equal specific surfaces. From Figures land 2 it is seen that these two ashes also showed almost identical reductions in alkalinity and silica releases.

Sample 4017 had a smaller specific surface than samples 3726 and 4024, and also gave a lower reduction in alkalinity and silica release. Sample 4021 had a specific surface smaller than that of sample 4017, and the reduction in alkalinity was also lower. However, the silica release was greater than for sample 4017.

Specific surfaces were measured for sample 3726 calcined at 520, 760 and 1065 deg. C. The specific surface of the sample calcined at 520 deg. was less than one-half the surface of the uncalcined ash, but the reduction in alkalinity of the calcined sample was nearly as large as that of the uncalcined ash, and the silica release was considerable greater. This implies a true activation of the ash by calcination. The specific surface of the ash calcined at 760 deg. was one-half as large as that of the ash calcined at 520 deg., and the reduction in alkalinity and silica release were correspondingly smaller. The ash calcined at 1065 deg. had a very small specific surface and the reduction in alkalinity was negative. However, the silica release was still one-half that of the sample calcined at 760 deg.

On the basis of these results, although the specific surface is decreased by calcination, activation of the ash occurs by calcination at 520 deg. to such an extent that the reactivity of the ash is increased. Calcination at 760 deg. and 1065 deg.C decreased both surface and reactivity of the ashes.

SUMMARY

An adsorption apparatus has been constructed and calibrated. A procedure for the use of the apparatus was worked out and has been described.

Using the apparatus, adsorption isotherms of several Saskatchewan volcanic ashes were determined, and the specific surfaces were calculated from the adsorption.

The Saskatchewan volcanic ashes were subjected to a reactivity test using sodium hydroxide solutions. By this test, the reduction in alkalinity of the solution and the silica released into the solution were determined. Ashes from the same locality were found to give similar results. Ashes from different localities did not necessarily give the same results. An abnormal result was observed with samples 4007 and 4008, which showed significant decreases in reduction in alkalinity as time of reaction increased. This was explained by assuming a greater uptake of water than sodium hydroxide by the ash.

Samples 4007, 4008, and 4009 (bentonite) swelled while in contact with sodium hydroxide solutions. This is characteristic of bentonites, and supported the belief (65,66) that samples 4007 and 4008 were contaminated with bentonite.

For the ashes which do not swell while in contact with the solution, the reduction in alkalinity was found to be approximately proportional to the surface area.

Samples 3726 and 4021 were calcined at a series of temperatures between 320 deg. and 1065 deg. C. These calcined samples were subjected to the reactivity test, the results of which indicated an activation of both ashes by calcination to 500deg. C, and deactivation at higher temperatures. Specific surface determinations of sample 3726 calcined at 520, 760 and 1065 deg. C showed that calcination decreased the specific surface. Therefore, a true activation of the surface of the ash by calcination to about 500 deg. C was indicated.

SUGGESTIONS FOR FURTHER WORK

In this investigation, only two ashes were subjected to calcination. A study of the effects of calcination on the other Saskatchewan volcanic ashes would be of interest to determine if they would be affected in the same manner and to the same extent as the samples studied.

Burwell (10) has investigated the formation of cellular products by calcination of Oklahoma volcanic ashes at ti

temperatures in excess of 1200 deg. C. A similar study of Saskatchewan volcanic ashes might result in discovery of a useful insulating substance.

Mills et. al.(36) have investigated acid activation of bentonites for use as catalysts. Sample 4009, a bentonite, might be studied to determine its activity.

Burroughs(12), Billings(13), and Draper(14) investigated adsorption of dyes from solution and decolorization of oils. by Saskatchewan volcanic ashes. A correlation of specific surfaces and efficiency in decolorization might be possible. Activation of the ashes was carried out by treatment with hot, concentrated sulphuric acid. The activation process probably results in an increase in specific surface, and specific surface determinations of the activated substances might indicate the most satisfactory method of activation. A study of the decolorizing properties and acid activation of calcined ashes might also prove valuable.

