THE BASIS OF ADSORPTION OF WATER POLLUTANTS BY COAL

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6

# ABSTRACT

An approach for studying the basis of adsorption of water pollutants, by coal, is presented.

Oxidized and non-oxidized coal samples, mined from the Hat Creek deposits of British Columbia, were evaluated.

During the first phase of the research, electron microanalysis, and macrochemical techniques were used to investigate the surface properties and the pore structure of the Hat Creek coal in comparison with activated carbon.

The second phase of the study was focussed on the extensive evaluation of the adsorption capacity and efficiency of the coal to remove some dissolved components from synthetic wastewaters using both batch and continuous leaching tests. Heavy metals, dissolved organics, nitrates, phosphates, ammonia, phenol and cyanide were tested either individually or mixed in some combinations. The selectivity exhibited by coal towards mixed metals is also discussed. Adsorption isotherms and break through curves were plotted and interpreted for each material.

A comparative study using other adsorbents such as activated carbon, soil and construction sand was also conducted. The effect of some factors in influencing the adsorption process were statistically analyzed.

During the third phase of the study two mechanisms for the adsorption of heavy metal ions and dissolved organics were investigated. Spectroscopic, electron microscopic, and chemical methods were used to confirm that metal ions are adsorbed by coal through a chemisorption type of mechanism where the adsorbed metal ions interact with the available acid groups (mostly carboxylic COOH and phenolic -OH) to form metal complexes.

In the case of removal of dissolved organics by coal, there was a combining effect of physical adsorption and biological oxidation. A material balance on the coal bed systems was utilized to estimate the bio-oxidizable fraction of the organic substrate.

The last phase of this work is concerned with some design applications using the actual flow from municipal and industrial sewage. Data from long term experiments on larger columns were utilized to predict the size and performance of a coal bed to treat large quantities of flow.

It appears from the research conducted that low rank coals will be a satisfactory material for the removal of pollutants from wastewaters.

TABLE OF CONTENTS

LIST OF TABLES

## LIST OF FIGURES

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## NOMENCLATURE

| | |
|---|---|
| AC | Activated carbon |
| AEI | Absorption Electron Image |
| A.W.A. | Acid washed activated carbon |
| A.W.C. | Acid washed core coal |
| A.W.S. | Acid washed surface coal |
| BOD | Biochemical oxygen demand, mg/1 |
| C.C. | Core coal (non-oxidized) |
| CEC | Cation exchange capacity |
| COD | Chemical oxygen demand, mg/1 |
| $gpm/ft^2$ | Gallons per minute per square foot of surface area = 6.79 X $10^{-5}$ $L/sec/cm^2$ |
| m.eq/gm | Milliequivalent per gram |
| mg/1 | Milligrams per liter |
| MGD | Million gallons per day |
| ppm | Parts per million = mg/1 |
| $NH_3-N$ | Ammonia nitrogen |
| $NO_3-N$ | Nitrate nitrogen |
| $O-PO_4-P$ | Ortho phosphate phosphorus |
| S.C. | Surface coal |
| TIC | Total inorganic carbon |
| T-N | Total nitrogen |
| T.K.N. | Total Kjeldahl nitrogen |
| TOC | Total organic carbon |
| T-P | Total phosphorus |
| % w/w | Percentage weight by weight |
| W.W.A. | Water washed activated carbon |
| W.W.C. | Water washed core coal |
| W.W.S. | Water washed surface coal |

# I. INTRODUCTION

## 1.1 Justification

The increasing population, industrial growth and increasing water use has already created pollution problems in many locations in the world.

During the past decade an increasing interest and concern has developed with regard to our environment. The detrimental effect of releasing wastes to soil or water "sinks" is only beginning to be understood, although that practice has been used for centuries.

Recently, the direction of concern is changing from the general pollution aspects to more specific problems such as the removal of organics, phosphates and nitrates from wastewaters. In particular, the problem of efficient heavy metal removal becomes important, since heavy metals have a high potential toxicity to various biological organisms at extremely low concentrations. Lead, zinc and copper represent the greatest "heavy" metal loading in surface waters (Hendren, 1973; Evans, 1973 and Sarter, 1972).

Therefore, advanced wastewater treatment is necessary to remove pollutants which are not adequately removed by conventional, secondary treatment processes. Activated carbon is now extensively used in tertiary treatment processes and

its use has become firmly established as a practical, reliable
new tool which has many uses in preserving water quality, and
meeting discharge requirements (Linstedt and O'Connor, 1971).
Because of the expensive cost of this process, a keen
interest in the creation of a new, less expensive method for
tertiary treatment has developed rapidly during the past few
years.

For many years, crushed anthracite coal has been
used as a mechanical filtering medium for water supplies
(Turner, 1943).

Recently, a renewed interest has developed for the
use of low fuel value coal as a material for water purification
(Office of coal research, Report No. 55, 1971). However, the
subsequent use of this material as an energy source may require
appropriate pretreatment to remove toxic matters.

Locally, the interest has been directed towards the
use of low grade coals from British Columbia in wastewater
purification. Some laboratory experiments indicated that
some of the B.C. coals do possess adsorptive characteristics
(Coulthard, 1974; Riaz, 1974 and Hendren, 1974).

Considerable interest has been generated in the
use of Hat Creek coal for water purification since it is
available in a large and economical reserve in British Columbia.

Because very little is known about the surface
chemistry and porous structure of this coal and the cause of
its effectiveness in the adsorption of metal ions and dissolved

organic constituents, the ability of this coal as an adsorbent material for use in water purification is still the subject of much discussion and many claims.

Accordingly, there is a need for more investigation with emphasis on surface structure of the Hat Creek coal, also, on the study of the mechanism involved in the adsorption of heavy metals and dissolved organics. Then, there is a definite need to conduct larger pilot experiments to treat actual sewage effluents in order to reinforce the encouraging results obtained from the laboratory experimentation.

1.2 Objectives

1) To evaluate the surface properties and porous structure of Hat Creek coal in comparison to activated carbon.

2) To determine the sorptive properties of the coal, through batch and continuous adsorption tests, to remove dissolved constituents from water including metal ions, dissolved organics, phosphates, nitrates, ammonia, phenol and cyanide.

3) To evaluate the effect of factors influencing the adsorption process.

4) To investigate the mechanisms involved in the adsorption of metal ions.

5) To investigate the mechanism involved in the adsorption of dissolved organics.

6) To predict the size and performance of the larger coal beds required to treat actual wastewater sewage discharges.

## II. LITERATURE REVIEW

### A. General on Coal

#### 1. Basic concept and definitions

Coal is not a uniform substance but rather a heterogeneous mixture of organic substances and mineral matter (Leonard and Mitchel, 1968). As coal is derived by metamorphism of plant debris, the terms "mineralized plants" and "mineral fuel" have been widely used to define coal (Spackman, 1966). However, coal is not a mineral of constant composition, but a mixture of organic and inorganic materials representing matter of different origins (Van Krevelen, 1961). Therefore, the composition and physical properties of coals vary among different deposits and even within single seams in some mines.

Coal is a compact stratified mass of combustible metamorphosed plant remains (Spackman, 1966). The diversity of the original plant materials and the degree of metamorphism or coalification that has affected these materials are the two major reasons for the variety of the physical components in coal.

Most coals are unstable, or more correctly, meta-stable solids, the most mature coals such as anthracite are the most stable. Coal is used commonly as a fuel, a source of carbon for the metallurgical industry and, to a lesser extent, as a source of organic chemicals (Lowry, 1963).

Methods have therefore been devised to classify coals according to properties of greatest importance to these industries and to the coal producers. The most important are rank (Table 4b), type and analysis for certain chemical components. These properties are described in details in Chapter IV.

For coal to be used in sewage treatment the first requirement is that it retains its physical integrity when wet. Most coals do so with the exception of lignite and subbituminous which have been found to disintegrate. The next variable of importance is the ability of a given coal to adsorb dissolved species from solutions.

Therefore, this literature review is focussed on discussing the research work conducted on the adsorptive properties of coal and other related characteristics such as surface properties, pore structure, chemical structure and similar factors.

2.   Impurities in Coal (Leonard, 1968)

These are classified into:

a)   Those components that form ash.

b)   Those that contribute sulphur to air pollution.

Both of these impurities may be subdivided into two types.

i)   Impurities that are structurally a part of coal, intimately mixed with it, and are named "True" or "Inherent" impurities.

ii)   Impurities that can be eliminated by appropriate cleaning methods.

2.1  Minerals in coal (Leonard, 1968)

The principal mineral groups in coal are: shale, kaolin, sulfides, carbonates, chlorides and numerous forms of silicates.

2.2  Elements in coal (Leonard, 1968)

The following table gives the approximate ranges of the major oxides present in the ash of bituminous coals of the United States.

| Constituent | Percentage |
|---|---|
| Silica ($SiO_2$) | 20-60 |
| $Al_2O_3$ | 10-35 |
| $Fe_2O_3$ | 5-35 |
| CaO | 1-20 |
| MgO | 0.3-4 |
| $TiO_2$ | 0.5-2.5 |
| Alkalis ($Na_2O + K_2O$) | 1-4 |
| $SO_3$ | 0.1-12 |

In addition, minor elements can also be present such as Li, Rb, Sr, Ba, Ag, As, B, Be, Bi, Sb, Co, Cr, Cu, Ga, Hg, Ge, Zn, P, N, Mn, Mo, U, V, W, Zr.

3.  Deterioration or Weathering During Storage

3.1  Dehydration and "slacking".

Berkowitz (1971) reported that dehydration of low rank coal with 20-30% moisture is accompanied by extensive and partially irreversible volume

shrinkage, after that the coal loses its cohesion and disintegrates into small pieces. This behavior is called "slacking". Sub-bituminous and lignite coals undergo "slacking" during storage while higher rank coals do not.

## 3.2 Oxidative deterioration

Oxidation takes place through chemisorption of oxygen at the exposed surface followed by the formation of ether (-O-), phenolic hydroxyl (-OH) and carboxyl (-COOH) groups on the surface layers. Phenolic hydroxyl and carboxyl groups render the coal more acidic and increase the contents of alkali-soluble "humic acids" (Berkowitz, 1971).

## 4. Surface Area

Many years of research have been spent in the testing of numerous adsorbates at various temperatures. The experimental results have then been interpreted in terms of theoretically derived isotherms. These studies have revealed an extreme complexity of the structure of coal from both chemical and physical viewpoints.

The theoretical BET adsorption equation, as developed by Brunauer, Emmett and Teller (1938), is extensively used for the measurement of specific surface areas by the adsorption of nitrogen gas at a temperature of $77^{\circ}K$.

Dubinin (1966) and Spencer (1966) questioned the use of the BET equation for microporous materials,

whenever micropore filling by an adsorbate occurs before
the monolayer formation.

Consequently, Dubinin (1966) modified the adsorption
potential theory, proposed by Polanyi in 1932, and developed
the Dubinin-Polanyi (DP) equation, from which the micropore
volume and a function of micropore size can be estimated.

Marsh et al. (1965) tested extensively the
application of the DP equation in adsorption of carbon dioxide
at room temperature on coals and proved that it is satisfactory.

Walker (1970) compared the surface areas of coal
calculated from the carbon dioxide adsorption isotherms at
$298^O K$ using BET and DP equations. He found no appreciable
differences between the two values and concluded that the
use of the DP equation is more advantageous and simpler.

In excellent reviews, Marsh (1965) and Spencer
(1967) discussed the problem of determining the surface
areas of coals which has been, up until now, the subject of
considerable controversy. Both pointed out that the area
calculated from nitrogen at $77^O K$ using the BET equation
is associated with the external area of the particle plus
the area contained in pores of diameter greater than
$5.0^O A$, while the area calculated from carbon dioxide at
a higher temperature of $298^O K$, also using the BET equation,

is considered to be a closer approximation to the total surface area of coals. The latter was also confirmed by Walker (1965). Any method applicable at ordinary temperatures indicates larger specific internal areas. In bituminous coals, these areas are found to be in the range of 30 to 100 $m^2$/gm situated almost entirely in the ultrafine capillaries with widths below 40 $\overset{o}{A}$ (Lowry, 1963). These surface areas can be measured only by methods using temperatures not too far below room temperature; the exact temperature depends on the nature of the gas used. Measurements at liquid air temperatures, as used for nitrogen adsorption, relate only to external surfaces of particles and those of macro capillaries and therefore yield values too low by a factor of up to 100; this is explained earlier by Maggs (1952) as an activated diffusion into the micro capillary system becoming exceedingly slow at low temperatures. Most recently, Gan and Nandi et al. (1972) showed that the surface area calculated from carbon dioxide adsorption at $298^o$K are consistently higher than those calculated from nitrogen at $77^o$K. The comparison is shown in Table 1.

TABLE 1.　　NITROGEN AND CARBON DIOXIDE AREAS OF
AMERICAN COALS

| Coal Sampling Location | Carbon (% daf)* | Surface Area ($m^2/g$, mm Cb)** | |
|---|---|---|---|
| | | Nitrogen | Carbon Dioxide |
| Pa | 91.2 | 6.1 | 426 |
| Pa | 90.8 | 7.0 | 408 |
| W. Va. | 90.5 | < 1.0 | 231 |
| Pa | 89.5 | < 1.0 | 253 |
| Alabama | 89.3 | < 1.0 | 197 |
| Alabama | 88.3 | < 1.0 | 214 |
| Kentucky | 83.8 | < 1.0 | 213 |
| Pa | 83.4 | < 1.0 | 141 |
| Indiana | 82.7 | 32.0 | 148 |
| Washington | 81.6 | < 1.0 | 168 |
| Indiana | 81.3 | 43.0 | 114 |
| Kentucky | 81.3 | 1.6 | 179 |
| Illinois | 80.0 | 2.2 | 228 |
| Indiana | 79.9 | 17.0 | 147 |
| Kentucky | 78.8 | 27.3 | 160 |
| Illinois | 78.7 | 88.4 | 169 |
| Illinois | 77.2 | 35.0 | 133 |
| Pa | 76.5 | - | - |
| Illinois | 75.9 | 46.6 | 127 |
| Illinois | 75.5 | 83.0 | 96 |
| Wyoming | 75.0 | < 1.0 | 359 |
| Texas | 74.3 | 2.2 | 225 |
| Wyoming | 72.0 | 2.6 | 308 |
| Texas | 71.7 | 2.3 | 250 |
| Montana | 71.5 | 2.0 | 264 |
| N. Dakota | 71.2 | < 1.0 | 268 |
| N. Dakota | 63.3 | < 1.0 | 238 |

*　Dry, ash-free basis.

**　Mineral matter containing basis.

Spencer and Bond (1966) feel that the "sorption uptake" (moles per unit weight or volume of a given adsorbent) under defined conditions is the correct parameter that should be used to describe the sorptive properties of porous materials, and that the concept of "specific surface" should not be applied since adequate reference materials are not available. They also advise to use of adsorption/desorption isotherms for revealing information on the pore structure of microporous solids and on the changes these undergo upon various treatment.

5.    Porosity of Coals

Hirsch (1954) used the scattering obtained in his X-ray diffraction studies of vitrinite to demonstrate the existence of two types of porosity present in coals:

a)    The "open structure" characteristic of low rank coals with high porosity.

b)    The "liquid structure" characteristic of coking coals, with very little porosity. The work by Bond in 1956 and 1957 has also indicated that "the holes" in coal tend to be flat rather than cylindrical or spherical.

More recently, Toda et al. (1971) concluded that:

a)   The micropore volume decreases with an increase in
     the rank of coal and shows a minimum at 85% carbon.

b)   The micropore volume decreases with an increase in
     the aliphatic, cyclic or aromatic C-H hydrogen,
     identified by infra-red spectroscopy.

The nature of porosity of a number of American
coals has been studied by Gan et al. (1972) who concluded
that coals vary widely in their total pore volumes
(porosites range between 4.1 and 23.2%). Most of the
internal surface area in a coal particle is contained
within the ultrafine region of the total porous structure,
which may represent only 50 to 80% of the internal free
volume.

In the lower rank coals (carbon content less than
75%), macropores predominate while in coals with 76-84%
carbon content, about 80% of the total open pore volume
is due to micro and transitional pores.

Their final conclusion is that coals having
about 35-55% of their total open pore volume in the
transitional range are expected to be most suitable
for use in the adsorption of dissolved molecules from
solutions and thus they are of interest as possible
materials for use in water purification.

The initial oxygen content of the coal is found to have an effect on the formation of transitional pores (Bonnet, 1970). The specific surface and the capillary values increases with the degree of oxidation of the coal and gives lower values for non-oxidized coal (Rusin, 1973).

Toda (1972) calculated the pore volume of coals by the measurement of the coal densities in various liquids. He then utilized this technique in the study of the changes in the pore structure of Japanese coals with heat treatment (Toda, 1973).

6. Colloidal Structure

Colloids are defined as materials with at least one dimension less than 0.5 um. According to McBain (1950), a single material cannot be defined as colloidal, rather a combination of materials must be specified to designate a colloid system. Accordingly, charcoal is not a true colloid, even though it has "colloidal" dimensions, while brown coals and lignites are considered as true colloids in their naturally occurring state (Evans, 1973a). The finely divided coal substance is dispersed in a continuous water medium to form a gel

stabilized by the carboxyl and hydroxyl groups in the
coal.  As these groups are removed, the coal loses
its colloidal nature.  Evans (1973b) reported that
any attempt to measure surface area or porosity after
removing the dispersing medium (water), for example
by drying, will at least measure the values of the
resultant xerogel, which may be different from
the original coal.

7.    Permeability

The permeability was found to be directly
proportional to the square of the size of particles of
coal at constant porosity (Kuprin, 1973), i.e. $K = C d^2$
where K is the permeability, d is the average diameter
of the particles (nm) and C is a constant ($4 \times 10^{-4}$).
He also derived the formulae for calculating the
permeability of coal and sand at different porosities
cited as follows:


$K = C c^2/R^{1.2}$ for coal (c = particle diameter of coal)


$K = C d^2/R^{0.8}$ for sand (d = particle diameter of sand)


R is a particle size parameter determined by data from a

sieve analysis. These equations can be used to control the filtration through coal media on the basis of particle size distribution.

8.  Infra-red Spectra

The infra-red methods can in situ detect the presence of chemical groups, preclude or limit the existence of proposed structures, and demonstrate similarities and differences in the chemical structure of coal.

Work on the infra-red spectroscopy of coal and coal products was originated in Great Britain by Sutherland (1944).

Early investigators (Cannon and Sutherland, 1945) were successful in assigning some of the absorption bands to specific chemical bonds. Cannon (1953) later made further assignments such as oxygen-containing functional groups, $CH_2$ and $CH_3$ groups and both single ring and condensed aromatic structures. He discussed the decrease in bands of oxygen-containing groups with increase in rank. Many studies have been carried out by Brown (1955) on the variation of infra-red spectra with the rank of coal.

Friedel et al. (1956) compiled in a report most of the spectral studies on the chemical composition of coal, including a comparison between various experimental techniques of which the potassium bromide pellet technique is the easiest and most successful one. Several new structural

assignments being made during this work for the absorption bands obtained. Interference due to minerals in the coal has been recognized, Kaolinite has been identified as the principal cause of a band hitherto assigned to aromatic ethers.

A complete survey of the positions of characteristic infra-red bands and their assignments by various authors is presented by Tschamler & De Riuter in Loury (1963), a modified list, including the recently assigned bands is shown in Table 2.

Fujii et al. (1970) concluded that the aromatic C-H hydrogen band at 3030 cm$^{-1}$ appears in coal with 81.1% carbon and becomes stronger as the coal rank increases. However, the aliphatic C-H hydrogen band at 2920 cm$^{-1}$ increases gradually with the rank until 86% carbon, but decreases sharply beyond that point. He also confirmed that the band at 1600 cm$^{-1}$ increases in intensity with increase of the oxygen content.

For the -OH absorption band at 3450 cm$^{-1}$, only semi-quantitative information can be obtained (Osawa et al. 1971) because this band is affected greatly by the moisture content of the KBr disc.

Recently, the infra-red spectra of tertiary lignites were measured and related to their chemical structure (Siskov, 1974).

TABLE 2.    BAND POSITIONS IN THE INFRA-RED SPECTRA
OF COALS AND THEIR ASSIGNMENTS

| Band Position | | Assignment |
|---|---|---|
| $cm^{-1}$ | $\mu$ | |
| 3300 | 3 | -OH Str. ) Phenolic OH......O<br>) -OH (hydroperoxide)<br>-NH Str. ) > NH.....N |
| 3030 | 3.3 | ar. CH Str. |
| 2978 Sh. | 3.36 | $CH_3$ Str. |
| 2925<br>2860 | 3.42 )<br>3.5 ) | $CH_3$ Str., $CH_2$ Str., al. CH Str. |
| 1700 | 5.9 | C = O Str. of COOH or ketonic carboxyl |
| 1600<br>v.intense | 6.25 | ar.  C = C Str.<br>C = O......HO-<br>Double band conjugated with carboxyl $COO^-$,<br>more recently graphitic structure. |
| 1450 | 6.9 | $CH_3$ sym. def., ar. C = C Str., al. C-H<br>also  $C{<}^{O}_{O}$ |
| 1300<br>to<br>1000 | 7.7<br>to<br>10.0 | C - O Str. (phenols)<br>OH def.<br>Car.-O-Car. str.<br>C - O Str. (alcohol)<br>Car.-O-Car. al. Str.<br>Cal.-O-Cal. Str. |
| 1050<br>to<br>900 | 9.6<br>to<br>11.0 | $S_i$ - O of silicate impurity<br><br>and other mineral matters |
| 900<br>to<br>700 | 11.0<br>to<br>14.3 | Aromatic bands |
| 860<br>to<br>750 | 11.5<br>to<br>13.3 | Substituted benzene rings,<br>Carbonates $CO_3^{--}$ |

$\mu$ (microns) = a measure for the wavelength ($\lambda$) in microns.
$cm^{-1}$ = a measure for the wave number $\bar{V}$.  The two units are connected by the relation

$$\bar{V} = \frac{1}{\lambda (cm)} = \frac{10,000}{\lambda (\mu)} = cm^{-1}$$

In comparison, the first scan of the spectrum of activated carbon in the infra-red shows complete or nearly complete electronic absorption. However, on expanded scale and using wider slit and slower scanning speeds, a spectrum has been observed by Friedel (1970 and 1972). This spectrum shows definite bands at 1735 $cm^{-1}$, 1590 $cm^{-1}$ and 1215 $cm^{-1}$. These are interpreted, respectively, in terms of carboxyl, aromatic structures or unconjugated chelated carbonyl and C-O groups.

However, due to the great magnification, it is possible to reach a point where the apparent transmittance may consist of an appreciable amount of instrumental scattered energy.

## 9. Chemical Structure

In the last several years, excellent work has been done which contributes to a better understanding of the basic structural models of the coal molecule (Given, 1960; Hill, 1962; Smirnov, 1973; Loewenber, 1973; Chakrabartty and Berkowitz, 1974).

Although Given's model is widely recognized by many coal chemists, it appears to be the least promising in relation to the research carried out for this report for the following reasons: a) The model is proposed for high rank coals with 82% carbon while all experiments in this research were performed on low rank lignite coals. b) The absence of methylene bridges, side chains and functional groups in Given's

model is contrary to our findings where there is an appreciable amount of acidic groups present in Hat Creek coal samples.

In comparison, the model proposed by Hill (1962) for the high volatile bituminous coal is more consistent with our objectives. It incorporates a large number of functional groups and other bonds.

Recently, Chakrabartty and Berkowitz (1974) developed a structural model for coal which shows that the skeletal carbon arrangements of coal are largely made up of non-aromatic structures and it is not therefore an aromatic solid as believed previously.

## 9.1  Oxygen-functional groups

A characteristic of low rank coals, peats and related humic materials is that much of the oxygen associated with their structure is present as carboxyl and phenolic hydroxyl groups (Brooks, 1957). The distribution of oxygen-containing functional groups in humic acids of the coal was measured by Moschopedis (1962) for some lignite samples, and found to have a total acidity of 7.3 m. eq/gm, carboxyl COOH of 4.4 m.eq/gm and phenolic OH of 2.9 m.eq/gm. Meanwhile, soil humic acids are found to have very similar values.

The acidity or exchange capacity of humic substances is due mainly to the presence of dissociable hydrogen in aromatic and aliphatic COOH and phenolic -OH groups. The active hydrogen in coal is determined using Grignard Reagent (methyl magnesium iodide). However, the reaction is not always stoichiometric and lower values are often obtained. (Jones et al. 1962).

Kasotochin et al. (1964) showed the fundamental structure of humic acids to consist of flat aromatic condensed rings with functional groups as well as other simple aromatic hydrocarbon chains. He pointed out that nitrogen occurred in cyclic and in aliphatic forms. The structure of brown coal is related to that of oxidized hard coal by Kukharenko et al. (1969). He oxidized humic acids extracted from brown coals and weathered coals, and then isolated carboxylic acids from the reaction mixture, using gas-liquid chromatography. It was shown that tri- and tetra-basic aromatic carboxylic acids predominated.

The proportions of oxygen in the major functional groups were calculated for coal humic acids (Moschopedis,1962) who found that only 74% of the oxygen present can be accounted for in functional-oxygen groups mainly the carboxyl COOH of > 49%, phenolic OH of >16% and methoxyl groups of $\simeq$ 9%.

At the present time, the characterization of this unaccountable oxygen has yet to be clearly achieved. A number of theories exist which confirm the presence of quinones and ether-like linkage units in the humic substances. Davies et al.

(1969) showed that blocking of the quinone groups produced
a significant decrease in the copper retention capacity of
the humic acid.

Rachid (1972a) has measured the quinone content of
humic substances isolated from a marine environment. More
recently, Goodman and Cheshire (1973) have suggested an
entirely different type of group containing nitrogen -
"porphyrin group". Because nitrogen is such a well-known
electron donor in coordination compounds, therefore, it is
likely that the "porphyrin group" also plays a role in
binding the heavy metal ions.

Schafer (1970a) studied the ion-exchange properties
of low rank coal with a view to obtaining optimum conditions
for the determination of carboxyl groups in the presence of
phenolic groups. He assessed the alternative procedures
known for estimating the carboxyl groups and he concluded that
exchange with barium acetate at pH 8.25 under reflux (single
for 4 hours) followed by potentiometric titration to pH 8.25
in the presence of the coal provided the most reliable
approach. In another work by Schafer (1970b) the procedure
for the determination of total acidity of low rank coal,
using barium hydroxide, was re-examined and it was concluded
that barium hydroxide reacts with acidic hydrogens in both
aliphatic and aromatic compounds. Therefore, it is a
successful reagent for measuring both phenolic OH and carboxyl
COOH groups defined as "total acidity".

Aliphatic hydroxyls are not thought to contribute significantly to the total acidity, so the difference between "total acidity" and carboxyl COOH groups gives a measure of phenolic OH (Brooks, 1957).

A recent study by Schafer (1972) suggested that the moisture content of low rank coals is directly related to the carboxyl content and to a lesser extent to phenolic hydroxyl content. The hydrophilic character of these groups leads to the interaction through hydrogen bonding between water and the functional groups.

10. Adsorption on Coal Surface

10.1 Adsorption of dissolved organics

10.1.1 Biodegradable organics

For many years crushed anthracite coals have been used for filtration in both water purification and sewage treatment (Turner, 1943).

Only during the past decade has the use of coal as an adsorbent for purifying wastewaters been examined.

Jhanson and Kunka (1962) reported that certain coals have the capacity to remove up to 4% of their weight of oxygen-demanding materials, measured in terms of COD, from settled raw sewage.

The Rand Corporation (U.S. Dept. of Interior
Report, 1971) operated a 10,000 U.S. gal/day pilot plant
coal filter recommending the use of coal for post or
tertiary treatment of secondary sewage effluent, since
it is far less expensive than activated carbon which is
now extensively used in tertiary treatment processes
(Hassler, 1974; Perrotti, 1973; Kalinske, 1972; and
Culp, 1971).

Shannon (1970) examined the adsorptive capacity
of some Canadian coals to remove some components from
sewage. He found a pronounced selectivity between
different components which were mixed in a form of
synthetic waste.

The biological oxidation activity during
sewage treatment with carbon or coal has been confirmed.

A study of Biospherics Research Inc. (1969)
showed that the surface of the coal particles provided
an enriched micro-environment for microbial growth,
therefore, enhancing the biological oxidation of the
organic matter.

The large surface area and the chemical
functionality of the available surface are found to be
the major factors responsible for the enhancement of
the biological oxidation activity (Perrotti, 1973).

A study on powdered coal (Kehoe, 1967) showed
that it is effective in agglomeration of the organic
particulates from the primary sewage.

10.1.2    Dyes

Some American coals were found to adsorb dyes from
an aqueous solution (Nandi et al., 1971). The removal of
dye by coal was shown to be partly due to the interaction with
some mineral constituents, mostly pyrite and soluble alkali
salts, and due to adsorption on the porous surface of the
coal. This study also proved that adsorption of dyes on
lignites was not influenced by the oxygen groups on the surface.

10.1.3    Oils

The use of coal in the removal of oil and other
organic contaminants from refinery wastes was studied
recently by Bunn (1974).

Other research on the removal of oil by powdered coal containing 10 mg/l of a coagulant (e.g. $Al_2(SO_4)_3$)) was conducted by Merkel (1972), who used the spent coal after treatment for combustion.

## 10.1.4    Alcohols and phenols

Oxidized coal was found to adsorb n-aliphatic alcohols (Vlasova, 1973). The oxygen-containing groups, especially phenolic -OH and carboxyl COOH form active centers for adsorption.

The adsorption of butanol, hexanol and phenol was proven to be greater on waste rock of 97% ash content than on high grade coal with 2% ash content.

## 10.1.5    Colors

The study of color removal by coal was carried out in Japan by Motohisa et al. (1973) who found that a mixture of coal with a small amount of activated charcoal showed considerable activity.

An earlier study on coal ash proved that the latter removed the color completely from effluents and residual liquors from yeast production (Drub, 1967). Other sorbents including activated carbon have been found to be less effective than coal.

10.2   Adsorption of heavy metals

In 1971, the Linfield Research Institute in McMinnville, Oregon completed a preliminary study on the removal of heavy metal ions from solutions by coal (Hinrichs, 1971).

During the last few years, research studies proved that some local B.C. coals possess a good adsorptive quality for the removal of heavy metals (Coulthard, 1976), (Hendren, 1974), (Riaz, 1974).

Other research studies in Japan by Kawazoe (1971) found that chromium was removed completely from electro-plating waste effluents when it was in contact with low grade coal for 24 hours.

Powdered lignite has been found first to reduce hexavalent chromium (Cr VI) to trivalent chromium (Cr III) in an acidic solution, then the latter is readily adsorbed by coal (Motoshi, 1974).

Other extensive studies have been carried out on the adsorption and desorption behavior of some heavy metals such as beryllium, titanium and gallium on coal and peat. The effect of pH and presence of other ion electrolytes was also studied (Eskenazy, 1972, 1970 and 1967).

Recently, process feasibility studies have been initiated in India to determine the possibility of extracting metallic nickel by a lignite-adsorption route (Altekar et al., 1974).

Lignite coal proved to be more effective for adsorption of nickel than other adsorbents such as coke, charcoal, activated carbon, sawdust, etc. as shown in Table 3.

TABLE 3.     COMPARISON OF ADSORBENTS FOR NICKEL*

| Adsorbent | Adsoprtion (% of Ni in solution) |
|---|---|
| Metallurgical coke | Trace |
| Charcoal | 1.6 |
| Hardwood sawdust | 27.2 |
| Petroleum coke | 39.6 |
| Activated carbon | 55.1 |
| Lignite | 98.4 |

11.  Suggested Mechanisms for Adsorption of Metal Ions

No definite mechanism for the adsorption of the metal ions by coal has, as yet, been proven because of the complexity of the chemical composition of coal.

Eskenazy (1970, 1972) supposed that the binding of beryllium to coal leads to the formation of chemical compounds of various stabilities and the presence of functional groups chiefly hydroxyl and carboxyl groups, making it possible for ion exchange reactions. He also noticed that a decrease of the functional groups brings about a reduction of beryllium adsorption per unit surface area;  he assumed

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*       Sorbent/Sorbate ratio for the above solution is 26.7g adsorbent per g. Ni.

that adsorption has a chemical nature due to its irreversibility, and that the metals slowly form more stable chemical bonds with coal. From the results of his experiments he concluded that a chemisorption process proceeds through an ion exchange.

Eskenazy's explanations for the mechanism involved in the adsorption of metals are not adequately confirmed and require further research work to support his hypothesis.

In Japan, Terajima (1973) studied the adsorption mechanism of removing heavy metal ions from wastewater using nitro-humic acid. He concluded that the adsorption of heavy metal ions by the humic acid is mainly due to the chelate formation at low concentration of metal ions and mainly due to ion exchange at high concentrations. He used infra-red spectroscopy to confirm his theory.

11.1 Complexing of metals with humic substances

Coal is considered as one of the naturally occurring humic substances and it contains humic acid in its structure. Therefore, theories related to the interaction of metal ions with the humic acids extracted from coal, peat, soil etc. can be assumed to be partially applicable to the adsorption of metal ions on coal.

As early as 1952, Broadbent and Bradford showed the importance of carboxyl COOH and phenolic hydroxyl -OH groups in cation exchange reactions of soil organic matter.

Davies et al. (1969) concluded that the retaining sites probably involved carboxyl and hydroxyl groups acting together. Although these workers suggested that alternate groups such as hydroxy quinones might also be implicated in the reaction.

Schnitzer and Skinner (1965) suggested a simultaneous involvement of acidic carboxyls and phenolic hydroxyls with $Fe^{3+}$, $Al^{3+}$, and $Cu^{2+}$, while alcohol hydroxyls are not involved in the interaction. They concluded that salicylic acid type structure was present in the humic organic matter.

Most recently, Cross (1975) provided additional evidence for the hypothesis that salicylic and phthalic acid-like functional groups play a significant role in the formation of metal-organic complexes in soil.

It can be seen that the metal reaction with acidic groups must involve a proton release; Van Dijk (1971) conducted titration curve experiments comparing the magnitude of the pH drop upon the addition of several inorganic salts to the solution. The pH reductions were related to the bond strengths of the complexes formed.

12.    Adsorption of Metals on Activated Carbon

Although the merits of activated carbon for the removal of organic compounds from water have been well

documented in the literature (Hassler, 1974), (Culp, 1971),
little, if any, work has been performed within the water
treatment field relevant to the use of activated carbon for
removing trace metals and compounds.

Sigworth et al. (1972) were able to extrapolate
the results of a test performed, and came to the conclusion
that activated carbon needs appropriate conditions of pH
to carry out an efficient purification of water from trace
metals. They predicted that several mechanisms are probably
involved as follows

1)  Carbon will physically adsorb on its tremendous internal
     surface molecular compounds such as acids,
     complexes and high molecular weight polymers.

2)  Because of the very small number of oxygen complexes and
     functional groups fixed on the carbon surface, a
     limited ion exchange action is expected to take
     place.

3)  Carbon can induce precipitation of a super saturated
     solution by nucleation and can reduce the solubility
     of a metallic salt.

4)  Commercial activated carbons contain traces of reduced
     forms of iron and other metals, which can enter
     into reactions with metallic ions lower in the
     electromotive series causing the heavy metal to
     be deposited on the surface.

B.    Hat Creek Coals

1.   History:    (Campbell and Jory, 1977).

"The Hat Creek coal deposits were first reported by
Dr. G.M. Dawson of the Geological Survey of Canada in 1877.
The coal exposures were limited to a small area along the bank
of Hat Creek, where erosion had stripped the cover of glacial
till.

By 1925, three shallow shafts and two short adits had
been driven into the coal and seven holes had been bored into
it.  No further work was done until 1933.  From 1933 until 1942,
a few hundred tons of coal were mined from the workings each
year and sold locally for thermal use;  this activity ceased
during World War II and was not renewed.  In 1957, Western
Development and Power Ltd., a subsidiary of B.C. Electric Co.
Ltd., optioned the property as a possible future source for
a major thermal electric generating plant.

The area of the exposed portion of the Hat Creek
deposit was explored by reconnaissance diamond drilling and
trenching during 1957 and 1959.

The work justified the subsequent purchase of the
property by B.C. Electric for two million dollars.

Following an expropriation of the B.C. Electric Co.
by the B.C. Provincial Government, the ownership of the coal
property passed to the B.C. Hydro and Power Authority.

No further work was conducted on it until 1974 when

the current program of more definitive investigation was begun.

At present studies are being conducted by various consultants on a conceptual thermal plant design, preliminary assessment of possible open pits, environmental impact and alternative coal uses".

2.   Geology

The general geological and economic features of the Hat Creek coal deposits were investigated by Campbell, Jory et al. (1977) who concluded from their preliminary study that the Hat Creek coal deposits occur within folded and faulted tertiary strata of the Cold Water group. This group comprises weakly claystone, shales, silt stones, and conglomerates underlying the floor and lower flanks of the valley of upper Hat Creek.

The main coal layer at upper Hat Creek is one of the thickest in the world (1500 ft.).  The deposits probably represent the world's greatest concentration of coal in such a small area. Investigation of the deposits is still in progress, and much remains to be learned, particularly concerning their combustion characteristics, their ultimate extent and their economic ability to be mined to the great depths which they reach.

3.   Rank

The relationship between ash and calorific value of the Hat Creek coal described by Campbell and Jory (1977) is nearly linear as shown in Figure 1. The calorific
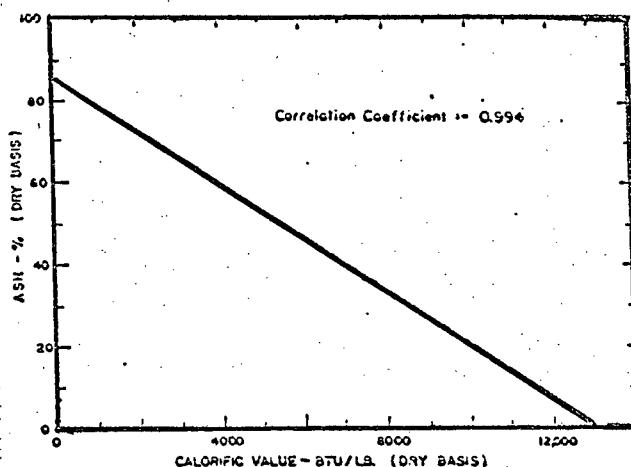
FIGURE 1 : ASH -CALORIFIC VALUE REGRESSION OF HAT CREEK
COAL. (Campbell and Jory, 1977)

value intercept, for dry, mineral matter-free coal is approxi-
mately 13,000 BTU/lb for coal samples from "holes" 76-135 and
136 which were drilled during the summer of 1976. If the
in situ equilibrium moisture content is assumed to be 25%
the calorific value of the moist, mineral matter-free coal is
then approximately 9750 BTU/lb making this sample of coal low
sub-bituminous B in rank.

The mean calorific values and ash contents of Hat
Creek coal samples from different zones are shown in Table 4a

TABLE 4a        SOME MEAN VALUES OF HAT CREEK COAL.

| Zone | Average Thickness (ft) | C.V. (BTU/lb) | Ash (%) | Vol. Mat. (%) | Fixed C (%) | Total S (%) |
|------|------------------------|---------------|---------|---------------|-------------|-------------|
| A | 407 | 5900 | 28.9 | 25.7 | 25.3 | 0.58 |
| B | 237 | 6300 | 26.6 | 25.6 | 27.8 | 0.66 |
| C | 110 | 4500 | 38.4 | 22.4 | 19.2 | 0.35 |
| D | 267 | 7580 | 19.0 | 27.4 | 33.6 | 0.22 |
| Mean* | | 6300 | 26.4 | 25.8 | 27.8 | 0.41 |

* Mean obtained by weighting each zone by the percentage of the coal reserve it represents.

However, if the rank of the Hat Creek coal were to be determined according to the Standard ASTM procedure D388 (1976), individual samples would be ranked variously from lignite to sub-bituminous C depending on the calorific value.

Table 4b shows the ASTM classification of coals by rank. It is obvious that classification is according to fixed carbon and calorific value expressed in BTU/lb calculated to the mineral matter-free basis.

The higher rank coals are classified according to fixed carbon on the dry basis, the lower rank coals are classed according to calorific value on the moist mineral matter-free basis.

4. Infra-red Spectra

Greenslade (1975) evaluated the infra-red spectra of Hat Creek coal in comparison with two other B.C. coals from Kaiser and Fording deposits. All of the main absorption bands

| Class | Group | Fixed Carbon Limits, percent (Dry, Mineral-Matter-Free Basis) | | Volatile Matter Limits, percent (Dry, Mineral-Matter-Free Basis) | | Calorific Value Limits, Btu per pound (Moist,[b] Mineral-Matter-Free Basis) | | Agglomerating Character |
|---|---|---|---|---|---|---|---|---|
| | | Equal or Greater Than | Less Than | Greater Than | Equal or Less Than | Equal or Greater Than | Less Than | |
| I. Anthracitic | 1. Meta-anthracite | 98 | ... | ... | 2 | ... | ... | nonagglomerating |
| | 2. Anthracite | 92 | 98 | 2 | 8 | ... | ... | |
| | 3. Semianthracite[c] | 86 | 92 | 8 | 14 | ... | ... | |
| II. Bituminous | 1. Low volatile bituminous coal | 78 | 86 | 14 | 22 | ... | ... | Commonly agglomerating[e] |
| | 2. Medium volatile bituminous coal | 69 | 78 | 22 | 31 | ... | ... | |
| | 3. High volatile A bituminous coal | ... | 69 | 31 | ... | 14 000[d] | ... | |
| | 4. High volatile B bituminous coal | ... | ... | ... | ... | 13 000[d] | 14 000 | |
| | 5. High volatile C bituminous coal | ... | ... | ... | ... { | 11 500 | 13 000 | |
| | | | | | | 10 500 | 11 500 | agglomerating |
| III. Subbituminous | 1. Subbituminous A coal | ... | ... | ... | ... | 10 500 | 11 500 | nonagglomerating |
| | 2. Subbituminous B coal | ... | ... | ... | ... | 9 500 | 10 500 | |
| | 3. Subbituminous C coal | ... | ... | ... | ... | 8 300 | 9 500 | |
| IV. Lignitic | 1. Lignite A | ... | ... | ... | ... | 6 300 | 8 300 | |
| | 2. Lignite B | ... | ... | ... | ... | ... | 6 300 | |

[a] This classification does not include a few coals, principally nonbanded varieties, which have unusual physical and chemical properties and which come within the limits of fixed carbon or calorific value of the high-volatile bituminous and subbituminous ranks. All of these coals either contain less than 48 percent dry, mineral-matter-free fixed carbon or have more than 15,500 moist, mineral-matter-free British thermal units per pound

[b] Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal

[c] If agglomerating, classify in low-volatile group of the bituminous class

[d] Coals having 69 percent or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of calorific value.

[e] It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and there are notable exceptions in high volatile C bituminous group.

TABLE 4b: ASTM CLASSIFICATION OF COALS BY RANK .

are similar to those previously assigned for Pittsburg and
Japanese coals by Fujii (1970) and Osawa (1971) respectively.

All of the three B.C. coals exhibit similar infra-
red spectra. In the case of Hat Creek coal, intense
absorption bands at the 1700 $cm^{-1}$ of the C = 0 bond of the
carboxyl groups COOH and at the 1600 $cm^{-1}$ of the C = 0 bond
of the carboxylate and the C = C bond were obtained. This
indicates that Hat Creek coal contains a relatively large
number of carboxyl groups. The strong absorption bands
obtained at the 1430 $cm^{-1}$ and 870 $cm^{-1}$ were explained to be
due to the presence of carbonate in mineral matter while
the kaolinite band is not present.

The degree of surface oxidation of the Hat Creek
coal is indicated by the combination of infra-red spectral
and salt flotation studies. Higher degrees of surface
oxidation in the coal is accompanied by an increase in the
carbonyl C = 0 groups which result in a decrease in the
flotation rate.

5.      Adsorption of Water Pollutants

The ability of Hat Creek coal to remove dissolved
constituents from water has been the subject of much
discussion and many claims in B.C.

The efficiency of the coal for removing dissolved
organic constituents from sewage seems to be very encouraging,
(Coulthard, 1976; Hendren, 1974).

This coal demonstrated that it possessed a good adsorptive capacity for the removal of heavy metal trace elements from water (Coulthard, 1976; Riaz, 1974; and Hendren, 1974).

III.  EXPERIMENTAL MATERIALS

1.  Hat Creek Coal

1.1  Description of the coal deposits

The type of coal used in this study is of lignite variety, mined from the Hat Creek deposit which is situated about 200 miles from Vancouver, British Columbia, as shown on the map, (Figure 2) where one billion metric tons, or more, of the coal exists.  This amount is contained partly within a Crown mineral grant area and coal licences owned by B.C. Hydro.  The coal deposit consists of five seams, each several hundred feet thick.  Figure 3 is a cross sectional view showing that the five seams are separated by relatively thin layers of clay, shale, and sandstone (Jones, 1973).

1.2  Sampling locations

Two samples of Hat Creek coal were provided for this research study by the exploration company (Dolmage, Campbell and Associates, 1976)*.  The samples mined from the area shown in Figure 4 were classified as follows:

a)  Oxidized, surface coal (S.C.) which was provided from location number (1) shown on the maps in Figure 5. The 150 kilogram samples was mined manually at the surface.

b)  Drill-hole coal or Core coal (C.C.) which was provided from the drill-hole marked on the map in Figure 5 as DDH 74-39.  The core sample is a composite of

*  Direct communication
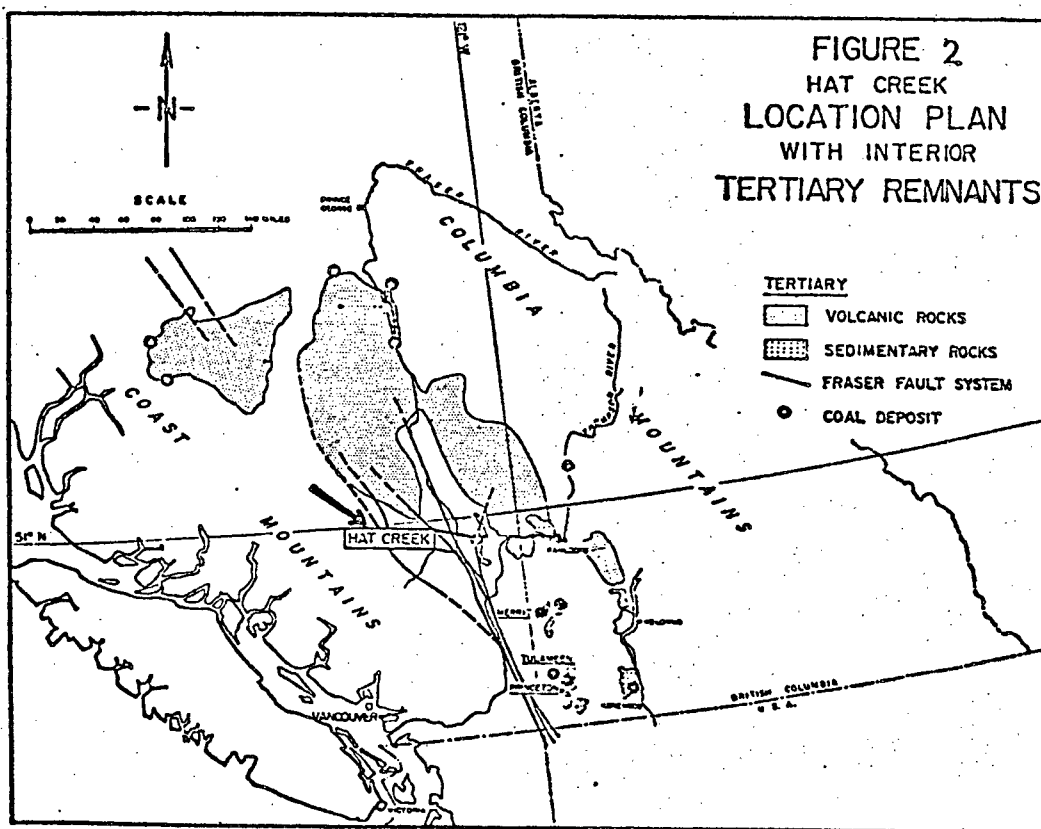
FIGURE 2 : HAT CREEK COAL LOCATION PLAN.

(Campbell and Jory, 1977)
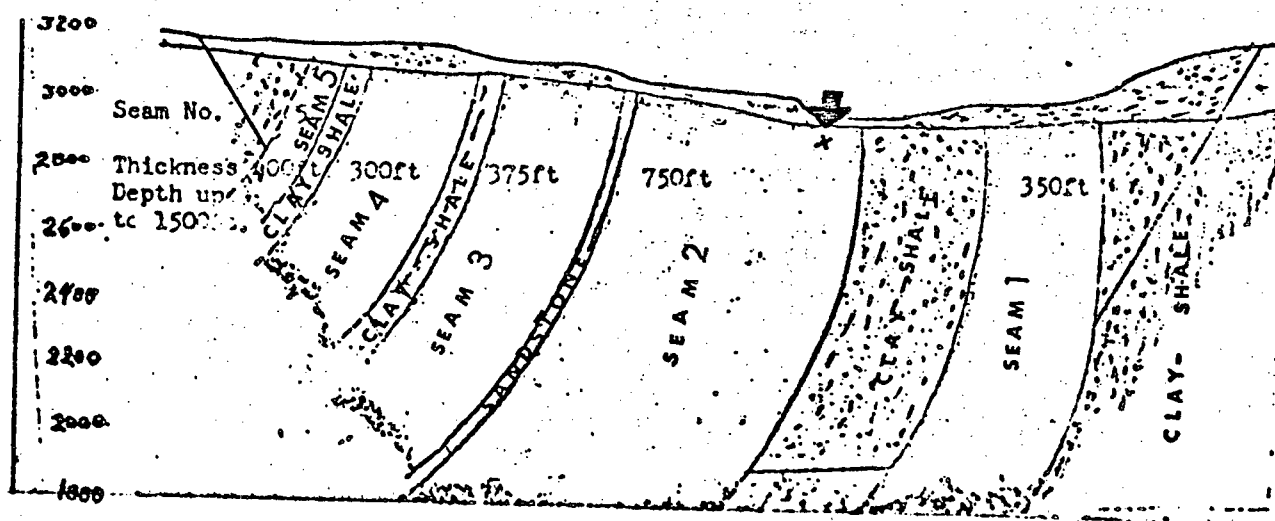


FIGURE 3 : CROSS SECTION VIEW SHOWING THE COAL SEAMS.

FIGURE 4

SCALE : ]" = 2000'
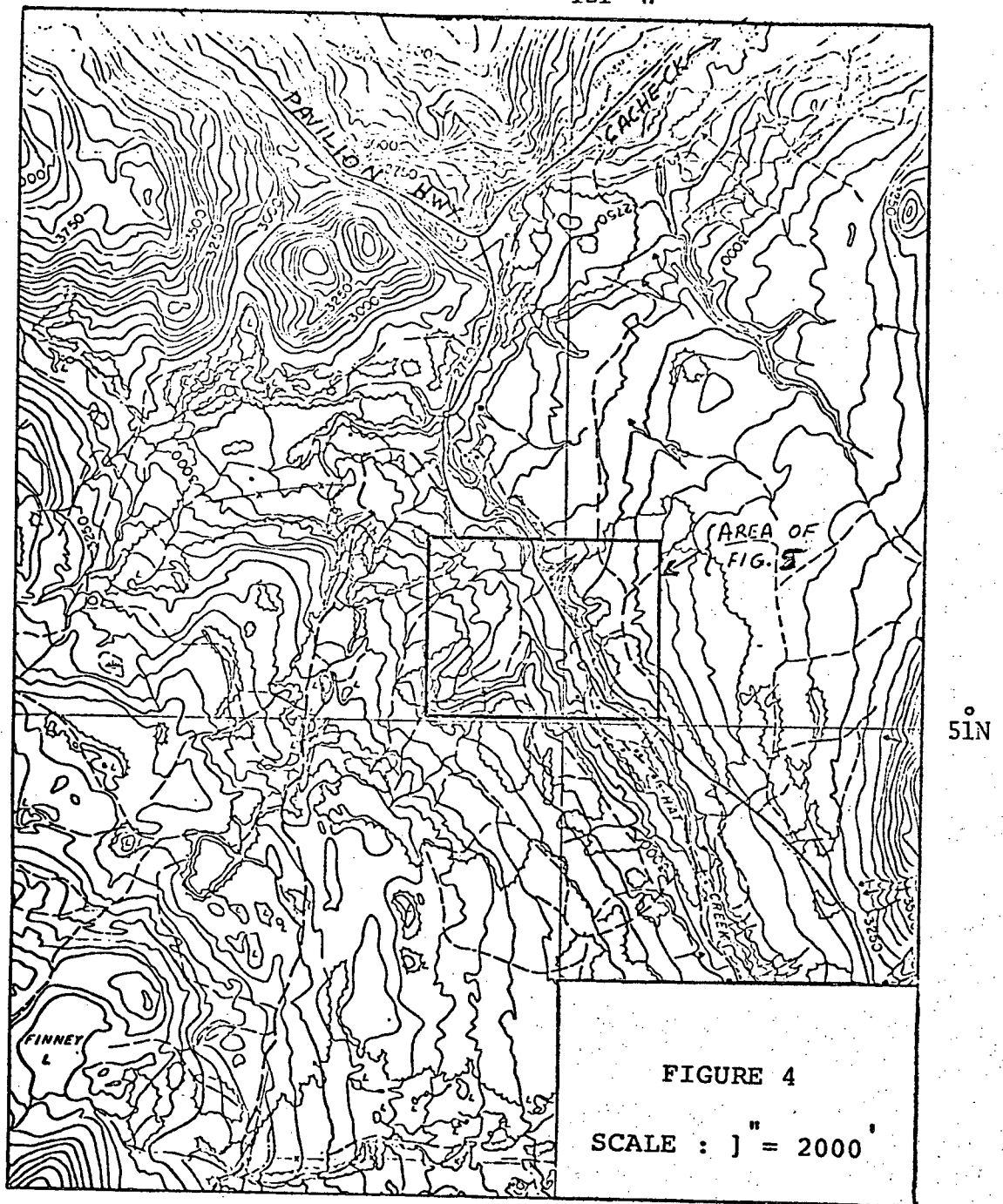
FIGURE 4 : INDEX PLAN FOR THE HAT CREEK COAL DEPOSITS.
(Dolmage and Campbell Associates)

FIGURE 5

(1) SURFACE COAL.

(2) CORE COAL
    D.D.H 74-39.
    SCALE :1"=400'
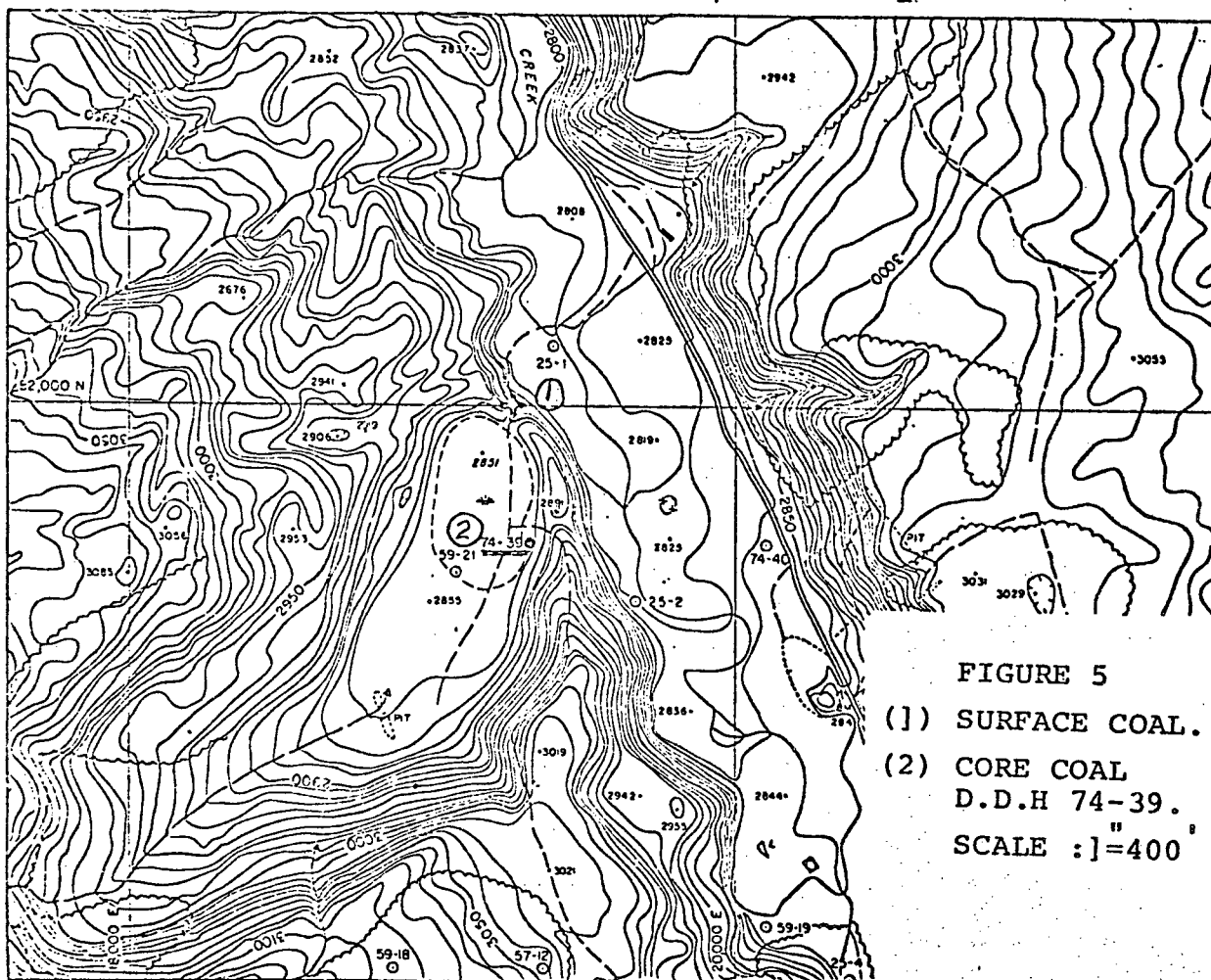
FIGURE 5 : HAT CREEK COAL DEPOSITS,

SAMPLING LOCATION PLAN.

(Dolmage and Campbell Associates)

two drill-hole samples. One was collected at a footage of 33 to 93 feet, while the other sample was collected at a footage of 98 to 438 feet.

## 1.3 Coal preparation

The 150 kilograms of the oxidized surface sample was received as large lumps and unwashed. The core sample received was crushed and washed prior to shipping from the site.

### 1.3.1 Crushing of the surface coal

The coal was first crushed in a BICO Jaw Crusher, then passed through a "BICO" Pulverizer to give a crushed material with particle sizes ranging from 4 mesh to less than 200 mesh size.

### 1.3.2 Sieving

Series of U.S. Standard Test Sieves were used for mechanical shaking on a "Roto-Tap" shaker. The coal was classified into coarse, medium, and fine particle sized samples. U.S. sieve numbers 4, 14, 20, 50, 60, 100, 140 and 325 mesh size were mostly used in the size classification. The particle sizes are usually reported, in this work, as the U.S. Standard Screen Scale Sieve Series. The actual dimensions of screen openings, the equivalent screen sizes, and the Tyler mesh numbers are listed in Appendix A, Table 1.

### 1.3.3 Washing and Drying

The samples were washed by slurrying first in water followed by decantation, and then oven dried at

$103 - 105^{\circ}C$ for three hours.

## 2. Activated Carbon

Calgon Filtrasorb 400, supplied by Calgon Canada in Ontario was used in some experiments to assess the adsorptive qualities of the Hat Creek coal in comparison to the activated carbon which is considered a very effective adsorbent and is used widely in the wastewater treatment processes.

The following materials were used in minor experiments for comparison purposes:

## 3. Centralia Anthracite

It is anthracite type, mined from a deposit in the State of Washington, U.S.A.

## 4. Union Bay Coal

Also known as Tsable River coal. The coal is mined from the Union Bay deposit on Vancouver Island, B.C.

A comparison between the levels of the different metal ions in the ash is shown in Table 5 for the above three coals.

TABLE 5.    LEVELS OF METALS IN THE COAL ASH*

| Location | Cu | Fe | Co | Ni | Pb | Mn | Zn | Na | Cd | Cr |
|----------|------|---------|------|------|-------|-------|------|--------|------|----|
| Hat Creek | 79.07 | 20917.4 | 16.3 | 43.5 | 20.98 | 848.3 | 62.9 | 1758.2 | 0.0 | 63 |
| Union Bay | 60.00 | 2922.2 | 8.8 | 34.4 | 11.8 | - | 96.6 | - | 3.35 | 49 |
| Anthracite Washington | 25.5 | 7202.0 | 9.2 | 18.3 | 11.8 | - | 19 | 97 | - | 0.0 | 72 |

Note:    Mercury for Hat Creek 27 - 28 ppb, other values in ppm. (mg/l).

* The analysis conducted at the geochemistry lab, Geological Science Dept., U.B.C.
  Sample of commercial coal.

5. Ottawa Sand

A special kind of construction sand which is mostly used for research work in the field of irrigation and soil studies.

6. Abbotsford Sandy Silt Loam

This sample obtained from Abbotsford, B.C., is classified as an orthic concretionary brown soil (Luttmerding, 1966). It is composed of a mixture of shallow aolian deposits mixed with, or, over glacial outwash.

IV.    PROPERTIES OF HAT CREEK COALS

## 1.    MATERIALS.

1.1  Prepared surface coal, particle size 100/140 mesh.

1.2  Unoxidized core coal, particle size 100/140 mesh.

1.3  Calgon activated carbon, particle size 100/140 mesh.

## 2.    METHODS.

The following chemical analyses were conducted at the Commercial Testing and Engineering Company, Vancouver Branch,* according to the ASTM standard procedures for coal and coke (ASTM, 1974).

2.1  Chemical analysis

2.1.1  Proximate analysis (Ode, W.H. in Lowry, 1963)

"This analysis represents the distribution of products obtained during heating under standard conditions, proximate analysis separates the compounds into four groups:-

1)  Water or moisture content.

2)  Volatile matter consisting of gases and vapors driven off during pyrolysis.

3)  Fixed carbon, remaining as the non-volatile fraction of the pyrolyzed coal.

4)  Ash, derived from the mineral impurities."

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* 147 Riverside Dr., North Vancouver, B.C., V7H 1T6.

The fixed carbon is a calculated figure obtained by subtracting from 100 the sum of the percentages of moisture, volatile matter and ash.

2.1.2 Ultimate analysis (Ode, W.H. in Lowry, 1963)

"This analysis expresses the composition of coal in percentages of carbon, hydrogen, nitrogen, sulfur, oxygen and ash, regardless of their origin.

The carbon includes that present in the organic coal substance as well as that in carbonates. The hydrogen includes that of the organic coal substance and the hydrogen present in the form of moisture and the water of constitution of the silicate minerals. All the nitrogen is present as a part of the organic substance. The sulfur normally is present in three forms - organic sulfur compounds, pyrite or marcasite, $(FeS_2)$, and inorganic sulfates."

2.1.3. Other standard determinations

The ash composition, distribution of sulfur forms, and heating value of the coal in BTU per pound are also determined for the surface and the core samples of the Hat Creek coal.

2.2   Contaminants in Hat Creek coal

This is expressed, in this study, as the major water and acid leachates from the coal.

The test was carried out on 100 gram quantities of each of the surface and the core coal samples. Each coal sample was either leached with one liter of water or a hydrochloric acid solution of 1N concentration. Each washing was collected and a composite sample then analyzed.

2.2.1  Heavy metals (APHA, 1975)

Analysis of the following heavy metals in each washing sample have been carried out with a Perkin Elmer Atomic Absorption Spectrophotometer, Model 306;  the following metals were determined:

Na, Zn, Pb, Cu, Mn, Cr, Ni, Fe, Ca, Mg, and Ba.

2.2.2  Ammonia and nitrates (APHA, 1975)

100 mls of distilled water was refluxed with 2%, 5% and 10% by weight of each of the surface and core samples for a period of two hours.  The coal was then separated by filtration.  The ammonia and nitrate were determined by the automated methods on the Technicon Industrial AutoAnalyser, Model II.

2.3  Surface properties

2.3.1  Surface features of the coal (Goldstein, 1975)

The low power light microscope and the Scanning Electron Microscope (SEM) were used for the preliminary examination of the coal surface.

A low magnification of 4.5X was used to photograph the surface features of the particles.

The SEM was used for the examination and analysis of the microstructural characteristics of the coal surface. Images with a three dimensional appearance could be obtained which is a direct result of the large depth of focus.  The coal sections preparation  is described in Appendix B-1-1.

## 2.3.2 Infra-red absorption

The potassium bromide technique was used for the preparation of the coal samples. The I.R. spectrum, in the range of wave numbers between 4000 - 250 $cm^{-1}$, for each of the surface and core coals were recorded and compared.

The absorbance for every main band was evaluated using the base line technique. The specific extinction coefficient $\varepsilon$ for each absorption band was thereby estimated according to Ewing (1960) and Fujii (1970).

A Perkin Elmer Infra-red Spectrophotometer, Model 521, was used for recording the I.R. absorption spectra. A detailed description for all of the techniques involved in this analysis is outlined in Apprendix B-2.

## 2.3.3 Surface area and pore structure

The BET surface area using nitrogen (Brunauer, Emmett and Teller, 1938), measured in $m^2$/gram, micropore volume in mls/gram and the average pore diameter in angstrom ($^oA$) have been determined for surface and core coal, and compared with those measured for activated carbon.

These measurements were conducted by the Fuel Sciences Division, Alberta Research Council, Edmonton. The Micromeritic Surface Area and Pore Volume Analyzer were used for those measurements.

All of the samples (-60 + 100 mesh) were evacuated to $\sim 10^{-6}$ Torr in situ overnight at $120^oC$ before nitrogen

adsorption measurements. The micropore volume covers the range
of pores of diameter between 28 - 400 $^O$A.

The BET equation and method of calculating the specific
surface area are shown in Appendix B-3.

2.3.4 Permeability test (Karol, 1969).

A prepared column sample of coal of certain particle
size, having a cross section A and length L was subjected to
a flow of water under a constant head h. From Darcy's law
(Q = KiAt) where i is equal to the hydraulic gradient h/L, there-
fore, the coefficient of permeability, K, can be expressed in
terms of these quantities as follows:

$$K = \frac{QL}{hAt} .$$

The test is performed by measuring the quantity of water Q
flowing through the coal sample of length L, the head of
liquid h and the time t.

# 3. RESULTS AND DISCUSSION

## 3.1 Chemical properties

Table 6 shows the comparison of the surface sample and the core sample which are used for the mechanism studies of the research reported. Surface coal has a relatively high calorific value of 8526 BTU/lb m.m.m.f.b.* while core coal exhibits a lower thermal value of 7623 BTU/lb m.m.m.f.b.

Therefore, both coal samples as tested can be ranked as a lignite variety.

Other individual samples of the core coal drilled from the same hole, at different footages, were analyzed and the data tabulated in Appendix C-1-1. The table shows a wide range of ash content for the analyzed samples. As the footage in depth increases the thermal value increases to reach a maximum value of 10760 BTU/lb d.b. at footage from 318 to 338 ft for a sample having an ash content as low as 16.25% d.b. A minimum calorific value of 2800 was obtained at a depth of 33 to 53 ft where the ash content reaches a maximum value of 61.71% d.b.

Consequently, the economic value of Hat Creek coal is expected to be very low if used for thermal generation. The hardness test was 3.0 on the mohr scale for the oxidized outcrop, while unoxidized samples show a hardness of 4.0, compared to a value of 2.62 obtained for the anthracite coal (Coulthard, 1974).

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\* m.m.m.f.b. moist, mineral matter-free basis.

TABLE 6.　　　CHEMICAL ANALYSIS OF HAT CREEK COAL SAMPLES

|  |  | SURFACE COAL | | CORE COAL Sample 39-401 Footage 33'-178',width.140' | |
|---|---|---|---|---|---|
|  |  | As Received | Dry Basis | As Received | Dry Basis |
| I. | PROXIMATE ANALYSIS |  |  |  |  |
|  | % Moisture | 14.38 | - | 19.04 | - |
|  | % Ash | 22.51 | 26.29 | 34.87 | 43.07 |
|  | % Volatile | 32.19 | 37.60 | 23.58 | 29.12 |
|  | % Fixed Carbon | 30.92 | 36.11 | 22.51 | 27.81 |
|  |  | 100.00 | 100.00 | 100.00 | 100.00 |
|  | BTU | 6607 | 7717 | 4965 | 6133 |
|  | % Sulfur | 0.38 | 0.44 | 0.63 | 0.78 |
|  | % Alk. as $Na_2O$ | 6.08 | 0.09 | 0.42 | 0.52 |
| II. | ULTIMATE ANALYSIS |  |  |  |  |
|  | % Moisture | 14.38 | - | 19.04 | - |
|  | % Carbon | 41.92 | 48.96 | 30.47 | 37.64 |
|  | % Hydrogen | 2.59 | 3.03 | 2.30 | 2.84 |
|  | % Nitrogen | 0.68 | 0.80 | 1.01 | 1.25 |
|  | % Chlorine | 0.07 | 0.08 | 0.03 | 0.03 |
|  | Sulfur | 0.38 | 0.44 | 0.63 | 0.78 |
|  | Ash | 22.51 | 26.29 | 34.87 | 43.07 |
|  | O (by diff.) | 17.47 | 20.40 | 11.65 | 14.39 |
|  |  | 100.00 | 100.00 | 100.00 | 100.00 |

| III. MINERAL ANALYSIS | IGNITED BASIS　　(%) | |
|---|---|---|
|  | SURFACE COAL | CORE COAL |
| $P_2O_5$ | 0.04 | 0.25 |
| $SiO_2$ | 85.22 | 49.93 |
| $Fe_2O_3$ | 0.81 | 12.31 |
| $Al_2O_3$ | 8.27 | 26.84 |
| $TiO_2$ | 0.31 | 0.89 |
| CaO | 2.68 | 2.57 |
| MgO | 0.48 | 2.01 |
| $SO_3$ | 1.62 | 3.48 |
| $K_2O$ | 0.08 | 0.76 |
| $Na_2O$ | 0.28 | 0.71 |
| Undetermined | 0.21 | 0.25 |
| Total: | 100.00 | 100.00 |

This good mechanical property exhibited by the Hat
Creek coal is considered promising for the coal to be utilized
in leaching processes.

The mineral analysis shows a very high level of
silica in the surface coal reaching 85.22% in the ash while
core coal contains half of this value. This may be due to the
contamination of the surface coal by the soil present in the
field. On the other hand, the core coal seems to be very rich
in iron, alumina and most of the other mineral constituents.

3.2    Contaminants in Hat Creek coal

3.2.1    pH of the coal

The pH measurements of the water leachates from sur-
face coal showed a drop in the pH values to an acidic range
of 4.5 - 4.6, indicating the acidic nature of the surface coal.
This may be attributed to the presence of some oxygen-containing
acidic groups. However, core coal does not exhibit any drop
in the pH but remains at the neutral level which indicates the
lesser acidic nature of this coal.

3.2.2    Ammonia and nitrate

The results summarized in Table 7 show that 18 mgs
$NH_3$-N per 100 grams of coal is washed out of surface coal
compared to only 7 mgs $NH_3$-N per 100 grams of coal leached
from a core sample. This confirms that the surface coal con-
tains higher ammonia content than the core coal. The washed
out nitrates seem to have the same levels in both coals of

TABLE 7.    LEACHING OF AMMONIA AND NITRATE
FROM HAT CREEK COAL

| | SURFACE COAL | | | CORE COAL | | |
|---|---|---|---|---|---|---|
| | Coal added | | | Coal added | | |
| | 2% | 5% | 10% | 2% | 5% | 10% |
| $NH_3$-N | | | | | | |
| ppm | 5.7 | 10.2 | 16.0 | 2.2 | 3.9 | 11.0 |
| mgs washed out per 100 gm coal | 22.0 | 18.0 | 15.0 | 5.0 | 5.0 | 10.0 |
| $NO_3$-N | | | | | | |
| ppm | 0.65 | 1.31 | 2.31 | 0.81 | 2.5 | 3.88 |
| mgs washed out per 100 gm coal | 2.0 | 2.0 | 2.0 | 3.0 | 5.0 | 4.0 |

Distilled water (control)

$NH_3$-N  =  1.3    ppm (mg/1)

$NO_3$-N  =  0.19    ppm (mg/1)

2 - 4 mgs $NO_3$-N per 100 gram of coal. The high ammonia level in surface coal is probably due to external contamination in the coal field.

The sorptive capacity of the coals were compared before and after washing out ammonia. The results are discussed in Chapter V.

### 3.2.3 Heavy metals

The results shown in Table 8 compare the levels of the different metals leached out of the coal upon washing with water or acid solution.

It is obvious that more metal ions can be removed through acid washing; this is due to the proton exchange with the metal cations.

Water-soluble salts of calcium, iron and magnesium were washed out with water from both types of Hat Creek coal.

Generally, the core coal leachates contain higher levels of metal ions than surface coal. This is due to the larger quantity of "gangue" materials in the core coal which contain metal ions such as sodium, manganese, chromium, iron and barium. However, higher lead levels are present in surface coal and this may be partially due to surface contamination.

### 3.3 Surface properties

### 3.3.1 General features of the coal surface

The images observed by the low power light microscope reveal the common features of the surface of the coal particles.

TABLE 8.          LEACHING OF HEAVY METALS FROM HAT CREEK COAL

| Metal Ion | SURFACE COAL | | CORE COAL | |
|---|---|---|---|---|
| | Acid Washing | Water Washing | Acid Washing | Water Washing |
| Na | 99.00 | 29.00 | 335.00 | 24.00 |
| Zn | 2.80 | 0.10 | 3.00 | 0.05 |
| Pb | 0.50 | N.D. | 0.150 | N.D. |
| Cu | 1.50 | 0.10 | 2.20 | 0.18 |
| Mn | 6.00 | N.D. | 25.00 | N.D. |
| Cr | 1.00 | N.D. | 3.60 | N.D. |
| Ni | 0.55 | N.D. | 1.00 | N.D. |
| Fe | 145.00 | 0.20 | 550.00 | 2.20 |
| Ca | 790.00 | 5.00 | 825.00 | N.D. |
| Mg | 125.00 | 3.00 | 155.00 | 0.25 |
| Ba | 3.00 | N.D. | 25.00 | N.D. |

The results are calculated in terms of mgs metal ions washed out/100 gm coal.

N.D.  =  Not detectable.

pH of water washings from surface coal   =   4.5-4.6
pH of water washings from core   coal   =   6.9-7.0

Figures 6a, 6b and 6c give a comparison between the activated carbon, oxidized surface coal and non-oxidized core coal respectively. The particles of the surface coal have less fractures and cracks than activated carbon, while the core particles appeared smoother with a layered shape.

Since the fractures expose larger areas of macro-pores and therefore tend towards more surface activity, one can expect that the surface deposit is likely to be more active than the non-oxidized core deposit. Nevertheless, the surface coal has less activity compared to activated carbon.

The scanned images shown in Figure 7a represent a cross section in the coal particles obtained after polishing the surface.

The corresponding X-ray energy dispersive analysis for particle under scrutiny is shown in Figure 7b.

This analysis reveals that silicon and to a lesser extent iron and sulfur are the main elements present in the layered particles, while lower levels of these elements are present in the fractured particles. Also, other elements can be identified in the latter case, such as sodium, potassium, calcium, titanium and chlorine.

3.3.2 Infra-red absorption

The infra-red spectra of the surface and core samples of Hat Creek coal, of carbon contents 48.96% d.b. and 37.64% d.b. respectively, are compared in Figure 8.
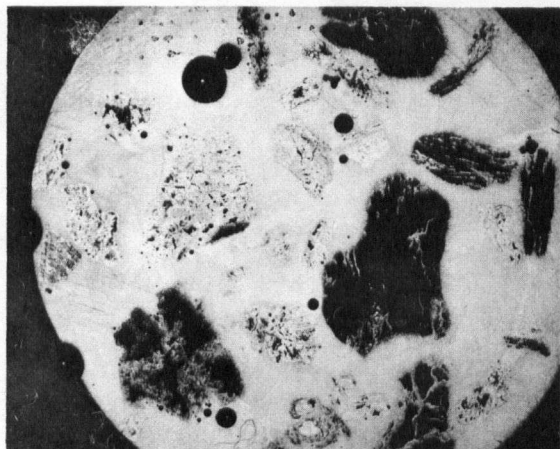
6-A   ACTIVATED CARBON   4.6X
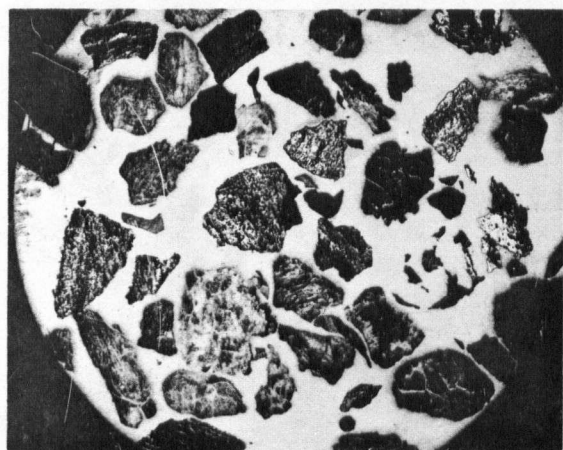
6-B   SURFACE   COAL   4.6X
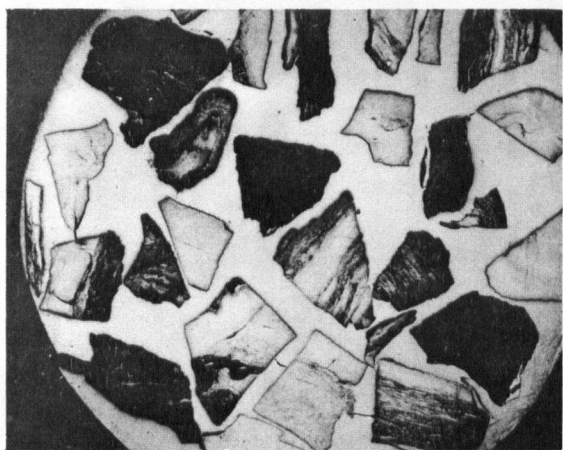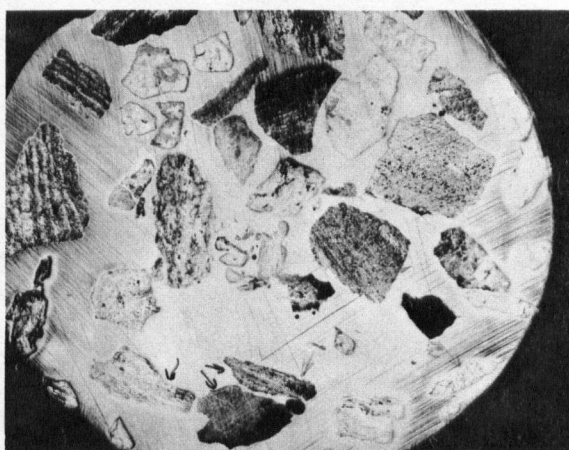
6-C   CORE   COAL   4.6X

FIGURE 6-    LOW POWER LIGHT MICROSCOPE IMAGES OF:

6-A.   ACTIVATED CARBON PARTICLES (8/14 MESH).

6-B.   OXIDIZED HAT CREEK COAL PARTICLES (8/14 MESH) FROM SURFACE DEPOSIT
           (SURFACE COAL).

6-C.   NON-OXIDIZED HAT CREEK COAL PARTICLES (8/14 MESH) FROM 400 FT DEPTH
           DEPOSIT (CORE COAL).

LIGHT MICROSCOPE IMAGE 4.6X
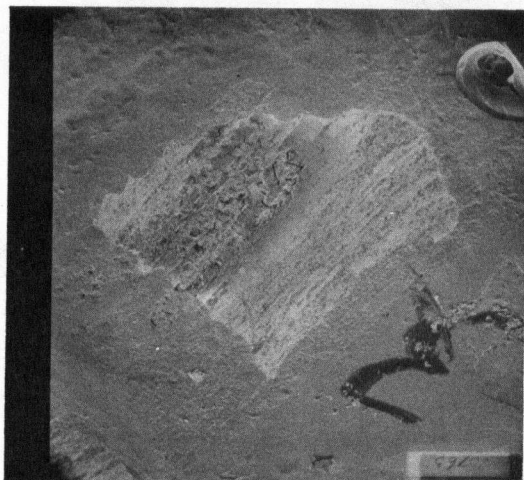
LAYERED PARTICLE WITH SOME FRACTURES 20X

LAYERED PARTICLE 20X.
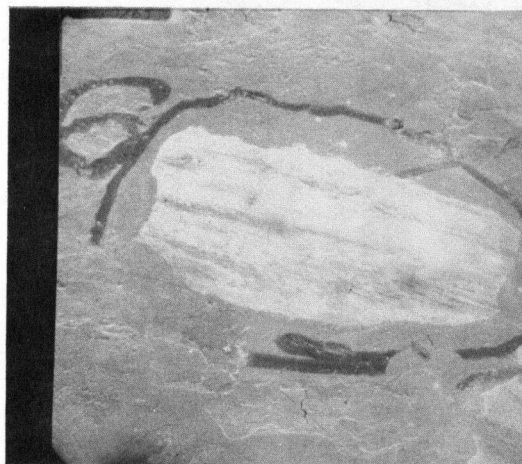
SMOOTH LAYERED PARTICLE 20X.

FRACTURED PARTICLE 20X.

FIGURE 7a- SCANNING ELECTRON MICROSCOPE IMAGES OF <u>POLISHED CROSS SECTION</u> OF DIFFERENT PARTICLES OF OXIDIZED HAT CREEK COAL FROM SURFACE DEPOSIT SHOWING LAYERED AND CRACKED NATURE OF THE PARTICLE SURFACE.

MEAN PARTICLE SIZE 8/14MESH

X-RAY INTENSITY    COUNTS PER SECONDS.
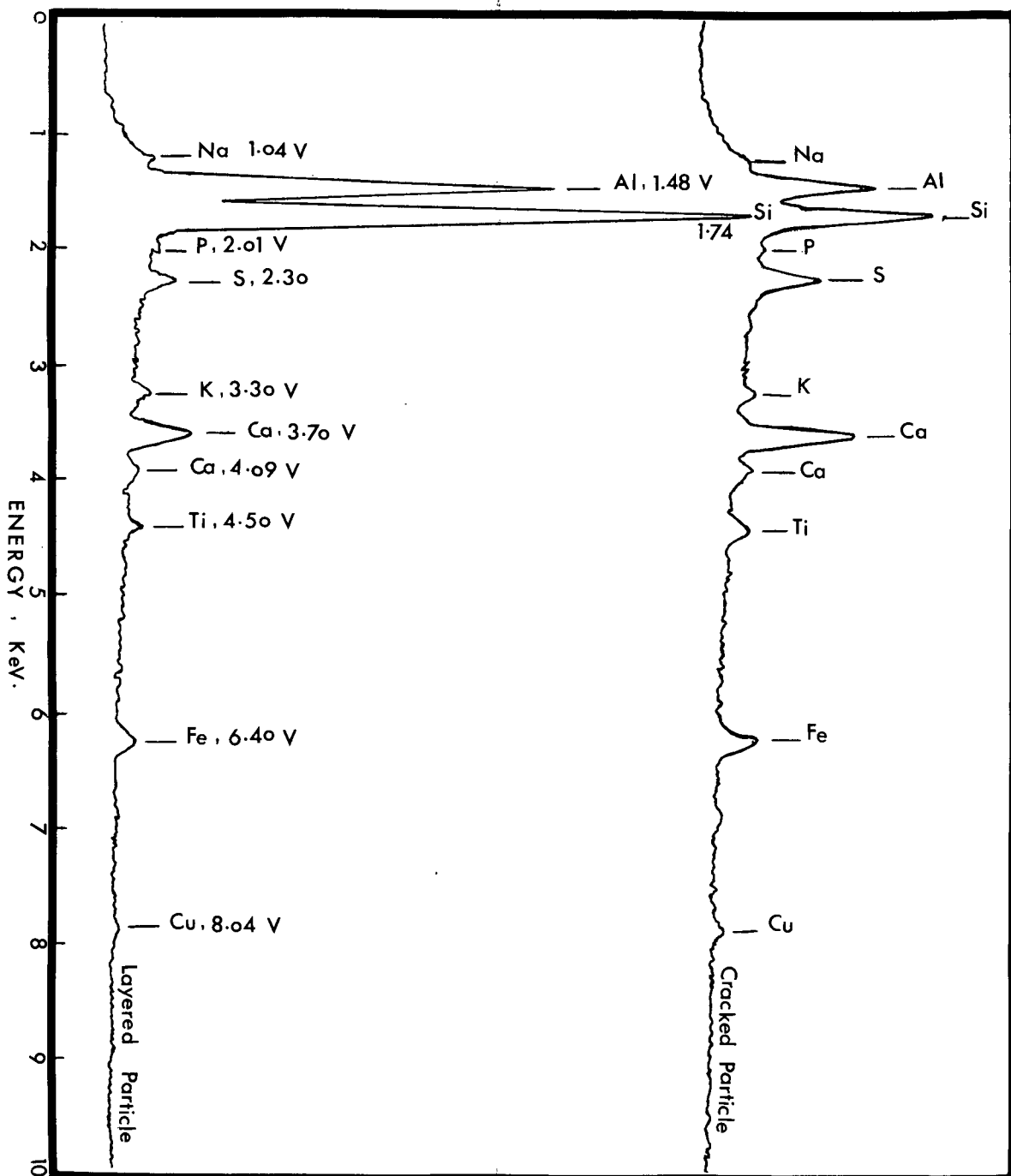
Figure 7b-X-ray energy spectrum showing the elemental distribution across tow Particles of Hat Creek Coal.

ENERGY , KeV.

Na 1.04 V
Al . 1.48 V
Si 1.74
P. 2.o1 V
S, 2.3o
K , 3.3o V
Ca . 3.7o V
Ca , 4.o9 V
Ti , 4.5o V
Fe , 6.4o V
Cu , 8.o4 V

Na
Al
Si
P
S
K
Ca
Ca
Ti
Fe
Cu

Layered Particle

Cracked Particle
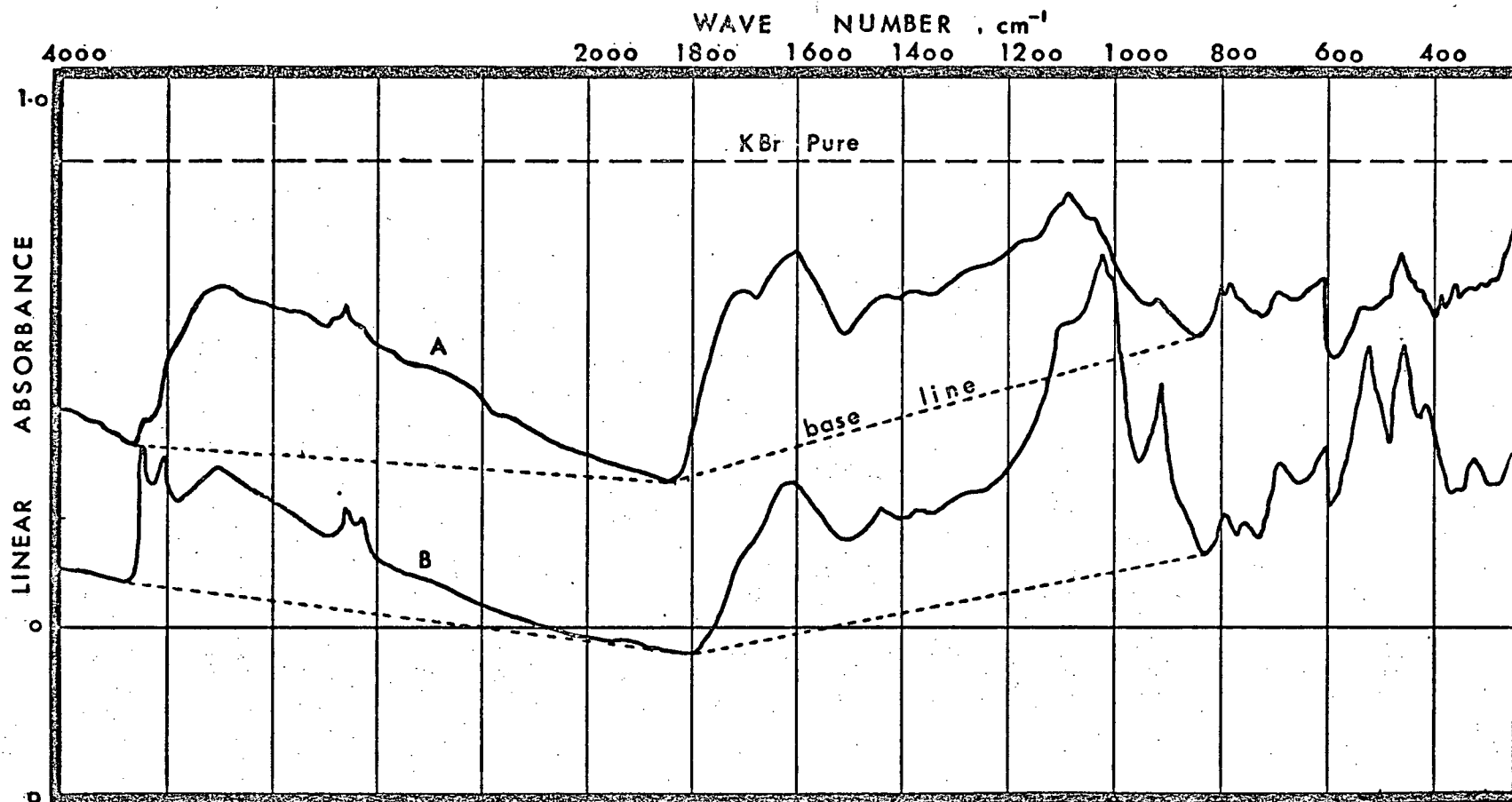
FIGURE 8 : INFRA - RED SPECTRA OF HAT CREEK COALS.

A - SURFACE DEPOSITS.

B - CORE DEPOSITS.

The main absorption bands and the specific extinction coefficient (K) values between 4000 - 250 $cm^{-1}$ range are listed in Table 9.

The bands appear broad because of the partial or even complete overlapping of the "characteristic" bands due to the complexity of the coal structure.

The -OH absorption band at 3400 $cm^{-1}$ (Friedel, 1956 and Osawa, 1971) exists in both surface and core coal with K values of 0.30 and 0.26 $cm^2$/mg respectively. The bands at 2920 $cm^{-1}$, assigned for $CH_3$ or $CH_2$ and aliphatic CH stretch (Fujii, 1970) have very small intensities of 0.06 and 0.08 $cm^2$/mg in surface and core coal respectively. This is usually the case with low rank coals where part of the aliphatic CH is substituted by a hydroxyl OH (Friedel, 1956 and Fujii, 1970).

A shoulder of K value 0.32 $cm^2$/mg appears at 1725 $cm^{-1}$ in the case of surface coal which is characteristic of the C = 0 of COOH or the ketonic carbonyl (Fujii, 1970; Schitzer, 1972). This shoulder is practically non-existent in the case of the core coal spectrum, indicating the absence of -COOH groups and therefore little oxidation of the coal sample.

The most important absorption band at 1600 $cm^{-1}$ has a relatively high K value of 0.55 $cm^2$/mg in the case of surface coal compared to 0.26 $cm^2$/mg in the case of core coal.

TABLE 9.    SPECIFIC EXTINCTION COEFFICIENTS K $(cm^2/mg)$* OF MAIN INFRA-RED
ABSORPTION BANDS OF SURFACE COAL AND CORE COAL.

| Absorption Band $cm^{-1}$ | Main Assignment | Surface Coal | Core Coal |
|---|---|---|---|
| 3700 | OH in kaolinite | - | 0.28 |
| 3620 | "      " | - | 0.3 |
| 3400 | OH | 0.30 | 0.26 |
| 2920 | Aliphatic - CH | 0.06 | 0.08 |
| 1725 | C=O unconjugated | 0.32 | Very weak shoulder |
| 1600 | C=O........OH conjugated | 0.55 | 0.26 |
| 1430 - 1450 | Aliph.CH and $C{<}^O_O$ | 0.28 | 0.20 |
| 1090 ) | ar. C - O C - O - C Mineral matter | 0.48 | 1.16 |
| 1035 ) | Kaolinite | - | 0.95 |

Wt. of sample = 0.8 grams.

ar. = aromatic.

\*    All values are calculated on "As received" basis.
It is recognized that by using a mineral matter-free
basis in calculating the specific extinction coefficients,
the possibility of large variations will be decreased.

This confirms that the oxidized surface coal possesses more carbon-oxygen groups, such as carboxylate $COO^-$, also conjugated carbonyl $C = O.....HO$ (Friedel, 1956; Fujii, 1970 and Schnitzer, 1972). Other weaker bands can be detected in the region between 1430 to 1450 $cm^{-1}$ in both coals with similar K values. These are assigned for the $C\begin{smallmatrix}O\\O\end{smallmatrix}$ structure which can be carbonate, also bands in that region are related to the aliphatic CH structure.

Considering the mineral matter, the bands at 1055, 1000, 970, 910 $cm^{-1}$ were assigned to minerals such as kaolinite (Friedel, 1956). The spectrum of the core coal exhibits sharp peaks at 1090 and 1035 $cm^{-1}$ with very high K values of 1.16 and 0.95, respectively, while surface coal shows very weak peaks with lower intensities. This can be explained by the presence of a large quantity of "gangue" material (mostly kaolinite) in the core samples since the alumina in the ash is equal to 8.27% d.b. This hypothesis is supported better by the presence of two sharp absorption bands at 3620 and 3700 $cm^{-1}$ in the spectrum of the core coal, while they are non existent in that of surface coal. These two bands were assigned to the water associated with the mineral kaolinite (Greenslade, 1975). Moreover, the possibility of the presence of a mixed carbonate and kaolinite "gangue" in both coals is supported by the presence of absorption peaks at 1430, 800

and 735 cm$^{-1}$ which are characteristic peaks of mineral calcite.

The spectra of activated carbon, shown in Figure 9 are quite different from that of coal. Activated carbon does not exhibit any significant absorption bands on the normal absorbance scale; with 5 times the expansion of the scale, a weak band appears at 1600 cm$^{-1}$ with very small intensity (K value = 0.006 cm$^2$/mg). This result is in good agreement with that obtained by Friedel in 1972.

### 3.3.3    Surface area

The results, shown in Table 10, summarize the experimental data which are listed in detail in Appendix C-1-2. The BET surface areas are calculated by the adsorption of nitrogen gas for both Hat Creek coal and activated carbon. The BET equation is described in Appendix B-3. The specific surface area measured by this method exhibits very small values for coal in comparison to activated carbon. Meanwhile, core coal shows about 4 times more surface area than surface coal. Although the micropore volumes follow the same pattern as the surface area values, the average pore diameter of the coal lies within the same range as activated carbon. This can be explained by the very large number of micropores present in the activated carbon which raise the micropore volume. In the case of coal, there are fewer pores with larger pore diameter, of
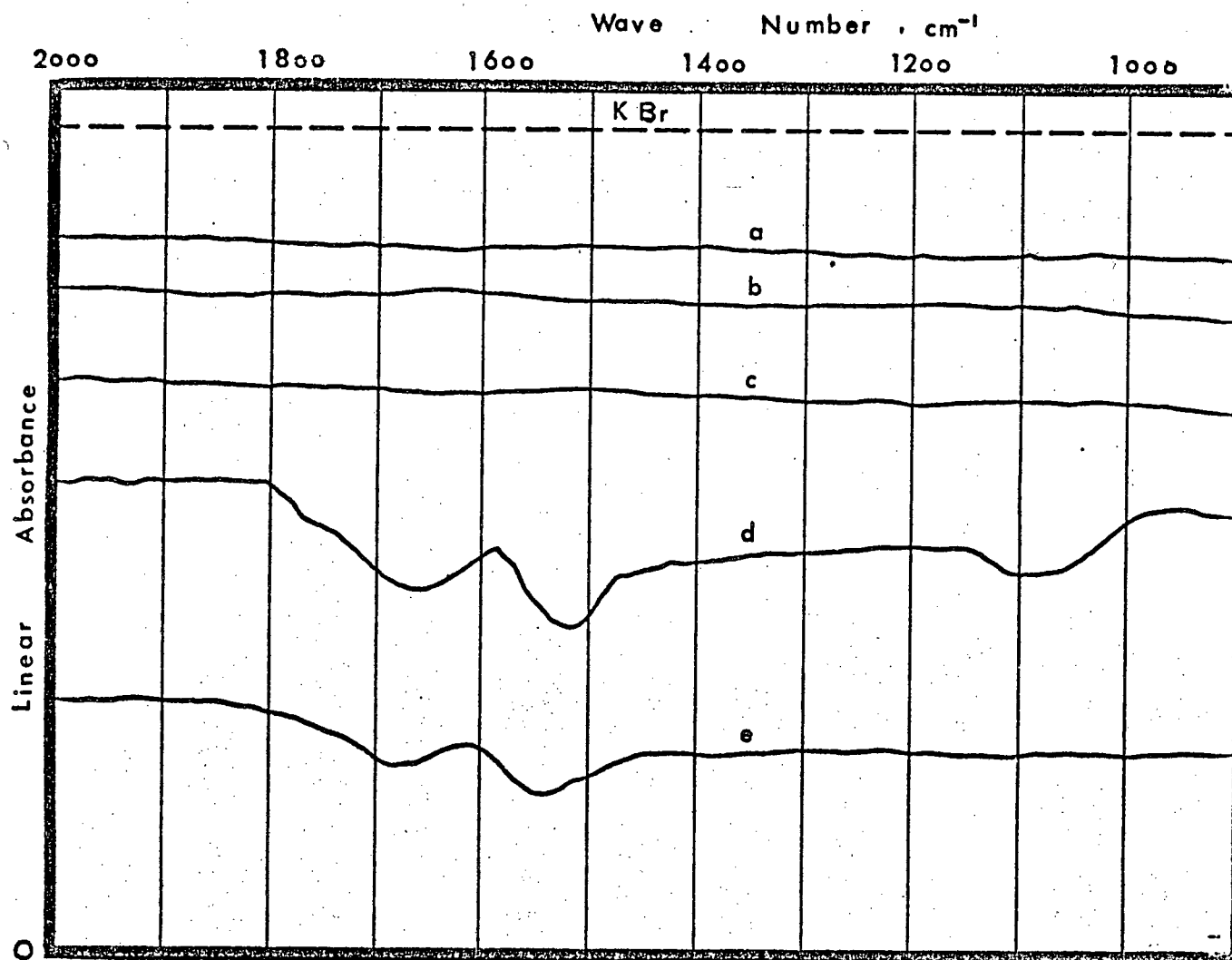
FIGURE 9: INFRA-RED SPECTRA OF ACTIVATED CARBON
a-water-washed sample
b-acid-washed sample
c-acid-washed after adsorption of lead
d-water-washed - expanded scale x5.
e-acid-washed - expanded scale x5.

TABLE 10.　　　SURFACE AREAS, MICROPORE VOLUMES AND
AVERAGE PORE DIAMETERS FOR COALS AND
ACTIVATED CARBON.

| | BET - surface area $(m^2/g)$ | Micropore volume $(ml/g)$ | Average pore diameter $(\overset{\circ}{A})$ |
|---|---|---|---|
| Core sample of coal | 11.8 | 0.067 | 255 |
| Surface sample of coal | 3.1 | 0.042 | 305 |
| Activated carbon (calgon) | 705.9 | 1.057 | 310 |

high average value comparable to that of activated carbon but the surface area and pore volumes have very small values.