At the present time an investigation of the minerals present in the Saskatchewan volcanic ashes is being carried out. X-ray diffraction and petrographic microscope studies are being carried out. An attempt should be made to relate the mineral content to the properties, of the volcanic ashes such as the reactivity, the decolorizing efficiency, and pozzolanic activity.

The use of sample 4024 as a pozzolan has been studied under the direction of Professor H. Douglas of the Department

of Civil Engineering, and sample 3726 is^{also} being studied. Compressive strength tests have been prepared by replacing a portion of the portland cement with volcanic ash. Tests performed using calcined volcanic ashes would be of interest, since it has been found that calcination often improves pozzolanic activity(24).

BIBLIOGRAPHY

- (1) Webster's New International Dictionary, 2nd. Edn., p. 161.
- (2) Ladoo, R.B. "Non- Metallic Minerals", Mc Graw-Hill, P. 455, (1925).
- (3) Eardley - Wilmot, V.L., "Abrasives", Department of Mines, Ottawa, Mines Branch No. 673 (1927)
- (4) Johannsen, A., "Petrography of Igneous Rocks, Vol. 1", Univ. Chicago Press, p. 7, (1929).
- (5) Spence, H.S., "Bentonite", Dept. of Mines of Canada, Bul. No.626 (1924).
- (6) Ries, H. "Clays, their Occurrences, Properties and Uses."
- (7) Alexander, J., Ind. Eng. Chem., 16, 1140, (1924).
- (8) Worcester, W.G., "A Report on Saskatchewan Volcanic Ash", (1943)
- (9) Crawford, G.S., Thesis, University of Saskatchewan (1948).
- (10) Burwell, A.L., Oklahoma Geological Survey, Circular No.27.
- (11) Reagan, M., Thesis, University of Saskatchewan, (1944).
- (12) Burroughs, G., Thesis, University of Saskatchewan, (1949).
- (13) Billings, M., Thesis, University of Saskatchewan, (1949).
- (14) Draper, R., Thesis, University of Saskatchewan, (1949).
- (15) Larsen, D.H., "Colloid Chemistry" edited by J. Alexander, Vol. VI, p.502-30.
- (16) Mills, G.A., Holmes, J., and Cornelius, E.B., J. Phys. and Colloid Chem., 54, 170-85, (1950).
- (17) Davis, R.E., A.S.T.M. Special Publication No. 99, 3 - 15, (1949)
- (18) Lea, F.M., "Symposium on the Chemistry of Cements", 406 - 83, (1938).
- (19) Blanks, R.F., J. Am. Concrete Inst. 21 - 2, 89-108, (1949).
- (20) Mielenz, R.C., Witte, L.P., and Glantz, O.J., A.S.T.M. Special Publication No.99, 43 - 91, (1949).
- (21) Lerch, W.C., A.S.T.M. Special Publication No. 99, 153 - 77, (1949).

- (22) Stanton, T.E., A.S.T.M. Special Publication No. 99, 178 - 202, (1949).
- (23) Davis, R.E., J. Am. Concrete Inst. 21-5, 377 - 84, (1950).
- (24) Moran, W.T., and Gilliland, J.L., A.S.T.M. Special Publication No. 99, 109-130, (1949).
- (25) Feret, R., Bureau of Reclamation, Denver, Technical Memorandum No. 461.
- (26) Feret, R., Bureau of Reclamation, Denver, Technical Memorandum No. 418.
- (27) Stanton, T.E., "A Study of Pozzolans and Pozzolanic or Blended Concretes", Department of Public Works, Sacramento, Calif., (1934).
- (28) Lea, F.M., Department of Scientific and Industrial Research, Teddington, England, Technical Paper, No.27, (1940).
- (29) Thorvaldson, T., Symposium on the Chemistry of Cements, Stockholm, 498-99, (1938).
- (30) Hanna, W.C., A.S.T.M. Special Publication No. 99, 92, (1949).
- (31) Schweyer, H.E., and Work L.T., A.S.T.M., Technical Publication No. 51, 1-23, (1941).
- (32) Schweyer, H.E., Ind. Eng. Chem., Anal. Ed., 14, 622-32, (1942).
- (33) 1939 A.S.T.M. Book of Standards, Part 11, p. 453.
- (34) Norton, F.H., and Spiel, S., J. Am. Ceramic. Soc., 21, 89, (1938).
- (35) Svedburg, T., "Colloid Chemistry", A.C.S. Monograph (1928).
- (36) Hauser, E.A., and Lynn, J.E., Ind. Eng. Chem., 32, 659 (1940).
- (37) 1939 A.S.T.M. Book of Standards, Part 11, 897.
- (38) Kenrick, F.B., J. Am. Chem. Soc. 62, 2838, (1940).
- (39) Palmer, W.G. and Clark, R.E.D.; Proc. Roy. Soc., A149, 360, (1935).
- (40) Carmen, P.C., J. Soc. Chem. Ind, 57, 225, (1938).
- (41) Carmen, P.C., J. Soc. Chem. Ind., 58, 1, (1939).