It has been suggested, not proven, that the areas calculated from the nitrogen isotherm using the BET equation are mostly associated with the external area of the particles plus that area contained in the pores of diameter greater than about 5 $\overset{o}{A}$ (Marsh, 1965). This explains the very small values of specific surface area obtained for coal.

Another possibility for the low $N_2$ area obtained for the coal is that the gel-like structure of lignite may be irreversibly altered upon drying conducted before the analysis and thus the low nitrogen areas may be apparent. It was seen that coals with a carbon content range of 75-81% tend to have BET nitrogen area of $> 10$ m$^2$, while the carbon dioxide area was in the order of 100-200 m$^2$/gm. on the other hand, the lignite-variety coal with less than 73% carbon content exhibits a negligible ($< 1.0$ m$^2$/gm) nitrogen area, while a very high carbon dioxide area - reached more than 300 m$^2$/gm.

3.3.4

Pore size distribution

The pore size distribution curve (Figure 10) was
obtained by plotting the incremental volume over the
incremental diameter against the average pore diameter $\bar{d}$
(Fornwalt, 1966). The distribution curve for the core coal
shows a very distinct peak corresponding to the transitional
pores with diameters between 60 - 300 $^O$A.

In comparison, surface coal shows a minor peak
in the transitional range and a major peak corresponding
to a higher percentage of pores with a larger micropore
region of > 200 $^O$A.

The points were insufficient to complete this peak
because the pore volume measurements were taken up to
only 372 $^O$A.

Activated carbon has the highest peak on the curve
within a range of diameters of 50 - 70 $^O$A. This represents
a system approaching micropores. The pore size distribu-
tion of activated carbon, using nitrogen, permits rapid
penetration by gases (with their widely separated molecules)
but not by liquids, especially those with long chain
molecules (Fornwalt, 1966). This is mainly the reason for
the large $N_2$ area obtained for activated carbon and the
negligible one obtained for coal.
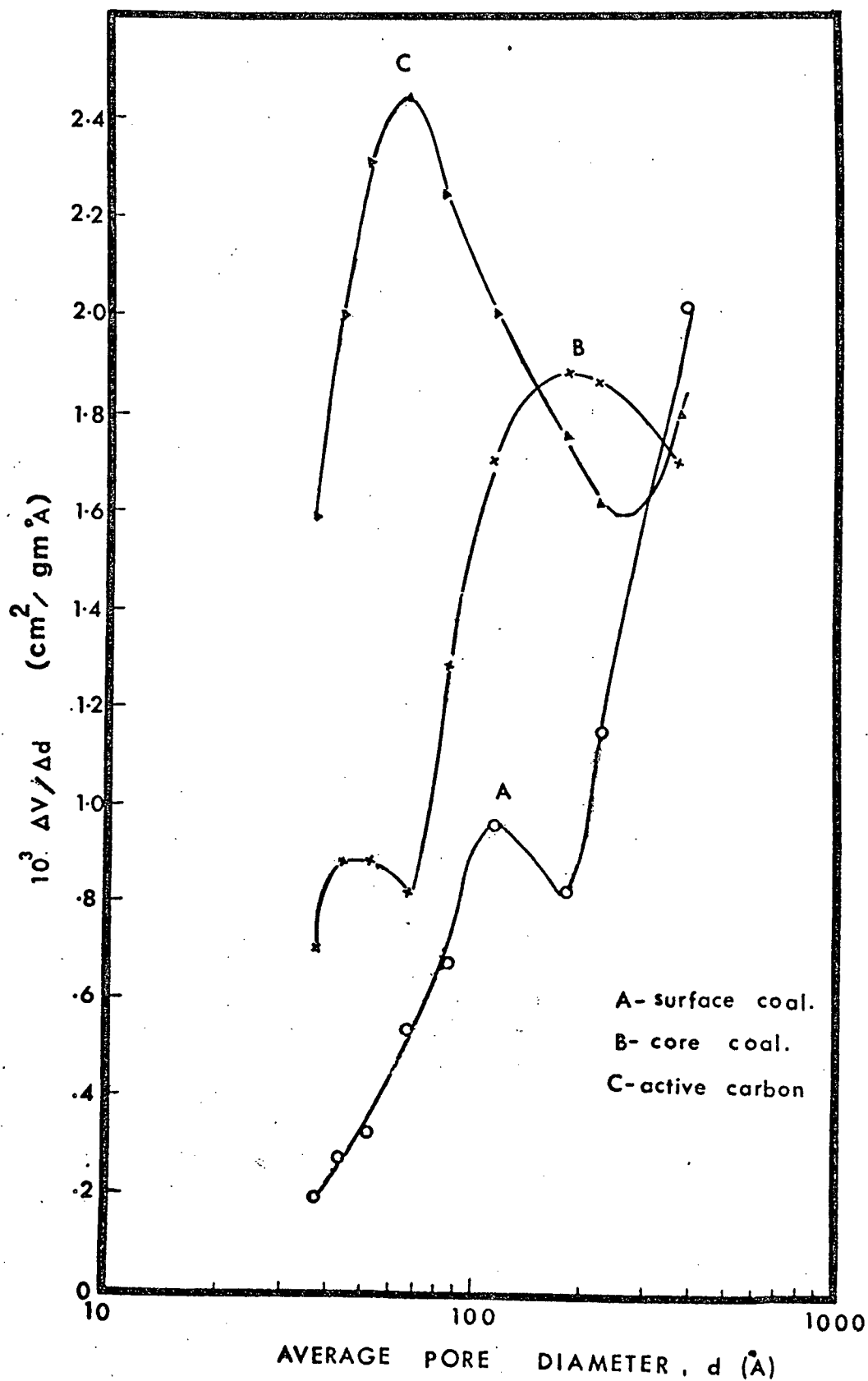
FIGURE 10 : PORE SIZE DISTRIBUTION CURVE FOR HAT CREEK
COAL AND ACTIVATED CARBON CALCULATED FROM
NITROGEN ADSORPTION ISOTHERM AT 77°K.

Therefore, coals with their highest percent of total pore volume lay in the transitional and macropore range. They are, accordingly, expected to be most suitable for use for adsorption of long chain molecules from liquid phases.

3.3.4 Permeability test

Table 11 shows the degree of permeability K in cm/sec at $20^{\circ}$C, which is calculated for four sizes of Hat Creek coals. These results compare favorably with those for soil or sand of comparable sizes (Karol, 1969).

The K values for the particle sizes 3 and 60 mesh Tyler proved to give a suitable hydraulic conductivity to pass satisfactory volumes of wastewater during the loading process, and therefore all the column leaching experiments have been conducted using these two granular particle sizes.

The 150 mesh and the fines show a very low degree of permeability and therefore they were not used in the adsorption processes during the course of this work.

TABLE 11. DEGREE OF PERMEABILITY OF SURFACE HAT CREEK COAL

| Sieve size Mesh | Permeability K cm/sec at $20^{\circ}$ C |
|---|---|
| 3 | $1.3 \times 10^{-2}$ |
| 60 | $4.4 \times 10^{-3}$ |
| 150 | $1.5 \times 10^{-4}$ |
| Fines | $9.87 \times 10^{-5}$ |

### 3.3.5   Iodine number

The iodine number of surface Hat Creek coal was compared with other types of coal of the same rank, activated carbon and construction sand.  The summary of the results are reported in Table 12.

TABLE 12. IODINE NUMBER OF HAT CREEK COAL
COMPARED WITH OTHER ADSORBENTS

| Absorbent | Range of Iodine Number (based on triplicate samples) |
|---|---|
| 1. Activated carbon | 750 - 950 |
| 2. Hat Creek coal | 105 - 158 |
| 3. Union Bay coal (Vancouver Island) | 110 - 160 |
| 4. Construction sand | 1.4 - 3.2 |

Activated carbon exhibits the largest adsorptive capacity towards iodine which is found to be numerically equal to the nitrogen area (U.S.E.P.A., 1973).

The value for activated carbon is approximately 7 times greater than that of coal, very similar values have been obtained for both Hat Creek and Union Bay coal, while in comparison with construction sand, the latter has a very small value of iodine number, approximately 60 times less than that of coal.

The iodine uptake is not only a function of surface area and porosity, but depends  rather complexly on the

iodine reagent interaction with the compounds of the coal as well as the type of the coal used (Roy, 1957).

The BET surface areas of coal are very small when compared with values obtained from the iodine numbers. The reason lies in the fact that thermal contraction of coal to liquid nitrogen temperatures makes nitrogen sorption at very low temperatures an <u>activated</u> process.

For all practical purposes, the BET surface area can be more or less equated with the external surface presented by the particles of the test sample.

The liquid phase adsorption, which is our interest, demonstrates clearly that the iodine number value is by far the better measure of the "real" surface area, which the sample would present to a reagent.

"In the case of activated carbon, the reasonable correspondence between the BET surface area and the iodine values are associated with the fact that activated carbon, unlike coal, offers a rigid carbon skeleton and does not therefore thermally contract to such an extent so that penetration of its pore volume at a very low temperature is much more difficult than at room temperature"(Berkowitz, 1977)*

* Berkowitz, N. Fuel Science Division, Alberta Research Council, Edmonton, Alberta. Direct communication.

## V.   SORPTIVE CHARACTERISTICS

Preface:

This part of the research program deals with the study of Hat Creek coal as a possible adsorbent material for water purification and the evaluation of its adsorptive capacity for the removal of the main pollutants which are not adequately removed by conventional secondary treatment processes.

In this work, synthetic wastewaters were used rather than actual wastes in order to control the strength and the composition of the tested materials, also to facilitate the measurements and to avoid the possibility of any complexation that may occur between organic and inorganic materials.

Table 13 indicates the simulated wastewaters, and the materials used in the synthetic wastewaters prepared for the experiments.

Descriptions of the reagents are included in Appendix B-4-1.

Both batch contact and column adsorption tests were performed to evaluate the adsorptive capacity of oxidized Hat Creek coal, mined from the surface, to remove each material either separately or in some combinations.

Several tests were conducted using activated carbon, Abbotsford silt loam and construction sand for comparison purposes. These materials were described earlier in Chapter III.

TABLE 13. SOLUTIONS TESTED

| Polluting Materials in Actual Wastewaters for Examination | Synthetic Wastewater Used for Tests |
|---|---|
| 1. <u>Heavy metal ions:</u><br>lead, cadmium, mercury, copper, zinc, and chromium | metal nitrate solutions (details in Appendix B-4-1) |
| 2. <u>Dissolved organics:</u><br>(oxygen demanding material) | beef extract solution (COD: TKN = 9:1) |
| 3. Phosphate ions $(PO_4^{-3})$ | sodium phosphate solution |
| 4. $NO_3$-N | sodium nitrate solution |
| 5. $NH_3$-N | ammonium sulfate solution ammonium nitrate solution |
| 6. Phenol | liquified phenol |
| 7. Cyanide $(CN^-)$ | potassium cyanide solution |

## 1.   DESIGN OF EXPERIMENTS (COULTHARD, 1974).

### 1.1   Batch contact process

A series of known concentrations, covering a wide range, were prepared from each material listed in Table 13. A volume of 100 mls of each concentration was then mixed with different percentages of coal 1, 5 and 10% w/w for each of the four average particle sizes 0.533 mm, 0.2965 mm, 0.117 mm and 0.03414 mm as shown in Appendix B-4-2.

The solutions were then shaken continuously at room temperature on a standard mechanical shaker at 150-200 cycles per minute for a contact time of 8 hours.

The contact time was determined by performing preliminary experiments in which fixed volumes of the solution were contacted with a fixed weight of coal for different periods of time ranging from 1 hour to 24 hours. A contact time sufficiently long to ensure a reasonable approach to equilibrium was chosen at 8 hours for all materials tested. Details are shown elsewhere (Coulthard, 1974).

The residual concentrations of the material have been determined and the adsorptive capacity of the coal toward such material was calculated in terms of milligrams of material removed per gram of coal. Data from the batch experiments were then utilized in plotting the adsorption isotherms.

### 1.2   Column test (Coulthard, 1974)

This semi-continuous test was conducted to compare the column process to the batch process in terms of adsorptive capacity.

Small columns of dimensions 20 cm X 7 cm I.D., containing approximately 600 grams of coal were used. Experimentation was carried out on the four particle sizes of coal using the same series of the solution strengths employed in the contact process.

The volume of solution was 500 mls applied at a flow rate of 1 ml/min. The effluents were withdrawn from the bottom of the column and subsequently analyzed for retention concentration.

1.3 Continuous column test (Coulthard, 1974)

A larger column of dimensions 2 meters X 15.24 cm I.D., was employed to evaluate the adsorptive capacity of the coal, and its life time to remove certain pollutants or combinations under stationary bed-type conditions.

About 28 Kgs of coal was contained in the column which consisted of a granular particle size of 0.533 mm average diameter.

The solution containing the material to be adsorbed was continuously applied to the column at a flow rate equivalent to 1 Imp gpm/ft$^2$ to provide 30-35 minutes of contact time. The "break through point" was arbitrarily set up at the lower limit of ionic concentration recommended by the Public Health Water Quality Standards (B.C. Dept. of Health Service, 1969; California Water Quality Criteria, 1963).

Filter candles were inserted at each 30.5 cm (1 ft) level in the column beginning at the 15.25 cm (6 in) level to enable sampling from various depths of the column.

A schematic diagram for the column is shown in Figure 11. Effluent samples were collected periodically from different levels for analyses.


## 2.    DESCRIPTION OF SORPTIVE TESTS.

### 2.1  Heavy metals

Known concentrations of the 6 heavy metal ions lead, copper, zinc, cadmium, chromium and mercury were prepared for the series of the outlined contact and leaching experiments.  The reagents used are included in Appendix B-4-1.  The concentration of metals in the charging stock solutions was varied and the lower limit of ionic concentration was guided by the Public Health Drinking Water Standards as shown in Table 14.


TABLE 14.  -    PUBLIC HEALTH DRINKING WATER STANDARDS

| Chemical | Limits mg/1 [a] | | U.S.P.H.S. [b] |
|----------|-----------------|--------------|----------------|
|          | Permissible | Objective | |
| Lead | 0.05 | N.D.* | 0.05 |
| Zinc | 5.00** | < 1.0 | 5.0 |
| Copper | 1.00** | < 0.01 | 1.0 |
| Cadmium | 0.01 | N.D. | 0.01 |
| Chromium | 0.05 | N.D. | 0.05 |
| Mercury | - | 0.005 mg/1*** | - |

a     B.C. Dept. of Health Service, 1969.
b     McKee and Wolfe, 1963
*     Not detectable
**    Recommended standard
***   U.S.S.R. objective
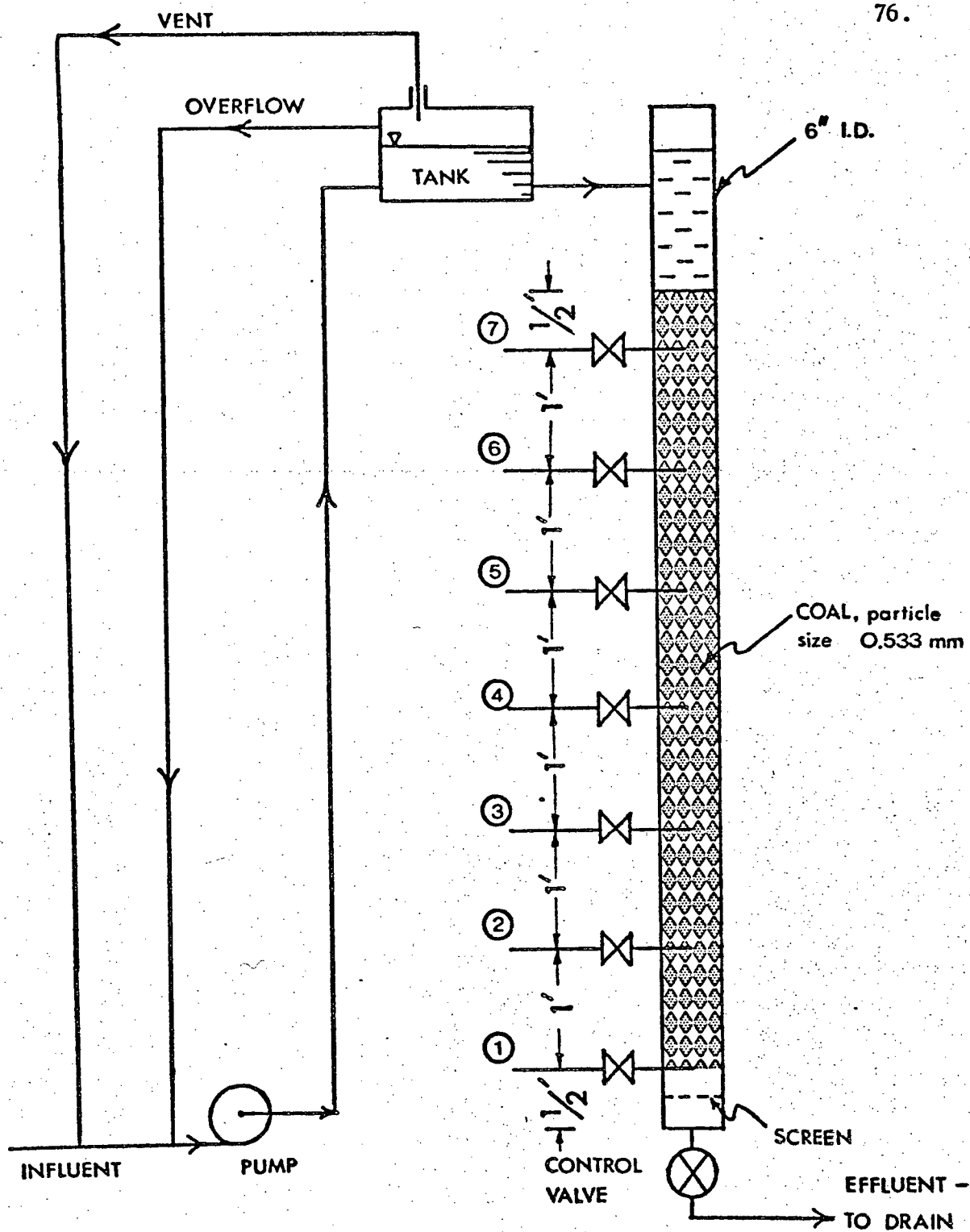
FIGURE 11 : SCHEMATIC DIAGRAM OF THE CONTINUOUS COLUMN
PROCESS.

For example, the lead solution tests contained a series of 0.05, 0.1, 0.2, 0.5, 5.0, 50 and 500 mg/1. The concentrations for the other metals are shown in the tables included in Appendix C-2.

In the case of using the larger bed for continuous leaching, a 5 mg/1 lead solution was applied continuously to the column at a flow rate of 1 gpm/ft$^2$ until the break through point (e.g. an effluent of 0.5 mg/1, Pb) was reached.

2.1.1 Selectivity towards heavy metals

The same test coal bed was then used to treat a synthetic effluent containing six elements in combination, lead, mercury, chromium, zinc, copper and cadmium, each contributing 5 ppm concentration respectively. The level of each element in the withdrawn sample was measured, the influent was applied continuously until the break through point of 0.5 mg/1 was attained.

2.2 Dissolved organics

A series of beef extract solutions were prepared for the organic tests. Beef extract is a material which contains all of the organic nutrients necessary as a substrate for the bacterial culture. In addition, beef extract solutions may be prepared to desirable and predictable concentrations without contamination from other elements. In this respect, there are, for example, only the BOD$_5$, COD and TOC values, excluding the side effects of other possible toxic compounds which would be experienced in sewage wastewater.

Both contact and column adsorption methods were employed.

The majority of the experiments, for organics however, were confined to the use of only two particle sizes of coal namely 0.533 mm and 0.2965 mm average value. Several experiments carried out with fine particle sizes, e.g. 0.03414 mm, especially in the column adsorption process, indicated that the small pores in the coal bed quickly "blocked" with organics and consequently the head loss increased and prevented the passage of any fluid through the column bed. Nevertheless the fine size (0.03414 mm) was used successfully in the contact (batch) process.

Mineral nutrients were added in the stock solution for some trials to determine if these elements (Fe, Ca, Mg, etc.) were in the coal in sufficient strengths to stimulate a good bacterial growth.

Some experiments were carried out with activated carbon and construction sand to compare their removal capacities with that of Hat Creek coal.

To explore the effect of heavy metals on organic solutions, measured amounts of lead were added to the influent beef extract solutions. Only a few experiments have been conducted owing to the time available.

Inoculation of the coal bed: One liter of the beef extract solution was applied to the fresh coal bed with a very slow flow rate 5-6 mls/min. The column was allowed to drain, then washed with clear tap water, drained, and allowed to "mature"

for three days before application of further organic solutions. This procedure allows the bacterial growths to establish within the coal and its pores.

## 2.3 Phosphates

Both column and contact process were employed to determine the capacity of the coal to adsorb phosphate ions. Tests to study the effect of particle size, coal dosage, contact time and phosphate concentration were carried out. It is known that most soils have a good capacity to remove and retain phosphates present in solution. To compare the coal's capacity with soil, some leaching trials with an Abbotsford sandy loam were carried out

## 2.4 Nitrates

Standard nitrate solutions of various concentrations were used for both the contact and column process. Some batch tests were also tried using coal samples after washing out the originally present nitrate in the coal and the results compared with that obtained with the unwashed samples.

## 2.5 Ammonia

A series of experiments have been conducted using both contact and column techniques. Both ammonium nitrate and ammonium sulfate have been utilized to provide known ammonia concentrations. Initial concentrations of ammonia of 50 mg/1 and 10 mg/1 were also employed. Results obtained with both surface and core coal samples were compared to that obtained with activated carbon.

## 2.6  Phenol

A phenol solution containing approximately 5 mg/l concentration was used in both the contact and the column experiments.  Also the effect of pH change on the removal of phenol was determined, and some tests were conducted using activated carbon for comparison.

## 2.7  Cyanide

A cyanide solution containing approximately 2 mg/l of cyanide ions was used in both the contact and the column tests. The effect of the pH was also studied.  Some tests were conducted using activated carbon for comparison.


## 3.  ANALYTICAL METHODS.

## 3.1  Heavy metals

The Atomic Absorption Spectrophotometer (Perkin-Elmer Model 303) was used for most of the measurements.  The flame atomic technique using a deuterium lamp for the background correction was used for all heavy metals, except mercury, which required a flameless or cold vapor technique for its release (Jarrel Ash report No.Hg-1, 1970).  In this technique the mercury samples were acidified with $H_2SO_4$ and later oxidized with K Mn $O_4$.  The permanganate additive was neutralized with hydroxylamine hydrochloride (HONO$_3$ Cl) and aerated after addition of stannous chloride (SnCl).  The mercury released was analyzed in a flameless cell on a Jarrel Ash Atomic Absorption Spectrophotometer.

The standardized instrument settings and detection limits for each metal were as shown in Appendix B-4-4. The samples containing the metals were acidified by adding enough nitric acid to lower the pH to below 2 before analyses.

Samples with low concentration levels below the detectable limits of the instruments were concentrated by evaporation.

3.2 $BOD_5$ and COD

These analyses were conducted in accordance with the chemical methods described with the A.P.H.A. Standard Methods for the examination of water and wastewaters, (14th Ed., 1975).

3.3 Total organic carbon

These analyses were determined by automated method on a Beckman Total Organic Carbon Analyzer, Model 915.

3.4 Phenol and cyanide

These analyses were carried out by the Pesticide Laboratory, B.C. Ministry of Agriculture in accordance with the A.P.H.A. Standard Methods, 1975.

The following analyses were determined by automated methods on a Technicon Industrial Auto Analyser II.

3.5 Ammonia Nitrogen ($NH_3$-N)

Ammonia was determined by means of the Berthlot Reaction in which a green colour is developed with phenol and sodium hypochlorite. The colour intensity is read at 630 nm. The detection limit is 0.2 mg/l $NH_3$-N.

## 3.6 Nitrate-Nitrogen ($NO_3$-N)

The nitrate is reduced to nitrite by hydrazine and a copper catalyst. The nitrite then forms a pink dye by diazotization. The colour is read at 520 nm. The detection limit is 0.02 mg/1 $NO_3$-N.

## 3.7 Orthophosphate Phosphorus (O-$PO_4$-P)

The orthophosphate reacts in acid solution with ammonium molybdate and ascorbic acid to give molybdenum blue which has an absorption maximum at 660 nm. The detection limit is 0.2 mg/1 O-$PO_4$-P.

## 3.8 Total-N and Total-P

The sample is automatically digested with concentrated $H_2SO_4$ containing selenium and perchloric acid. Organic nitrogen is converted to ammonia, and organic phosphorus to orthophosphate which is then determined simultaneously by the Berthlot and molybdenum blue procedures respectively. The detection limit is 0.05 mg/1 N and P.

# 4. RESULTS AND DISCUSSION

General

<u>Adsorption isotherms</u>: The sorptive capacity of the coal can be measured by determining the adsorption isotherms (Culp, 1971) which are considered the most convenient form for representing the experimental data obtained from the batch tests for the various substances. The adsorption isotherm is the relationship, at a given temperature, between the amount of a substance adsorbed and its concentration in the surrounding solution.

In dilute solutions, such as wastewaters, the values are plotted on a logarithmic scale usually yielding a straight line. In this connection, a useful empirical formula is the Freundlich equation which is not derived from theoretical concepts such as the Langmuir and BET equations, but is nonetheless useful in relating the amount of impurity in the solution to that adsorbed as follows (Hassler, 1974).

where

$$X/m = K \ C^{\frac{1}{n}}$$

X    = amount of substance adsorbed

m    = weight of coal or carbon

X/m  = amount of substance adsorbed per unit weight of coal

K and n = are constants (log K is the intercept & $\frac{1}{n}$ is the slope)

C    = unadsorbed concentration of substance in the solution

A reading, therefore, taken at any point on the isotherm gives the amount of substance adsorbed per unit weight of coal which is the adsorptive capacity at a particular concentration. The effectiveness of the removal is measured in this work by two parameters.

a)    The milligrams of substance removed per gram of coal applied.

b)    The percentage removal efficiency which is the amount removed compared to the amount in the original solution.

The calculation of these values is based on the sensitivity of the measuring instrument used for the analysis as well as its detectable limit for each substance. For example, with weak solutions, the sensitivity of the instrument would not allow detection of metal ions left in the solution and therefore the detectable amount removed was found to approach 100% in the weak solutions for all of the heavy metals tested.

4.1     Heavy Metals

4.1.1   Batch Tests

Complete randomized design were applied in the experiments for batch tests (Leclerg, 1966) in which four independent variables were considered; these are: type of heavy metal ions, solution concentration, coal dosage and particle size of coal.

The dependent variable in all experiments is the adsorptive capacity of the coal in mgs metal ions removed per 1 gram of coal.

A total of 648 isotherm tests are included in this experimental design; each test deals with one variable at a time while the others remain constant. The results obtained from the tests are tabulated in detail in Appendix C-2-1, Table 1 to Table 20 inclusive.

The applicability of the Freundlich isotherm was tested for each of the 648 sorption tests using linear regression analysis. Slopes, intercepts and correlation coefficients were then calculated for the isotherms and the data is included in Appendix C-2-2. The isotherms obtained with lead, mercury, copper and zinc show linear relationships in Figure 12a, and therefore they can be interpreted by using the Freundlich isotherm equation. Cadmium and chromium behave differently; relatively poor correlation coefficients are obtained for their isotherm data while the levelling out of the points at equilibrium concentration higher than 100 mg/l indicates a saturation stage is probably reached as shown in Figure 12b. This may be due to the insufficient coal dosage used in this test (1% by wt). Therefore, for cadmium and chromium adsorption systems, a Freundlich isotherm may not be applied for interpretation of the data obtained.
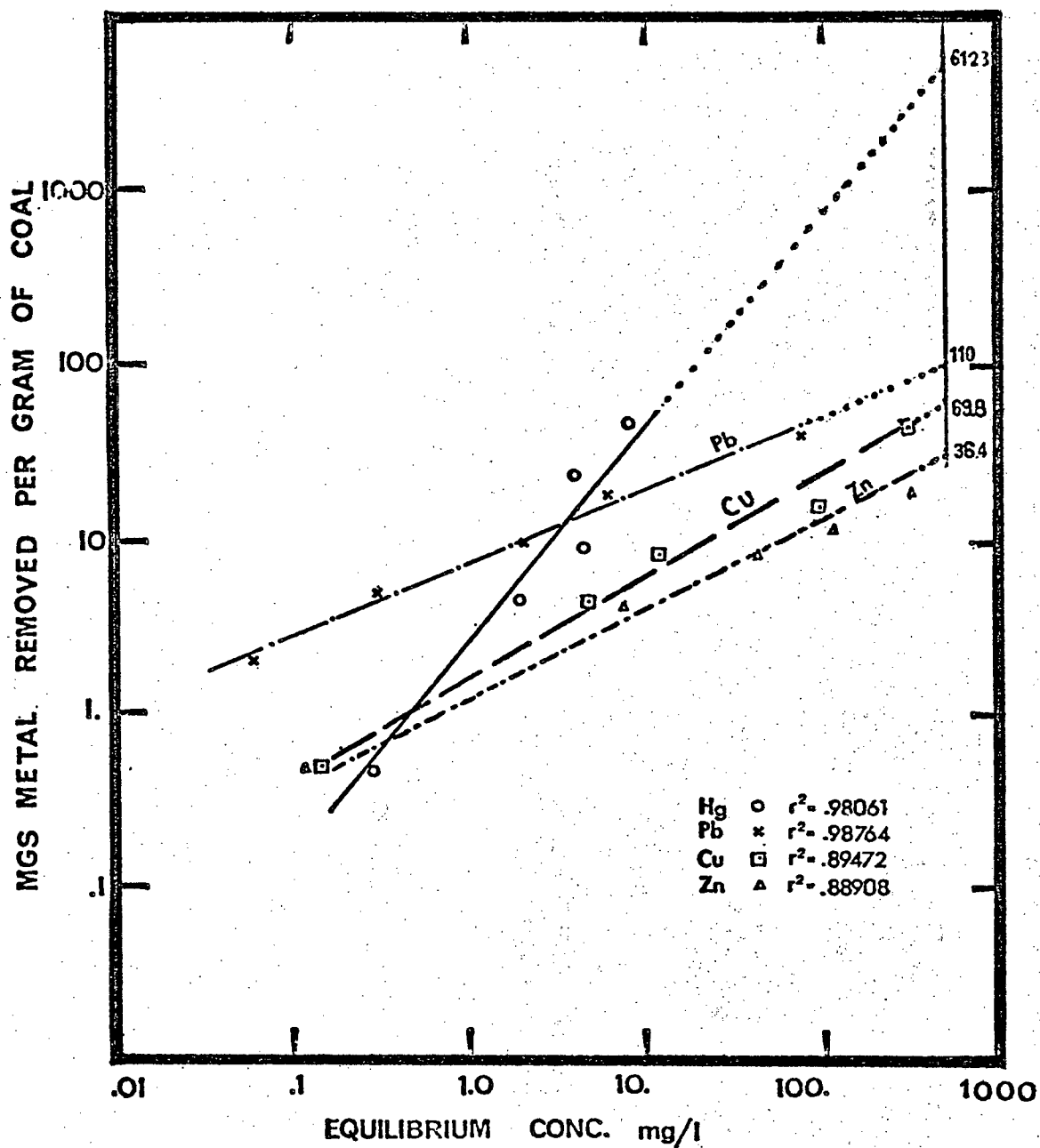
FIGURE 12A. ADSORPTION ISOTHERMS FOR REMOVAL OF
HEAVY METAL IONS BY COAL.
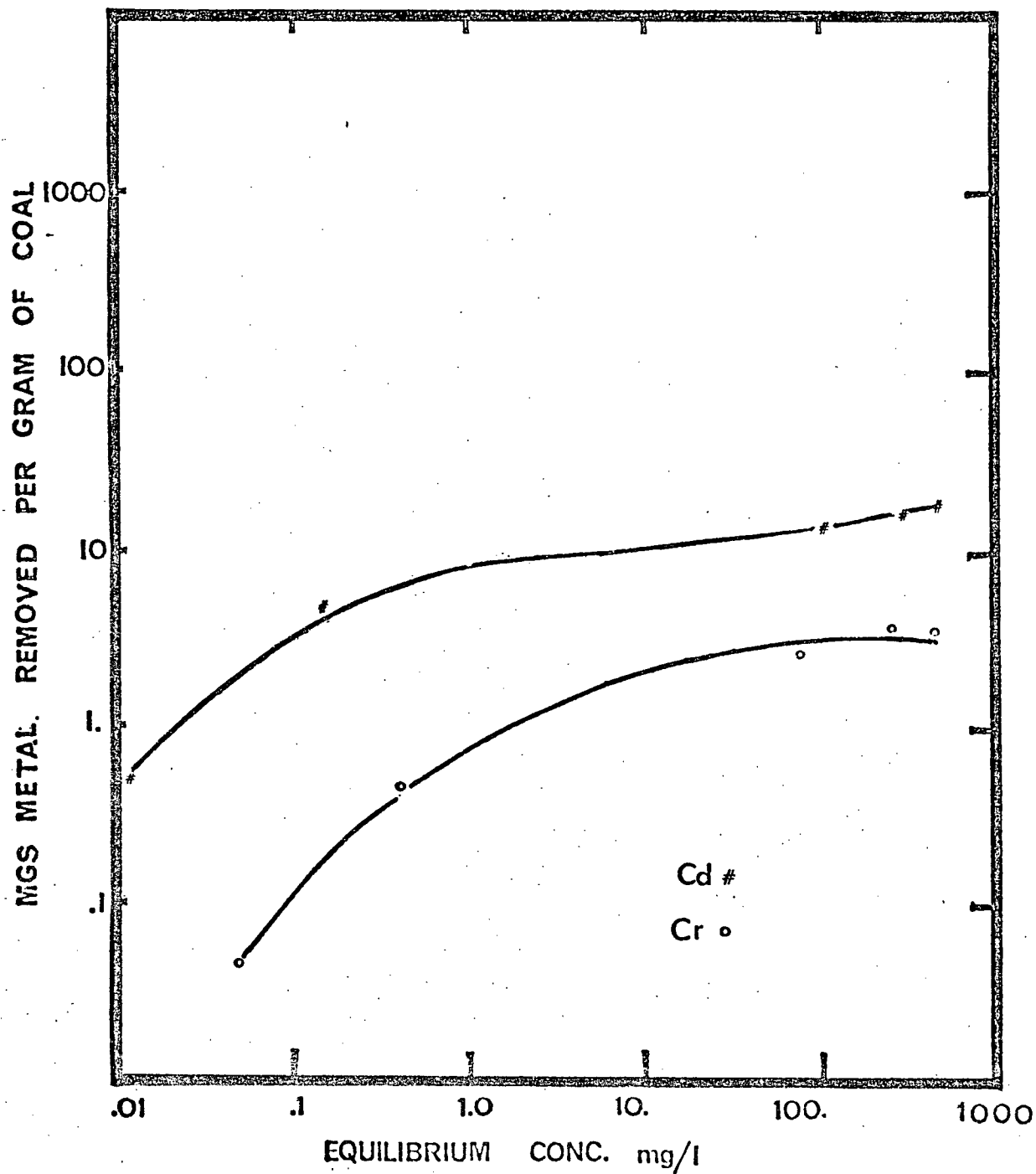
FIGURE 12B. ADSORPTION ISOTHERMS FOR REMOVAL OF
HEAVY METAL IONS BY COAL.

The maximum adsorptive capacities for all metals at an
initial concentration of 500 ppm were estimated by extrapolation
of the isotherm line. Some values are compared in Table 15.
All results show that the mercury isotherm line has the steepest
slope indicating the highest adsorptive capacity as well as the
greatest efficiency in column operation, while the chromium
isotherm line has the least slope and correspondingly the
poorest efficiency of removal. Lead exhibits a very high
removal efficiency and is categorized as second after mercury.
Copper, zinc and cadmium can be categorized together as they
have intermediate adsorptive affinities towards coal and
exhibit similar values.

Therefore, the six heavy metals may be listed in
sequence according to their affinity towards coal as follows,
starting at the highest affinity:

$$Hg > Pb > Cu > Zn > Cd > Cr.$$
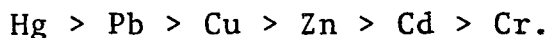
4.1.2 Comparison with activated carbon

Figure 13 shows a comparison between the three adsorp-
tion isotherm lines obtained for the adsorption of lead by
oxidized surface coal, unoxidized core coal and Calgon activated
carbon. The data are tabulated in Appendix C-2-3. When the
maximum adsorptive capacity is measured at 50 ppm, the oxidized
coal exhibits the greatest adsorptive capacity of 217 mgs lead

TABLE 15.     COMPARISON OF THE ADSORPTIVE CAPACITIES OF SURFACE COAL
              TOWARDS SIX METAL IONS

              Contact time = 8 hrs
              Coal dosage  = 1%
              Particle size = 0.03414 mm

| Metal ion | Maximum adsorptive capacity $(x/m)_{500}$* mgs metal ion/gram coal | Correlation coefficient for the isotherm $r^2$ data |
|---|---|---|
| Mercury | 6123 | 0.9806 |
| Lead | 110 | 0.9876 |
| Copper | 70 | 0.8947 |
| Zinc | 36 | 0.8891 |
| Cadmium | 19 | 0.7947 |
| Chromium | 8 | 0.8478 |

*   $(x/m)_{500}$ = maximum adsorptive capacity obtained by extrapolation of
    the isotherm line to initial concentration of 500 mg/1.
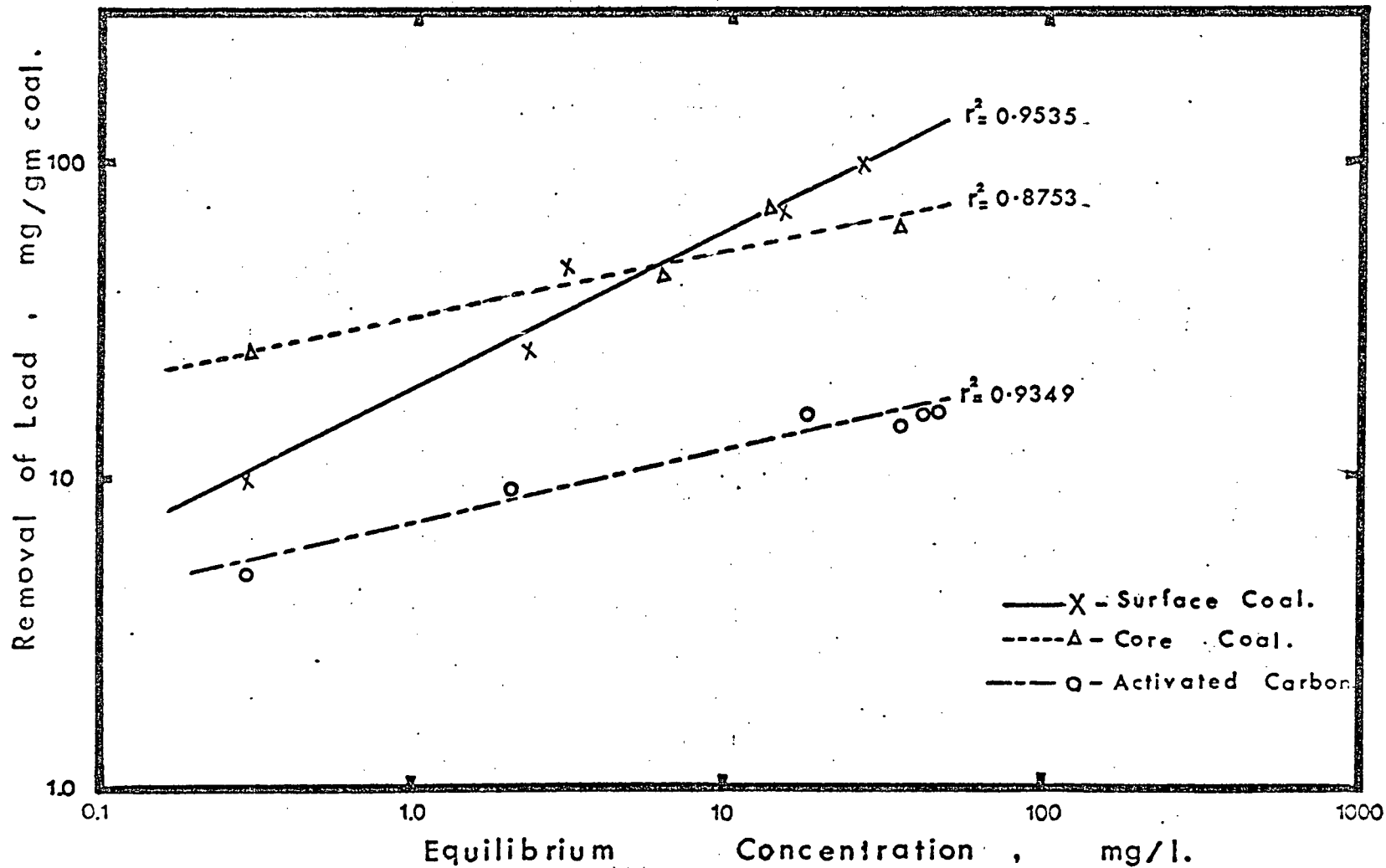
FIGURE 13 : ADSORPTION ISOTHERMS FOR REMOVAL OF LEAD
BY HAT CREEK COAL AND ACTIVATED CARBON.

per gram coal while unoxidized coal shows about half of this value in the order of approximately 125 mgs lead per gram coal. This indicates that surface oxides on the coal likely play an important role in the adsorption mechanisms concerning heavy metals. Therefore interest was focussed in this study on determining the role of surface oxides in removing lead ions from solutions by coal.

In comparing Hat Creek coal with the activated carbon, the latter exhibits very poor adsorptive capacity towards lead, only 19.3 mgs lead ions per gram of coal. Therefore activated carbon will not be competitive with coal in adsorption of heavy metals from a solution.

4.1.3  Variables influencing adsorption

A qualitative evaluation of the effects of some of the experimental variables on the adsorption efficiency was made using the data shown in Appendix C-2-1.

4.1.3.1 Contact time

Preliminary batch tests were conducted for exposure periods of between 1 hour and 24 hours to determine the optimum contact time. All results are included in Appendix C-2-4-1. Figure 14 shows the adsorption of lead as a function of contact time. A rapid approach towards equilibrium was evident.

Reduction of the effluent concentration was continued as the contact time increased until at about 8 hours, when the reduction obtained was the same as those obtained at a longer time of exposure. Therefore, 8 hours was considered sufficiently long to ensure a reasonable approach to equilibrium, and was

The figure shows a plot of EFFLUENT CONC., mg/l (y-axis, 0 to 50) versus CONTACT TIME, hrs. (x-axis, 0 to 24). The curve decreases sharply from 50 mg/l.

ADSORBENT: oxidized Hat Creek coal
DOSAGE : 1 % w/w
AVG. COAL SIZE: 0.533 mm dia.
INFLUENT CONC: 50 mg/l

equilibrium time 8 hr.
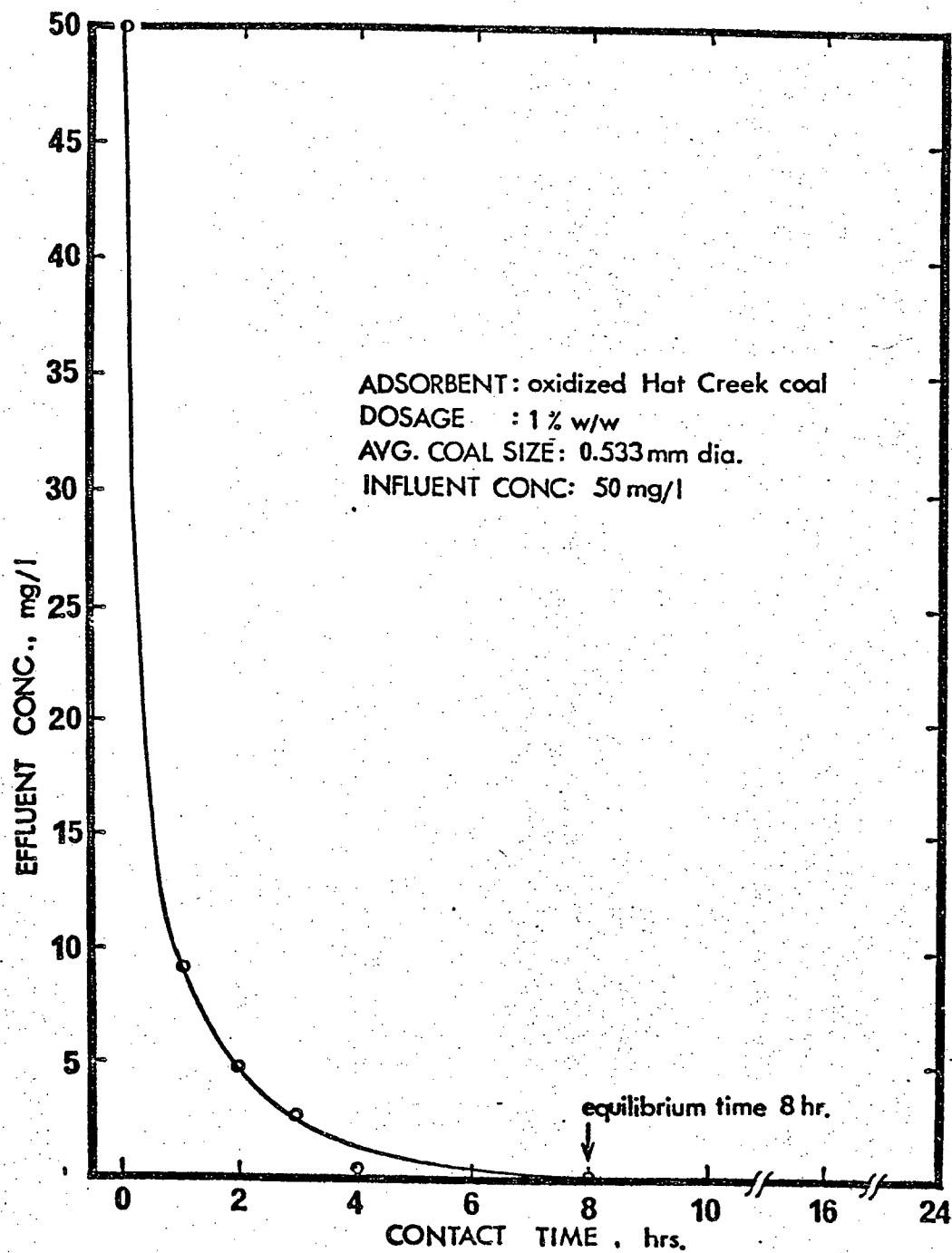
FIGURE 14 : EFFECT OF CONTACT TIME ON ADSORPTION OF LEAD.

adopted for all further batch testing.

4.1.3.2   Coal dosage

The minimum amount of coal necessary for the effective
removal of heavy metals from a known volume of solution of cer-
tain concentration was determined.

The test results listed in Appendix C-2-4-2 show that
more reduction in the residual concentration is obtained by
increasing the coal dosage with a greater increase in the removal
efficiency.   The increase in efficiency is more significant
at high influent concentration, mostly about 50 ppm.

Figures 15a and 15b show the effect of a coal dosage on
the remaining concentration and the removal efficiency of copper
by coal.   The efficiency of removal of copper from a solution
concentration of 500 ppm increases from 32.9% when 1% w/w coal
is used to over 92% when the coal dosage is increased to 5% w/w.

The same conclusions were obtained with other heavy
metals tested except with mercury where the effect of carbon
dosage is not significant because of the great affinity of
mercury to be adsorbed with a minimum efficiency of not less
than 90% at all concentration levels.