- (42) Brunauer, S., Emmett, P., and Teller, E., J. Am. Chem. Soc. 60, 309, (1938).
- (43) Brunauer, S., "The Adsorption of Gases and Vapors-- Physical Adsorption", Princeton University Press, (1945).
- (44) Emmett, P., A.S.T.M. Technical Publication No. 51, 95-106, (1941).
- (45) Bugge, P. and Kerlogue, R., J. Soc. Chem. Ind., 66, 337-81, (1947).
- (46) Harkins, W. and Jura, G., J. Am. Chem. Soc. 66, 1358, (1944).
- (47) McBain, J., and Bakr, A., J. Am. Chem. Soc. 48, 690, (1926).
- (48) Langmuir, I., J. Am. Chem. Soc., 40, 1361 (1918).
- (49) Tolman, R.C., "Statistical Mechanics with Applications in Physics and Chemistry." *Chemical Catalog Co. Inc. (1927)*
- (50) Brunauer, S., Deming, W., Deming, L., and Teller, E., J. Am. Chem. Soc., 62, 1723, (1940).
- (51) Barrett, H., Birnie, A., and Cohen, M., J. Am. Chem. Soc., 62, 2839, (1940).
- (52) Emmett, P., in E.O. Kraemer's "Advances in Colloid Science," New York, (1942), Ch. 1.
- (53) McMillan, W., and Teller, E. J. Ch. Phys., 19, 23, (1951).
- (54) McMillan, W., J.Ch. Phys., 15, 390, (1947)
- (55) Walker, W. and Zettlemyer, A., J. Phys. and Colloid Chem., 52, 47-58, (1948).
- (56) Ross, S., J. Phys, and Colloid Chem., 53, 385, (1948).
- (57) Corrin, M.L., J. Phys. and Colloid Chem., 55, 612, (1951).
- (58) Hill, T., J. Am. Chem. Soc, 72, 5389, (1950).
- (59) Hill, T., J. Chem.Phys., 14, 263, (1946).
- (60) Harkins, W. and Jura, G., "Colloid Chemistry", Vol. VI, edited by Jerome Alexander.

- (61) Livingston, H.K., J. Chem. Phys., 15, 617, (1947).
- (62) Emmett, P., J. Am. Chem. Soc., 68, 1784, (1946).
- (63) Mackower, B., Shaw, T. and Alexander, L., Proc. Soil Sci. Soc. America 2, 101-8, (1941).
- (64) Farkas and Melville, "Experimental Methods in Gas Reactions."
- (65) Worcester, W.G., Personal Communication.
- (66). Cowie, W.G., Canadian Pacific, Synopsis No. 3. (1951)

APPENDIXTABLE I

Calibration of Mercury Cutoff

Graduation Mark	Volume ml.	Graduation Mark	Volume ml.
1	0.0626	16	0.0690
2	0.0711	17	0.0719
3	0.0669	18	0.0695
4	0.0682	19	0.0643
5	0.0722	20	0.0670
6	0.0639	21	0.0759
7	0.0689	22	0.0661
8	0.0668	23	0.0709
9	0.0696	24	0.0593
10	0.0687	25	0.0748
11	0.0658	26	0.0649
12	0.0681	27	0.0676
13	0.0684	28	0.0650
14	0.0665	29	0.0567
15	0.0719	30	0.0685

TABLE II

Vapor Pressures of Nitrogen and Oxygen
as a
Function of Temperature

Temperature deg. K	Vapor Pressure of Oxygen cm.	Vapor Pressure of Nitrogen cm.
77.0	14.89	73.35
77.1	15.11	74.20
77.2	15.34	75.09
77.3	15.56	75.98
77.4	15.79	76.90
77.5	16.03	77.80
77.6	16.25	78.72
77.7	16.50	79.65
77.8	16.04	80.58
77.9	16.98	81.52
78.0	17.23	82.48

In tables III, IV and V of the Appendix, abbreviations are used at the heads of the columns. The significance of the abbreviations are as follows:

"J.T." is the temperature of the water jacket in deg. C.

"R.T." is the temperature of the room in deg. C.

"P." is the pressure observed, in cm. of mercury.

"V. at J.T." is the volume in ml. of apparatus at the jacket temperature.

"V. at R.T." is the volume in ml. of tubing at room temperature. This volume is 5.0 ml. (table III) when stopcock G is closed, and is 15.2, 16.3 or 17.1 when stopcock G is open.

"V.P. of O₂" is the vapor pressure of oxygen in cm. as measured on the oxygen vapor pressure thermometer.

"V." is the volume at S.T.P. calculated from the foregoing data. When the dead space was determined V. gave the dead space volume in ml./gm. When the adsorbed volume was determined, V. was in ml.

The volume of the tubing joining the gas buret and the mercury cutoff was measured by varying the volume of helium in the gas buret(B) while stopcock G was closed. Table III gives the experimental data and volume calculated from the data.

TABLE III

Measurement of the Volume of Tubing
Joining the Buret and the Cutoff

J.T. :	R.T. :	P. :	V. at J.T.:	V at RT:	V.P. of O ₂ :	V.
25.0	24.8	30.377	76.39	a	-----	-----
25.0	24.8	49.04	45.40	a	-----	-----

TABLE IV

Measurement of the Volume of Tubing
Between Stopcocks G and H
Bulb I

25.0	24.8	30.37	76.39	5.0	-----	-----
25.0	24.8	26.99	76.39	5.0† b	-----	-----
Bulb II						
25.5	27.9	30.82	76.26	5.0	-----	-----
25.5	27.9	27.24	76.26	5.0‡ c	-----	-----
Bulb III						
25.2	25.5	28.18	76.26	5.0	-----	-----
25.2	25.5	24.53	76.26	5.0† d	-----	-----

Using the ideal gas law,

$$b = 10.2 \text{ ml.}$$

$$c = 11.3 \text{ ml.}$$

$$d = 12.1 \text{ ml.}$$

*b, c, d, are volumes
to be determined*

By using the ideal gas law, volume "a" was calculated to be 5.0 ml.

Three different adsorption bulbs were used in the determinations. The volume of tubing from stopcock G to stopcock H was different for each bulb. These volumes were measured by, measuring the pressure of helium with the stopcock

G closed, then opening G while stopcock H was closed and measuring the pressure again. Table IV gives the experimental data measured in this way, and the volumes calculated from the data.

Table V gives the experimental data measured in the adsorption determinations.

TABLE V

Primary Adsorption Data
 Volcanic Ash 3726
 Sample Weight 2.429 gm.
 Calibration of Dead Space

J.T.	R.T.	P.	V. at J.T.	V at RT	V.P of O ₂	V.
25.0	25.5	32.40	76.39	5.0	-----	-----
25.0	25.5	16.82	10.74	15.2	14.91	2.090

Adsorption Data

25.0	27.0	50.08	76.39	5.0	-----	-----
25.0	27.2	9.26	76.39	15.2	14.90	25.37
25.0	27.5	10.91	22.72	15.2	14.90	27.16

Stopcock G turned off after lowering mercury so volume was 76.39. Pressure returned to 9.26

25.0	27.6	37.89	76.39	5.0	-----	-----
25.0	27.3	16.77	76.39	15.2	14.94	29.82
25.0	27.4	21.53	10.74	15.2	14.94	31.65

Stopcock G turned off after lowering mercury in buret as above.