4.1.3.3   Concentration of solute

The dependence of adsorption capacity of coal upon the
concentration of the metal ions in the solution phase is expressed
by data summarized in Table 16 for the adsorption of mercury. For
all metals, it is obvious that the adsorptive capacity of coal
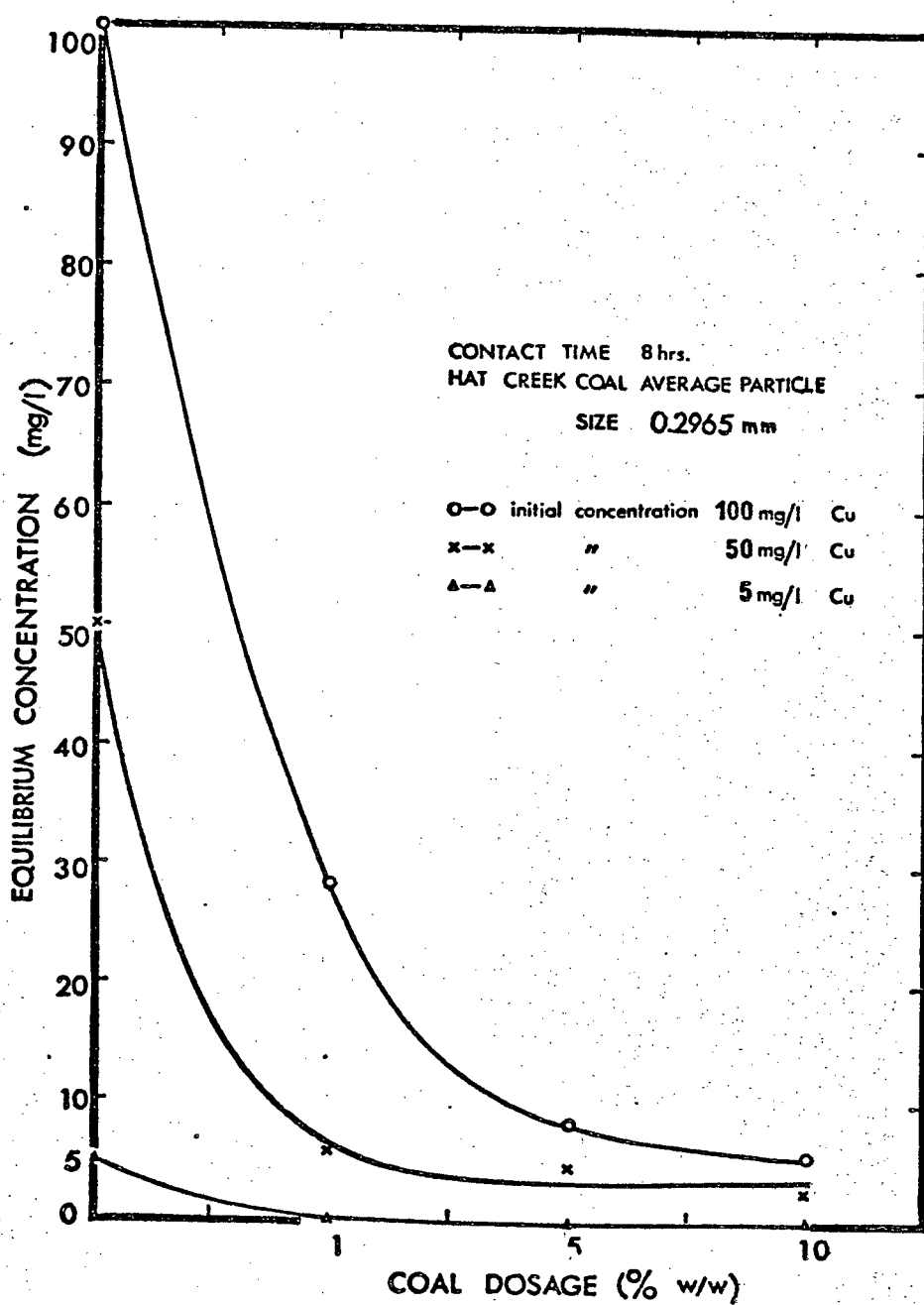
FIGURE 15a : EFFECT OF COAL DOSAGE ON ADSORPTION OF COPPER.
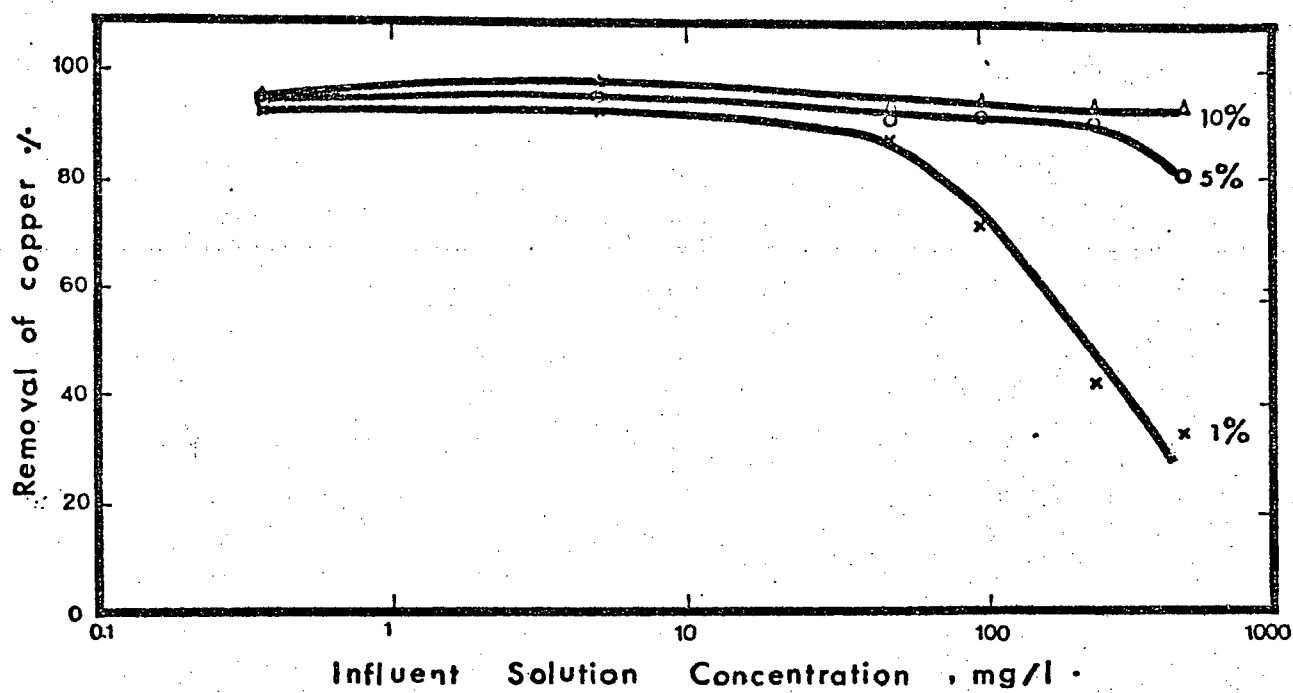
FIGURE 15b : CONTACT PROCESS, COPPER.
EFFECT OF COAL DOSAGE.

coal particle size:0.2965mm.
contact time:8 hours.

TABLE 16. EFFECT OF SOLUTE CONCENTRATION ON THE ADSORPTIVE CAPACITY OF MERCURY.

Contact Time: 4 hours
Coal dosage: 1% w/w
Mean coal particle size: 0.2965 mm.

| Influent Solution Conc. mg/1 | Effluent Conc. mg/1 | mg Hg Removed per gm Coal | % Removal |
|---|---|---|---|
| 0.1 | <0.031 | 0.0069 | >69 |
| 0.5 | <0.04 | 0.046 | >92 |
| 5 | 0.112 | 0.4888 | 97.76 |
| 50 | 0.35 | 4.965 | 99.3 |
| 100 | 0.5 | 9.95 | 99.5 |
| 250 | 12.56 | 23.744 | 94.98 |
| 500 | 56 | 44.4 | 88.8 |

increases with increasing the equilibrium concentration of the metal ions. The rate of increase differs for different metal ions, as shown in results included in Appendix C-2-4-3.

In the case of mercury the rate of increase is linear as shown in Figure 16a which indicates the direct proportionality of the increase in coal capacity with the increase of metal concentration. The results confirm that a multiple increase of 5 times the concentration of mercury will be equivalent to 5 times the increase in the adsorptive capacity of coal. A similar linear relationship is obtained in the case of adsorption of lead. With other metals, such as copper, zinc and cadmium, a non-linear increase in capacity with increasing concentration is obtained which is shown in Figure 16b for copper. Cadmium and zinc show the same shape of a curved line. Also this graph shows that the increase in the solute concentration is accompanied by a gradual drop in the removal efficiency of such metals, while in the case of mercury no appreciable drop in efficiency is noticed.

Chromium exhibits a different behavior as it has the poorest adsorptive capacity among the metals examined. The results indicate that the adsorptive capacity continues to increase with an increase in the concentration up to 200 ppm, after which a significant drop in capacity was noticed. Therefore, the relationship between solute concentration and adsorptive capacity can be considered rather than a system-specific which exhibits different behaviors in different adsorption systems.
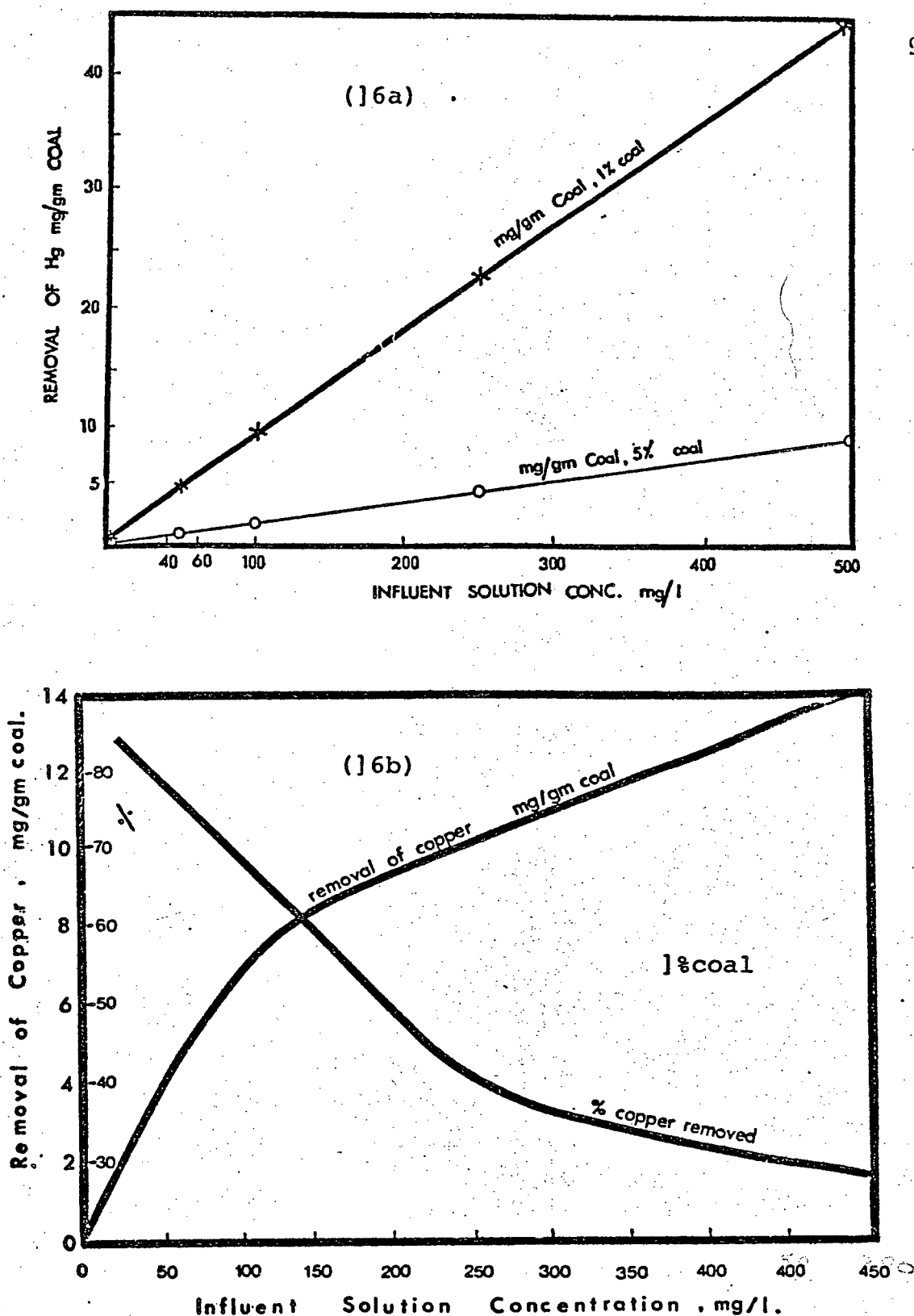
FIGURE 16 : EFFECT OF METAL ION COCENTRATION ON ADSORPTION.

a- MERCURY.

b-COPPER.
coal size:0.2965, contact time:4hrs.

Apparently, the affinity of the metals towards coal controls the nature of such a relationship. For example, metals with the highest affinity exhibit a linear relationship.

4.1.3.4 Particle size of coal

The isotherm tests conducted with four different particle sizes of coal ranged from granular 0.533 mm average to less than 0.03414 mm.

Generally, all the results (Appendix C-2-4-4) show that reduction in the particle size of coal would increase the adsorptive capacity. However, the breaking up of large particles to form smaller ones quite probably serves to open some tiny channels in the coal which then become available for adsorption, thus slightly increasing the dependence of equilibrium capacity on particle size above a simple variation with the inverse of the diameter (Weber, 1963).

Figure 17a shows that the effect of particle size is less significant at lower concentrations. The inverse relationship between the particle size and the adsorptive efficiency is illustrated in Figure 17b. Higher equilibrium concentrations are obtained when larger particle sizes of coal were used. Also the data show that the effect of the particle size on the adsorption process is not significant when higher carbon dosages are used. The obtained relationship, shown on the above mentioned figures, indicates that the variation should be with the reciprocal of some higher power of diameter rather than a simple power. This means that intraparticle
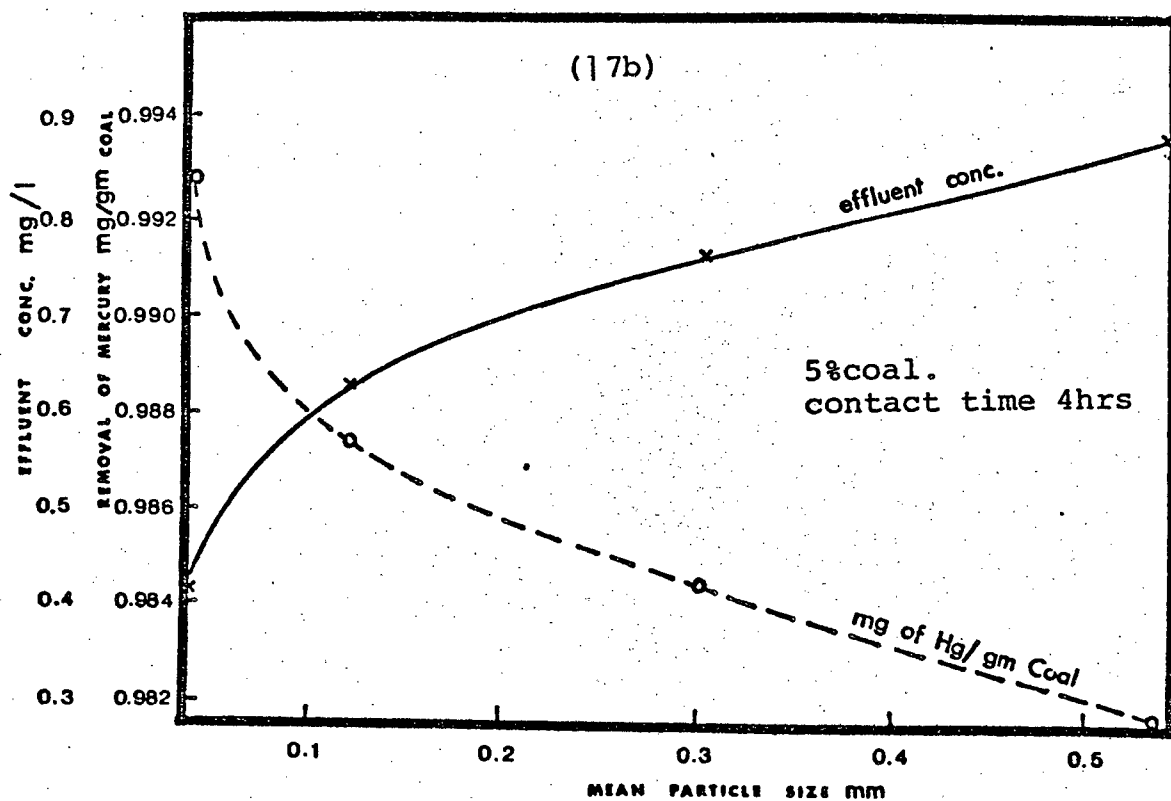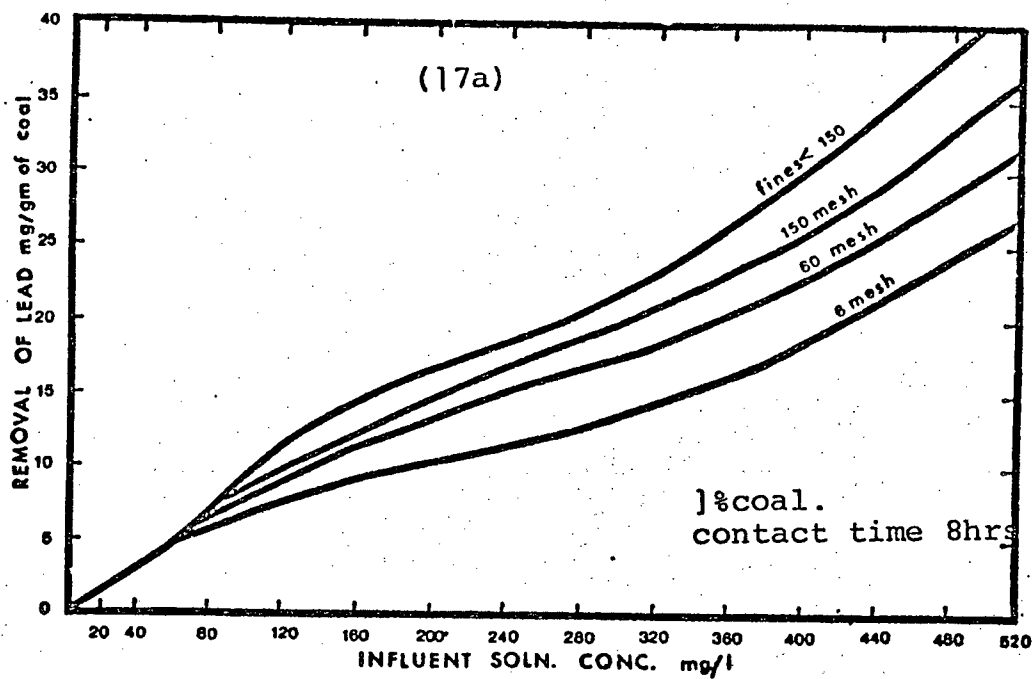
FIGURE 17 : EFFECT OF PARTICLE SIZE OF COAL ON ADSORPTION.
a- LEAD.          b- MERCURY.

transport is involved rather than a simple mechanism of adsorption on specific external sites (Crank, 1956).

However, upon statistical analysis of all factors considered, the effect of particle size is relatively the least significant parameter. The point is shown clearly in the table of analysis, included in Appendix C-2-5.

4.1.4 Statistical analysis

The 4-way analysis of variance technique (Leclerg 1966) was applied to test the significance of the main variables (described in Section 4.1.3) and their interaction. A summary of this analysis is included in Appendix C-2-5. The results show that the main variables are highly significant. In addition, a highly significant two-way and three-way interaction between variables is shown, which are very difficult to interpret statistically and usually lead to misleading conclusions.

Therefore, it is not recommended by statisticians*
to consider the result of a statistical analysis in the discussion of this work.

Neglecting the interaction problem, the results of the analysis regarding the main effects are in very good agreement with the expected conclusions from the experimental data.

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* Kozac, A., Professor of Statistics and Biometrics, Dept. of Forestry, U.B.C., personal communication.

4.1.5   Column adsorption tests

In this semi-continuous experiment, the same magnitude

and order of metal ion concentrations was employed as in the

batch tests.

The detailed tables of results including the test of

the effect of different variables on the process are listed in

Appendix C-2- 6.   Further tables and the corresponding graphs

may be found elsewhere (Coulthard, 1974).

The graphical representation of the data obtained for

mercury when 500 mls of solution of different concentrations

was applied through the coal bed, are shown in Figure 18 .

The results and graphs obtained with the other heavy metals are

very similar to that shown for mercury.   All experimental results

show that the column   process is the most effective method to

be applied for the adsorption of metal ions by coal.   All metal

ions were removed with an efficiency approaching 100% for all

initial concentration levels.

A comparison between the adsorption efficiency of the

six metals is summarized in Table 17.

It is obvious that the order of affinity of the six

metals from the  column  test is very similar to that obtained

with batch tests.   While mercury and lead have the highest

affinity, chromium exhibits the lowest one and the other metals

range between these two.
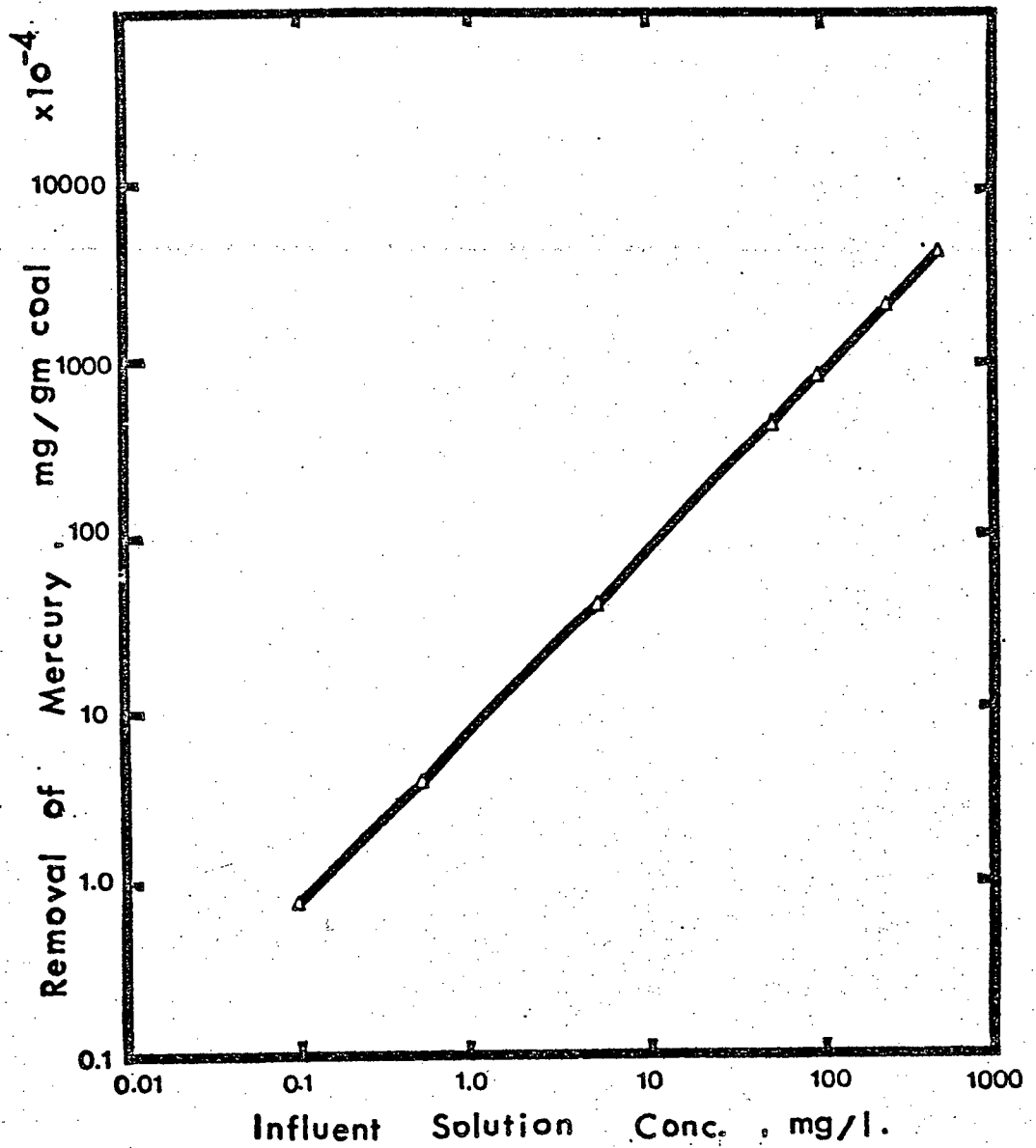
FIGURE 18 : COLUMN ADSORPTION PROCESS , MERCURY.

        flow rate:0.3gpm/ft$^2$,

        contact time: 30 minutes,

        coal particle sizes:0.533,0.2965,0.117&0.03414 mm

# TABLE 17. COLUMN ADSORPTION PROCESS

COMPARISON BETWEEN ADSORPTION OF
DIFFERENT HEAVY METALS.

Volume of Solution = 500 mls
Rate of Flow = 0.3 gpm/ft$^2$
Contact Time = 30 minutes
Depth of Column = 9 inch
(600 gms Coal) 0.2965 mm

| Heavy Metals Tested | 1 MERCURY | | 2 LEAD | | 3 COPPER | | 4 CADMIUM | | 5 ZINC | | 6 CHROMIUM | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solution Conc. mg/l | $C_e$* | % Removal | $C_e$ | % Removal | $C_e$ | % Removal | $C_e$ | % Removal | $C_e$ | % Removal | $C_e$ | % Removal |
| 0.1 | >0.002 | >98-100 | <0.018 | >91-100 | - | - | <0.003 | > 98.5 | - | - | <0.02 | >80.0 |
| 0.2 | - | - | <0.018 | >95.5-100 | - | - | <0.003 | > 98.5 | - | - | - | - |
| 0.5 | 0.0055 | 98.9 | <0.02 | >98-100 | <0.048 | >90.4-100 | <0.004 | > 99.2 | 0.057 | 88.60 | <0.02 | >96.0 |
| 5.0 | >0.002 | 99.96 | <0.02 | >99.8-100 | 0.056 | 98.88 | <0.03 | > 99.7 | 0.067 | 98.66 | <0.045 | >99.0 |
| 50.0 | 0.008 | 99.98 | <0.02 | > 99.98 | 0.087 | 99.83 | <0.03 | > 99.97 | 0.050 | 99.90 | 0.08 | 99.84 |
| 100.0 | 0.0088 | 99.99 | - | - | 0.156 | 99.84 | - | - | 0.059 | 99.94 | 0.16 | 99.84 |
| 250.0 | 0.0110 | 99.99 | - | - | 0.139 | 99.94 | - | - | 0.075 | 99.97 | 0.08 | 99.96 |
| 500 | 0.0045 | 100.0 | <0.02 | >99.99 | 3.401 | 99.34 | <0.03 | > 99.997 | 2.39 | 99.52 | 0.27 | 99.95 |

* $C_e$ = equilibrium concentration mg/l

SENSITIVITIES: Pb = 0.06    Cu = 0.003 )
Hg = 0.002    Zn = 0.01 ) mg/l
Cd = 0.005    Cr = 0.05 )

In column adsorption tests, the time of contact is of
greater importance than solute concentration or particle
size as shown in the analysis listed in Appendix C-2-6.
This gives a great advantage for the coal when used in
practice for wastewater treatment. This short term column
test allowed only a rough evaluation of the method's
effectiveness. The throughput volume of 500 milliliters
was not sufficient to estimate the adsorptive capacity and
service life of the coal in the bed and therefore the longer
term experiments were conducted.

4.1.6    Long term column adsorption

The results reported in Appendix C-2-7 are a record
for the daily effluent concentration of lead influent and the
corresponding effluent at each 1 foot level throughout the bed
depth, beginning at the 15.25 cm level. The data displayed
in Figure 19 show the beneficial effectiveness of the coal
to adsorb lead ions by operating continuously for approximately
32 days. During that period of time, 1007 Imp gallons of
solution reduced the 1½ ft level effluent concentration to
0.03 mg/l of lead which is well below the drinking water
standard of 0.05 mg/l, recommended by both B.C. guidelines
and APHA.

The adsorption capacity during this period was
evaluated as 9.66 mgs lead ions per gram of coal on the basis
of the break through point at 0.5 mg/l effluent concentration
from the 6" level. The efficiency of removal was high and
approaching more than 80% in value. The details of this
estimation is described in Appendix C-2-7.
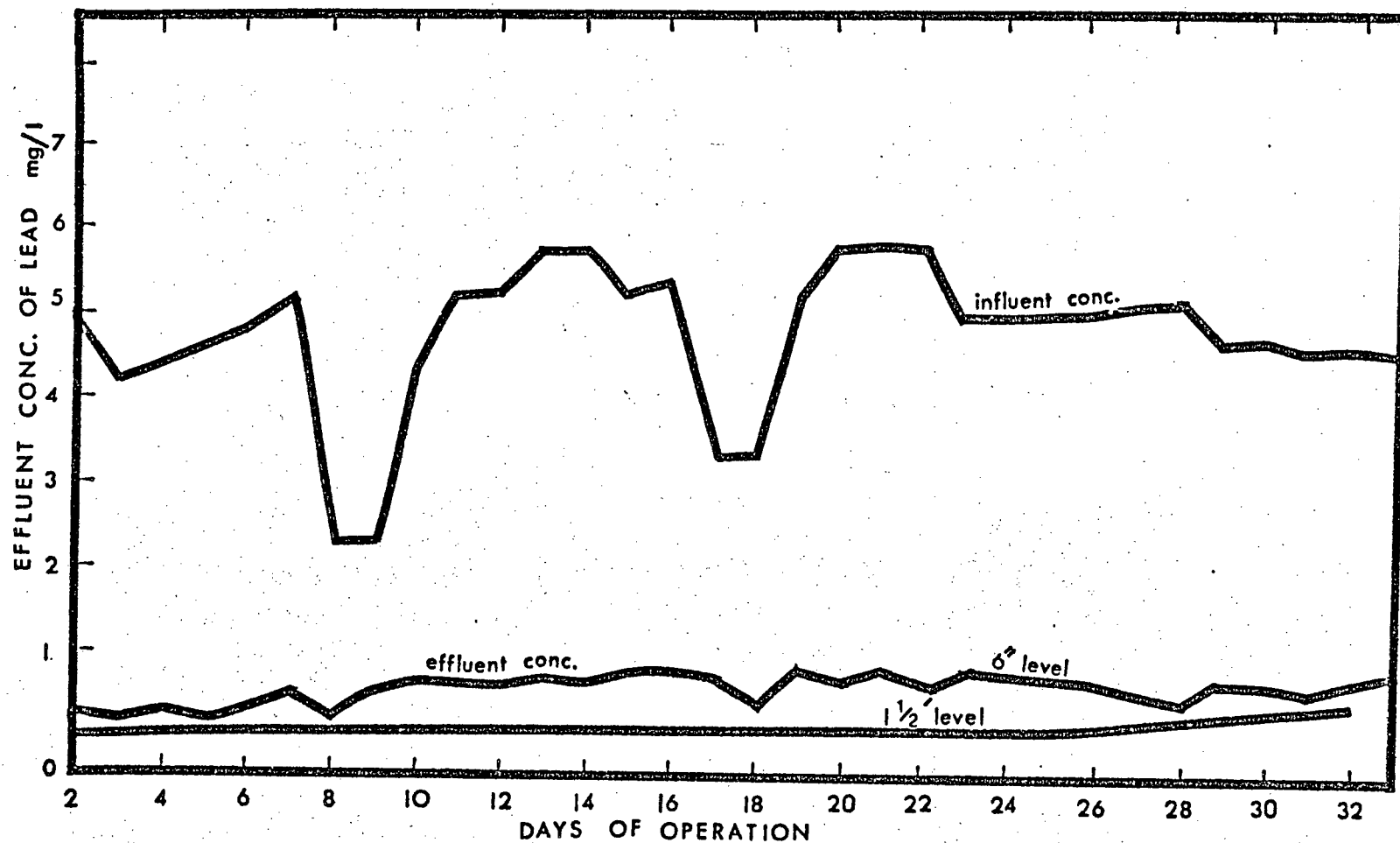
FIGURE 19 :   REMOVAL OF LEAD THROUGH COAL COLUMN
diam.6"(15.24cm.) x 2m. length.

4.1.7     Selectivity in adsorption of mixed metals

A mixture of the six metals, consisting of about 5 mg/1 of each were applied through the same bed, previously used for the adsorption of lead.

Results from monitoring the equilibrium concentrations during a period of operation of 19 days continuous operation are shown in Appendix C-2-8, while some of the data are displayed in Table 18.

Surface coal appears to have a specific selectivity towards each metal ion when they are present in combinations. A comparison between the effluent concentrations of each metal at the 45 cm level after 19 days is represented by a bar graph shown in Figure 20. The graph shows that coal exhibits the highest selectivity towards mercury, then lead, while zinc seems to be the least selective metal.  Here the sequence is as follows:  Hg > lead > chromium > copper > Cd > Zn.  This result is in accordance with that obtained by Riaz for the sequence of Pb > Cu > Zn, (Riaz, 1974).

The sequence of affinity of the six metals combined towards coal is generally in accordance with that obtained on an individual basis which was previously discussed in Section 4.1.1.  The only exception is with chromium which exhibits much higher adsorption when it is in the mixed state than in a case of the individual state.  The reason for this behavior was not studied during this work, but it may be suggested to be due to some synergistic effect when the chromium ions are mixed with the other metal ions.

TABLE 18. LONG TERM ADSORPTION PROCESS THROUGH LARGER COLUMN. COMPARISON BETWEEN THE ADSORPTION OF DIFFERENT HEAVY METALS. DAYS OF OPERATION 19 DAYS.

Column diameter 6" (15.24 cm)  Coal depth 2 meters  Coal size 0.533 mm

| Sampling Point | 1 Mercury | 2 Lead | 3 Chromium | 4 Copper | 5 Cadmium | 6 Zinc |
|---|---|---|---|---|---|---|
| Influent | 6.0 | 5.790 | 6.040 | 5.986 | 5.48 | 5.56 |
| 6" Level | 1.780 | 6.200 | 3.87 | 6.204 | 5.73 | 5.97 |
| 1½ ft Level | 0.08 | 0.306 | 0.441 | 1.59 | 5.42 | 6.58 |
| 2½ ft Level | 0.023 | 0.0234 | 0.098 | 0.0717 | 0.220 | 0.761 |
| 3½ ft Level | 0.0124 | 0.0127 | 0.057 | 0.0431 | 0.0016 | 0.033 |
| 4½ ft Level | 0.0094 | -- | 0.037 | 0.0528 | 0.0013 | 0.072 |
| 5½ ft Level | 0.0068 | - | 0.034 | 0.0604 | 0.00087 | 0.0475 |
| 6½ ft Level | 0.0062 | - | 0.032 | 0.085 | - | 0.072 |
| 7 ft Level | 0.0066 | 0.0151 | 0.0304 | 0.066 | - | 0.129 |

Values in mg/l.

106.
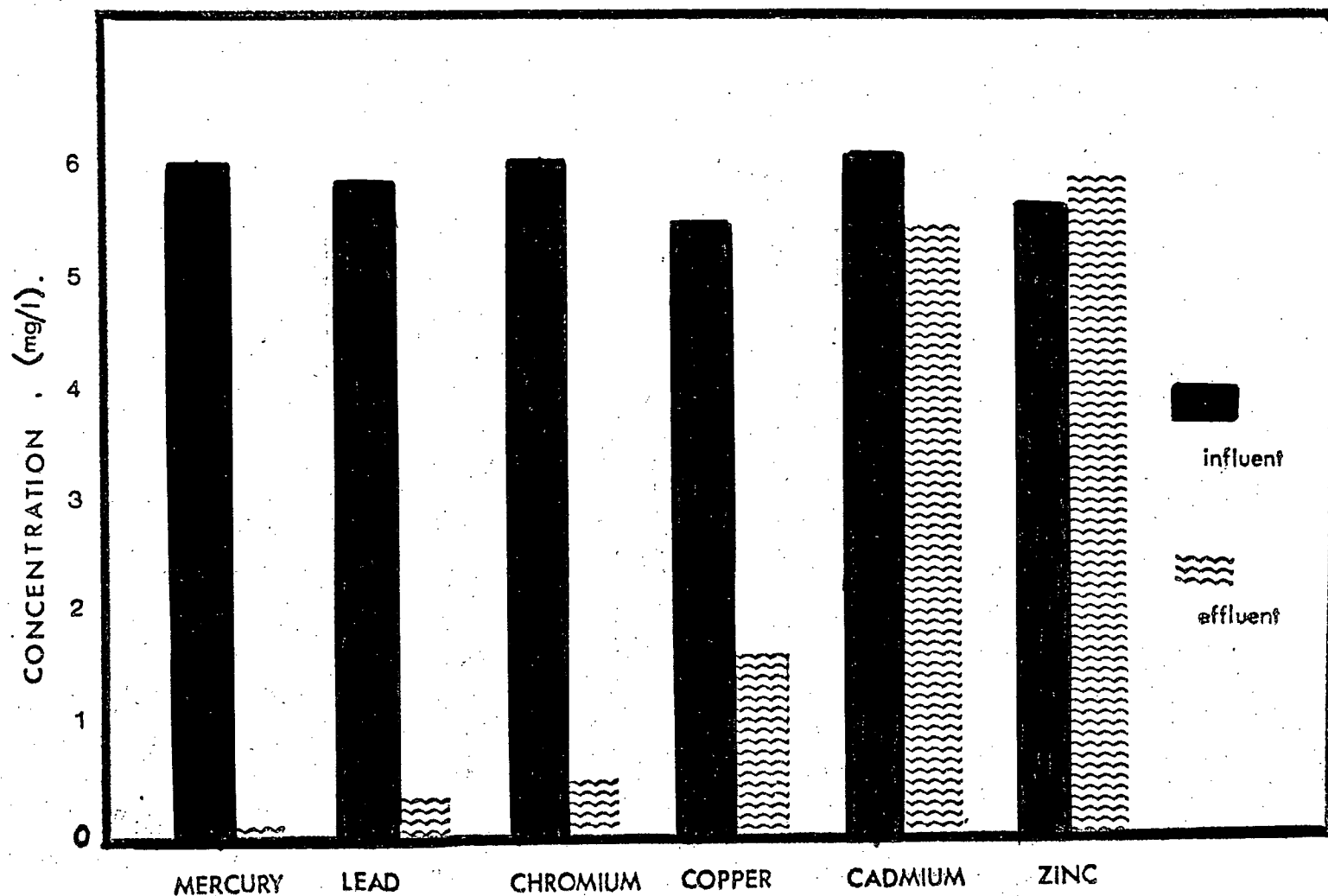
FIGURE 20 : SELECTIVITY IN ADSORPTION OF MIXED METALS BY COAL.

operation:19days ,1.5ft.(46cm.)level,
column size:15.24cm.I.D.X2m.length.
coal particle size:0.533mm.

It is obvious that the presence of other metals in the solution detract from the removal capacity for the single metal. A much more rapid break through of these metals was noticed. As a general conclusion, the coal seems to retain its capability of reducing the effluent concentration of different metals in the mixture to a level comparable with that of single metals.

4.2  Dissolved organics

4.2.1 Contact process

The tables of results, included in Appendix C-3-1 are represented in Figures 21a and b which show the adsorption isotherm regression lines for Hat Creek coal in comparison to activated carbon for the removal of $BOD_5$ and COD respectively.

The isotherms are the Freundlich type, therefore, the empirical Freundlich formula can be applied in this case up to an equilibrium concentration of 400 mg/1 $BOD_5$ and the adsorptive capacities for different systems are estimated by the extrapolation of the isotherm line to the initial concentration $C_i$ as shown in Figures 21a and b. Table 19 compares the estimated capacities for coal and activated carbon in terms of $BOD_5$ and COD.

The above results show that granular activated carbon has approximately 6 times the adsorptive capacity of granular coal with the same particle size, while the powdered coal seems to have a comparable capacity with granular activated carbon as measured on a COD basis.
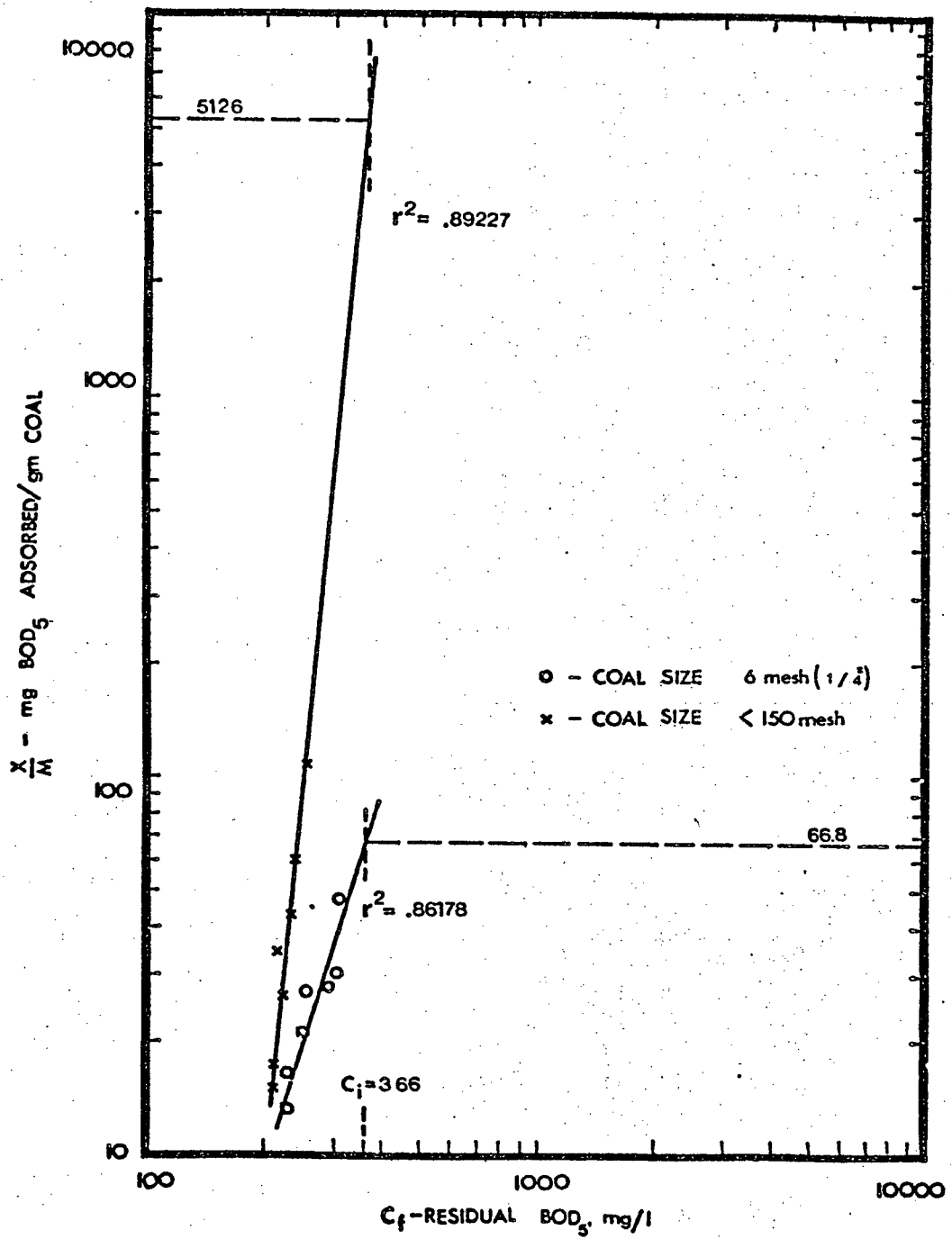
FIGURE 2|a : ADSORPTION ISOTHERMS FOR REMOVAL OF $BOD_5$ BY COAL.

contact time : 4 hours.
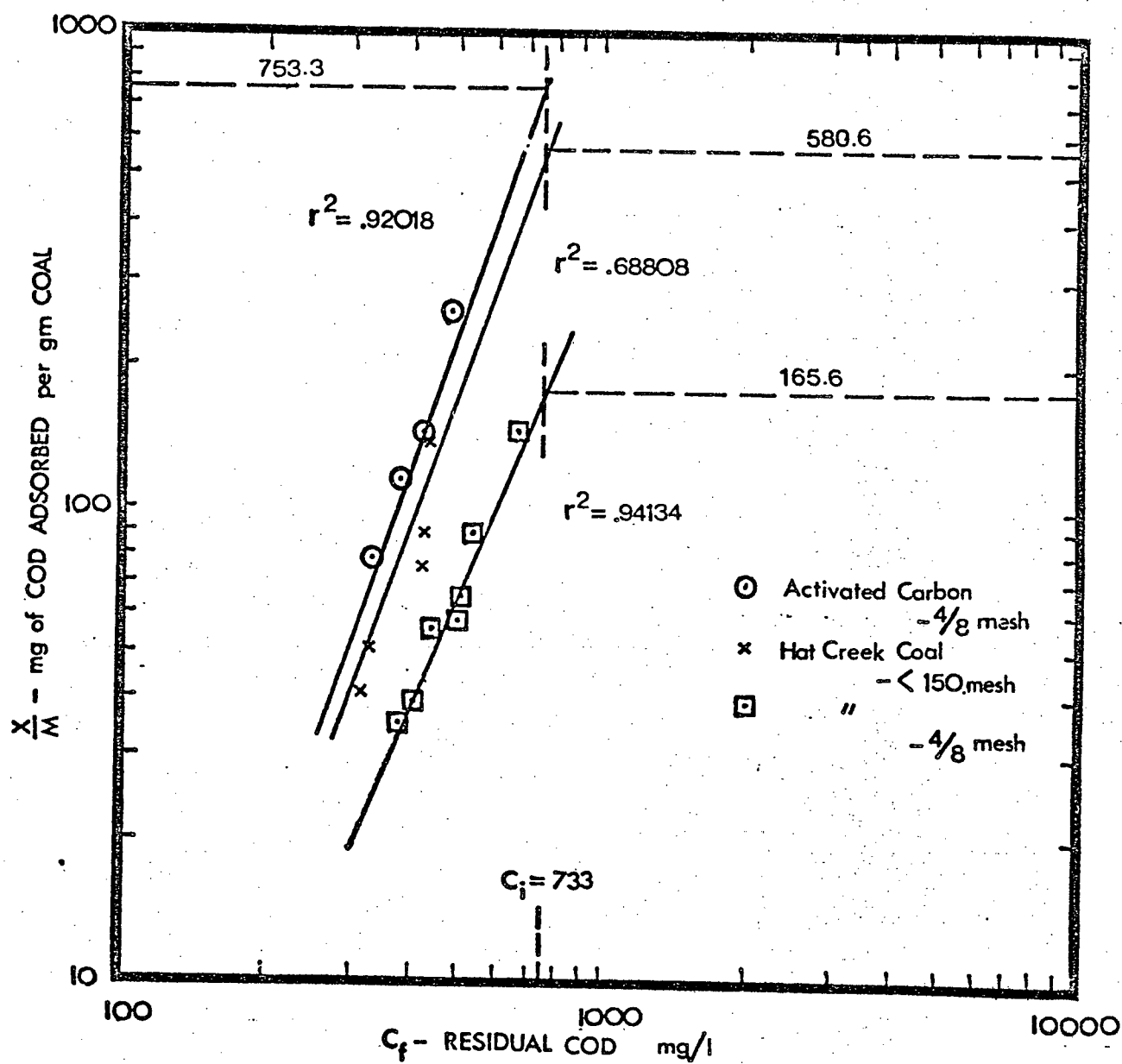
FIGURE 21b : ADSORPTION ISOTHERMS FOR REMOVAL OF COD BY COAL.
contact time : 4 hours.

TABLE 19.    COMPARISON OF ADSORPTIVE CAPACITIES OF COAL
            AND ACTIVATED CARBON

| Adsorbent | Estimated adsorptive capacity mgs/gm adsorbent | |
| --- | --- | --- |
| | BOD$_5$ | COD |
| Activated carbon 4/8 mesh | — | 753.3 |
| Hat Creek coal 4/8 mesh | 66.4 | 165.6 |
| Hat Creek coal < 140 mesh | 5126.0 | 580.6 |

Also, the reduction of the coal particle size seems to have a great effect on the increase of the capacity to remove BOD$_5$ from organic solutions.

4.2.2  Column process

The results of the adsorption experiments on columns containing coal of the 0.533 mm and 0.2965 mm particle sizes are listed in Tables 1 and 2 respectively in Appendix C-3-2.