25.0	27.4	47.17	76.39	5.0	-----	-----
25.0	27.4	25.20	76.39	15.2	14.96	32.62
25.0	27.5	30.90	22.72	15.2	14.96	34.39

Stopcock G turned off as above

Table V (ctd.)

Volcanic Ash 4009
Sample Weight = 2.167 gm.

J.T. : R.T. : P. : V. at J.T. : V at RT : V.P of O₂ : V.

Determination of Dead Space

25.2	28.1	36.43	76.26	5.0	-----	-----
25.2	28.2	22.08	10.39	17.1	15.28	1.284

Adsorption Data

25.2	29.0	20.84	76.26	5.0	-----	-----
25.2	29.0	0.23	76.26	17.1	15.28	20.03
25.2	29.0	19.68	76.26	5.0	-----	-----
25.2	29.0	3.99	76.26	17.1	15.30	29.95
25.2	28.5	37.40	76.26	5.0	-----	-----
25.2	29.0	14.81	76.26	17.1	15.31	36.66
25.2	28.9	31.93	76.26	5.0	-----	-----
25.2	29.0	20.51	76.26	17.1	15.30	39.75
25.2	29.0	23.52	45.27	17.1	15.30	41.27

Stopcock G closed, then mercury in buret lowered

25.2	29.0	40.55	76.26	5.0	-----	-----
25.2	29.1	29.13	76.26	17.1	15.32	44.44
25.2	29.1	45.25	76.26	5.0	-----	-----
25.2	28.5	34.43	76.26	17.1	15.32	49.65

Volcanic Ash 4017
Weight of Sample = 1.04 gm.
Determination of Dead Space

25.0	26.4	38.88	76.39	5.0	-----	-----
25.0	25.4	12.30	78.39	15.2	15.75	1.960

Adsorption Data.

25.0	25.3	38.00	76.39	5.0	-----	-----
25.0	25.2	10.07	76.39	15.2	15.70	7.16
25.0	25.8	46.56	76.39	5.0	-----	-----
25.0	26.7	21.05	76.39	15.2	15.73	5.90
25.0	26.3	41.93	76.39	5.0	-----	-----
25.0	25.9	27.33	76.39	15.2	15.74	77.76
25.0	26.2	63.13	76.39	5.0	-----	-----
25.0	26.5	37.99	76.39	15.2	15.72	8.86
25.0	26.7	41.31	22.72	15.2	15.72	9.63
25.0	26.8	51.60	4.24	15.2	15.72	10.05

Table V (ctd)
 Volcanic Ash 4021
 Sample Weight 14.20 gm.

J.T.	R.T.	P.	V. at J.T.	V at RT	V.P. of O ₂	V.
Determination of Dead Space						
25.5	26.6	31.99	76.39	5.0	-----	-----
25.5	26.6	10.96	76.39	15.2	15.98	2.052

Adsorption Data

25.0	25.1	5.48	76.39	5.0	-----	-----
25.0	24.0	0.82	76.39	15.2	15.97	38.29
25.0	24.6	31.14	76.39	5.0	-----	-----
25.0	24.0	6.93	76.39	15.2	15.98	46.49
25.0	25.2	8.30	22.72	15.2	15.98	47.45
25.0	25.5	8.96	4.24	15.2	15.98	47.75

Stopcock G turned off after mercury in buret lowered

25.0	25.5	44.57	76.39	5.0	-----	-----
25.0	25.5	16.87	76.39	15.2	16.01	51.27
25.0	25.7	19.93	22.72	15.2	16.01	54.20
25.0	25.9	21.42	4.24	15.2	16.01	55.03

Stopcock G turned off after mercury in buret lowered

25.0	25.9	59.94	76.39	5.0	-----	-----
25.0	25.9	27.93	76.39	15.2	16.03	57.75
25.0	25.9	30.82	45.40	15.2	16.03	59.75
25.0	25.9	35.09	10.74	15.2	16.03	61.87

Volcanic Ash 4024
 Sample Weight 1.903 gm.