The BOD$_5$ and COD values for the 0.2965 mm size coal bed are displayed graphically in Figure 22a. The results indicate clearly that BOD$_5$ and COD values can be lowered substantially with a granular coal media bed. However, it is necessary to allow the bacteria to develop for a short period of time as shown by the comparison of values for analysis of the first liter of application to that of subsequent sampling analysis. The efficiency of removal of BOD$_5$ reaches up to 90% while 75 to 80% for COD values as shown in
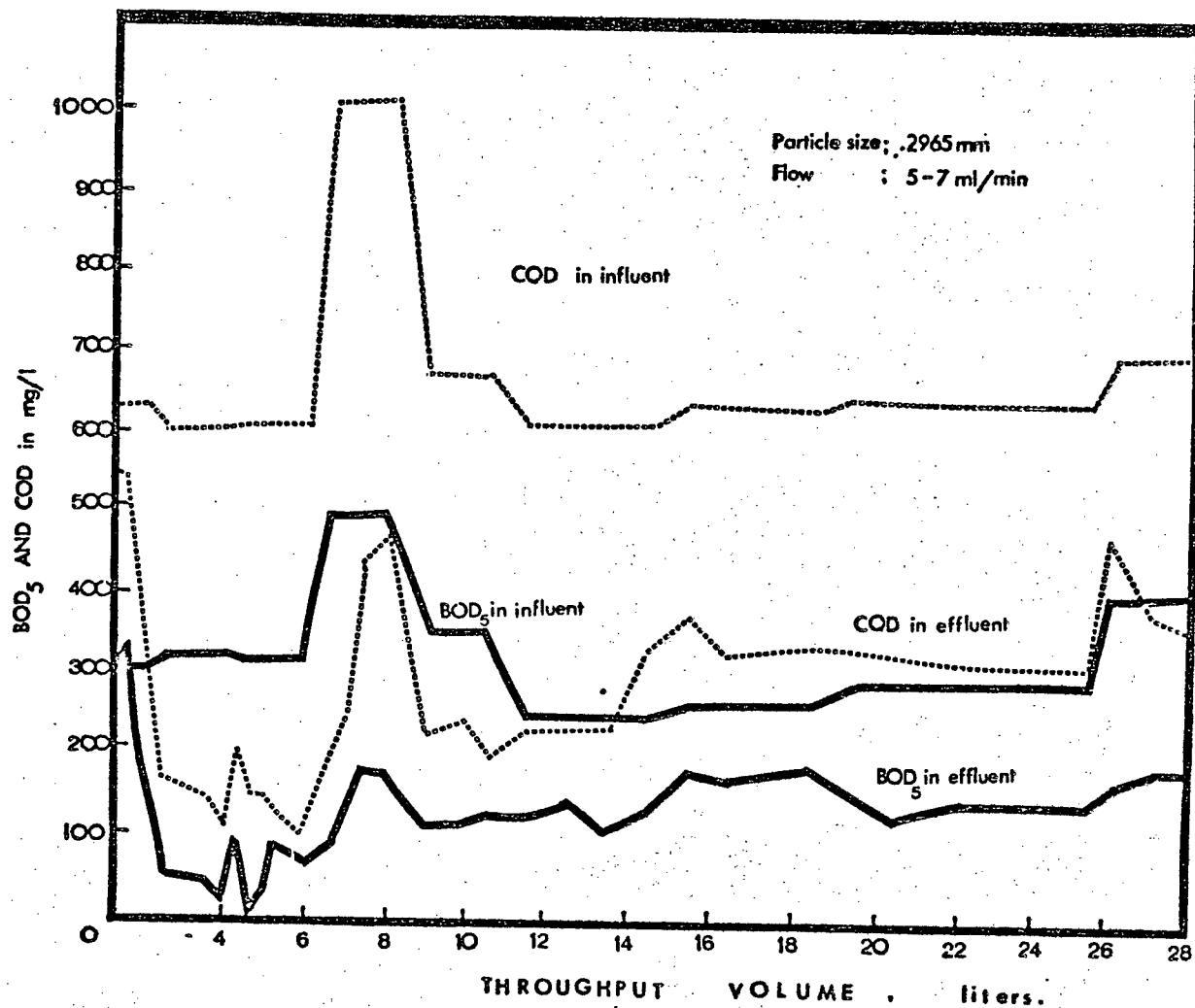
FIGURE 22a : REDUCTION OF BOD$_5$ & COD BY LEACHING OF BEEF
EXTRACT SOLUTION THROUGH COAL COLUMN
SIZE : 7cm.I.D. X 20cm. length.
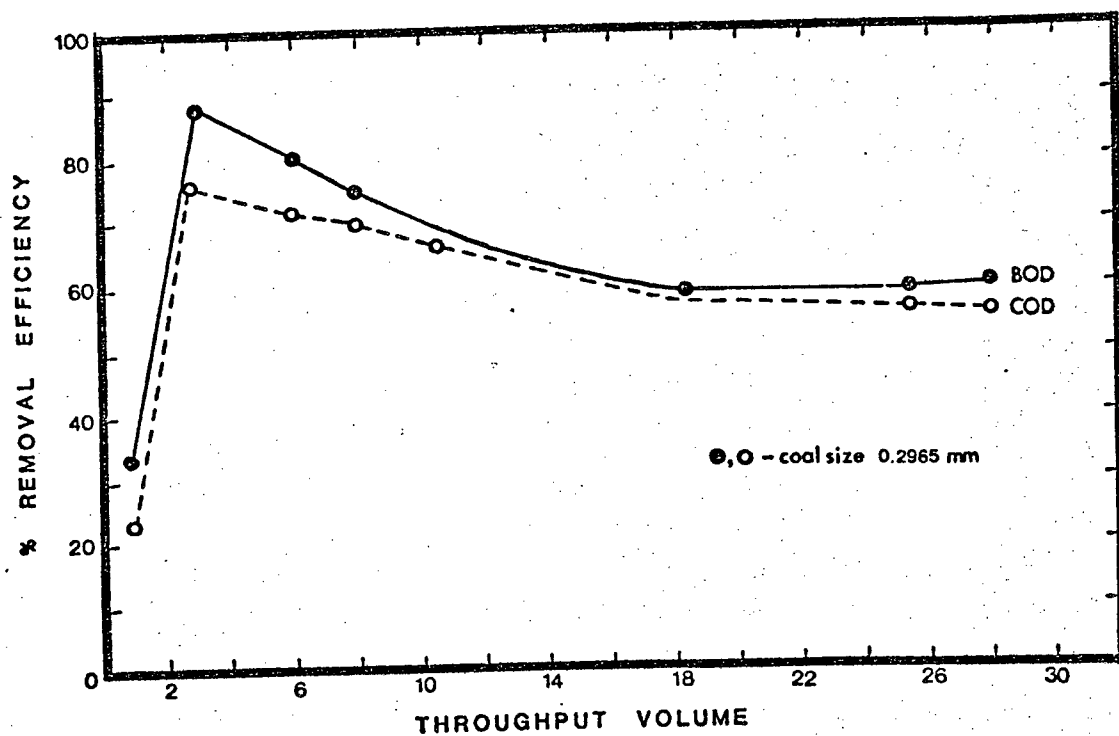
FIGURE 22b : EFFICIENCY OF REMOVAL OF $BOD_5$ &COD BY LEACHING
OF BEEF EXTRACT THROUGH COAL COLUMN
SIZE : 7cm.I.D. X 20cm. length.

Figure 22b; continuing efficient levels are shown to continue up to 28-30 liters of volume throughput. Nevertheless, the efficiencies slightly declined from the maximum levels due to the formation of multiple layers of bacterial slime indicated by a leakage of the $BOD_5$ and COD (appreciable values in the effluents) in addition to the gradual decrease in the hydraulic conductivity. To improve this condition, backwashing with tap water was used, but it does not bring the column back to its full original effectiveness.

A comparison of the results for the 0.533 mm and the 0.2965 mm particle sizes of coal indicates that the larger coal size is advantageous because it allows for lower head loss and consequently better hydraulic conductivity. However, one must recognize the lower organic removal capacity at the high flow rate, as shown for the 50 ml/min rate, compared to the 5 to 7 ml/min flow rate. The cumulative effect of a bed loading and the corresponding cumulative removal is shown in Figures 23a and b for $BOD_5$ and COD respectively for the two sizes of coal. It would appear that both columns have the capacity to accept much higher total load before they reach a saturated condition. A "levelling out" of the curve would indicate the saturated conditions.

The relationship between $BOD_5$ and COD cumulative for the two coal sizes is plotted graphically in Figure 23c which shows an almost linear relationship. The linear regression analyses of the data for a coal size of 0.533 mm is as follows:
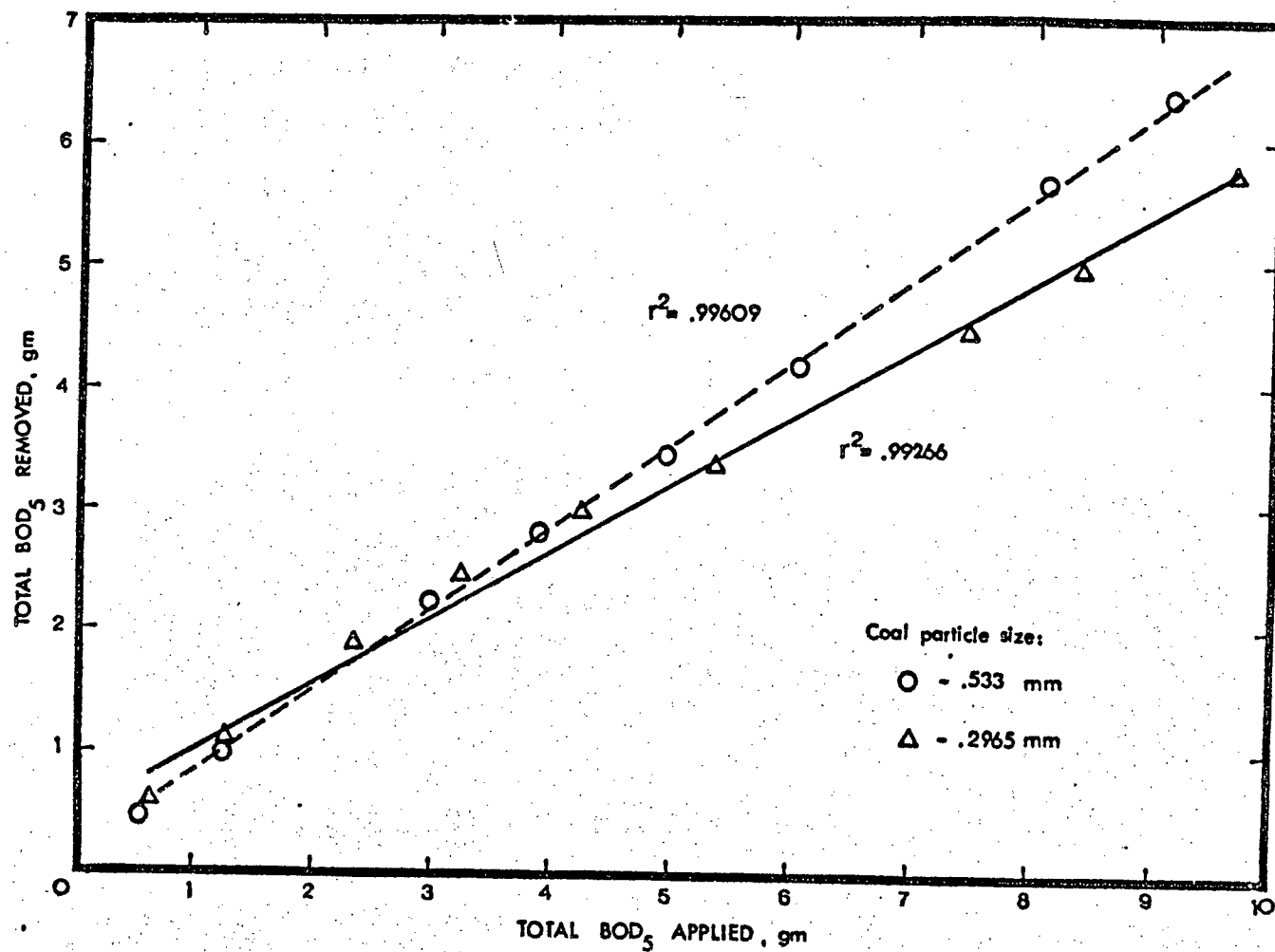
FIGURE 23a : CUMULATIVE REMOVAL OF $BOD_5$

LEACHING OF BEEF EXTRACT SOLUTION THROUGH

COAL COLUMN (20cm X 7cmI.D.).
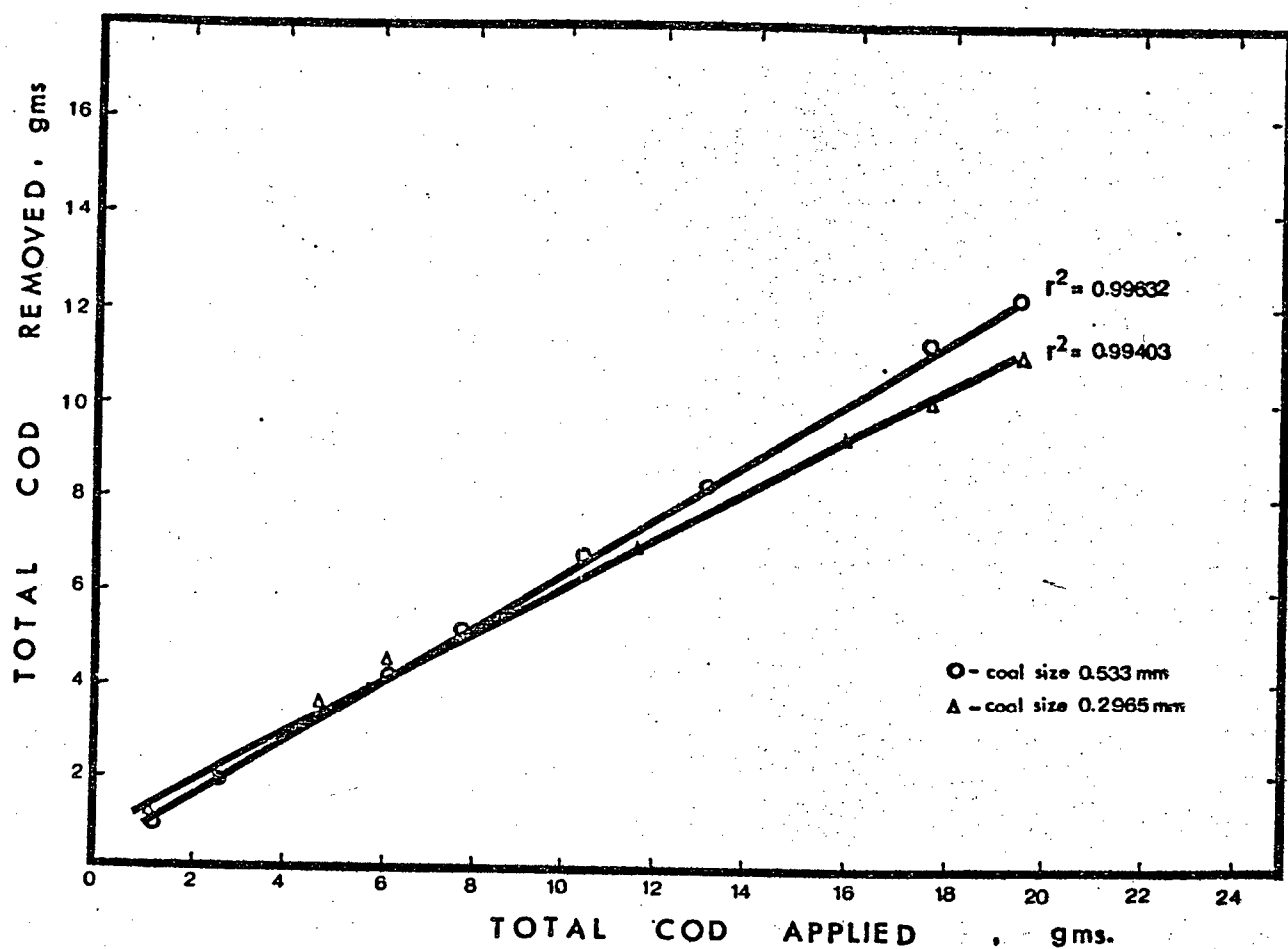
FIGURE 23b : CUMULATIVE REMOVAL OF COD ,
        LEACHING OF BEEF EXTRACT SOLUTION THROUGH
            COAL COLUMN (20cm. X 7cm.I.D.).
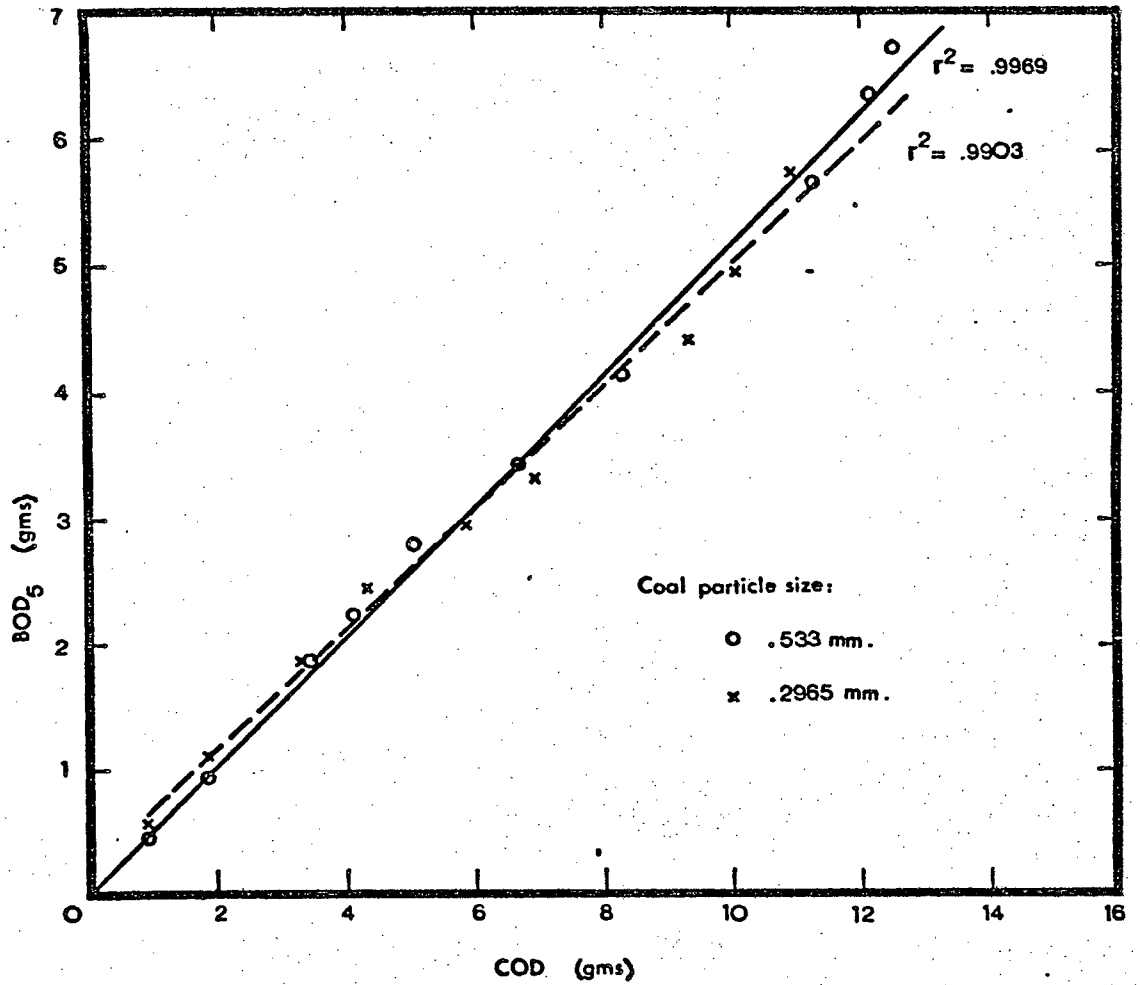
FIGURE 23c : RELATIONSHIP BETWEEN $BOD_5$ AND COD.

CUMULATIVE REMOVAL.

$$BOD_5 \text{ value} = 0.01485 + 1.91085 \text{ COD value}$$
$$(r^2 = 0.9969)$$

For a coal size of 0.2965 mm the relationship would be

$$BOD_5 \text{ value} = -0.29356 + 2.052 \quad \text{COD value}$$
$$(r^2 = 0.99017)$$

In both cases, it is noted that the two lines have very similar slopes and intercepts. Therefore these constants can be used to correlate approximately the $BOD_5$ to the COD values.

4.2.3 Mixed organics and toxic metals

To investigate the effect of mixed organics and toxic metals in sewage effluent, beef extract solution was mixed with 0.2 mg per liter of lead. This concentration of lead applied in this experiment was based on the average lead concentration in Iona Sewage effluent. It is evident from the results shown in Table 20 that $BOD_5$, COD and lead were removed to a satisfactory level. During the inoculation "run" the lead was removed almost completely, reaching a level in the effluent of < 0.05 mg/l. Also removal efficiency for $BOD_5$ and COD seems to be higher than that previously obtained for only dissolved organics. Enhancement of the dissolved organic removal, in the presence of metal ions, can be due possibly to a co-adsorption phenomenon which is a result of a cooperative action of adsorbates in which solutes are able to enhance the adsorption of certain other solutes (Hassler, 1974).

4.2.4 Comparison of coal with sand

The value of coal as an adsorbent is compared with that of construction sand which is considered as a porous medium.

TABLE 20. COLUMN LEACHING OF DISSOLVED ORGANICS

REMOVAL OF $BOD_5$, COD AND LEAD

(20 cm X 7 cm I.D.) COLUMN

Coal Size: 0.533 mm
Rate of Flow: 6-8 ml/min.

| | FIRST RUN VOLUME = 2 LITERS | | | | | | SECOND RUN VOLUME = 2 LITERS | | | | | | REMARKS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Influent I | Effluent (1) | Eff. (2) | Eff. (3) | Eff. (4) | Eff. (5) | Influent II | Effluent (1) | Eff. (2) | Eff. (3) | Eff. (4) | Eff. (5) | |
| Service Time $BOD_5$ Test | | 1 hr | 2hr | 3hr | 4hr | 5hr | | 1 hr | 2hr | 3hr | 4hr | 5hr | |
| $BOD_5$ mg/l | | 125 | 85 | 78 | 95 | 15 | | 2C0 | 117 | 128 | 142 | 46 | A bacterial inocula-tion of the column with 1 liter of about 300 mg/l beef extract followed by washing & drying preceded the first run. |
| $BOD_5$ Removed mg/l | 330 * | 205 | 245 | 252 | 235 | 315 | 580 * | 380 | 463 | 452 | 438 | 534 | |
| % Removal | | 62 | 74 | 76 | 71 | 96 | | 66 | 80 | 78 | 76 | 92 | |
| COD TEST | | | | | | | | | | | | | |
| COD mg/l | | 296 | 208 | 208 | 232 | 144 | | 400 | 320 | 296 | 265 | 173 | |
| COD Removed mg/l | 688 * | 392 | 480 | 480 | 456 | 544 | 1120 * | 720 | 800 | 824 | 855 | 947 | |
| % Removal | | 57 | 70 | 70 | 66 | 79 | | 64 | 71 | 74 | 77 | 85 | |
| LEAD TEST | | | | | | | | | | | | | Since maximum sensitivity of the machine is 0.02 mg/l the percentage de-tectable removal expected to be 100% for all con-centrations below 0.02 mg/l Pb. |
| Pb mg/l | | 0.03 | 0.03 | <0.02 | <0.02 | <0.02 | | 0.05 | 0.03 | <0.02 | <0.02 | <0.02 | |
| Pb Removed mg/l | 0.2 * | 0.17 | 0.17 | >0.18 | >0.18 | >0.18 | 0.2 * | 0.15 | 0.17 | >0.18 | >0.18 | >0.18 | |
| % Removal | | 85 | 85 | > 90 | > 90 | > 90 | | 75 | 85 | > 90 | > 90 | > 90 | |

* Concentration of the influent solution applied.

119.

The results of comparison for reduction of $BOD_5$ and COD are shown in Table 21 and the corresponding graph 24.

The results clearly indicate the superior value of coal over that of sand, especially after the inoculation period which allows for development of a good bacterial culture on the coal surface compared to the sand. This may be due to the presence of mineral nutrients as well as the carbon as a major constituent of the coal, while the major constituent in sand is silica which does not allow the bacterial development as significantly as in the case of coal. In addition, the coal has a larger internal surface area due to its numerous fractures and porosity while the sand particles do not possess these properties.

The results obtained may be compared to experiments conducted by the FMC Corporation (1971) which shows that the coal bed had little adsorption compared to activated carbon but had an effective biological capacity activity and correspondingly an increase in its adsorptive capacity to a highly acceptable level.

4.3  Phosphates

4.3.1  Contact process

The results from the various batch tests conducted under different conditions are shown in Tables 1 to 6 inclusive in Appendix C-4-1.

The effect of the contact time was first studied at 1 hour, 3 hours and 6 hours. The results indicate that 6 hours

TABLE 21. COMPARISON BETWEEN HAT CREEK COAL
AND CONSTRUCTION SAND FOR REMOVAL
OF DISSOLVED ORGANICS.

Coal Size:            0.2965 mm
Sand Size:   From 60 to <300 mesh

| Times, hrs | First Run: 1 liter (Inoculation) 3 hrs | | Second Run: 2 liters 6 hrs | |
|---|---|---|---|---|
| | Coal | Sand | Coal | Sand |
| **I: BOD TESTS** | | | | |
| — BOD of the Influent mg/l | 310 | 312 | 326 | 295 |
| — BOD of the Effluent mg/l | 245 | 196 | 52<br>44<br>22 | 194<br>252 |
| — BOD Removed mg/l | 65 | 116 | 274<br>282<br>304 | 101<br>43 |
| — % Removal | 21 | 37 | 84%<br>87%<br>93% | 34%<br>15% |
| **II: COD TESTS** | | | | |
| — COD of the Influent mg/l | 640 | 648 | 620 | 635 |
| — COD of the Effluent mg/l | 494 | 471 | 176<br>150<br>120 | 467<br>454 |
| — COD Removed mg/l | 146 | 177 | 444<br>470<br>500 | 168<br>181 |
| — % Removal | 30 | 27 | 72%<br>76%<br>86% | 27<br>29 |
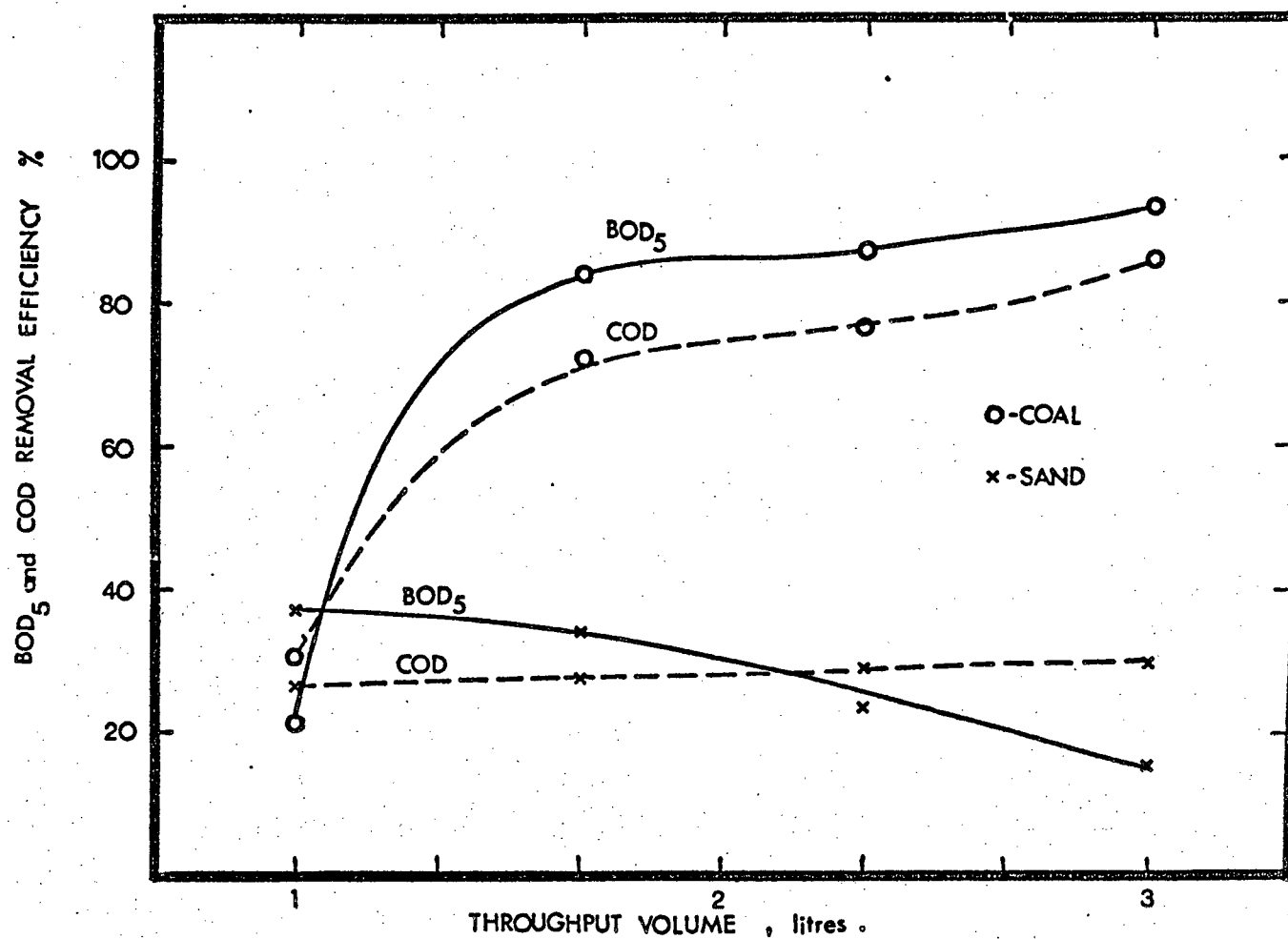
FIGURE 24 : COMPARISON BETWEEN THE EFFICIENCY OF REMOVAL
OF DISSOLVED ORGANICS BY COAL AND SAND BEDS.

123. 

contact is sufficient to attain equilibrium in the adsorption
system, and therefore all isotherm tests for phosphate have
been conducted at 6 hours contact.

Regarding the effect of particle size, the larger
particle sizes of coal exhibit poor adsorptive capacity for
phosphate. However, with finer sizes, the capacity gradually
increases as shown in Figure 25, also the efficiency of removal
reaches approximately 70% when a 1% addition of coal of
< 0.03414 mm (140 mesh) particle size was used.

For the same coal size, other adsorption isotherms
have been constructed using different amounts of coal -- 0.5%,
1% and 5% w/w. The results are in Table 22, and indicate
that by increasing the amount of coal added to 5% w/w, effective
removal could be obtained up to more than 90% with concentra-
tions of 5 mg/l and 10 mg/l of phosphate in the solution. This
is considered an excessive amount of coal for the contact
process in a commercial application.

4.3.2 Column process

The column adsorption process is more attractive for the
removal of phosphates. The tables of results are included in
Appendix C-4-2 and are represented by the break through curves
shown in Figure 26, respectively which are obtained with
coarse and fine coal sizes. The break through point for the
larger particle size, e.g. 0.533 mm is reached at a much
lower volume, while the smaller size gives better efficiency
of removal.
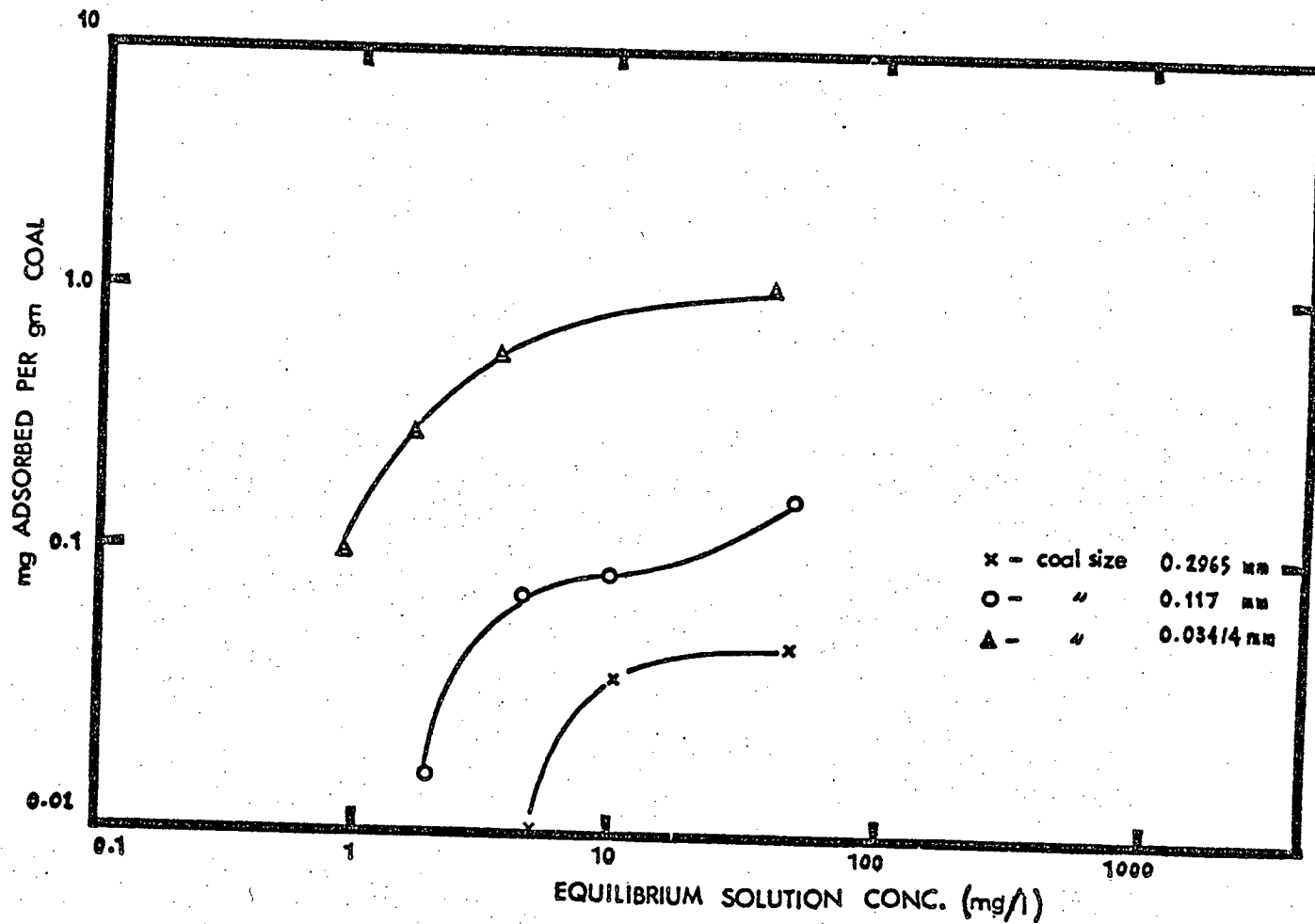
FIGURE 25 : ADSORPTION ISOTHERMS FOR REMOVAL OF PHOSPHATE
BY COAL.
contact time = 6hours.
coal dosage = 1%w/w.

Time:      6 hrs
Coal Size:      0.03414 mm av.

BATCH PROCESS

| % Coal Added | Influent conc.mg/l → 2 mg/l | | | 5 mg/l | | | 10 mg/l | | | 50 mg/l | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc mg/l | mg Removed per gm coal | % Removal | Effluent conc mg/l | mg Removed per gm coal | % Removal | Effluent conc mg/l | mg Removed per gm coal | % Removal | Effluent conc mg/l | mg Removed per gm coal | % Removal |
| 0.5 | 0.92 | 0.216 | 54.0 | 2.94 | 0.412 | 41.2 | 6.25 | 0.75 | 37.5 | 39.53 | 2.094 | 20.9 |
| 1.0 | 0.858 | 0.1142 | 57.1 | 1.56 | 0.344 | 68.8 | 3.46 | 0.654 | 65.4 | 38.0 | 1.2 | 24.0 |
| 5.0 | 0.46 | 0.0308 | 77.0 | 0.43 | 0.0914 | 91.4 | 0.64 | 0.1872 | 93.6 | 13.45 | 0.731 | 73.1 |
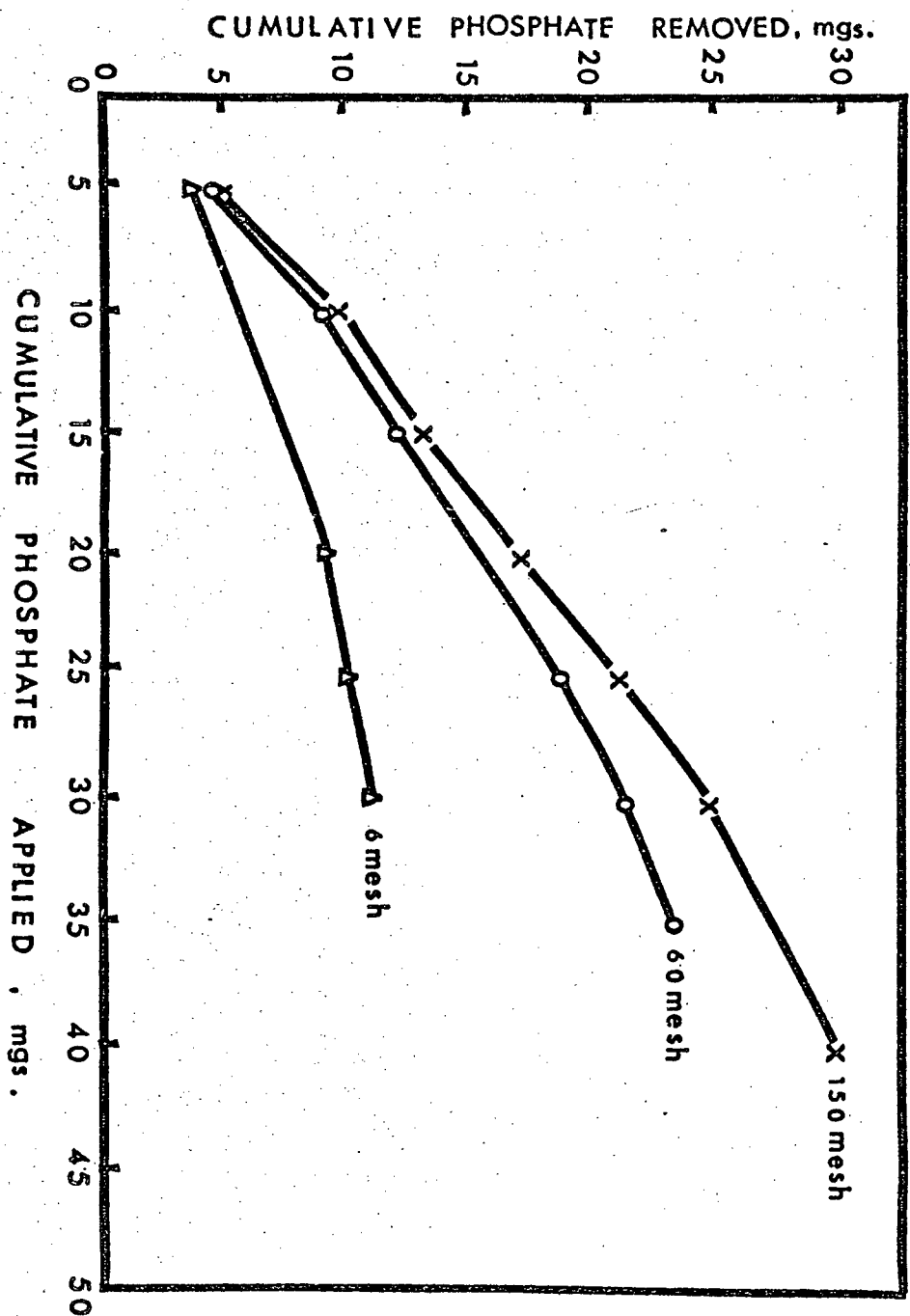
FIGURE 26 : COLUMN ADSORPTION PROCESS.
CUMULATIVE REMOVAL OF PHOSPHATES.

The very fine particle size < 150 mesh is not practical in column test since it allows very poor hydraulic conductivity.

### 4.3.3    Comparison between coal and soil

The Abbotsford sandy loam described earlier in Chapter IV, of similar texture to coal, was subjected to both contact and leaching trials to compare the value of soil to coal for phosphate adsorption.  Results from the contact process summarized in Table 23, show that there is not a great difference in their adsorptive characteristics.  Meanwhile, the column process shows clearly that soil is definitely superior to coal as shown in Figure 27.  In the case of soil, a break-through point of 75% removal is reached after 8½ liter volume of throughput with an adsorptive capacity of 3.4 mgs phosphate removed per gram soil.  In comparison, only 0.815 mgs phosphate is removed per gram of coal.

### 4.4    Nitrates

Neither the contact process nor the column process are encouraging for the removal of nitrate-nitrogen.  The results of the contact process, shown in Table 24a indicate that none of the coal particle sizes were effective.  In fact there is an accretion of $NO_3$ into the solution for each of the various sizes.  An increase of 2 mg/l or more was experienced in the smaller sizes and this value increased with the increasing percentage of coal added.  This indicates that nitrates are removed from the original coal.  The average quantity of

TABLE 23. CONTACT PROCESS - REMOVAL OF PHOSPHATE
COMPARISON BETWEEN HAT CREEK COAL AND
ABBOTSFORD SANDY LOAM.

Time of Contact:                    3 hours

| Influent Solution Conc ppm (mg.l) | % Coal or Sand | HAT CREEK COAL Size 0.03414 mm (<150 mesh) | | | ABBOTSFORD SANDY LOAM Size 150-250 mesh | | |
|---|---|---|---|---|---|---|---|
| | | Effluent conc mg/l | mg Removed per gm coal | % Removal | Effluent conc mg/l | mg Removed per gm loam | % Removal |
| 5 | 0.5 | 3.25 | 0.35 | 35.00 | 3.09 | 0.382 | 38.20 |
| | 1.0 | 2.51 | 0.249 | 49.80 | 1.35 | 0.365 | 73.00 |
| | 5.0 | 0.73 | 0.0854 | 85.4 | <0.31 | >0.094 | >94.00 |
| 50 | 0.5 | 41.37 | 1.726 | 17.26 | 42.9 | 1.42 | 14.2 |
| | 1.0 | 38.92 | 1.108 | 22.2 | 38.9 | 1.11 | 22.2 |
| | 5.0 | 18.48 | 0.6304 | 63.04 | 14.4 | 0.712 | 71.2 |
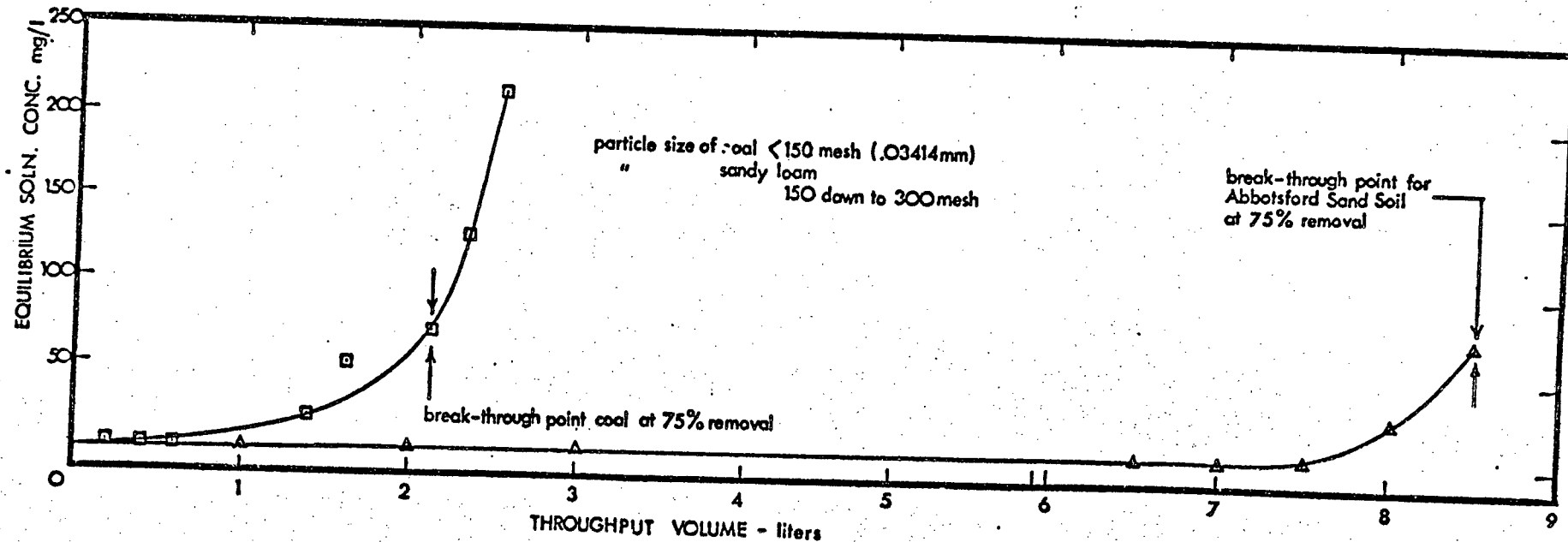
FIGURE 27 : BREAK-THROUGH CURVES FOR PHOSPHATE REMOVAL

BY COAL AND ABBOTSFORD SANDY LOAM.

# TABLE 24a. CONTACT PROCESS
## NITRATE-N REMOVAL
### Influent conc. =   10 mg/l

| Contact Time | % Coal | Coal Size 0.533 mm | | Coal size 0.2965 mm | | Coal size 0.117 mm | |
|---|---|---|---|---|---|---|---|
| | | $NO_3^-$-N mg/l | $NO_3^-$ mg/l | $NO_3^-$-N mg/l | $NO_3^-$ mg/l | $NO_3^-$-N mg/l | $NO_3^-$ mg/l |
| 1 hr. | 1% | 2.41 | 10.67 | 2.48 | 10.98 | 2.56 | 11.34 |
| | 5% | 2.56 | 11.34 | 2.64 | 11.69 | 2.72 | 12.05 |
| 3 hrs. | 1% | 2.48 | 10.98 | 2.51 | 11.11 | 2.43 | 10.76 |
| | 5% | 2.61 | 11.56 | 2.67 | 11.82 | 2.77 | 12.27 |
| | | INFLUENT CONC. 50 mg/l $NO_3^-$ | | | | | |
| 3 hrs. | 1% | 11.3 | 50 | | | 11.4 | 50.5 |
| | 5% | 11.2 | 49.6 | | | 11.9 | 52.7 |

nitrate-nitrogen leached out from Hat Creek coal was determined earlier in Chapter V, an average of 2 - 4 mgs of $NO_3$-N was found to be leached from each 100 gram of coal, this is equivalent to 2 - 4 mgs/liter.

The results of the column process, table 24b, show that at the beginning, a slight physical adsorption of $NO_3$ by coal, but only after 2 liters of volume throughput. The removal capacity is nil.

The inability of the coal to adsorb nitrates may be explained by the great solubility of the nitrate anions which make it difficult to be separated from its solutions and adsorbed on the coal surface. Also, by the possibility of releasing nitrates, being present in the coal, into the solution due to its high solubility.

4.5  Ammonia

4.5.1  Contact process

Table 25a shows the adsorption of ammonia with different percentages of both the surface coal and the activated carbon, when the initial ammonia concentration is 50 mg/l.

Both adsorbents exhibit poor adsorptive capacity which do not exceed 0.5 mg/gm adsorbent with not higher than 30% removal efficiency.  Slightly higher values were obtained with activated carbon.

Table 25b gives a comparison between the non-oxidized and oxidized coal for the removal of ammonia.  The results

TABLE 24b. COLUMN TEST
NITRATE REMOVAL

Coal size    = 0.2965 mm
Influent conc. =   10 mg/l $NO_3^-$.
Flow rate    = 8-10 ml/min.

| Throughput Volume Liters | $NO_3^-$-N mg/l | $NO_3^-$ mg/l | $NO_3^-$ Removed | % Removal |
|---|---|---|---|---|
| 0.5 | 1.8 | 8.4 | 1.6 | 16.0 |
| 1.5 | 2.0 | 8.86 | 1.14 | 11.4 |
| 2.0 | 2.31 | 10.2 | 0 | 0 |

## TABLE 25a.

### REMOVAL OF AMMONIA

#### COMPARISON BETWEEN ACTIVATED CARBON AND HAT CREEK COAL

CONDITIONS OF EXPERIMENTS

Material used for stock solution = $NH_4NO_3$
Initial concentration = 50 ppm
Contact time = 24 hrs
Mean particle size = 0.9 - 1 mm

| Code Samples | Conc ppm | Removed ppm | % Removal | mgs Removed per gm Carbon |
|---|---|---|---|---|
| 0 - $NH_3$ | 50.0 | | | |
| 0.5% ac | 47.75 | 2.25 | 4.5 | 0.4500 |
| 1.0% ac | 43.25 | 6.75 | 13.5 | 0.675 |
| 2.0% ac | 42.0 | 8.00 | 16.0 | 0.400 |
| 5.0% ac | 35.0 | 15.00 | 30.0 | 0.3000 |
| 0 - $NH_3$ | 50.0 | | | |
| 0.5% sc | 47.5 | 2.5 | 5.0 | 0.50 |
| 1.0% sc | 46.75 | 3.25 | 6.5 | 0.33 |
| 2.0% sc | 44.75 | 5.25 | 10.5 | 0.26 |
| 5.0% sc | 40.5 | 9.5 | 19.0 | 0.19 |

NOTE

ac = activated carbon

sc = surface coal

TABLE 25b. BATCH PROCESS

REMOVAL OF AMMONIA BY COAL

| Type of Coal | % Coal Added w/w | AMMONIUM NITRATE | | | AMMONIUM SULFATE | | |
|---|---|---|---|---|---|---|---|
| | | Effluent Conc mg/l | mgs Removed per gm coal | % Removal | Effluent conc mg/l | mgs Removed per gm coal | % Removal |
| - | 0 | 9.25 | - | - | 9.5 | - | - |
| NON- | 0.5% | 5.9 | 0.67 | 36.2 | 7.2 | 0.46 | 24.2 |
| OXIDIZED | 1.0% | 5.9 | 0.34 | 36.2 | 4.6 | 0.49 | 51.6 |
| CORE | 2.0% | 3.25 | 0.3 | 64.9 | 2.53 | 0.35 | 73.5 |
| COAL | 5.0% | 3.78 | 0.11 | 59.1 | 2.3 | 0.14 | 75.8 |
| SURFACE | 0.5% | 9.53 | - | - | 9.3 | 0.04 | 2.1 |
| COAL | 1.0% | 10.15 | AMMONIA LEACHED OUT INTO THE SOLUTION | | 10.1 | - | - |
| (OXIDIZED) | 2.0% | 11.0 | | | 14.0 | - | - |
| | 5.0% | 14.75 | | | 12.35 | AMMONIA LEACHED OUT INTO THE SOLUTION | |

indicate that the non-oxidized coal removes ammonia more efficiently than surface coal when either $NH_4NO_3$ or $(NH_4)_2SO_4$ solution is used as synthetic waste. With higher quantities of surface coal applied, the ammonia level increases in the effluent even higher than the original concentration. This confirms the suggestion that some soluble components, containing ammonium ions, were leached from the surface coal and add to the level originally present.

The leaching of ammonium ions from coal as studied during this period, and the results shown in Chapter V indicates that the ammonia leached from the surface coal is in the order of 16 mg/1 which is equivalent to 18 mgs $NH_3$-N per 100 grams of coal, while an average of 7 mgs $NH_3$-N was leached from the non-oxidized core coal. This explains the very poor adsorptive quality of the surface coal for ammonia.

4.5.2 Adsorption of ammonia with leached coal

After leaching ammonia from the surface and core coal, the coals were dried and used in a batch test to check the effect of removal of the originally present ammonia in coal on improving the adsorption behavior towards ammonia from waste-water.

Table 25c shows that in both types of coal the adsorptive capacity and the removal efficiency are increased by washing the coal. A 30% removal was obtained when the ammonia solution was treated with 5% coal without any further release

of ammonia into the solution. In comparison, about 63% removal
was obtained when 5% of core coal was used.

TABLE 25c. ADSORPTION OF AMMONIA WITH
WATER WASHED COAL.

- Particle size of coal 48/100 mesh; Contact time = 14 hours
- Volume of solution - 100 cc.
- Influent concentration = 7.55 mg/1 $NH_3$-N

| Coal sample | % coal added w/w | Effluent conc. mg/1 $NH_3$-N | Removed $NH_3$-N mg/1 | % Efficiency of removal |
|---|---|---|---|---|
| Surface coal | 1 | 5.75 | 1.80 | 24 |
| | 5 | 5.30 | 2.25 | 30 |
| Core coal | 1 | 3.75 | 3.80 | 50 |
| | 5 | 2.80 | 4.75 | 63 |

4.5.3 Column process

Table 25d shows that much high efficiency of removal
is achieved by a column leaching process rather than the con-
tact process. Up to 95% removal can be obtained using core
coal, while surface coal yields a lower efficiency, about 61%.
In comparison, the activated carbon has the highest effective-
ness where more than 99% removal is shown.

TABLE 25d.   COLUMN TEST FOR REMOVAL OF
AMMONIA

- Particle size of coal 14/20;   Contact time = 30 min.

- Flow rate 1 gpm/ft$^2$ (15 ml/min).

- Original influent concentration = 9.5 mg/1 $NH_3$-N

| Type of coal | Volume throughput liters | AMMONIUM SULFATE | |
| --- | --- | --- | --- |
| | | Effl. conc. mg/1 | % Removal |
| Non-oxidized core sample | 1 | 0.7 | 92.6 |
| | 2 | 0.6 | 93.7 |
| | 3 | 0.8 | 91.6 |
| | 4 | 0.45 | 95.0 |
| Oxidized surface coal | 1 | 3.9 | 59.0 |
| | 2 | 3.75 | 60.5 |
| | 3 | 3.6 | 61.0 |
| | 4 | 3.7 | 61.0 |
| Activated carbon | 1 | < 0.1 | > 99.0 |
| | 2 | < 0.1 | > 99.0 |
| | 3 | < 0.1 | > 99.0 |
| | 4 | < 0.1 | > 99.0 |

4.6   Phenol

Several batch and column adsorption tests were conducted
to check the adsorptivity of the surface coal toward phenol
in comparison to activated carbon.

The results from the batch test are summarized in
Table 26a, indicating that phenol is readily removed by surface
coal;   80% removal was obtained when 2% coal of size 100/150
mesh was used in a solution containing 4.12 mg/1 of phenol.

TABLE 26a.  REMOVAL OF PHENOL (BATCH PROCESS)

Initial concentration of phenol solution  =  4.12 mg/1

Mean particle size of coal or carbon  =  14/20 mesh (0.9-1 mm)

Contact time  =  24 hours

Volume of solution  =  100 cc

| Absorbent added % w/w | Phenol conc. mg/1 | Phenol Removed | % Removal | mgs removed per gm coal |
|---|---|---|---|---|
| 0 | 4.12 | | | |
| **Activated carbon** | | | | |
| 0.5% | 0.02 | 4.10 | 99.5 | 0.820 |
| **Surface coal** | | | | |
| 0.5% (14/20 mesh) | 2.73 | 1.39 | 33.9 | 0.278 |
| 2.0% (14/20 mesh) | 1.69 | 2.43 | 59.0 | 0.122 |
| 2.0% (100/150 mesh) | 0.81 | 3.31 | 80.3 | 0.166 |

In comparison, activated carbon is superior since
its efficiency for the removal of phenol is more than 99%.

Regarding the column adsorption test, 4 liters of
solution were applied through a column (20 cm X 7 cm I.D.) at
a flow rate of 1 gpm/ft$^2$. The results obtained from this test
are shown in Table 26b, and confirm that both surface and
core coal have appreciable adsorptive capacity towards phenol,
although surface coal has a greater efficiency reaching more
than 91% after passing through 3 liters. In comparison
activated carbon still possesses a superior efficiency of
99.9% for the removal of phenol.

4.7 Cyanide

Table 27a shows the result of the batch test for the
removal of cyanide which indicates that cyanide is removed
readily by surface coal with a very high efficiency from
90 - 96% while in comparison activated carbon completely
removes the cyanide from solutions.

The results of the column adsorption tests in Table 27b
show that the surface coal exhibits higher efficiency than
the core coal for the removal of cyanide from solutions.
Nevertheless, activated carbon exhibits superior activity. The
higher efficiency of surface coal more than core coal for
removal of phenol and cyanide may be attributed to the presence
of surface oxides (oxygen-containing functional groups)
which are likely to play a role in the adsorption mechanism.
This point was not investigated during this portion of the
research.

TABLE 26b COLUMN ADSORPTION PROCESS- REMOVAL OF PHENOL

Column size (20 cm X 7 cm I.D.)

Flow rate = 1 gpm/ft$^2$ (165 ml/min)

Particle size of adsorbent = 14/20 mesh

Contact time = 2-3 min

Influent = 4.08 mg/l phenol

| Volume throughput liters | ACTIVATED CARBON | | SURFACE COAL | | CORE COAL | |
|---|---|---|---|---|---|---|
| | Effl. conc. mg/l | % Removal | Effl. conc. mg/l | % Removal | Effl. conc. mg/l | % Removal |
| 0 | 4.08 | - | 4.08 | - | 4.08 | - |
| 1 | 0.02 | 99.5 | 0.56 | 86.3 | 0.58 | 85.8 |
| 2 | 0.07 | 98.3 | 2.00 | 51.0 | 1.43 | 65.0 |
| 3 | 0.025 | 99.4 | 0.35 | 91.4 | 1.91 | 53.2 |
| 4 | 0.005 | 99.9 | 0.50 | 87.8 | 2.50 | 38.7 |

TABLE 27a             REMOVAL OF CYANIDE (CONTACT PROCESS)

Initial concentration of cyanide        = 1.66 mg/1
Mean particle sizes                     = 14/20 and 100/150 mesh

Contact time                            = 24 hours
Volume of solution                      = 100 cc.
Influent concentration                  = 1.66 mg/1 phenol

| Adsorbent added % w/w | Phenol conc. mg/1 | Phenol Removed | % Removal | mgs removed per gm coal |
|---|---|---|---|---|
| 0 | 1.66 | - | - | - |
| **Activated carbon** | | | | |
| 0.5% (14/20) | N.D. | All removed | $\geq$ 99.9 | 0.330-0.332 |
| **Surface coal** | | | | |
| 0.5% (14/20 mesh) | 0.14 | 1.52 | 91.6 | 0.304 |
| 2.0%    " | 0.16 | 1.5 | 90.4 | 0.075 |
| 2.0% (100/150 mesh) | 0.07 | 1.59 | 95.8 | 0.080 |

TABLE 27b                    COLUMN ADSORPTION PROCESS

Column size (20cm X 7 cm I.D.)

Flow rate   =  1 gpm/ft$^2$ (165 ml/min)

Particle size of adsorbent - 14/20 mesh

Contact time  =  203 min

Influent concentration = 1.46 mg/1 CN

| Volume throughput liters | ACTIVATED CARBON | | SURFACE COAL | | CORE COAL | |
|---|---|---|---|---|---|---|
| | Effl. conc. mg/1 | % Removal | Effl. conc. mg/1 | % Removal | Effl. conc. mg/1 | % Removal |
| 0 | 1.46 | - | 1.46 | - | 1.46 | - |
| 1 | 0.054 | 96.3 | 0.02 | 98.6 | 0.24 | 83.6 |
| 2 | 0.054 | 96.3 | 0.77 | 47.2 | 0.62 | 57.5 |
| 3 | 0.071 | 95.1 | 0.54 | 63.0 | 0.54 | 63.0 |
| 4 | 0.074 | 94.9 | 0.03 | 97.9 | 0.12 | 91.8 |

## VI.   MECHANISM STUDIES.

A.      Mechanism of Adsorption of Heavy Metals by Coal

Preface:

Coal is a very complex humic material, therefore its high activity in removing heavy metals from solutions is not expected to be a simple mechanism, because it may involve one or more of the following mechanisms in combination: ion-exchange, surface adsorption, chelation, coagulation or peptization reactions (Mortensen, 1963). During the course of this study the interest was focussed on the ion-exchange type of mechanism.

A characteristic of low rank coals such as Hat Creek, and related humic materials is that much of the oxygen associated with their structure is present as carboxyl and phenolic hydroxyl groups (Brooks, 1957).

The study of the ion-exchange mechanism is directed toward providing sufficient evidence for the involvement of the acid groups of coal in the interaction with heavy metals and therefore the following approaches were considered:

1.      Microscopic Approach. The Electron Microprobe and the Scanning Electron Microscope were both used to confirm that the adsorbed lead ions would be sited on the organic part of the coal and not on the silicon contained in inorganic minerals.

2.      Spectroscopic Approach.  The Infra-Red absorption spectroscopy was applied, using a semi-quantitative technique, to show the interaction of the acid groups in the coal with the adsorbed metal ions.

The same technique is also employed to check the
proximity of the carboxyl groups present in the
coal. The infra-red spectra of the anhydride
form of the coal are compared with those obtained
after adsorption of lead, the similarity between
them would indicate the possibility of a complex
formation between two adjacent carboxyl groups
and the metal ion.

3.    Chemical Approach.

3.1   Measuring the number and the nature of the active
      sites available for cation exchange reaction with
      the metal ions.  Both the exchangeable cations
      and the total exchange capacity (CEC) of the coal
      are determined and used in this study.

3.2   A quantitative determination of the ratio between
      the number of lead ions adsorbed and the corres-
      ponding number of hydrogen ions released.

3.3   A quantitative determination of the number of
      carboxyl and phenolic hydroxyl groups present in
      the coal, as well as the number of these groups
      which are involved in the interaction with the
      metal ions.  An evaluation of the relation
      between these values and the values obtained by
      the lead ions which reacted and released hydrogen
      as described in the previous 3.2 Section.

All of the above studies are correlated and used to suggest an overall mechanism which may be expected to take place during the adsorption of metal ions by coal carbon.

## 1. MATERIALS

### 1.1 The Hat Creek coal samples

These were prepared as described previously in Chapter III and IV. The following samples were used:

a) Water-washed oxidized surface coal (W.W.S.)

b) Acid-washed oxidized surface coal (A.W.S.)

c) Water-washed unoxidized core coal (W.W.C.)

d) Acid-washed unoxidized core coal (A.W.C.)

### 1.2 Calgon Activated Carbon samples

These included:

a) Water-washed activated carbon (W.W.A.)

b) Acid-washed activated carbon (A.W.A.)

### 1.3 Stock solutions of lead nitrate of 500 mg/1 and 5000 mg/1 concentration respectively to provide the lead ions required for the adsorption process.

## 2. METHODS

### 2.1 Electron Microanalysis

The Electron Microprobe and the Scanning Electron Microscope, were used to obtain an elemental mapping for the distribution of the adsorbed lead ions with respect to other elements across the surface of the coal particles.

A description of the two instruments and the theory of their operation are included in Appendices A, and B-1.

A very important feature of these methods is that the coal samples are analyzed non-destructively without damaging the features of the surface.

The special technique used for the preparation of the coal specimen for such analyses is described in Appendix B-1 (Goldstein, 1975). Micrograph pictures obtained by the low power microscope are used to choose the suitable coal particles used in the study of the mechanism. Then the Scanning Electron Microscope micrographs are used to describe the features of the coal particles under scrutiny.

A set of electron images were produced which show the elemental distribution or mapping across certain areas of the specimen. Each image gives the concentration of a particular element in the given area. In places of high concentration of elements, the picture will be nearly white, it will be gray when the element concentration is lower and black when the element is absent.

The adsorption of lead ions on the surface of the coal particles: The coating material (carbon) was first removed from the surface by washing thoroughly with ethyl alcohol, then with acetone, and finally air dried. Each specimen under scrutiny was then soaked in a 200 cc solution of lead nitrate at a concentration of 500 mg/1 at room temperature. A contact time of

72 hours allowed the specimen to reach an equilibrium state.
Each specimen was then removed from the solution, washed
thoroughly with distilled water, dried in air for about 2 days
before starting the electron microanalysis.

## 2.2 Infra-red Spectra

A solution of lead nitrate containing 500 mg/1 concen-
tration was shaken with 1% w/w coal or carbon of a particle size
of 50/100 mesh for a contact time of 8 hours, then the coal
particles were rinsed with distilled water and air dried. KBr
pellets technique (Lowry, 1963 and Fujii, 1970) described in
Appendix B-2-2 was applied. The infra-red absorption spectra
were then recorded between the region of 200 to 900 $cm^{-1}$.
The specific extinction coefficient for the acidic
groups were evaluated using the base line technique described
in Appendix B-2-3 (Ewing, 1960 and Fuji, 1970).

Another set of coal samples was prepared by adsorbing
barium ions on the coal from a saturated solution of 1 N barium
acetate. The coal was refluxed in the barium acetate solution
for 4 hours. The infra-red spectra of these samples were com-
pared with those obtained when lead was adsorbed.

Preparation of the acid anhydride of coal. The coal
was heated at $170^{o}C$ for about 50 hours (Wright and Schnitzer,
1961). The samples were cooled carefully in a desiccator.
Infra-red spectra of the anhydrides were then measured on
potassium bromide discs.

## 2.3 Chemical Methods

## 2.3.1 The determination of exchangeable cations and total
exchange capacity (Black, 1965).

Cation exchange capacity (C.E.C.) denotes the total cations that can be replaced from a given substance under a given set of conditions. Usually, it is expressed as milli-equivalent/100 grams. The exchange capacity depends on the pH of the solution used in the determination. For this reason, neutral solutions at pH = 7 are used throughout, by leaching with a neutral ammonium acetate. With this salt, the exchange capacity of humic substances can be determined reasonably accurately even when the substance contains soluble salts and calcium carbonate.

The amount of $NH_4$ adsorbed from neutral ammonium acetate merely represents the amount of cations the coal is capable of holding in replaceable form at pH = 7.

Through this analysis both the exchangeable cations Na, K, Mg and Ca and the total exchange capacity were calculated. The detailed technique and method of calculation are included in Appendix B-5.

This method is based on the assumption that a complete replacement of all exchangeable cations is carried out by cations (in this case ammonium ions $NH_4^+$) which are not present in the sample (Kelley, 1948).

2.3.2 Determination of the ratio of adsorbed lead ions to hydrogen ions released from coal. A lead nitrate solution con-taining 500 mg/1 leadwas shaken with 1% w/w of coal or carbon of a particle size of 50/100 mesh for 8 hours. The mixture was then filtered and the pH of the clear filtrate measured and

used to calculate the hydrogen ions released upon the adsorption of lead.

The remaining lead ions in the solution after the interaction were measured using the Atomic Absorption Spectrophotometer.

The ratio of the lead ions adsorbed and the corresponding hydrogen ions released was calculated and is reported as follows.

2.3.3  Determination of acid groups.

The filtered coal from the above described procedure was then rinsed with distilled water and air dried.  The acid groups (carboxyls and phenolic hydroxyls) were then determined for the coal and the carbon samples before and after lead adsorption, using the following techniques:

2.3.3.1  Total acidity (Schafer, 1970;  Schnitzer and Gupta, 1965).

To 200 milligrams of each coal sample, previously ground to pass a 200 mesh sieve size, 20 mls of 0.25 N Barium hydroxide solution was added.  Simultaneously, a blank was set up consisting of 20 mls of 0.25 N $Ba(OH_2)$ only.  The air in the flask was displaced by nitrogen and the system was shaken for 24 hours at room temperature.

Following this, the suspension was filtered, the residue washed thoroughly with $CO_2$-free distilled water and the filtrate plus washings titrated potentiometrically (glass-calomel) with a  standard 0.5 N HCl solution to a pH of 8.4. The total acid is then calculated as follows:

$$\frac{(\text{Titer of blank - titer of sample}) \times \text{N acid} \times 1000}{\text{Weight of sample, mg}}$$

= m.eq. Total Acidity/gram of organic matter

## 2.3.3.2 Carboxy groups

Two methods were employed and compared:

(A) Barium Acetate Method (Schafter, 1970)

Coal (125 mgs) was refluxed in air with barium acetate (50 mls) (the pH being adjusted to 8.25) for 4 hours. The acid released was titrated poteniometrically under nitrogen in the presence of coal, with alkali (0.05 N) until the pH value 8.25 was restored.

A glass-calomel electrode combination, used in conjunction with a pH meter, served as the measuring system.

The carboxyl groups were then calculated as follows:

$$\frac{\text{Titer for sample - titer for the blank}}{\text{Weight of sample, mgs}} \text{ N base} \times 1000$$

= m.eq. COOH groups/gram of organic matter.

(B) Calcium Acetate Method (Schnitzer and Gupta, 1965)

Coal (200 mgs) was mixed with 10 mls of 1 N calcium acetate solution and 40 mls of $CO_2$-free distilled water, then the mixture was shaken for 24 hours at room temperature, filtered and the residue was then washed. The filtrate and washings titrated potentiometrically with standard 0.1 N NaOH to pH 9.8.

A blank consisting of 10 mls calcium acetate and 40 mls of distilled water was run simultaneously. The carboxyl groups were calculated as follows:

$$\frac{\text{Titer of sample - titer of blank}}{\text{Weight of sample, mgs}} \times \text{N base} \times 1000$$

= m/eq/COOH groups per gram coal.

Therefore, phenolic hydroxyls are evaluated as the difference between the total acidity and the carboxyl COOH.

2.3.4    Lead ions exchanged with calcium or barium during the determination of the acid groups

It is possible during the measurement of residual acidic groups after the lead adsorption test that part of the previously adsorbed lead ions on the coal will be released into the system.  This is due to their exchange with Ca or Ba ions used to perform the test.

The Atomic Absorption Spectrophotometer was used for the lead analysis, therefore, the percentage of released lead ions would be as follows:

$$\frac{\text{mgs lead released from 1 gram coal}}{\text{total mgs of adsorbed lead/gram coal}} \times 100$$

= % lead released.

## 3.  RESULTS AND DISCUSSION

### 3.1      Microscopic Studies

The X-ray images shown in Figure 28a reveal the distribution of carbon, silicon, oxygen and calcium across a layered particle of oxidized coal;  the distribution of the adsorbed lead is shown by a dense pattern of white dots.

The lead obviously located on areas containing carbon and not on those areas containing silicon, indicated that the mineral matter does not participate in the adsorption mechanism. Figure 28b shows a different shape of particle for the Hat Creek coal where the mineral matter appears in segregated form, not mixed with the organic part in which the organic carbon is located in two streaks.  The patterns of the carbon and lead distribution, represented by trace, indicate that the lead is predominantly adsorbed on the carbon and not on the mineral part that contains silicon.  However, the lead distribution is not uniform, some areas appear to have more lead adsorbed than others.  It was found that high levels of lead are shown on areas containing both carbon and oxygen in the same site, while less adsorption was noticed on sites containing only carbon.  It is expected, therefore, that lead is more readily adsorbed on functional groups containing oxygen such as carboxyl or phenolic hydroxyl groups.  This will be further confirmed by additional studies in the following sections of this chapter.
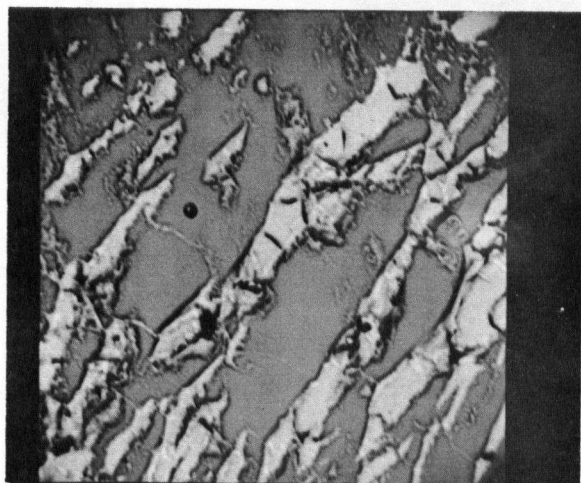
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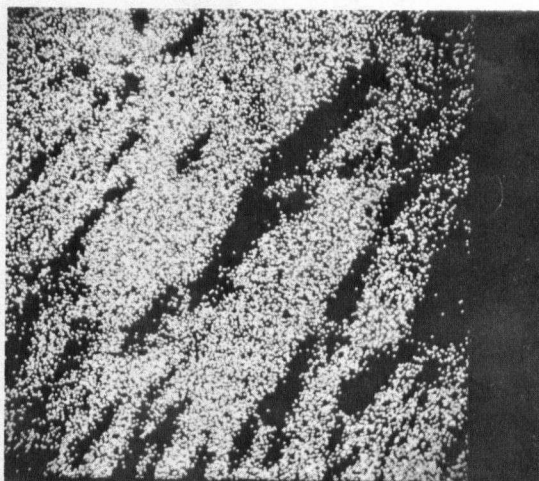
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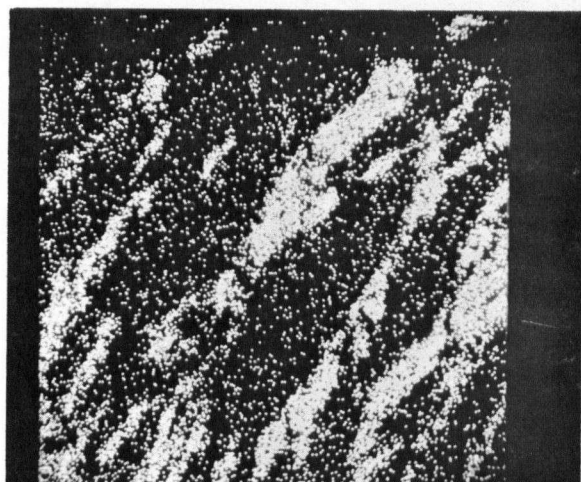
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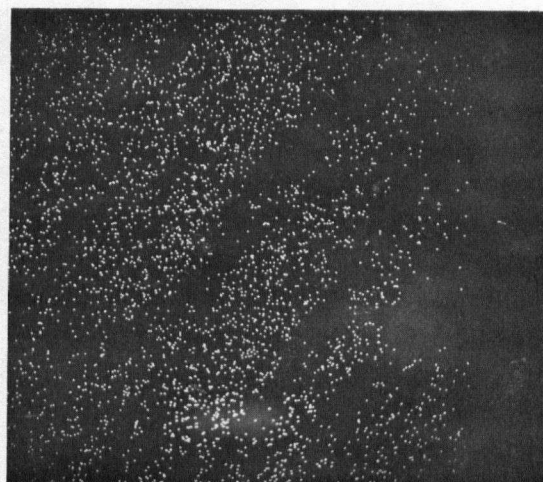
CALCIUM 290X.

ADSORBED LEAD 290X
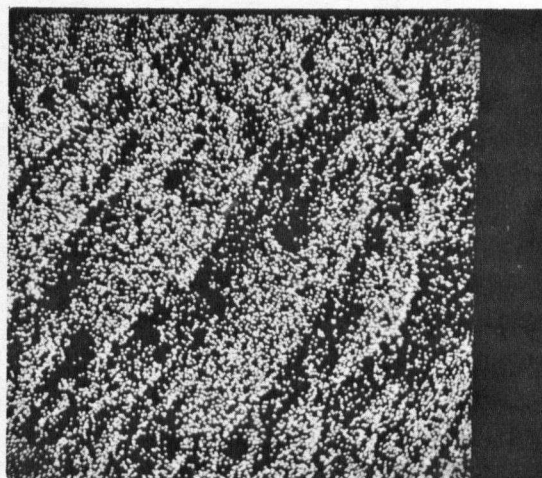
OXYGEN 290X.

FIGURE 28a- A SET OF X-RAY IMAGES SHOWING THE ELEMENTAL MAPPING AND THE
DISTRIBUTION OF ADSORBED LEAD ACROSS CERTAIN AREAS OF A LAYERED
PARTICLE OF OXIDIZED H.C. COAL FROM SURFACE DEPOSIT.
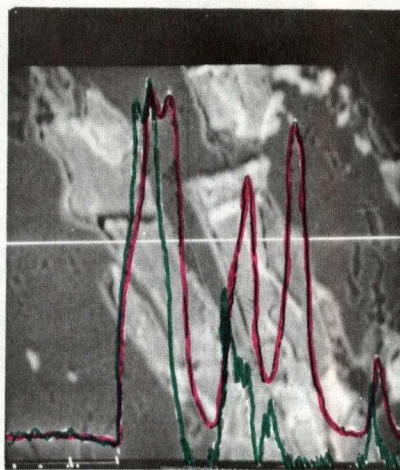
AEI WITH Y-AXIS DISPLAY ACROSS THE GIVEN AREA 620X
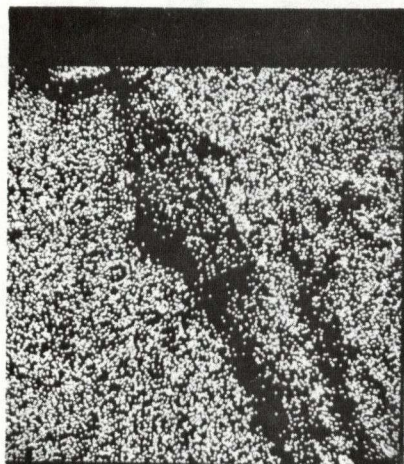
OXYGEN  620X

SILICON  620X
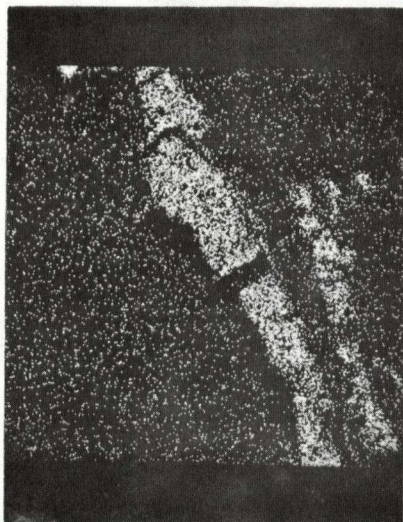
CARBON  620X

ADSORBED  LEAD  620X

FIGURE 28b - A SET OF X-RAY IMAGES ACROSS AN AREA OF SPECIMEN OF SURFACE H.C. COAL
CONTAINING TWO LAYERS OF CARBON IN SEGREGATED FORM AND NOT DISPERSED
WITH THE INORGANIC MINERALS.

RED  TRACE  SHOWS  THE  CARBON  DISTRIBUTION

GREEN  TRACE  SHOWS  THE  ADSORBED  LEAD  DISTRIBUTION.

A dispersed form of mineral matter, finely mixed with the carbon was noticed in the structure of some coal particles as shown by the X-ray images in Figure 29.  It can be seen that some adsorbed lead is interspersed with the silicon, but this is no doubt due to intimately mixed carbon and silicon particles.  In the X-ray images the intimately mixed particles are not easily discernible.

Figures 30a and 30b show the electron micrograph images on a sample of non-oxidized core coal which still confirms the adsorption of lead on an area containing carbon.  The similarity obtained between the sulfur and the carbon distribution in this particle can be explained by the occurrence of organic forms of sulfur.

The Absorbed Electron Images (AEI) of a cracked particle of core coal shows some interfacial deposition of lead on the boundaries between the carbon and silicon; but, in general, the distribution of lead follows to agreat extent the distribution of carbon.

The fact of adsorption of lead on carbon is further confirmed by applying the microprobe study on two particles of surface and core coal.  Figure 31 shows the X-ray images where both particles do not appear to have any appreciable silicon but consist mostly of coal.  The lead appears to be readily adsorbed on carbon in both particles.

In comparison with activated carbon, the pattern of the distribution of the adsorbed lead is completely different than those of either carbon or silicon across the particle. The X-ray images in Figures 32a and 32b show that the adsorbed lead
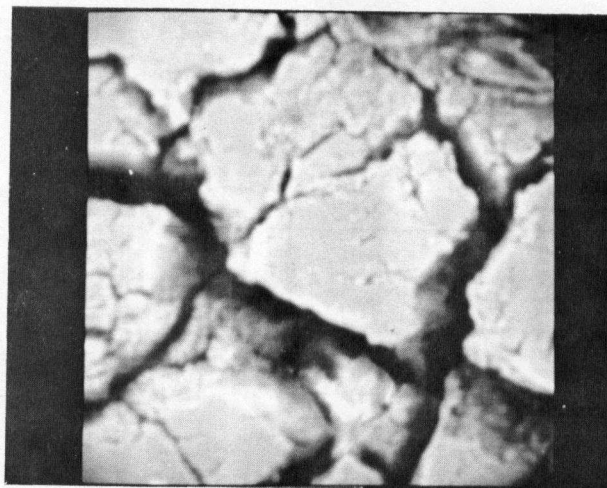
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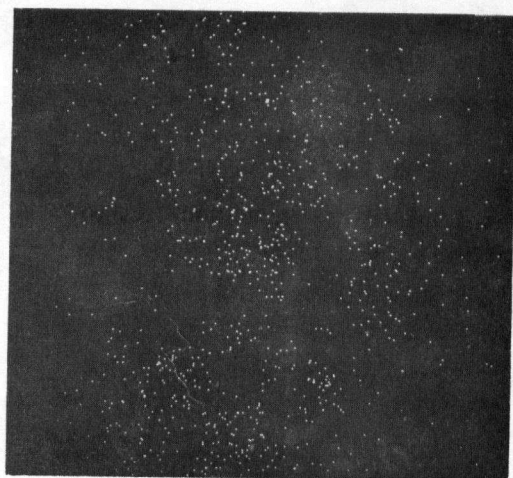
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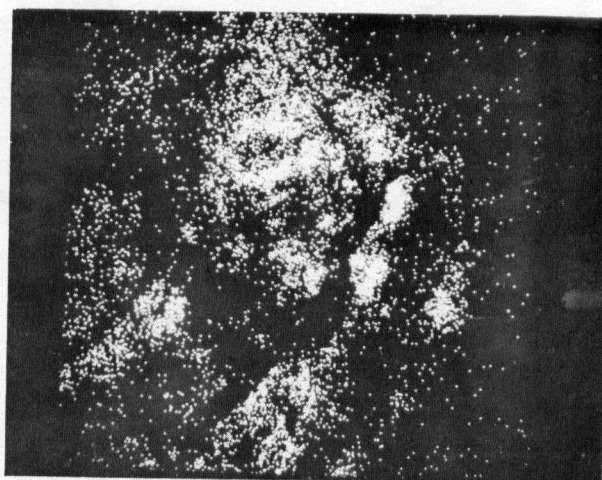
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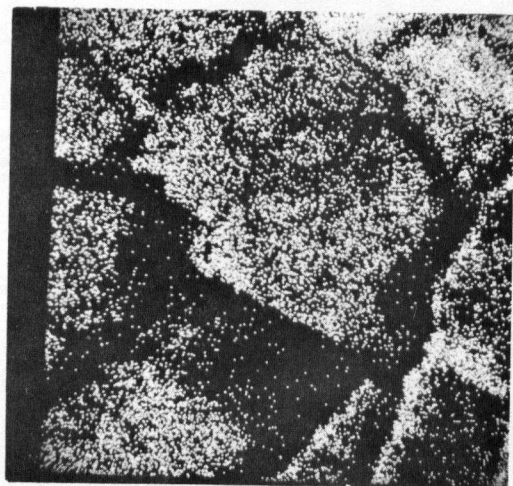
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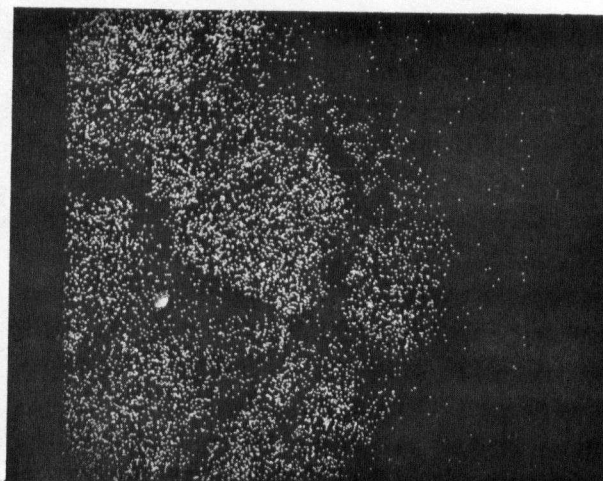
ADSORBED LEAD 500X

FIGURE 29- ELEMENTAL MAPPING ACROSS FRACTURED PARTICLE CROSS SECTION OF OXIDIZED HAT CREEK COAL FROM SURFACE DEPOSIT AFTER ADSORPTION OF LEAD.

157.
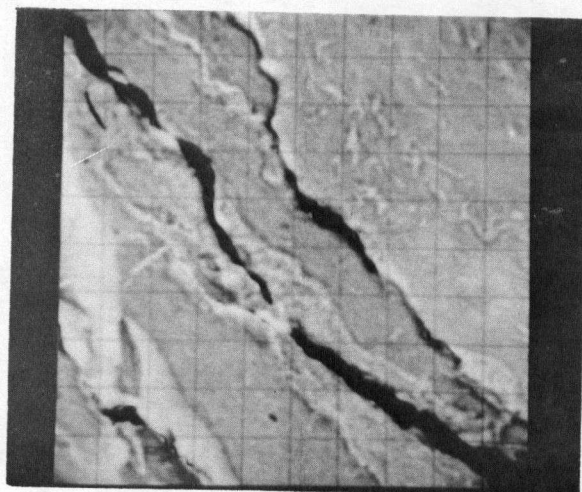


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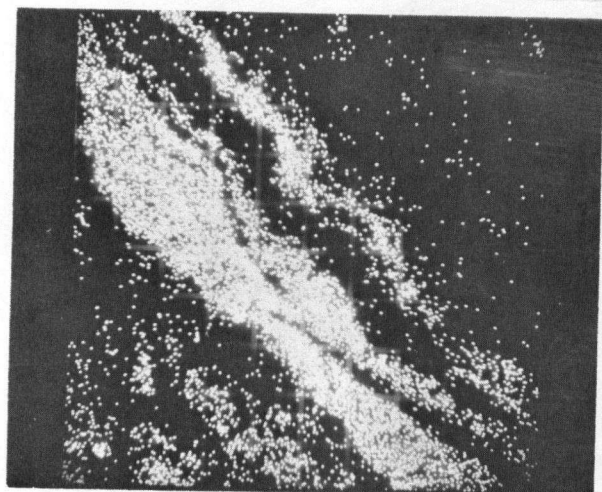
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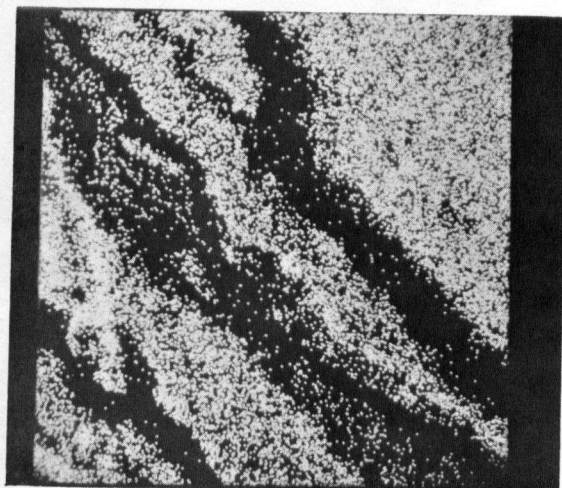
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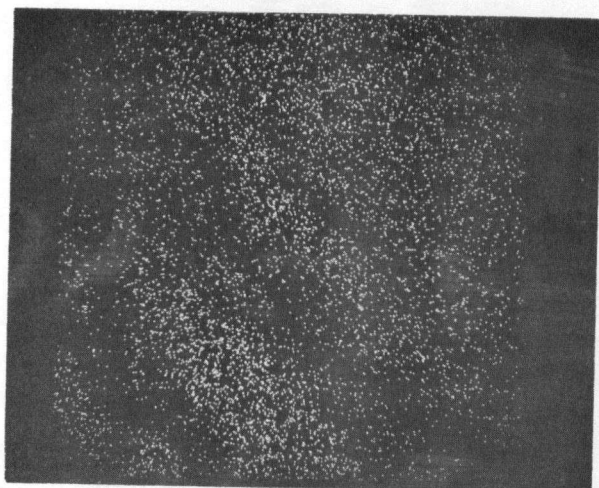
SULFUR 620X
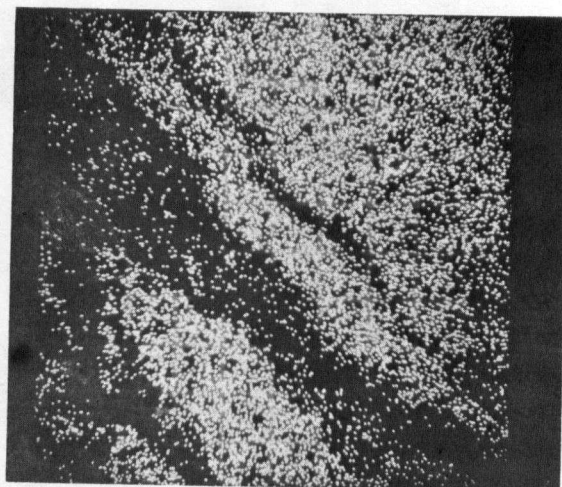
ADSORBED LEAD 620X

FIGURE 30a - ELEMENTAL MAPPING OF LAYERED PARTICLE CROSS SECTION OF NON-
OXIDIZED HAT CREEK SURFACE DEPOSIT AFTER ADSORPTION OF LEAD IONS.

158.
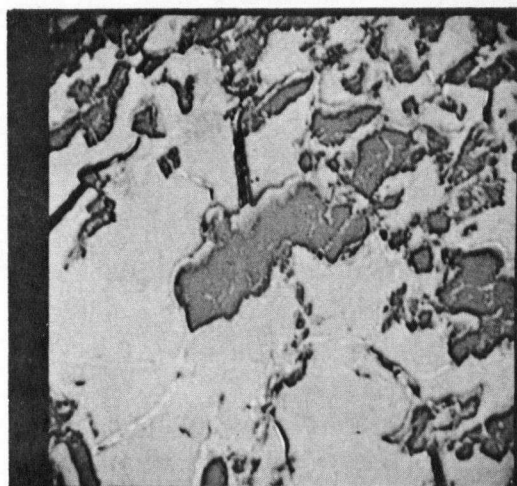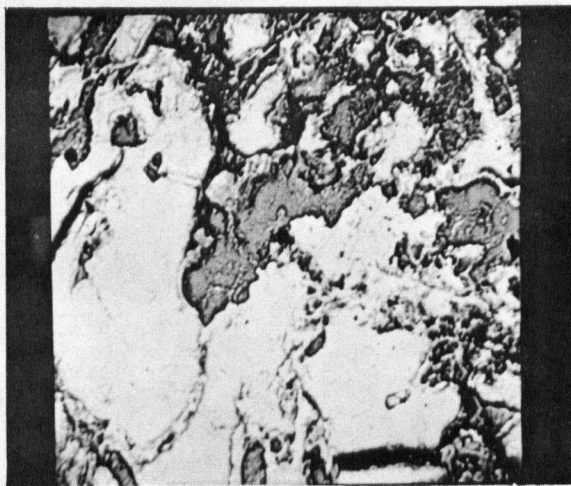


7A AEI 290X

7B AEI 290X
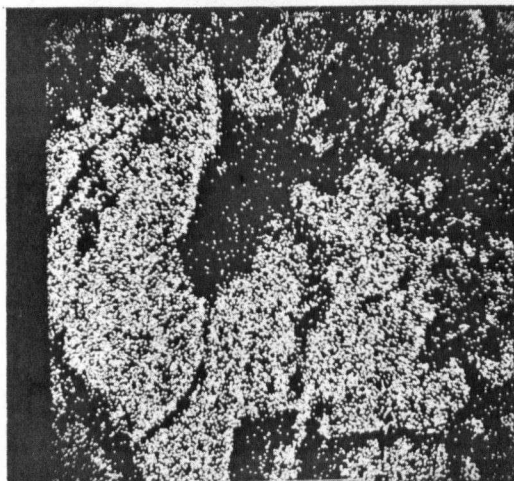
CARBON 290X

ADSORBED LEAD 290X
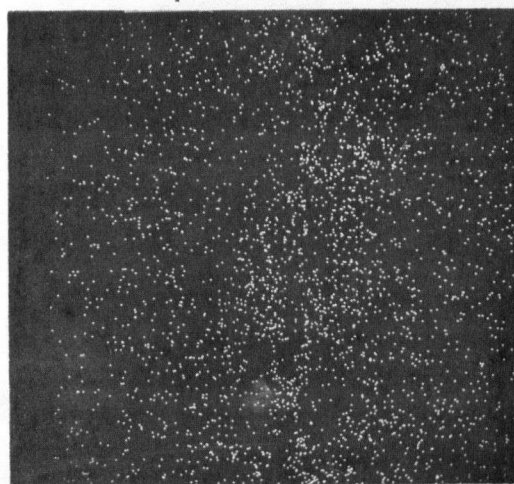
SULFUR 290X
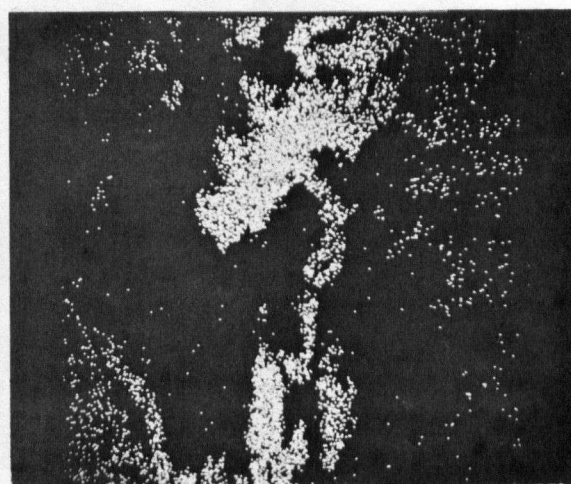
SILICON 290X

FIGURE 30b - ELEMENTAL MAPPING ACROSS AN AREA OF CRACKED PARTICLE OF NON-
OXIDIZED H.C. COAL FROM CORE DEPOSIT.

FIG. 7a & b ARE THE ABSORPTION ELECTRON IMAGES BEFORE AND AFTER
ADSORPTION OF LEAD SHOWING THAT LEAD MAY HAVE INCORPORATED ITSELF
NEAR THE BOUNDARY INTERFACES BETWEEN CARBON AND SILICON.
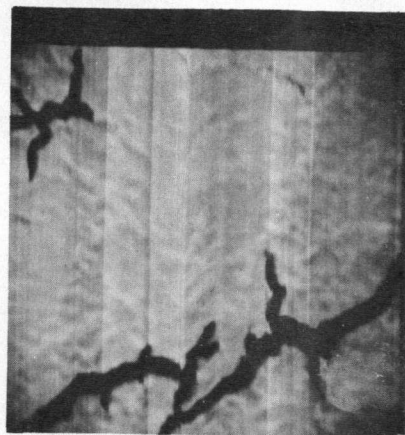
A1    AEI    620x      A2   SILICON   620x      A3   CARBON    620x      A4   LEAD    620x
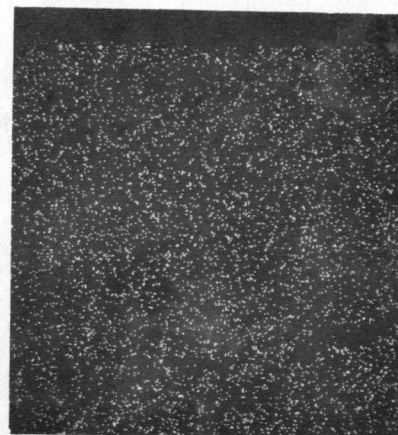
B1    AEI    29ox      B2   SILICON   29ox      B3   CARBON    29ox      B4   LEAD    29ox

FIGURE 31 - COMPARISON BETWEEN ELEMENTAL MAPPING OF PARTICLE CROSS SECTION OF SURFACE DEPOSIT AND CORE DEPOSIT OF HAT CREEK COAL SHOWING PURE CARBON SECTION OF THE PARTICLE WITH NO SILICON DETECTED AND THE ADSORBED LEAD DISTRIBUTION FOLLOWS THE CARBON DISTRIBUTION.    ( A:surface coal . ;   B : core coal.)

A1  AEI  290X

A2  SILICON  290X
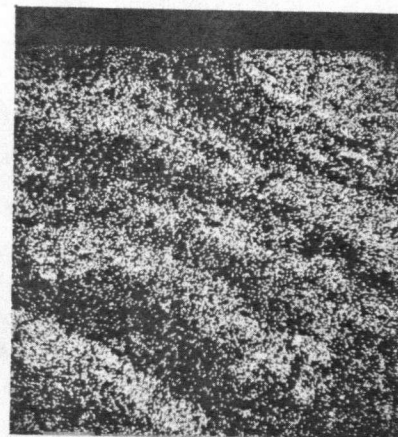
A3  CARBON  290X
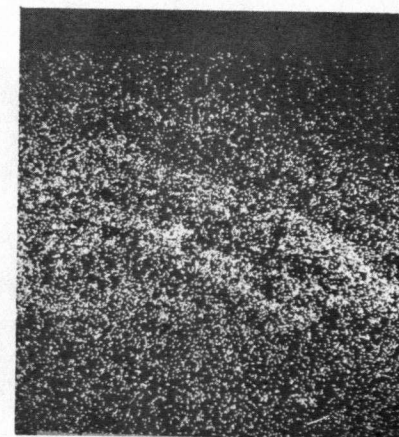
A4  ADSORBED  LEAD  290X
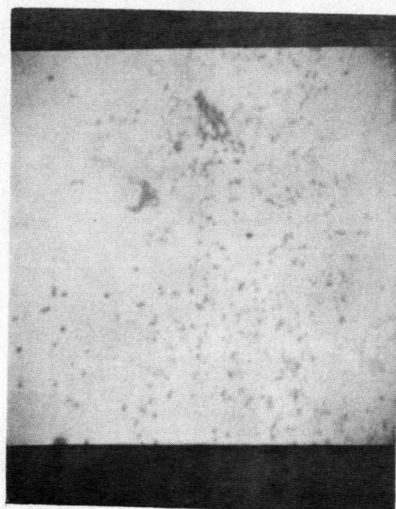
B1  AEI  290X
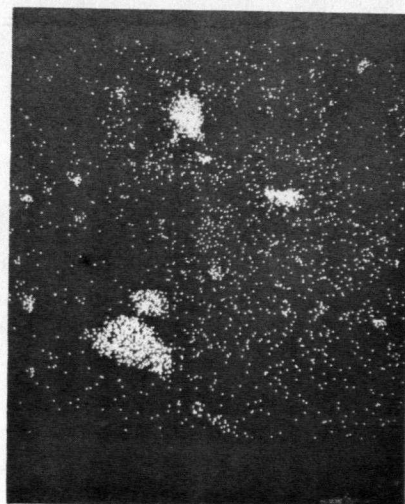
B2  SILICON  290X
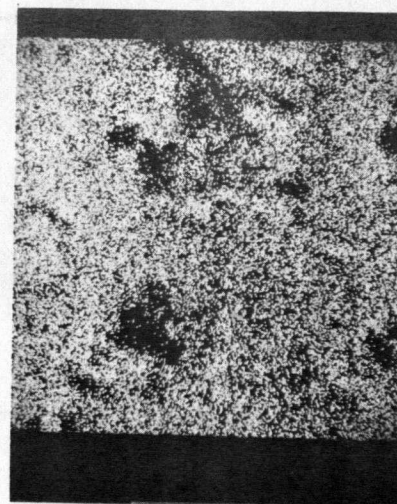
B3  CARBON  290X
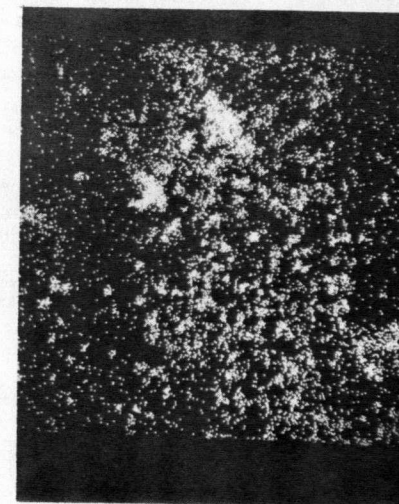
B4  ADSORBED  LEAD  290X

FIGURE 32a. ELEMENTAL MAPPING FOR AREAS OF TWO DIFFERENT ACTIVATED CARBON PARTICLES A & B. BOTH SHOWING THAT THE DISTRIBUTION OF ADSORBED LEAD IONS DOES NOT FOLLOW THE CARBON DISTRIBUTION AND LEAD APPEARS AS BLACK SPOTS SUPERIMPOSED ON THE SURFACE.

160.

A1- AEI 620x    A2 LEAD 620x    A3 CARBON 620x    A4 SILICON 620x

B1 SEM LEAD 5600x    B2 SEM 5600x    B3 SEM 1500x    B4 SEM 600x
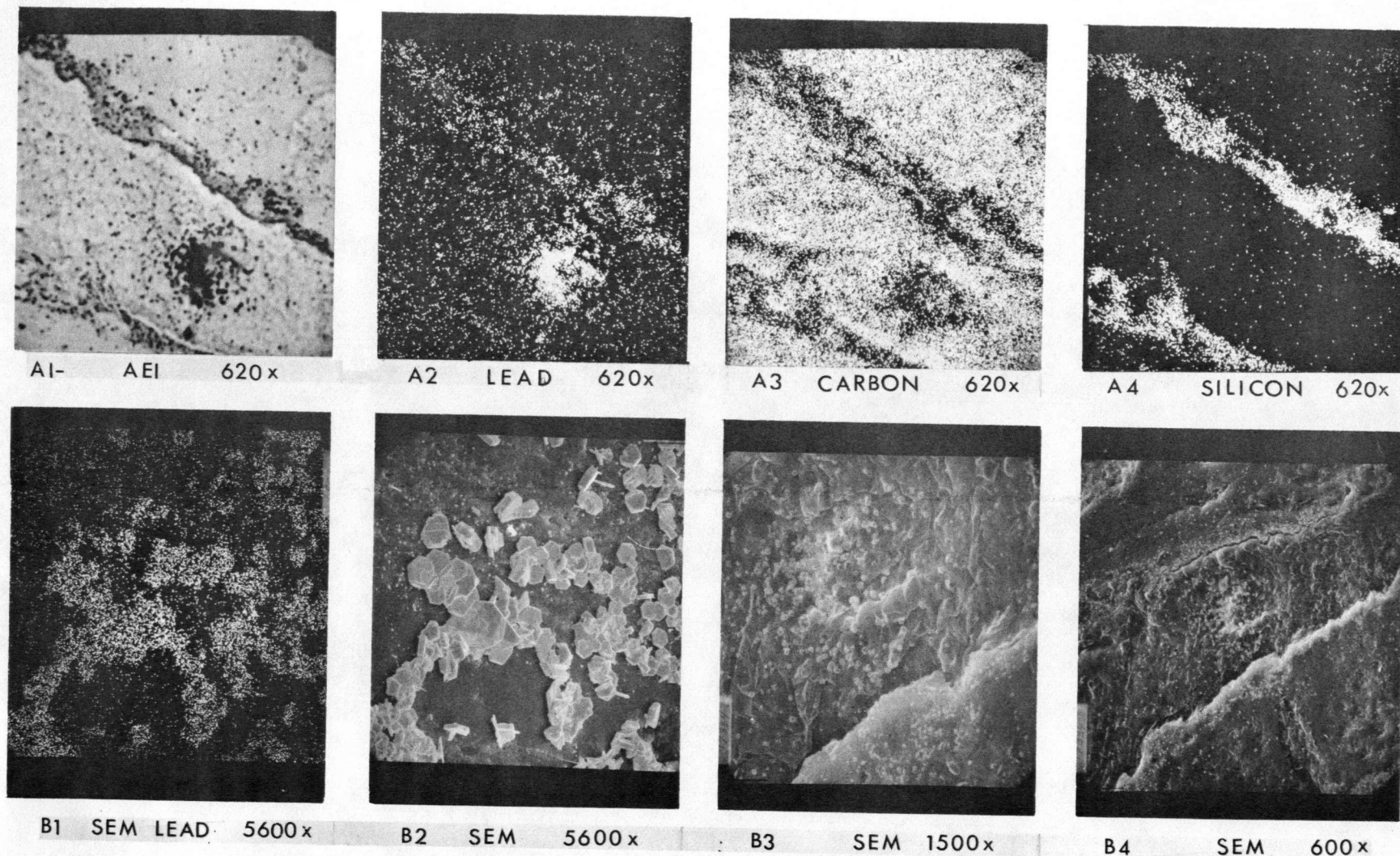
FIGURE 32b -ADSORPTION OF LEAD ON THE ACTIVATED CARBON PARTICLES.