Determination of Dead Space						
25.5	27.9	30.82	76.26	5.0	-----	-----
25.5	27.9	14.41	45.27	16.3	15.26	1.354

Adsorption Data

25.1	27.1	36.35	76.26	5.0	-----	-----
25.1	26.9	8.70	76.26	15.3	15.28	19.56
25.1	25.5	11.48	22.59	16.3	15.28	20.30

Stopcock G turned off, then mercury level in buret lowered

25.0	25.8	36.08	76.26	5.0	-----	-----
25.0	26.3	26.44	76.26	16.3	15.30	25.05
25.1	26.5	30.47	45.27	16.3	15.30	26.28

TABLE V (ctd)

J.T.	R.T.	P.	V at J.T.	V at R.T.	V.P. of O ₂	V.
25.1	26.3	34.30	22.59	16.3	15.30	27.36
25.1	26.5	46.44	76.26	5.0	-----	-----
25.1	26.9	38.42	76.26	16.3	15.33	28.69
25.1	26.5	49.55	29.59	16.3	15.33	32.36

Volcanic Ash 3726
 Calcined at 520 deg. C
 Sample Weight 2.040 gm.

Determination of Dead Space

24.2	25.0	24.52	76.26	5.0	-----	-----
25.2	25.0	14.64	10.61	16.3	15.25	1.321

Adsorption Data

25.2	25.2	18.71	76.26	5.0	-----	-----
25.2	25.4	4.20	76.26	16.3	15.26	7.67
25.2	25.5	28.62	76.26	5.0	-----	-----
25.2	25.8	12.26	76.26	16.3	15.28	11.88
25.2	25.8	38.80	76.26	5.0	-----	-----
25.2	25.8	22.67	76.26	16.3	15.30	12.22
25.2	25.8	32.22	10.61	16.3	15.30	14.05

Volcanic Ash 3726
 Calcined at 760 deg. C
 Sample Weight 2.048 gm.

Determination of Dead Space

25.2	25.5	26.22	76.26	5.0	-----	-----
25.1	25.1	11.73	4.11	15.2	15.30	1.976

Adsorption Data

25.2	26.2	23.05	76.26	5.0	-----	-----
25.2	26.0	6.19	76.26	15.2	15.29	4.13
25.2	26.0	30.65	76.26	5.0	-----	-----
25.3	26.4	13.64	76.26	15.2	15.30	5.03
25.4	26.5	31.93	76.26	5.0	-----	-----
25.4	25.9	19.20	76.26	15.2	15.29	5.71
25.4	26.0	21.71	45.27	15.2	15.32	66.03

TABLE V (ctd)

J.T.	R.T.	P.	V. at	J.T.	V. at	R.T.	V.P. of O ₂	V.
Volcanic Ash 3726 Calcined at 1065 deg. C Sample Weight 2.987 gm.								
Determination of Dead Space								
25.2	25.5	28.14	76.26	5.0	-----	-----	-----	-----
25.2	25.4	17.75	10.62	17.1	15.29	1.996		
Adsorption Data								
25.4	25.6	31.18	76.26	5.0	-----	-----	-----	-----
25.4	25.3	12.60	76.26	17.1	15.26	0.84		
25.3	25.3	21.74	76.26	5.0	-----	-----	-----	-----
25.3	24.9	16.34	76.26	17.1	15.28	0.92		
25.3	24.8	24.70	76.26	5.0	-----	-----	-----	-----
25.3	25.0	19.78	76.26	17.1	15.29	0.95		
25.4	25.5	23.39	45.27	17.1	15.30	1.08		

TABLE VI

Adsorption Data
Calculated for Figures 11 to 15
Volcanic Ash 3726

P.	$\frac{p(1+p)}{v}$	$\frac{p}{p_0}$	$\frac{p}{v(p_0 - p)}$	$\log_{10} p$	$\frac{1}{v^2}$
9.26	0.997	0.126	1.38	0.967	91.5
10.91	1.120	0.149	1.568	1.038	80.0
16.77	1.68	0.228	2.41	1.225	66.6
21.53	2.14	0.293	3.18	1.333	58.9
25.20	2.62	0.344	3.88	1.402	55.4
30.90	3.10	0.420	5.12	1.490	50.0
Bentonite 4009					
0.23	0.03	0.003	0.001	1.362	117
3.99	0.30	0.053	0.4	0.601	52.5
14.81	1.05	0.196	1.45	1.171	35.0
20.51	1.43	0.274	2.05	1.312	29.9
23.52	1.63	0.314	2.41	1.371	27.7
29.13	1.98	0.388	3.20	1.464	23.9
34.43	2.20	0.459	3.78	1.537	19.0

TABLE VI (ctd)

p	$\frac{p(1+p)}{v}$	$\frac{p}{D_0}$	$\frac{p}{v(D_0 - p)}$	$\log_{10} p$	$\frac{1}{v^2}$
Volcanic Ash 4017					
10.07	2.00	0.131	2.67	1.003	311
21.05	3.91	0.275	5.51	1.323	211
27.33	4.97	0.356	7.42	1.437	180
37.99	6.42	0.496	11.1	1.580	138
41.31	8.27	0.616	17.5	1.675	117
51.60	8.85	0.674	21.1	1.713	107
Volcanic Ash 4021					
0.82	0.332	0.010	0.43	1.914	1600
66.93	2.30	0.089	22.99	0.841	930
8.30	2.75	0.107	3.58	0.919	896
8.96	2.98	0.115	3.88	0.952	885
16.87	5.38	0.213	7.23	1.214	724
19.93	6.57	0.256	9.03	1.300	686
21.42	7.05	0.275	9.81	1.331	664
27.93	9.34	0.359	13.80	1.446	607
30.82	10.20	0.396	15.62	1.489	565
35.09	11.71	0.451	18.71	1.545	528
Volcanic Ash 4024					
8.70	0.95	0.116	1.28	0.940	94.9
11.48	1.24	0.153	1.70	1.060	88.0
15.36	1.73	0.218	2.42	1.214	75.3
21.12	2.09	0.282	3.02	1.325	60.6
26.44	2.69	0.340	4.13	1.422	57.6
30.47	3.10	0.407	4.97	1.484	52.5
34.30	3.48	0.458	5.86	1.535	48.5
38.42	3.86	0.512	6.96	1.584	44.0
49.55	4.85	0.661	11.49	1.695	34.6
Volcanic Ash 3726 Calcined at 520 deg. C					
4.2	1.18	0.056	1.58	0.623	707
13.26	3.38	0.177	4.65	1.123	468
22.67	4.98	0.313	7.23	1.355	278
32.22	6.70	0.430	10.92	1.508	210

TABLE VI (ctd)

p.	$\frac{p(1+p)}{v p_0}$	$\frac{p}{p_0}$	$\frac{p}{v(p_0 - p)}$	$\log_{10} p$	$\frac{1}{v^2}$
Volcanic Ash 3726 Calcined at 760 deg. C					
6.19	3.32	0.083	4.45	0.792	2460
13.64	6.05	0.182	9.10	1.135	1670
19.70	8.65	0.257	12.30	1.283	1290
21.71	9.54	0.290	13.90	1.337	1160
Volcanic Ash 3726 Calcined at 1065 deg. C					
12.60	17.5	0.169	24.1	1.100	14150
16.34	21.6	0.218	30.3	1.213	11810
19.78	26.3	0.264	37.7	1.296	11110
23.39	28.4	0.312	42.0	1.369	8590

Results for sample 3726 calcined at 1065 deg. C. were calculated on the basis of sample weight, since the ordinates based on one gram would be excessively large.