A1 TO A4 - ELEMENTAL MAPPING USING THE ELECTRON MICROPROBE SHOWING THAT LEAD DOES NOT ADSORB.

B1 TO B4 - SEM IMAGES SHOWING THAT LEAD IS PHYSICALLY ADSORBED ON THE SURFACE OF THE PARTICLE.

is precipitated in a certain form on the surface of the particle. This precipitation appears as black dotes on the surface. The scanning of this area, using the Scanning Electron microscope, reveals a hexagonal shape of crystals precipitated.

The phenomenon can be explained more likely as a surface phenomenon exhibited by the activated carbon where its large surface area and its greater micropore volume are both contributing to enhance the crystallization of the lead nitrate into hexagonal crystals upon evaporation of the solution. These crystals are therefore precipitated on the surface of activated carbon.

It is suggested that a true chemisorption is not likely taking place in this case.

3.2   Infra-red spectra

Infra-red spectroscopy is used as another useful diagnostic tool to ascertain the interaction of the adsorbed heavy metal ions with the acidic function groups of coal, mainly carboxyls - COOH and phenolic hydroxyls - OH.

Water washed and acid washed samples of surface and core coal have been used in this study.

The results are summarized in four groups of infra-red absorption spectra in the region of 1900 to 800 $cm^{-1}$ which are shown in Figures 33A, B, C, and D.

Each group consists of four infra-red spectra named as follows:
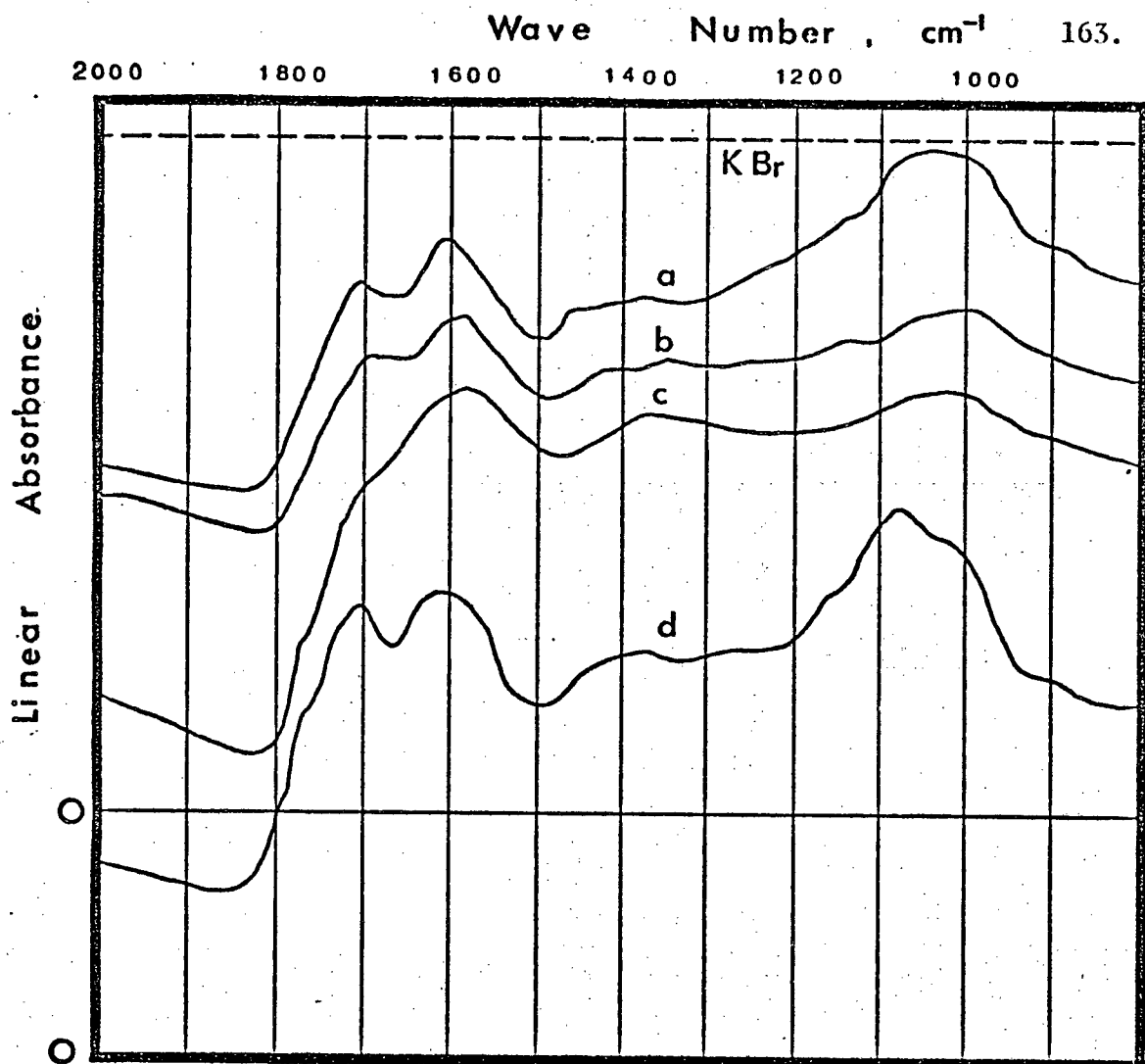
FIGURE 33A : INFRA-RED SPECTRA OF WATER-WASHED OXIDIZED
SURFACE COAL SAMPLES,SHOWING THE CHANGES
IN THE ABSORPTION BANDS AT 1720,1600&1100 cm$^{-1}$

|  | | K(cm$^2$/gm.) at | |
|---|---|---|---|
|  | 1720 | 1600 | 1100 |
| a- original coal | 0.3] | 0.43 | 0.42 |
| b- after adsorption of lead (1Pb/2coal) | 0.11 | 0.65 | 0.25 |
| c- after adsorption of barium (]7.2Ba/1coal) | 0.07 | 0.82 | 0.]7 |
| d- acid anhydride derivative | 0.44 | 0.49 | 0.44 |
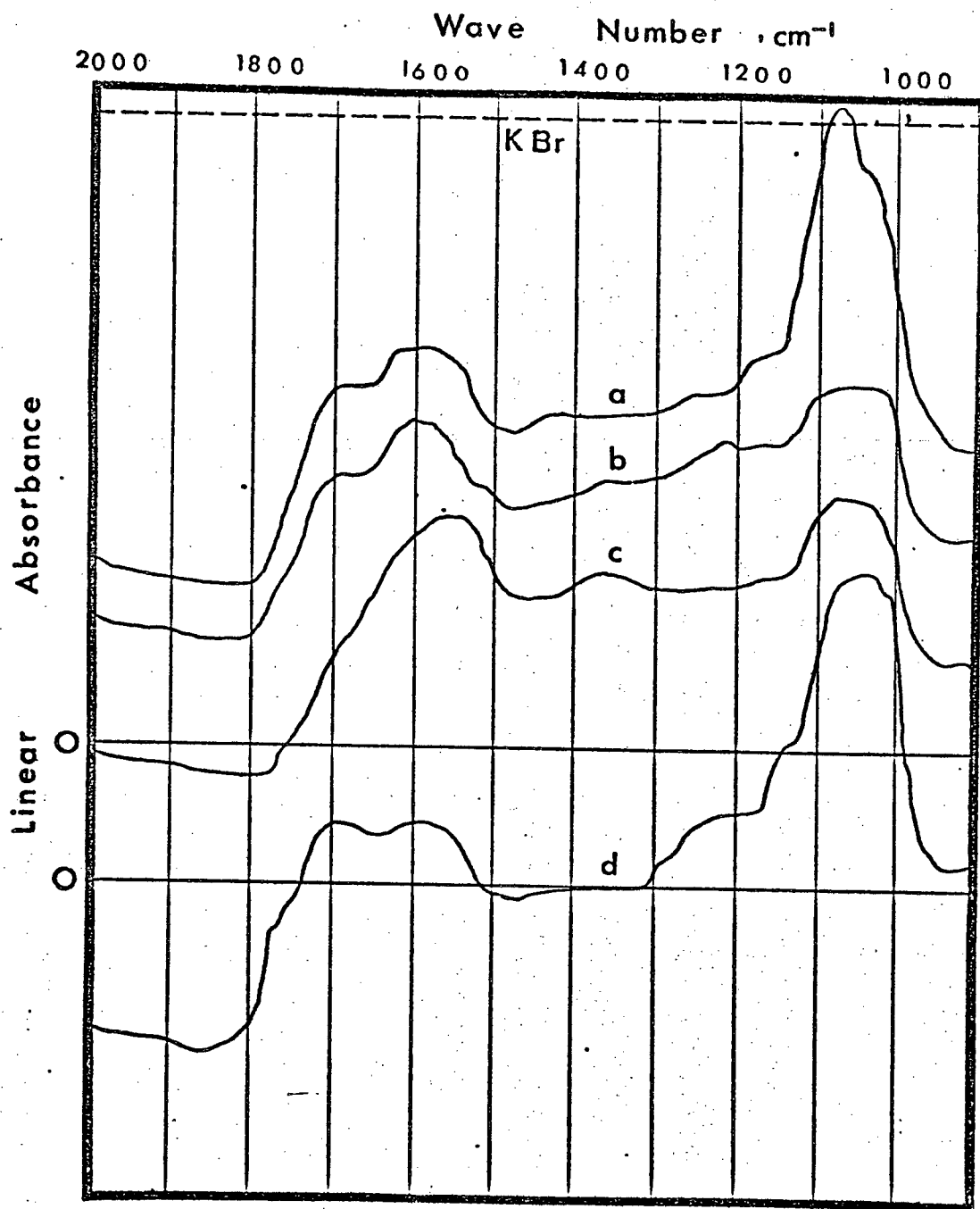
FIGURE 33B : INFRA-RED SPECTRA OF ACID-WASHED OXIDIZED
SURFACE COAL SAMPLES, SHOWING THE CHANGES
IN THE ABSORPTION BANDS AT 1720, 1600 & 1100 $cm^{-1}$.

|  | $K(cm^2/gm.)$ at | | |
|---|---|---|---|
|  | 1720 | 1600 | 1100 |
| a- original coal | 0.41 | 0.50 | 0.70 |
| b- after adsorption of lead (1Pb/2coal) | 0.33 | 0.45 | 0.30 |
| c- after adsorption of barium (17.2Ba/1coal) | 0.0 | 0.54 | 0.30 |
| d- acid anhydride derivative | 0.48 | 0.48 | 0.72 |
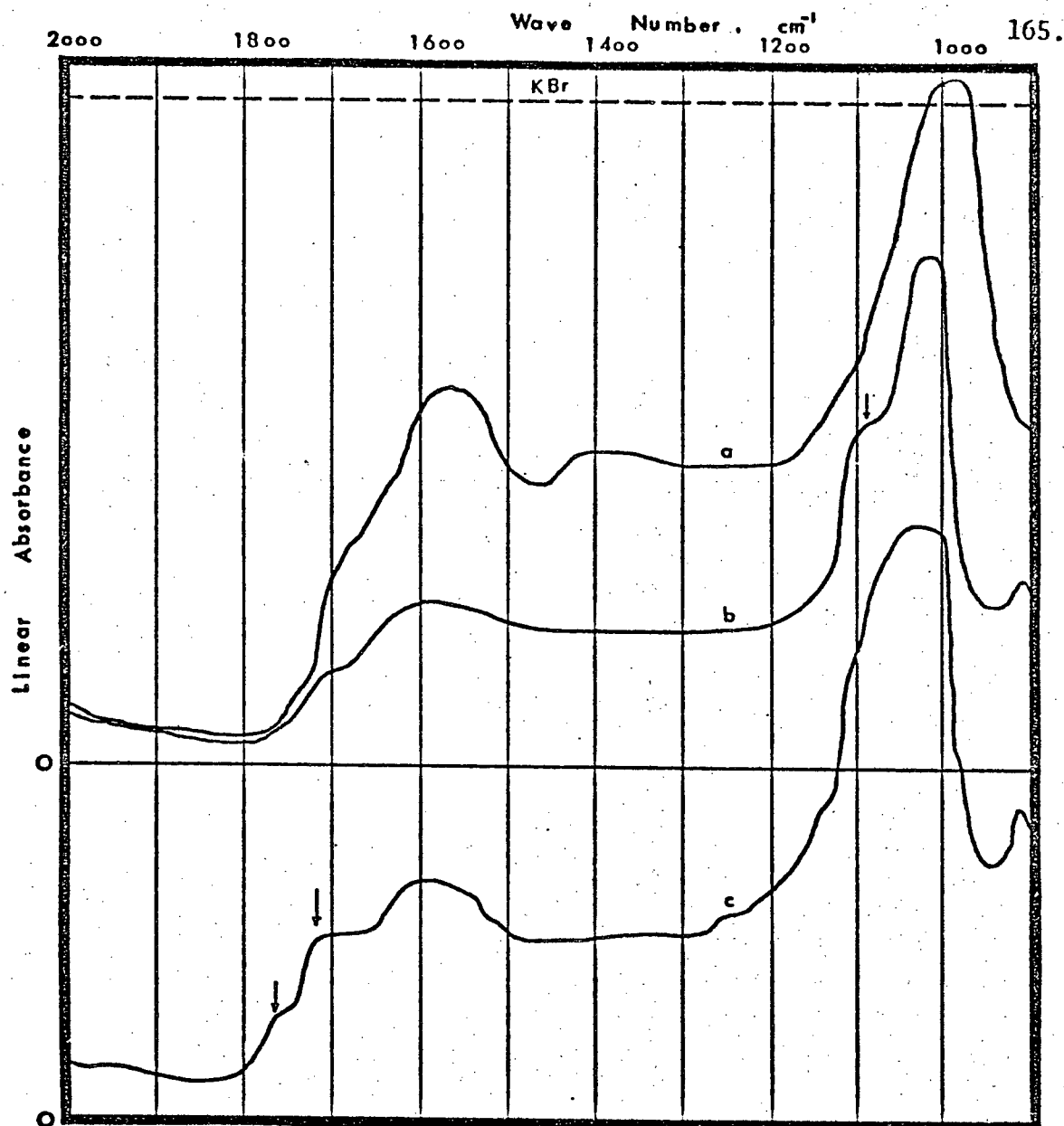
FIGURE 33 C:INFRA-RED SPECTRA OF WATER-WASHED,NON-OXIDIZED
CORE COAL SAMPLES,SHOWING THE CHANGES IN
THE ABSORPTION BANDS AT 1720,1600,1100cm$^{-1}$.

| | K(cm$^2$/gm) at | | |
|---|---|---|---|
| | 1720 | 1600 | 1100 |
| a- original coal | -- | 0.60 | 0.81 |
| b- after adsorption of lead (1Pb/2coal) | 0.13 | 0.23 | 0.76 |
| c- acid anhydride derivative | 0.26 | 0.34 | 0.69 |
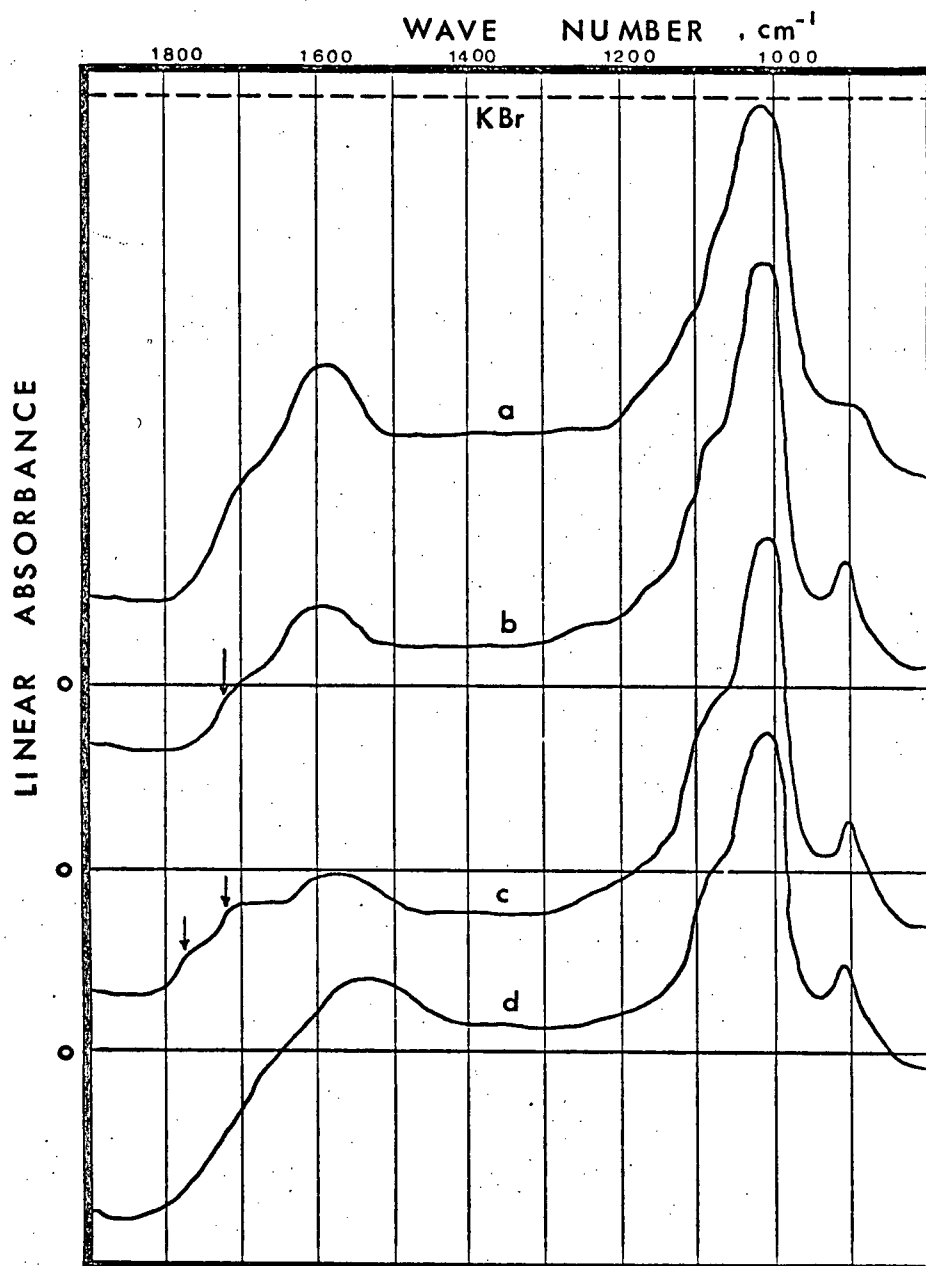
FIGURE 33D : INFRA-RED SPECTRA OF ACID-WASHED,NON-OXIDIZED
CORE COAL SAMPLES,SHOWING THE CHANGES IN
THE ABSORPTION BANDS AT 1720,1600,1100cm-1.

|  | K(cm$^2$/gm) at | | |
| --- | --- | --- | --- |
|  | 1720 | 1600 | 1100 |
| a-original coal | 0.25 | 0.51 | 0.76 |
| b- after adsorption of lead (1Pb/2coal) | 0.13 | 0.32 | 0.72 |
| c-acid anhydride derivative | 0.20 | 0.55 | 0.66 |
| d- after adsorption of barium (17.2Ba/1c0al) | ---- | 0.27 | 0.84 |

Spectrum "a"    --    original coal sample.

Spectrum "b"    ---    coal sample after adsorption of lead.

Spectrum "c"    ---    coal sample after adsorption of barium.

Spectrum "d"    ---    anhydride form of the coal sample.

It is obvious that the main changes, upon adsorption of metal ions, occur in the 1700 $cm^{-1}$ to 1600 $cm^{-1}$ and in the 1400 to near 1100 $cm^{-1}$ regions.

Therefore, the specific extinction coefficient "K" is calculated for each spectrum mentioned above for the absorption bands at near 1100, 1725 and 1600 $cm^{-1}$, the K values are listed on each figure mentioned above, while detailed tables, including the corresponding values of the absorbance, are outlined in Appendix C-5.

This infra-red analyses cannot be considered a quantitative method for coal because of the high overlapping and broadening of the peaks which make it very difficult to draw an accurate base line for measuring the band intensities. Therefore, all the calculated K values during this course of study should be considered as approximate values.

Upon adsorption of metal ions by water-washed surface coal (Figure 33A) the 1720 $cm^{-1}$ band decreases (K 1720 drops from 0.31 to 0.11 $cm^2/mg$) while the 1600 band increases (K 1600 increases from 0.43 to 0.65). These changes are also accompanied by a decrease in the intensity of the 1100 $cm^{-1}$ band (K 1100 drops from 0.42 to 0.25 $cm^2/mg$) and also a slight increase in the 1400 band. In the case of adsorption of the

barium ions, the changes are much greater and the 1720 band (assigned for COOH) almost disappears. These changes are likely due to the conversion of -COOH to COO⁻ carboxylate form to which metal ions are expected to be bonded by electro-valent bonding.

These results are in a good agreement with that obtained by Schnitzer, 1969 for metal-soil humic acid complexes. The great decrease in the intensity of the 1100 $cm^{-1}$ band is likely due to the partial participation of phenolic -OH groups in the interaction with the metal ions. Since the broad band exists in the region between 1100 - 1200 $cm^{-1}$ in all the infrared spectra values of humic materials they are assigned as due to phenoxy C-O vibrations of phenolic -OH groups (Schnitzer, 1964; Wright, 1960).

Spectrum "a" in Figure 33B shows that washing the coal with acid, increases the intensity of the 1720 $cm^{-1}$ and the 1100 $cm^{-1}$ bands and this is due to the conversion of the carboxylate form to the acid form COOH. Also, a sharpening of the 1100 is noticed which may be due to the dissolution of some of the "gangue" mineral matter which absorbs infra-red at the same wave length leaving the organic matter band with less broadening. Spectra "b" and "c" of Figure 33B indicate that the changes in the main bands are the same as in the case of water-washed coal, and therefore confirms the involvement of both carboxyl and to some extent phenolic hydroxyl in the mechanism of adsorption of metal ions by coal.

A greater decrease is noted in the 1720 $cm^{-1}$ band where the K 1720 drops from 0.41 to almost zero, while K 1100 decreases from 0.7 to 0.3 $cm^2/mg$. In addition, the new band starts to appear at the 1400 $cm^{-1}$, is also assigned for carboxylate formation ($COO^-$) (Schnitzer, 1971).

Accordingly, acid washed coal may be expected to exhibit more reactivity than water washed coal due to the increased availability of the free COOH groups upon acidification.

Figures 33C and D are the infra-red spectra of water washed and acid washed core coal samples respectively.

Spectrum "a" in Figure 33C shows that the core coal does not contain any appreciable free carboxylic groups compared to the oxidized surface coal. However upon acid washing a very slight shoulder at the 1720 $cm^{-1}$ appears which is mainly due to carbon oxygen double band (C = O) stretching vibration. This indicates that there are very few $COO^-$ groups in the structure of the core coal which is considerably less oxidized than the surface coal.

By adsorption of the metal ions, the changes obtained in the main infra-red absorption bands of the spectra are completely different than those obtained in the case of surface coal. Spectra "b" and "c" in Figures 33C and D show a great decrease in the intensity of the 1600 $cm^{-1}$ band (K 1600 drops from 0.6 to 0.23 $cm^2/mg$ while no appreciable change in the K 1100 is noticed. A sharp decrease is also noticed in the

K 3450 values from 0.63 to 0.25 $cm^2$/mg. This band is usually assigned to hydrogen bonded -OH, while in the case of surface coal no change in the 3450 can be noticed. This change can be explained by the participation of the phenolic hydroxyl -OH groups in the mechanisms of the adsorption of metal ions by core coal to a higher degree than that in the case of surface coal, where the carboxyl groups show the greater involvement in the mechanism.

A formation of coordinate covalent bonds, involving oxygen, phenolic OH groups, and the metal ions is expected in this case.

However, it should be mentioned that it is possible that decreases in absorption in this frequency region are offset by increased absorption arising from OH groups of water or other sources.

3.2.1  Proximity of carboxyls in coal

Spectra marked "d" in Figures 33A, B, C and D describe the spectra obtained for the anhydride form of each coal sample under scrutiny.

These shoulders at 1775, 1800 and 1190 $cm^{-1}$ assigned to stretching vibration of anhydride form of humic acids (Wood, 1961).

The peaks near 1100 $cm^{-1}$, in the spectra of the anhydride form are mainly due to the increase of the C-O bond formation.

In both types of coals, acid anhydrides may already be formed, therefore, there is likely to be a substantial

portion of the COOH and phenolic -OH groups already present
in the coal, which are likely to occupy positions adjacent
enough to each other to form 5-membered cyclic anhydrides of
the following (Wood, 1961).

Type I:  By interaction of 2 adjacent -COOH groups
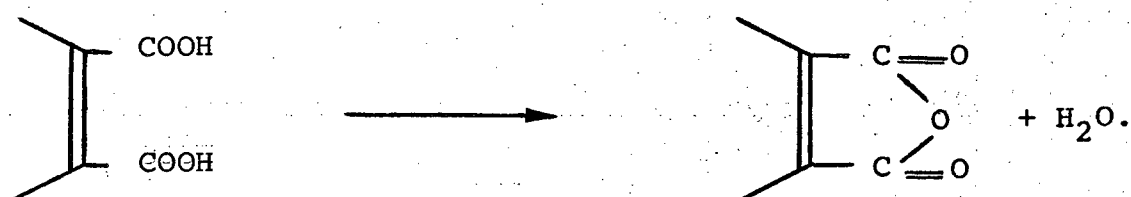


Type II:  By interaction of one COOH with an adjacent phenolic
OH group to form either cyclic esters

or open chain aliphatic esters
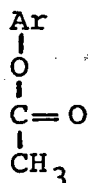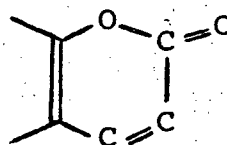


The increase in intensity of the 1720 $cm^{-1}$ band
after anhydride formation is probably due to the ester forma-
tion.

Between 10-90% of the COOH groups in eight different
humic acid preparations were found to form cyclic anhydrides
(Butler, 1966).  From this result, it appears that a  sub-
stantial portion of the COOH groups in coal may occupy positions

close enough to each other to form metal complexes which have a cyclic structure similar to that of the cyclic anhydride; this is further supported by the great similarity obtained between the infra-red spectra of the coal treated with the metal ions and that of the acid anhydride form of the coal.

More study and research are required to prove this hypothesis on a quantitative basis and to determine the percentage of the COOH forming a cyclic anhydride.

## 3.3 Cation exchange capacity

The results shown in Table 28 compare the value of the exchangeable Ca, Mg. K and Na cations with the total cation exchange capacity (CEC) for coal and activated carbon.

It is obvious that acid washed coal possesses the highest CEC value at 132.5    m.eq./100 gm coal, value of 0.3 m.eq/100 gram is obtained for the four exchangeable cations mentioned above. This result shows that surface coal can be ranked as a good cation exchange material. Its reactivity is therefore mainly attributed to the available cation exchange sites which do not include exchangeable cations of Na, K, Ca or Mg ions but may be mainly due to an organic type of cation exchange which exists in the organic part of the coal.

This type of cation exchange makes the coal capable of forming complexes, or chelates, upon interaction with the metal ions.

TABLE 28.    EXCHANGEABLE CATIONS AND TOTAL EXCHANGE
             CAPACITY OF HAT CREEK COALS AND ACTIVATED
             CARBON

| Material | Exchangeable Cations m.eq/100 gm | | | | | Total cation exchange capacity (CEC) m.eq/100 gm |
|---|---|---|---|---|---|---|
| | Ca | Mg | K | Na | Total | |
| Water washed surface coal | 9.24 | 4.52 | 0.218 | 0.97 | ~ 15 | 84.8 |
| Acid washed surface coal | 0.14 | 0.06 | 0.046 | 0.04 | ~ 0.3 | 132.5 |
| Water washed core coal | 19.84 | 7.81 | 0.557 | 8.81 | ~ 37 | 38.7* |
| Water washed activated carbon | 7.11 | 2.76 | 0.091 | 3.92 | ~ 14 | 14.4* |

*  Acid washed samples for core coal and activated carbon do not

   have any significant differences in the CEC values than that

   of the water washed samples.

This fact has been previously proven for soil (Kelley, 1948) where the part played by organic matter in cation exchange was traceable to the so-called humic acids.

Water washed surface coal exhibits slightly lower values of CEC than the acid washed coal, indicating that washing with acid helps to increase the reactivity of the coal through the introduction of more $H^+$ protons into the organic molecules.

The core coal exhibits much lower values for the exchangeable cations and the total CEC compared to that of surface coal. A value of 37 m.eq/100 gm is obtained for the exchangeable cation while 38.7 m.eq/100 gm is the total CEC of the core coal.

These results indicate that the exchangeable reactivity of the core coal is only due to the cations of Ca, Mg, K and Na which are likely present in the mineral part of the coal. No substantial organic cations seem to be involved.

In comparison, activated carbon possesses the least value for exchange reactivity (CEC = 14.4 m.eq/100 gram) which is mostly the inorganic exchangeables of Ca, Mg, Na and K.

This explains the low efficiency exhibited by activated carbon for the removal of heavy metal ions in comparison with the superior efficiencies of the Hat Creek coal.

3.4 Molar ratio between reacted lead and released hydrogen

Detailed results of the lead adsorption experiments and the corresponding pH reductions are included in Appendix C-6. The statistical calculations and the percentage errors, which are calculated from duplicate experiments, confirm the high reliability of the measurement with an error ranging from 0.4 to a maximum of 2%.

Table 29 summarizes the calculated molar ratio between the reacted lead and released hydrogen.

A sample calculation of this ratio is described in Appendix C-6.

It is usually known that the magnitude of the pH reduction attained upon the addition of metal ions to aqueous solutions of humic substances is often taken as a qualitative indicator of complex formation, (Schnitzer and Khan, 1972).

The greatest reduction in pH is obtained with acid washed surface coal which leads to a molar ratio of $\frac{Pb^{++}}{H^{+}} = 1/2$.

This means that surface coal has the highest binding capacity towards metal ions to form a stable complex with a displacement of 2 H ions for each lead ion adsorbed.

In the case of water washed surface coal, the drop in pH obtained is much less and $\frac{Pb^{++}}{H^{+}}$ ratio is equal to 1/1.

In comparison, the molar ratio $\frac{Pb^{++}}{H^{+}}$ obtained when water washed core coal is used, is in order of 1/0.05 which indicates that there is no appreciable hydrogen reduction on the addition of metal ions and therefore the possibility for complex

TABLE 29.    MOLAR RATIO OF ADSORBED $Pb^{++}$ and EXCHANGEABLE $H^+$
(Details in Appendix C-6)

| Material | pH reduction | $\dfrac{Pb^{++}}{H^+}$ * |
|---|---|---|
| 1. <u>Surface coal</u> | | |
| water washed | 1.535 | 1 :0.89 |
| acid washed | 1.810 | 1.07:2.0 |
| | | |
| 2. <u>Core coal</u> | | |
| water washed | 0.555 | 1 :0.055 |
| acid washed | 1.530 | 0.8 :2 |

$\dfrac{Pb^{++}}{H^+}$ = ratio between the adsorbed lead ions and the corres-
ponding exchanged hydrogen which are replaced by
lead ions and released in the solution.

formation is very small, and a rather ordinary salt formation is the predominant mechanism in this case.

Acid washing of the core coal seems to increase greatly its ability for complex formation and in this case a higher magnitude of pH reduction is obtained with a corresponding $\frac{Pb^{++}}{H^+}$ ratio equal to 0.8/2

3.5 Acid groups in coal.

Acid groups are defined as the carboxyl COOH plus the phenolic hydroxyl -OH.

The latter is considered to be the difference between the measured total acidity and the measured carboxyl groups. The values of the total acidity and carboxyl groups are presented both in milliequivalents per gram of coal and also in terms of millequivalent per unit BET surface area for interpretation of the results with reference to the surface area available.

The effects of some variables such as type of coal, type of washing applied and the magnitude of the change in the acid groups which occur upon lead adsorption are determined statistically using a three way analysis of variance technique also the comparison with activated carbon is carried out using a two way analysis of variance methods as the factor of the effect of lead adsorption is not included in this case. All the obtained results and their statistical analysis are included in Appendix C-7.

### 3.5.1 Carboxyl groups

Table 30a gives a summary of the carboxyl groups of coal and carbon samples in milliequivalent per unit BET surface area.

It is obvious that, acid washed surface coal has the highest number of carboxyl groups and therefore is expected to be the most efficient in the interaction with metal ions. This result is in good agreement with that obtained from other studies of the mechanism discussed in this chapter.

The three way analysis of variance gives the significance of the effect of different variables on the values of the carboxyl groups. The F values included in Appendix C-7-1 show that carboxyl groups vary significantly when different coal samples are used. As an example, surface coal possesses the highest number of carboxyl groups, approximately 8 times more than core coal, while activated carbon has a negligible carboxyl value which is approximately 500 times less than that of core coal.

The statistical analysis also show that acid washing affects in a highly significant manner the number of carboxyl groups in coal. The number of carboxyl groups increases after acid washing due to more conversion of $COO^-$ to the free carboxyl COOH. This fact has been proven also in other sections of this chapter.

It is important to prove through this study that upon adsorption of lead ions the carboxyl groups of coal decrease significantly and this confirms the view that the carboxyl

TABLE 30a. MEAN VALUES OF CARBOXYL GROUPS IN COAL AND
CARBON IN M.EQUIV./UNIT "BET" AREA. EFFECT
OF WASHING AND ADSORPTION OF LEAD.*

| | Surface coal | Core coal | Activated Carbon |
|---|---|---|---|
| Water washed | | | |
| Untreated | 0.717 | 0.0696 | 0.0001 |
| Treated with lead | 0.662 | 0.0854 | N.D. |
| Acid washed | | | |
| Untreated | 0.861 | 0.1081 | 0.0002 |
| Treated with lead | 0.713 | 0.0928 | N.D. |

N.D.  Not detectable

* - All values quoted in milliequivalents per unit B.E.T. area.
  - Methods outlined in section 2, pp.146.
  - The relationship between the carboxyl groups in coal and
    the lead ions adsorbed is shown in section 4, pp. 188.

groups are highly involved in the adsorption mechanism of metal ions by coal. The F-test also showed significant interaction between the type of washing and the treatment with lead ions. This can be explained by the increase of the free carboxyl group obtained as a result of acid washing which will enhance the interaction with the lead ions and therefore create an increase in the adsorptive capacity as expected.

Also, the interaction between the type of coal and the treatment with lead is conclusive in affecting the carboxyl values in a way which can be explained by the different levels of carboxyl groups obtained from the two coals and the activated carbon tested. This consequently would affect the adsorption capacity obtained for each type of material.

3.5.2   Phenolic hydroxyl -OH

Two way and three way analyses of variance have been applied to the data obtained for total acidity and the calculated phenolic -OH values for the two types of coal, as well as the activated carbon. All results are included in Appendix C-7-2. The type of coal reflects significantly the values of the phenolic -OH groups. Surface coal still possesses the highest number of phenolic -OH groups reaching about 1.8 milliequivalents per unit BET surface area. In comparison, core coal has only 0.4 m.eq./unit BET area, while activated carbon seems to have no appreciable value; a calculated value being as low as 0.0006 m.eq./unit BET area is obtained, as shown in Table 30b.

TABLE 30b.  MEAN VALUES OF PHENOLIC -OH (TOTAL ACIDITY
— CARBOXYL COOH) FOR HAT CREEK COALS AND
ACTIVATED CARBON.  EFFECT OF TREATMENT WITH
LEAD. VALUES IN M. EQUIV/UNIT "BET" AREA.

|  | Surface coal | Core coal | Activated Carbon |
|---|---|---|---|
| **Water washed** | | | |
| Untreated | 1.830 | 0.339 | 0.0006 |
| Treated with lead | 2.182 | 0.276 | N.D. |
| **Acid washed** | | | |
| Untreated | 1.940 | 0.271 | 0.0016 |
| Treated with lead | 1.919 | 0.375 | N.D. |

N.D.  Not detectable

Acid washing has a non-significant effect on the
values of phenolic -OH in contrast to the effect obtained on
the carboxyl groups discussed earlier.

After adsorption of lead, no appreciable reduction in
the phenolic -OH values are noticed. This cannot be inter-
preted as the phenolic -OH does not participate in the inter-
action with metal ions since there are other factors which
still control the calculated values of the phenolic -OH.
Some of these factors are as follows:

1) The possibility that the decrease in the number of phenolic
   -OH groups obtained upon interaction of the metal is
   offset by the presence of OH groups of complexed
   hydroxylated metal and aluminum compounds already
   present in the coal. This interpretation is in
   agreement with that obtained from the infra-red
   spectral studies where the intensity of OH absorption
   near the 3450 $m^{-1}$ band remains undiminished after
   metal adsorption.

2) The possibility of physical adsorption of barium hydroxide
   during the determination of total acidity gives rise
   to the values higher than the true values;
   this effect is therefore impossible to exclude
   (Schaffer, 1970).

3) The possibility of the exchange of some adsorbed lead ions
   by barium ions used in the test, and therefore, the
   measured value of total acidity would be very similar
   before and after treatment with lead.

The following Section 3.6 will show the extent of exchange obtained during the total acidity test and carboxyl group tests using barium hydroxide and barium and calcium acetate respectively.

## 3.6 Lead exchanged with barium or calcium during the acid group tests.

The released lead ions during the total acidity and the carboxyl group measurements are determined and shown in Appendix C-7-3 (Table 1).

The highest level of exchange of lead is obtained during the determination of carboxyl groups using the reflux-barium acetate method. Up to 23.5% of the adsorbed lead is released during the test. This means that the carboxyl COOH values for coal treated with lead does not represent only the unreacted carboxyl because some of the barium ions are also consumed in the exchange with the adsorbed lead and therefore the values from this test are expected to be higher than the true values.

During the calcium acetate test for the carboxyl group, only 3.24% lead is released and therefore the carboxyl values obtained from this test can be considered as the closest to the true carboxyl values and therefore, it is possible to use these values in the estimation of the number of carboxyl groups actually participating in the interaction with lead, from which an approximate mechanism of reaction can be suggested.

Table 30c. Released lead ions during the total acidity and carboxy group measurements.

| Coal Samples | Total Acidity Using Ba(OH)$_2$ Lead Released | | | Carboxyl Groups | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | Using Barium Acetate Lead Released | | | Using Calcium Acetate Lead Released | | |
| | mg/l | mg/gm coal | % | mg/l | mg/gm coal | % | mg/l | mg/gm coal | % |
| Blank (no coal added) | 1 | N.D. | - | 3.5 | N.D. | - | 0.5 | N.D. | - |
| **1 Water-washed coal** | | | | | | | | | |
| Original | 1 | N.D. | - | 3.5 | N.D. | - | 0.5 | - | - |
| Treated with Lead | 25 | 3.07 | 6.93 | 30 | 7.76 | 17.52 | 12 | 3.05 | 6.89 |
| **2 Acid-washed coal** | | | | | | | | | |
| Original | 0.5 | N.D. | - | N.D. | N.D. | - | 1 | N.D. | - |
| Treated with Lead | 29 | 3.54 | 8.69 | 36.0 | 9.59 | 23.53 | 6 | 1.32 | 3.24 |

$$\text{* The percentage of lead released} = \frac{\text{lead released (mg/gm coal)}}{\text{lead absorbed (mg/gm coal)}} \times 100$$

During the total acidity determination, the lead released is in the order of 7-9% from that already adsorbed, and this makes it difficult to calculate the true number of phenolic -OH groups which interact with lead. Therefore, the infra-red spectra may be taken as the only evidence for the contribution of the phenolic -OH groups in the mechanism.

### 4. SUGGESTED MECHANISM FOR ADSORPTION OF LEAD BY COAL

The main approaches used in this research, to study the nature of the mechanism involved in the adsorption of metal ions by coal, would provide strong evidences for the interaction of the organic acid groups of the coal, mainly carboxyls and phenolic hydroxyls, with the metal ions, to form metal complexes and/or simple carboxylates.

The evidences, derived from the results obtained in Section 3, can be summarized as follows:

1) <u>Electron micro study</u>. Lead ions are predominantly adsorbed on areas containing carbon and oxygen and not on mineral matter containing silicon.

2) <u>I.R. spectral study</u>:

(a) Upon adsorption of lead ions by coal the 1725 and 1100 $cm^{-1}$ bands decrease in intensity while the 1600 and 1400 $cm^{-1}$ bands increase indicating the conversion of COOH to COO$^-$ groups to which positively charged metal ions are probably bonded

by electrovalent linkages. It is concluded that
phenolic -OH is likely participating and the metal
ions are probably bonded in this case to -OH by
coordinate covalent bands, (Schnitzer, 1969).

(b) The formation of an acid anhydride form is indicated
and therefore, adjacent carboxyl and/or phenolic
groups are confirmed to be in the structure of the
coal which raises the possibility of complex forma-
tions.

(c) The similarity of the spectrum of the cyclic acid
anhydride form to the spectrum obtained after
adsorption of lead gives evidence that a metal complex
similar to a cyclic anhydride form might be formed.

3) Chemical study

(a) The high value of the cation exchange capacity CEC
obtained for surface coal highly exceeds the total
exchangeable cations of Ca, Mg, K and Na. This
indicates the presence of other exchangeable sites in
the coal, which are likely the organic acidic func-
tional groups.

(b) The chemical analysis confirms that oxygen containing
functional groups (carboxyls and phenolic hydroxyls)
are abundant in Hat Creek coal especially the
oxidized surface coal.

(c) The number of lead ions adsorbed, hydrogen ions released
and carboxyl groups blocked are correlated for acid
washed surface coal. The result is, approximately,

one lead ion interacts with two carboxyl groups

(measured by the calcium acetate method) releasing

$2H^+$ into the solution.

4)    Possible clay - interference

This section will discuss the possibility of any

interference in the adsorption mechanism by the presence of

clay minerals present in the coal.

(a)    Clay-minerals, mainly kaolinite and bentonite (Monto-

morillonite and illite) differ greatly in their surface

properties.        Kaolinite possesses a very small

surface area of 5-20 $m^2/g$  and a low capacity to adsorb

cations.  Montomorillonite has a large surface area of

700-800 $m^2/g$  and a high cation adsorption capacity,

perhaps 10-15 times that of kaolinite (Brady, 1974).

In comparison, humic substances have a cation exchange

capacity (C.E.C.) which far exceeds even that of

montomorillonite.

The following values show a comparison between the C.E.C.

of clays and humic substances as given by Brady (1974)

| Material | C.E.C. (m.eq/100 gm) |
| --- | --- |
| Kaolinite | 8 |
| Montomorillonite | 100 |
| Humic substances | 150-200 |

A measurement of oxidized acid washed Hat Creek coal

gives a C.E.C. value of 132 m.eq/100 gms.

(b)   The mineral matter content in the oxidized coal samples

(water and acid washed) used in studying the

mechanism was determined using a low temperature-

ashing technique.   An average value of 30% (d.w.b.)

mineral matter was found in the samples tested.

The X-ray diffraction analysis was used to identify

qualitatively the type of minerals.   A range of 70-80%

(d.w.b.) of the minerals is present as quartz ($SiO_2$),

while less than 20-30% (d.w.b.) is present as kaolinite.

No detectable bentonite was noticed.   Therefore,

kaolinite is the only detectable clay mineral found

in the coal, it represents not more than 6-9% (d.w.b.)

of the coal sample.   Because of the poor surface

activity of kaolinite as described previously, the

contribution of this kaolinite in retaining of metal

ions is presumed to be negligible compared to that of

the organic portion of the coal.   The absence of bentonite

from the tested samples further confirms that clay

interference is negligible.

(c)   A direct proportionality is shown between the amount of

carboxyl groups of the coal and the lead ions removed

as previously described in details in this chapter

(section 3-4 and 3-5 and data included in Appendix C-6

and C-7.   This proportionality is tested and outlined

for both surface and core coal samples in the following

table.

| Coal Sample | (A) -COOH m.eq/gm coal | (B)Pb$^{++}$ adsorbed m.eq/gm coal | Propor. Constant (A) : (B) |
|---|---|---|---|
| S.W | 2.222 | 0.392 | 5.67 |
| S.A | 2.670 | 0.426 | 6.26 |
| C.W | 0.821 | 0.158 | 5.20 |
| C.A | 1.275 | 0.393 | 3.24 |

The above data show that the amount of lead adsorbed is directly proportional to the amount of carboxyl groups originally present in the coal sample the ratio of -COOH to Pb$^{++}$ are ranged between 5-6 for all coal samples except for the acid washed core sample which has a value of about 3.2. This can be explained by significant participation of the phenolic -OH groups in this sample in the interaction with lead ions.

> If clay were responsible for any lead retention the proportionality, explained above, would not be so evident.

(d) The electron microprobe study shows clearly that lead ions are predominantly adsorbed on areas containing carbon and oxygen and not on mineral matter containing silicon. The silicon is also one component of the kaolinite found in the coal samples.

As a conclusion, the above evidences confirm clearly that clay-mineral in the coal does not contribute significantly in the removal of lead ions and therefore the main adsorption

mechanism takes place through the organic acid functional groups without any interference of the clay mineral of coal.

Suggested mechanism:    The above mentioned evidences confirm the fact that chemisorption rather than physical adsorption is involved in the adsorption of lead by coal, and a mechanism of cation exchange nature is assumed to be the predominant mechanism in which carboxyls and partially phenolic hydroxyls are bonded with the metal ions by electrovalent and coordinate covalent bonds respectively to form metal complexes with the coal.

These conclusions were previously confirmed for the interaction of humic acids extracted from either lignite or soil with divalent metal ions (Schnitzer and Skinner, 1965).

Accordingly, three types of mechanisms may be suggested to take place during the adsorption of lead ions by coal:

It was suggested earlier that Type I mechanism is the predominant one at high metal ion concentration with a development of electrovalent bonds, while Type II or III mechanisms are the predominant ones at low metal ion concentration with the development of coordinate covalent bonds (Gamble and Schnitzer, 1970).

In the case of coal, Type I is suggested to be likely the most predominant one in the case of acid washed oxidized surface coal.    While Type II or III are suggested to be the predominant ones when core coal is used.

TYPE I : TWO ADJACENT CARBOXYL GROUPS.
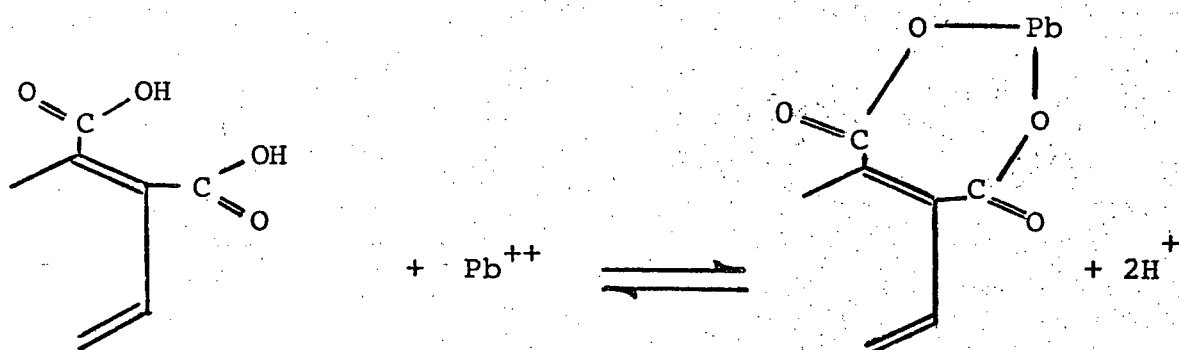


TYPE II : CARBOXYL GROUPS IS ORTHO TO A PHENOLIC GROUP.
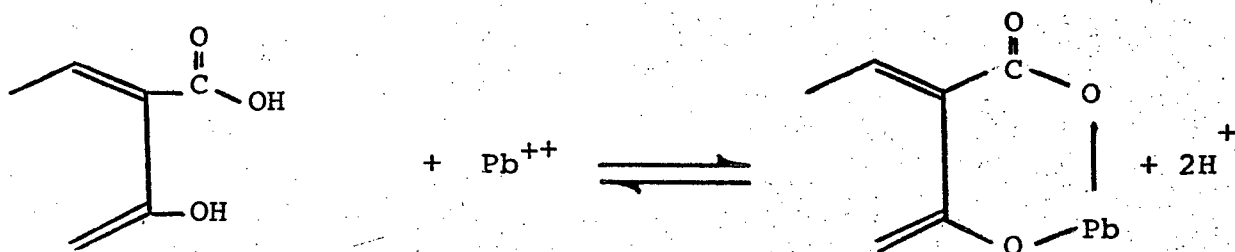


TYPE III : TWO ADJACENT CARBOXYL AND ONE ORTHO PHENOLIC
HYDROXYL.
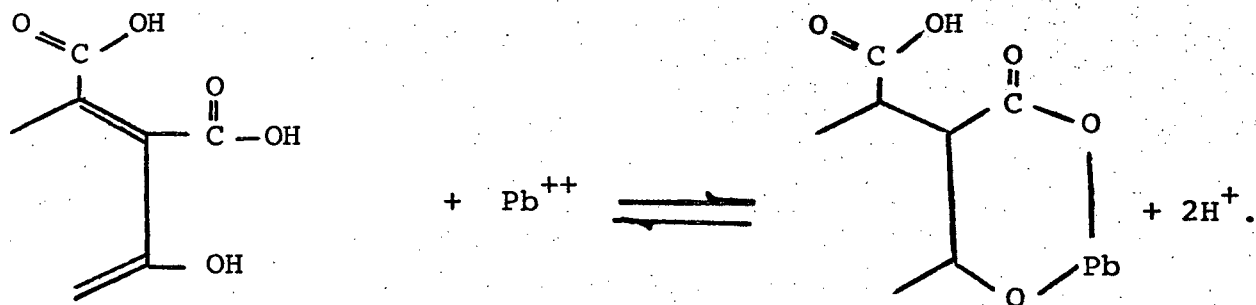
B.    Mechanism of Adsorption of Dissolved Organics by Coal

Preface:

Earlier work, discussed in Chapter VI has shown that Hat Creek coal is effective in the removal of biodegradable dissolved organic materials from solutions. This part of the research deals with the investigation of a mechanism for the removal of dissolved organics on the coal surface and to estimate the magnitude and the effect of biological activity in fixed coal beds for removal of the organics.

A material balance study on the coal bed system was utilized to estimate approximately the biooxidizable fraction of the organic substrate.

## 1.  MATERIALS

1.1  Adsorbent

Granular Hat Creek surface coal is used in all of the experiments. Two particle sizes of coal were used:

1.    0.533 mm average size.

2.    0.2965 mm average size.

1.2  Adsorbate

"OXO"[*]Beef Bouillon cubes were used as an organic substrate. The $BOD_5$ and COD obtained by dissolving a certain weight of cube in water was calibrated for a particular concentration.

---

* Supplier:   OXO Foods Division, Brooke Bond Foods Limited, Belleville, Canada.

However, "OXO" cubes contain other non-dissolved or partially dissolved biodegradable organic or inorganic matter such as spicy materials, starches, flavoring agents, synthetic colors, etc. These materials were responsible for most of the problems encountered during the course of the experiments.

2. DESIGN OF EXPERIMENTS

Three sets of experiments were conducted using fixed bed techniques under saturated (anaerobic) conditions. Several small columns of size 20 cm X 7 cm I.D. were used.

2.1 Using a coal bed with average coal particle size of 0.2965 mm

The bed was previously inoculated with two liters of the same substrate, drained, and left for 72 hours to enhance the bacterial growth on the coal surface. Then the influent with certain levels of $BOD_5$, COD and TOC were leached-through continuously at a flow rate of 50 ml/min to allow a contact time of 18 minutes along the column. Grab samples were collected periodically for analysis. After passing 40 liters of the solution, the bed was "blocked" due to the increase in the head loss. Backwashing was conducted using 20 liters of sodium hydroxide solution of pH = 11 (FMC Corporation, July, 1971). Composite samples from the washings were analyzed for $BOD_5$, COD and TOC. After rinsing and draining the bed, further volumes of substrate were leached continuously and the effluent samples were analyzed.

2.2 Using coal bed with an average coal size of
0.533 mm

Applying the above mentioned technique with a larger

size of coal in order to overcome the "blocking" problem

which occurred in the case of using the smaller size of coal.

2.3 Effect of inoculation

A third coal bed with average coal size of 0.533 mm

was set up and run anaerobically without an initial inocula-

tion until a break through point was reached.

2.4 Analytical methods

2.4.1 Total carbon (TC) and inorganic carbon (TIC) analyses

were conducted on the Beckman Total Organic Carbon Analyzer

Model 915.

2.4.2 $BOD_5$ and COD analyses were conducted by chemical

methods in accordance with the APHA Standard Methods, 14th

edition, 1975.

## 3. RESULTS AND DISCUSSION

The results shown in Appendix C-8, Table 1 indicate clearly that TOC, COD and $BOD_5$ values can be lowered by more than 50% using a coal media bed of particle size 0.2965 mm. The efficiency of removal declined slightly due to the development of anaerobic conditions throughout the column. Multiple layers of bacterial slime were formed on the coal surface which led to a leakage (increase) in the TOC, $BOD_5$ and COD values of the effluent in addition to a gradual decrease of the hydraulic conductivity; backwashing with 4 runs of 5 liters each of sodium hydroxide solution (pH = 11) removed the physically adsorbed organic materials from the coal surface. The washed materials were evaluated in terms of $BOD_5$, COD and TOC as shown in Table 2, Appendix C-8. The results indicate that the first five liters of wash solution removed most of the organic matter. Further washing was continued until no further change in the $BOD_5$, COD, TOC was obtained. This indicated that most and possibly all of the physically held materials were removed. Meanwhile, a control experiment was conducted to evaluate the organic components which might be washed from the coal with the organic materials of the substrate. This value was subtracted from all of the washing analyses to obtain the net value of the organic matter of the subtrate which was adsorbed by the coal. Table 31 shows that no more than approximately 103 mg of organic components of the coal were leached out by sodium hydroxide.

TABLE 31.   MATERIAL BALANCE FOR CALCULATION OF THE BIO-OXIDIZABLE FRACTION
OF THE ORGANIC SUBSTRATE

Average Particle Size of coal = 0.2965 mm

|  | ON TOC BASIS mgs | ON COD BASIS mgs | ON BOD$_5$ BASIS mgs |
|---|---|---|---|
| 1. Total amount applied | 3280 | 8840 | 6280 |
| 2. Amount removed by the coal | 1680 | 4480 | 3640 |
| 3. Organics washed out by backwashing | 1015 | 2155 | 1215 |
| 4. Amount washed from the coal surface by NaOH (Control) | 103 | -- | -- |
| 5. Estimated physically adsorbed fraction (3)-(4) | 912 | 2155 | 1215 |
| 6. Estimated bio-oxidized or consumed fraction through bacterial action (2)-(5) | 768 | 2325 | 2425 |
| PERCENTAGE PHYSICALLY ADSORBED | 54% | 48% | 33% |
| PERCENTAGE BIO-OXIDIZED | 46% | 52% | 67% |

Earlier work showed that the surface of the coal particles provided an enriched micro-environment for the microbial metabolism which enhanced the biological activity and the bacterial growth on the surface. Therefore, biological degradation or biooxidation of part of the organic matter could be expected. In order to estimate the biooxidized organics, an overall material balance on the coal bed was determined. The results shown in Table 31 indicate that 46% of the TOC was oxidized in a 60 mesh size coal bed, while 54% was physically adsorbed. On the COD basis, 52% was biooxidized while the highest value obtained was on the $BOD_5$ basis reaching 67%. This indicates that bacterial biodegradation is the dominating process on the surface.

Other forms of organics found in the "OXO" substrate were not readily biodegradable such as flavoring agents, cyclic organic compounds, spices etc. These materials are difficult to oxidize by bacterial action and this fact also explains the relatively lower values obtained for oxidized fractions in terms of TOC and COD.

3.1  Effect of backwashing on the regeneration of coal beds.

A second batch of organic solution was run through the backwashed columns and the cumulative TOC, COD and $BOD_5$ effluent from 16 liters applied on the spent coal are represented in Figures 34a, b and c respectively. All figures show a linear relationship between the load applied and the total amounts

FIGURE 34a. CUMULATIVE REMOVAL OF TOC BY SPENT COAL
AFTER BACKWASHING WITH SODIUM HYDROXIDE

$r^2 = 0.99970$
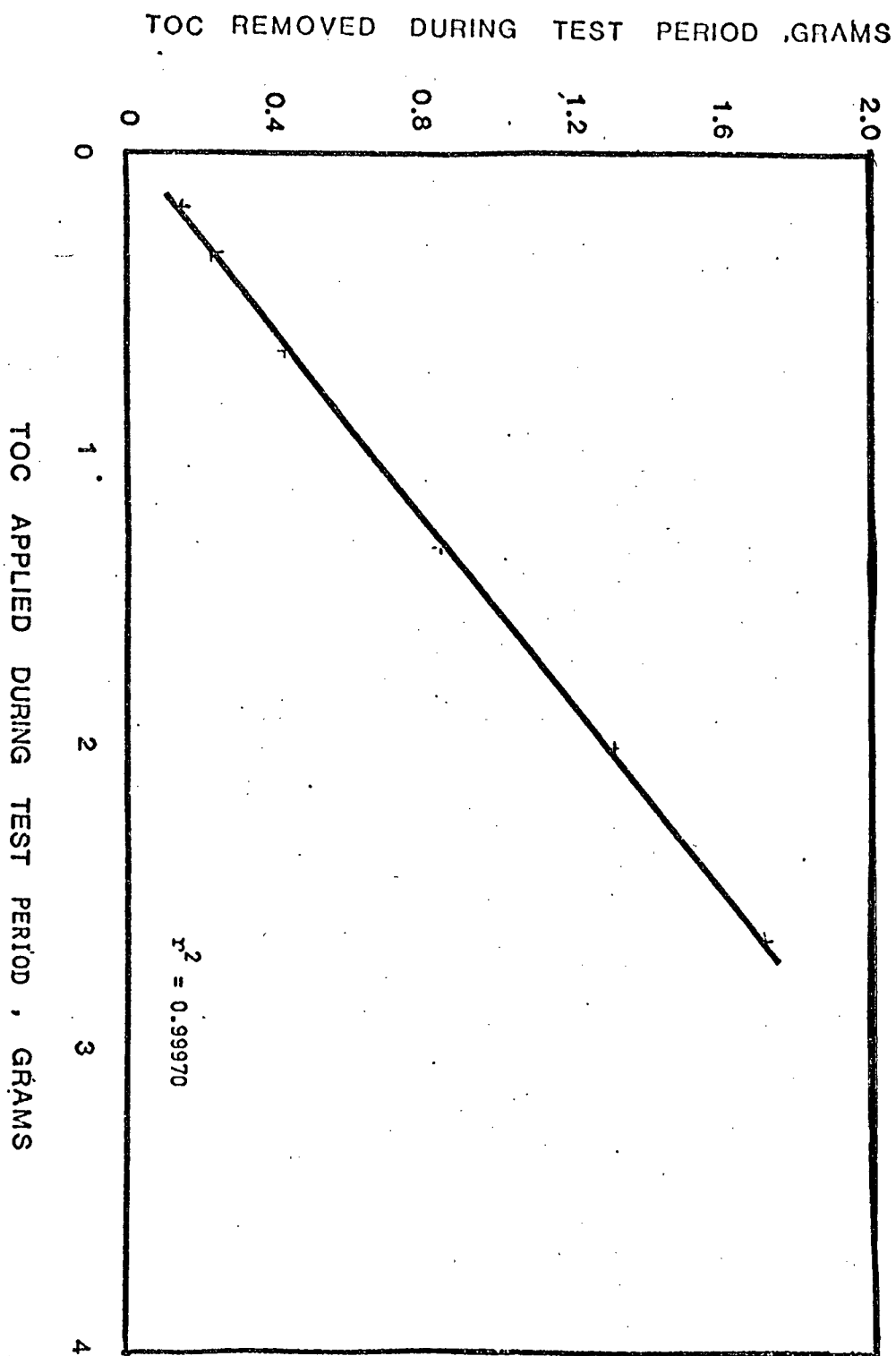
FIGURE 34b. CUMULATIVE REMOVAL OF COD BY SPENT COAL
AFTER BACK WASHING WITH SODIUM HYDROXIDE

COD REMOVED DURING TEST PERIOD , GRAMS.

COD APPLIED DURING TEST PERIOD , GRAMS.

$r^2 = 0.99196$
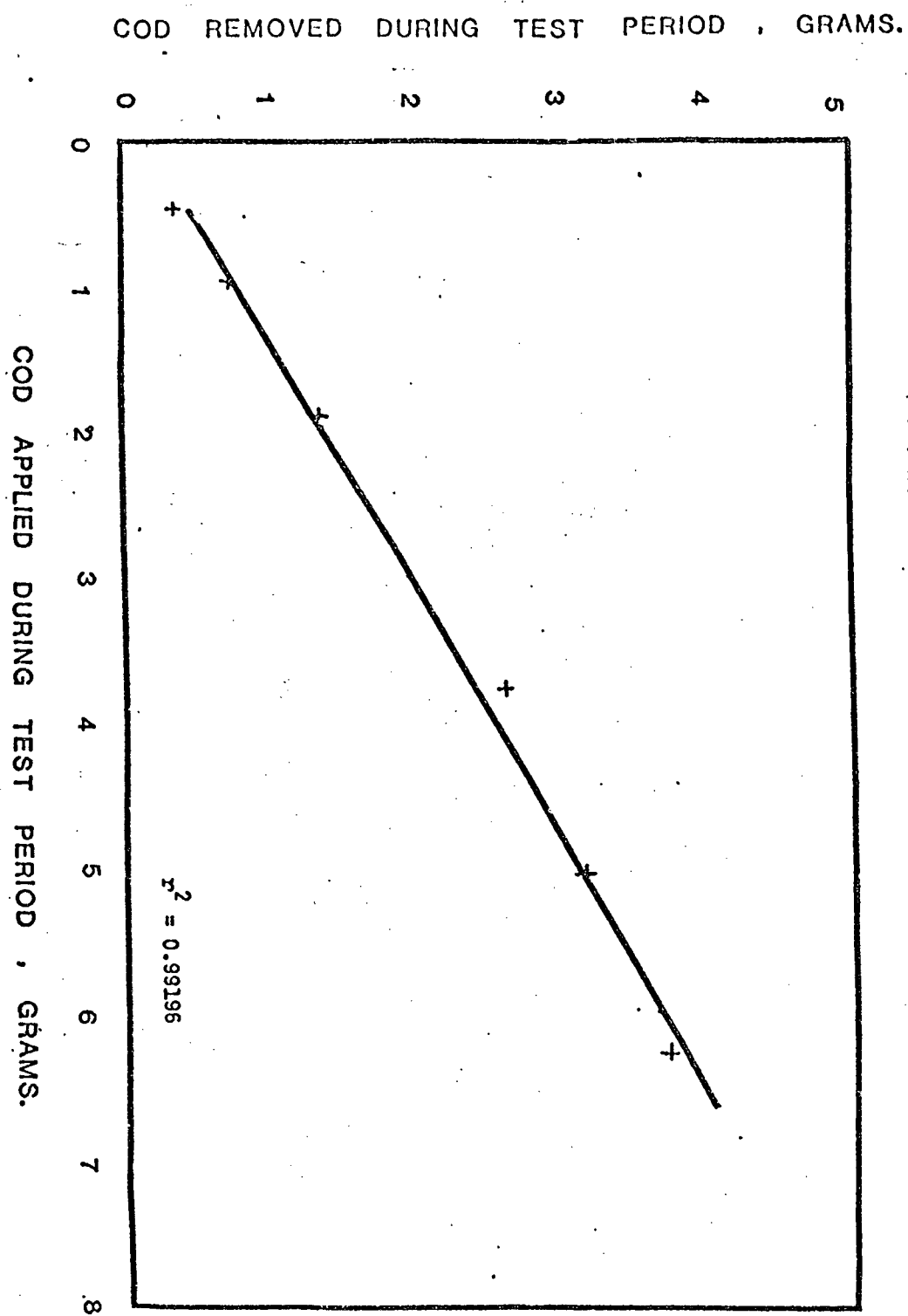
FIGURE 34c. CUMULATIVE REMOVAL OF $BOD_5$ BY SPENT COAL
AFTER BACKWASHING WITH SODIUM HYDROXIDE

$r^2 = 0.99058$

BOD REMOVED DURING TEST PERIOD, GRAMS

BOD APPLIED DURING TEST PERIOD, GRAMS
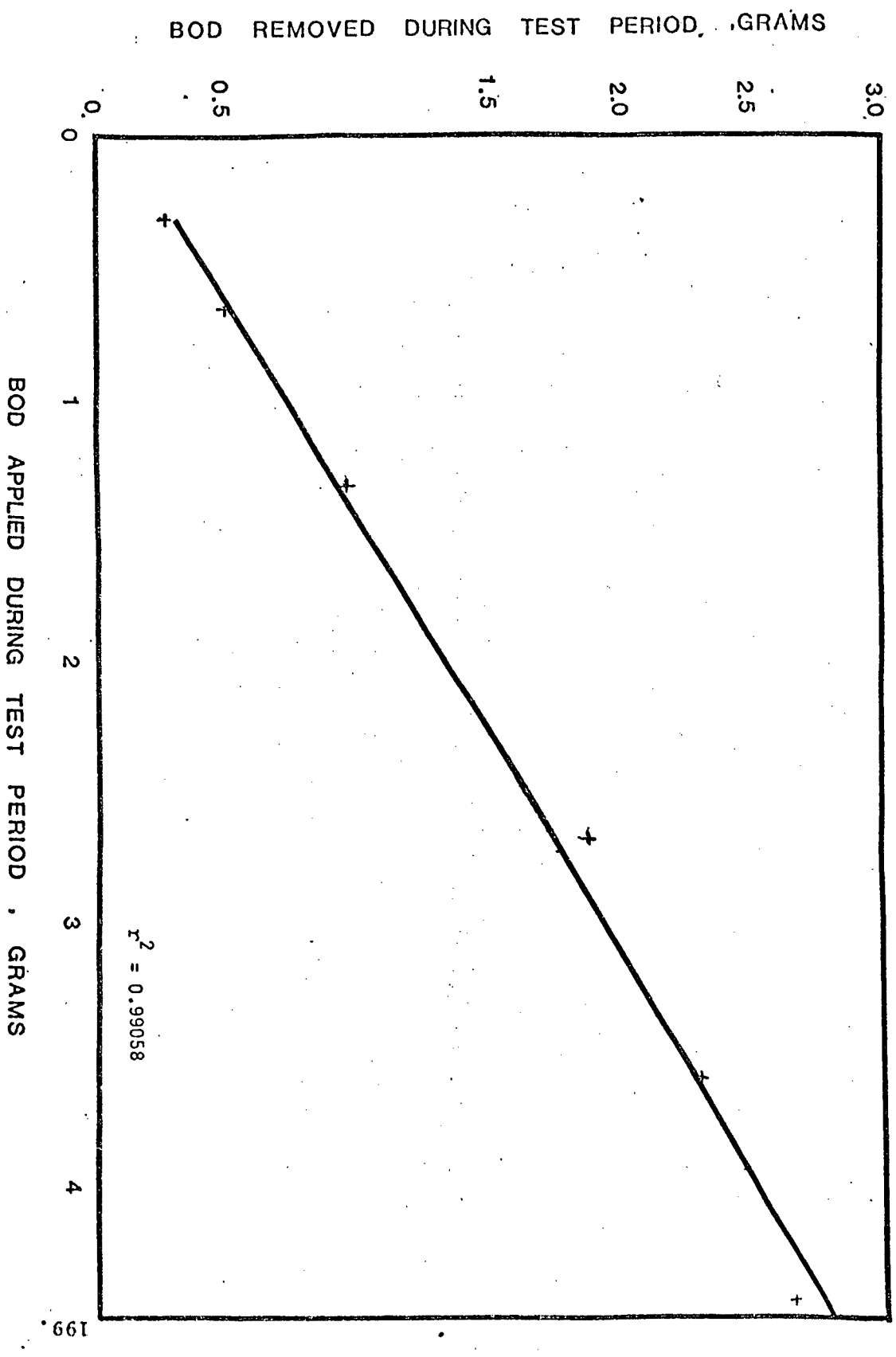
removed by the coal under this limited loading. From these results, it is obvious that NaOH can be a good regenerant for spent coal since the adsorptive quality of the coal is regained partially after backwashing. Table 3, Appendix C-8 summarizes the reduction in TOC, COD and $BOD_5$. When a larger size of coal (0.533 mm diameter) was used, a better hydraulic conductivity was obtained allowing a longer time period for effluent application before "blocking" occurred. Prior to applying the effluent, the coal bed was seeded with two liters of substrate solution and left for three days drainage. This period of inoculation aids in the initiation of bacterial growth and as a consequence more biological activity is expected by continuous running of the substrate solution through the bed, resulting in a continuous improvement in the efficiency of removal due to the biological oxidation. This means that the nine liters applied in this experiment were not enough to give adequate time for bacterial growth and metabolism on the coal surface. However, other workers have proved that continuous throughput improves the efficiency (F.M.C. Corporation, 1971), also aerobic conditions give better removal than anaerobic conditions. These factors should be taken into consideration in future work when studying the effect of inoculation of the coal bed on the removal efficiency of organics.

A series of experiments using the 0.533 mm size coal were conducted but without initial inoculation and the results compared with that obtained with the inoculated beds. The

comparison is shown in Figure 34d and verifies that inoculation gives better efficiency for reduction of TOC, COD and $BOD_5$ levels. An appreciable gradual drop in the efficiency was observed when a non-inoculated column was used; by running eight liters through the column an average of 28% reduction of TOC was achieved, while only 15% for $BOD_5$ and 25% for COD. These values are about one-half the efficiencies obtained with the inoculated bed.

Backwashing with NaOH was applied on the inoculated bed with the larger coal size and a material balance calculation on the total organic carbon showed that about 43.5% of the organic matter is oxidized while 56.5% is adsorbed.

In comparison, these results are very similar to those obtained by using the finer particle size of coal of 0.2965 mm.

## 3.2 Suggested mechanism for reduction of dissolved organics by coal

One possible explanation of the observed phenomonen may be that shown in Figure 35. It is assumed for this explanation that two biologically active films surround each coal particle. The interior film is anaerobic, the external film is aerobic. Adsorbable molecules pass through the films to the coal surface where partial anaerobic degradation may take place, forming low molecular weight degradation products such as organic acid, and alcohols, which have an inherently low relative energy for adsorption, this will diffuse through the external boundary film to the bulk solution. If an aerobic state is maintained

FIGURE 34a. EFFECT OF INOCULATION ON THE EFFICIENCY OF REMOVAL OF ORGANIC CARBON BY COAL

+ INOCULATED
$r^2 = 0.99728$

⊕ NON-INOCULATED
$r^2 = 0.99379$

TOTAL ORGANIC CARBON REMOVED MGS.

TOTAL ORGANIC CARBON APPLIED , MGS.
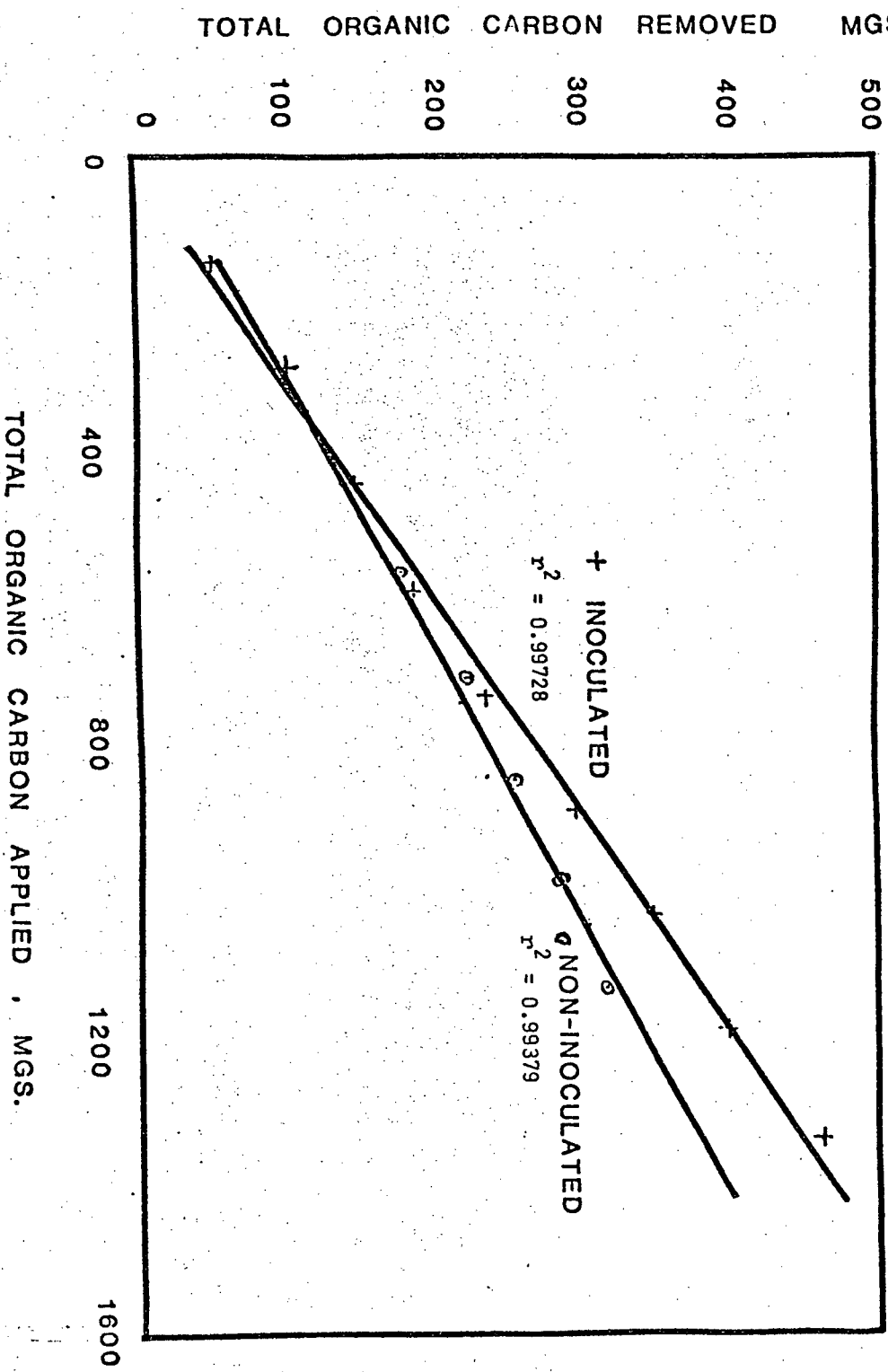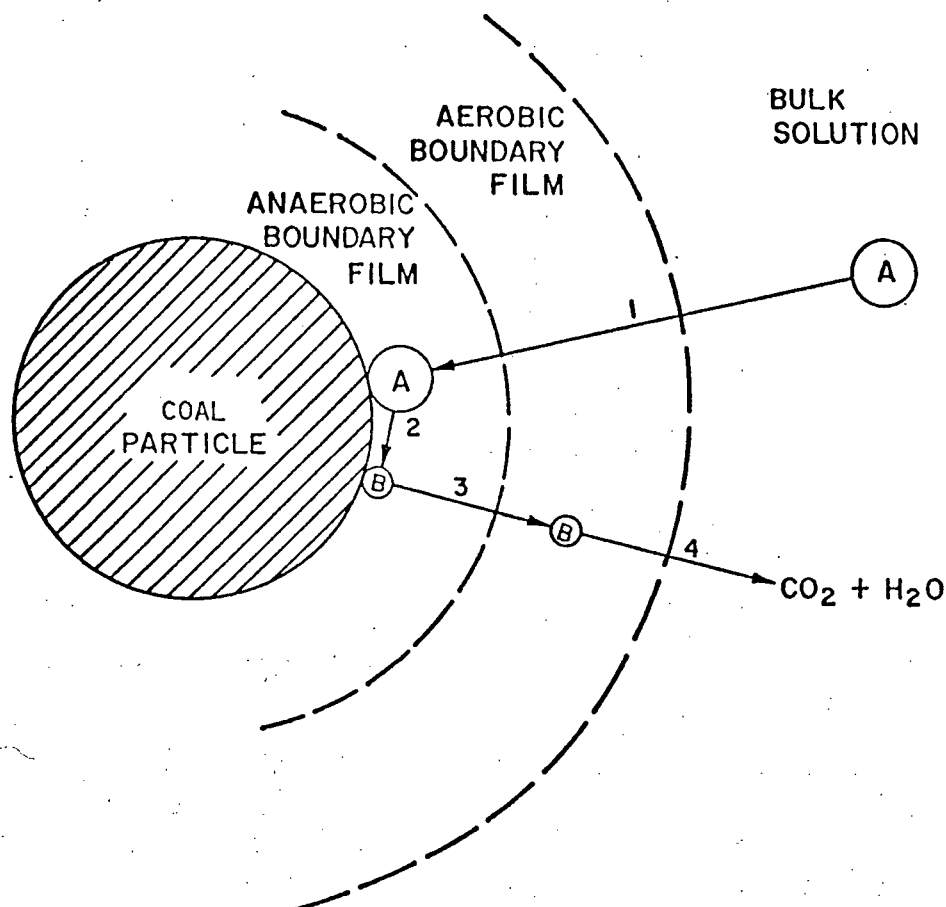
EVENT SEQUENCES: 1. DIFFUSION OF LARGE ADSORBING ORGANIC MOLE-
CULE (A) TO SURFACE OF CARBON.

2. ANAEROBIC DEGRADATION OF LARGE MOLECULE
(A) TO SMALL MOLECULE (B).

3. DIFFUSION OF SMALL NON-ADSORBING ORGANIC
MOLECULE (B) AWAY FROM SURFACE OF CARBON.

4. AEROBIC DEGRADATION OF SMALL MOLECULE (B)
TO $CO_2$ AND $H_2O$.

FIGURE 35— SCHEMATIC INTERPRETATION OF THE MODE OF IN
SITU BIOLOGIC EXTENSION OF ADSORPTION CAPACITY

(From: FMC Corporation)

in the outer layer of the boundary film on the coal and in the
solution phase, aerobic microorganisms are expected to grow
and oxidize the outward diffusing products of the anaerobic
decomposition.    This is consistent with the observation that
the effluents from the anaerobic coal beds used for this
research contain appreciable leakages to TOC, COD, and $BOD_5$
which were due to non-adsorbable organic matter, either from
the additives found in the "OXO" beef cubes or from the
anaerobic decomposition of the substrate.    This interpretation
is of course speculative.

# VII. APPLICATIONS IN SEWAGE TREATMENT

## Preface

The overall objective of this program of research and experimentation was to apply the coal sorption process to the treatment of municipal and industrial sewage for the removal of undesirable dissolved pollutants. Many of the pollutants, which are of organic or inorganic nature, are difficult to remove during the primary and secondary treatment of sewage.

Therefore in this chapter the applied aspects of the research are focussed upon the following sewage effluents:

1) Municipal sewage effluent emanating from the City of Vancouver was investigated for the removal of major dissolved pollutants such as $BOD_5$, COD, phosphorus, nitrogen, organic carbon and lead.

2) Industrial sewage effluent was obtained from an oil refinery to investigate the removal of the major pollutants such as phenol, cyanide, ammonia and dissolved organics.

In each case both batch, continuous, and long-term experiments were conducted to evaluate the adsorptive capacity and the service life of Hat Creek coal to treat such effluents.

Tentative calculations for the design of a coal bed based on the test data obtained indicated the design parameters which should be considered.

# 1.    MATERIALS

## 1.1  Hat Creek coal

Oxidized coal from the surface deposit was used in most of the experiments.  Unoxidized core coal and activated carbon were used occasionally for comparison.  The descriptions of these materials were previously mentioned in Chapter III.

## 1.2  Municipal sewage effluent

Samples of primary treated sewage were obtained from the Greater Vancouver Sewerage and Drainage District at the sewage treatment plant on Iona Island.  This effluent flows at a rate of 70 MGD and had been subjected to settlement and removal of the solids.

## 1.3  Industrial sewage effluent

This was a refinery wastewater supplied by the B.C. Petroleum Corporation.  The effluent had been previously passed through a trickling filter.

Both the municipal and the industrial effluents were stored in a $34^O$F cold room prior to the laboratory experiments.

# 2.    METHODS

## 2.1  Batch tests

The methods used were described in Chapter VI. Several coal particle sizes were tried during these tests.

## 2.2  Column tests

The method was described earlier in Chapter VI. Small

columns of size 20 cm X 7 cm I.D. filled with granular coal of sizes 4/14, 6/20 and 14/20 were used for the tests.

## 2.3 Design applications

The following long-term leaching processes were performed on a semi-pilot scale for the express purpose of obtaining sufficient data for the tentative calculation of the size of the coal bed required and the rate of consumption of the coal to treat certain sewage effluents.

## 2.3.1 Removal of lead from the artificial sewage effluent

Three columns of 4.76 cm I.D. and 35 cm, 70 cm and 140 cm lengths respectively were constructed and filled with fresh washed Hat Creek coal of 4/14 mesh size. A 5 mg/l lead solution was fed to each column at a rate of approximately 1 gal (Imp.) per minute per square foot of surface area $(gpm/ft^2)$. Daily effluent grab samples were collected from each column and analyzed for the residual lead. Leaching continued until a "break through point" of 0.5 mg/l of lead appeared in the effluent solutions.

## 2.3.2 Removal of dissolved organics from Iona sewage effluent

A continuous column process was set up at the Greater Vancouver Sewerage and Drainage District sewage treatment plant on Iona Island to provide for a steady supply of fresh sewage to the coal bed column.

A larger column (described earlier in Chapter VI, Figure 11 ) of dimensions 2m X 15.24 cm I.D., containing approximately 23 kgs of Hat Creek coal of particle size 6/20

mesh was employed. The sewage effluent was first pumped through the bed continuously under fixed-bed flow conditions. After 4 days of operation, the head loss increased greatly due to fouling from the sediment and subsequent blocking of the bed. The flow was then reversed to an expanded-type flow at a steady flow rate ranging between 300 - 315 mls/min which is equivalent to 1 gpm/ft$^2$ of area, allowing 30 minutes contact time. Grab samples were collected periodically from the 0, 0.5, 1 and 2 meters levels along the bed. The samples were then analyzed for $BOD_5$, COD, TOC and occasionally for pH as well as total and volatile residue.

The break through point was arbitrarily set up at $BOD_5$ concentration of 50 mg/l in the effluent.

2.3.3 Removal of phenol, cyanide and ammonia from the refinery effluent

A mixture of cyanide, phenol and ammonia, approximating concentrations of 1, 2 and 50 mg/l respectively was used as a synthetic waste effluent. The effluent was filtered through the larger column (2 m X 15.24 cm I.D.) containing approximately 18 kgs of coal. Water washed surface coal from the Hat Creek deposit of particle size 4/14 mesh was used. The flow rate was adjusted at 300 - 350 ml/min which is equivalent to 1 gpm/ft$^2$ at a contact time of approximately 30 minutes.

Grab samples were collected periodically from the 0, 1ft (30.5 cm), 3ft (91.4 cm) and 5½ft (167.8 cm) levels respectively and analyzed. The break through point was set

at 1/10 of the applied influent concentrations which are equivalent to approximately 0.2 mg/l of phenol, 0.1 mg/l of cyanide and 5.0 mg/l of ammonia.

The analytical methods used for all of the above analyses were previously described in Chapter VI.

### 3. RESULTS AND DISCUSSION

### 3.1 Municipal sewage

The Iona sewage samples used in these tests appeared to be diluted with storm water. The $BOD_5$ and COD values shown in Table 1 , Appendix C-9-1 are relatively low compared to a dry weather sample obtained earlier in the season with a $BOD_5$ analysis of 160 mg/l.

### 3.1.1 Batch tests

Two sets of experiments were applied using two different coal sizes of 48/60 mesh and < 150 mesh respectively. The test results are summarized in Tables 1 and 2 included in Appendix C-9-1.

Apparently a 1% w/w addition of coal is quite effective, yielding a $BOD_5$ reduction from 103 to 11 $BOD_5$ in the first hour of contact. The removal is greater than 89% rising to more than 94% in 24 hours of contact, while a 5% w/w addition of coal did not improve the removal value. Similar results with slightly lower removal values are shown for the COD analysis. The nitrogen content may account for this

change. The total nitrogen removal shows a more encouraging result than that for previous nitrate removal. This is likely due to an ammonia content in the sewage which formed a cationic radical ($NH_4^+$); this radical was then readily adsorbed on the coal surface more so than the anionic $NO_3^-$ which is quite soluble and less likely to adsorb on the coal surface. Also, the results show that lead ions are removed completely from the sewage to a non-detectable value when 1% coal is added.

Figure 36 gives a comparison between the efficiency of removal of all the mentioned pollutants by the coal.

### 3.1.2 Column test

This process gives a better removal of pollutants than the batch tests. The contact time in the column was approximately 25 minutes which is considered slightly lower than that used in the large scale applications with activated carbon when the contact time usually ranges from 35 - 50 minutes.

After 8 liters of continuous application of the sewage to the column, the coal appears to be continuing its normal rate of removal of different pollutants, namely $BOD_5$, COD, T-N, T-P, O-P and lead as shown in the data listed in Table 1, Appendix C-9-2.

It appears that a greater throughput volume should be applied to reach the break through point before the column becomes exhausted.
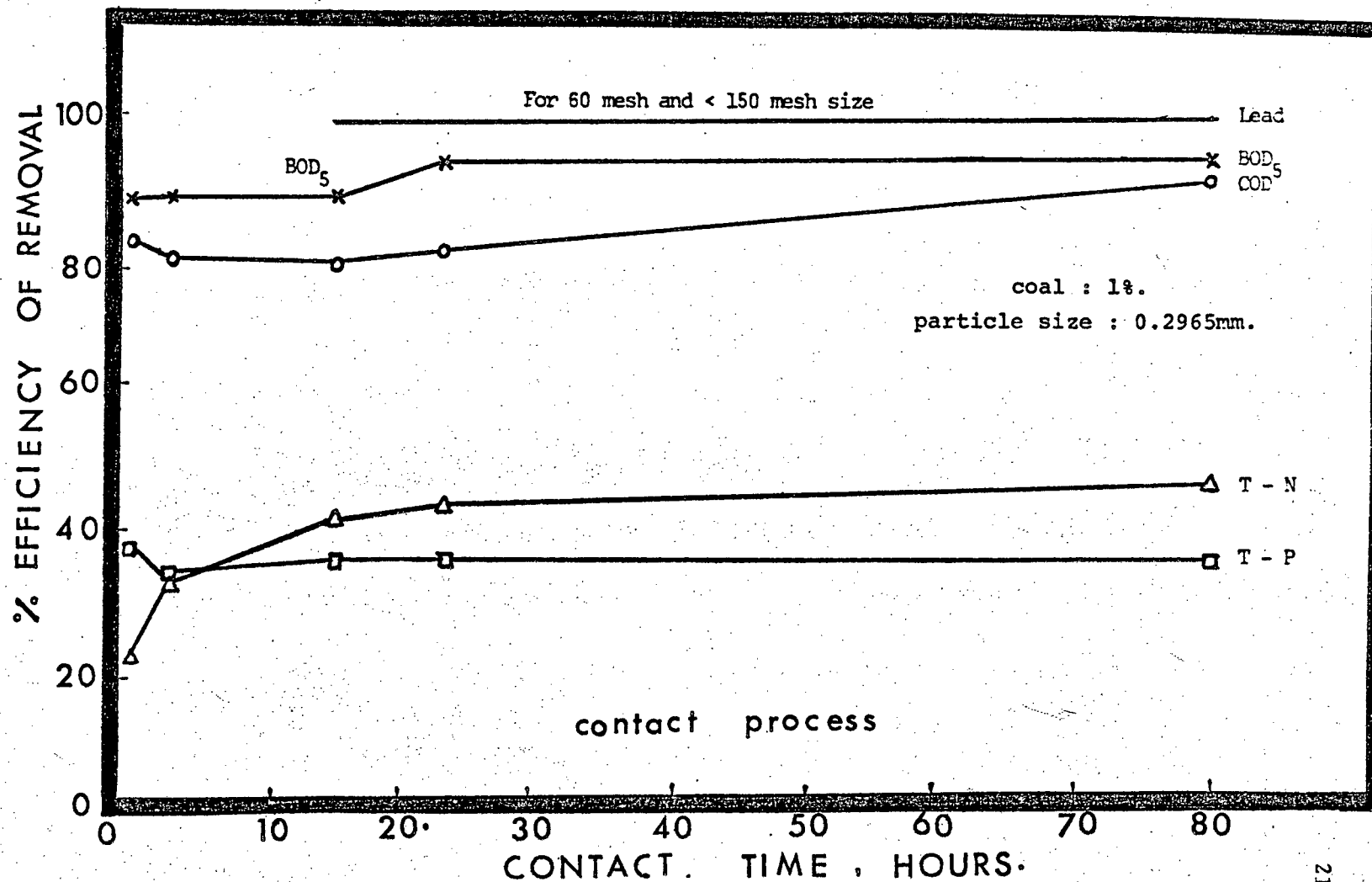
FIGURE 36 : EFFICIENCY OF REMVAL OF POLLUTANTS FROM IONA SEWAGE EFFLUENTS.

It seems fortunate that total nitrogen is removed which may contain ammonia in larger proportions. The $NO_3$-N value is not as serious a factor in Iona sewage since it is at very low concentrations.

Both the O-P and T-P are removed almost equally by column leaching but the removal declined slightly after 8 liters of application. However, the highest efficiency of removal was obtained for lead in both the contact and the leaching process. More than 80% of the lead was removed, calculated on a detectable basis. However this should, in essence, approximate a 100% removal value.

Figure 37 gives a comparison of the efficiency of the coal to remove each pollutant under observation from the municipal sewage.

3.1.3 Design applications

3.1.3.1 To remove lead ions from Iona sewage

The long-term experiment, described in section 2.3.1, was conducted for 58 days (1129 hours) of continuous leaching using the three coal bed depths of 30, 60 and 120 cm respectively. The columns and capacity data are tabulated in Appendix D-1. Table 1, while the break through curve for the 30 cm column is shown in Figure 38 indicating that the break through point at 0.5 mg/1 of retained lead is reached after passing approximately 380 gals of flow through the 30 cm column.

Coal size = 0.533 mm
Flow rate = 10-12 ml/min
Contact time = 25 minutes

Pb Removal > 80%

T-N

BOD₅

COD

T-P

O-P

BOD

COD

% EFFICIENCY OF REMOVAL

Throughput Values Liters
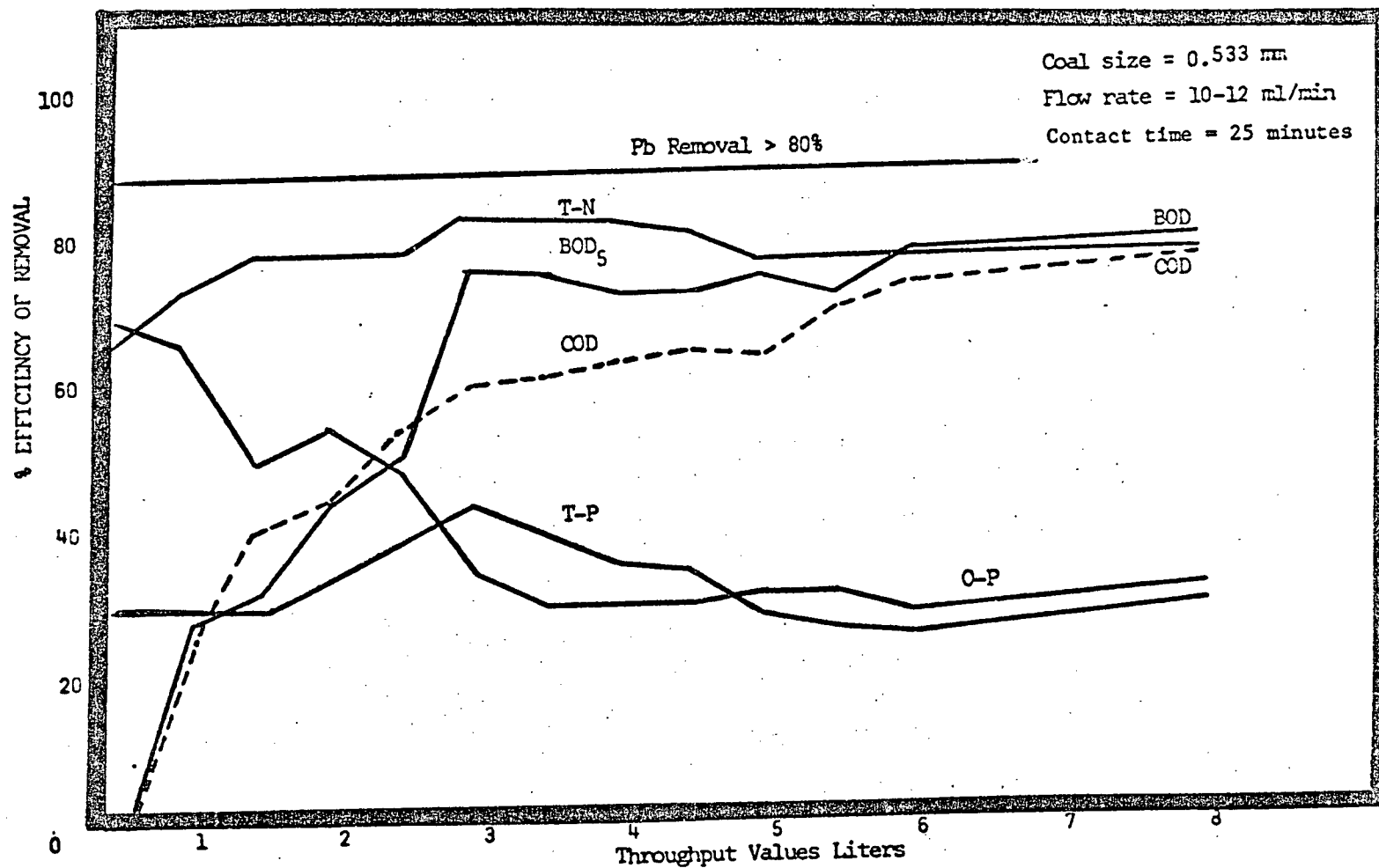
FIGURE 37 : EFFICIENCY OF REMOVAL OF ORGANIC & INORGANIC POLLUTANTS
FROM IONA SEWAGE BY COAL.
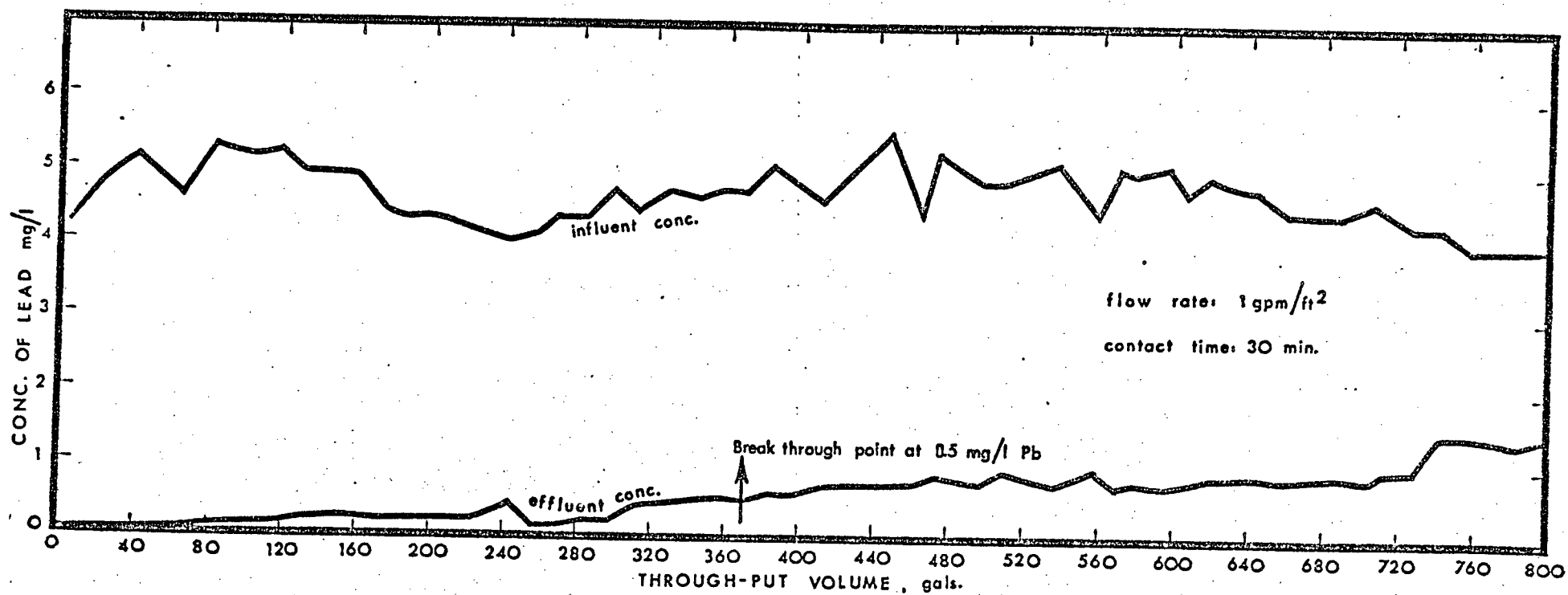
FIGURE 38 : BREAK-THROUGH CURVE AT 30cm LEVEL FOR LEACHING OF LEAD
SOLUTION THROUGH COAL BED.

214.

According to the Bohart Adam design relationship (Eckenfelder, 1970) if the service time to reach the break through point is plotted vs. depth of the bed in feet for the three columns, a straight line is obtained as shown in Figure 1 in Appendix D-1 as an evaluation of the design parameters of a coal bed. The application of the Bohart Adams relationship is utilized to estimate the size of the bed required as well as its performance. A tentative calculation based on the available data and the application of the Bohart Adams relationship, to treat Iona sewage effluent, is outlined in detail in Appendix D-1.

The estimated size and performance of this bed are found as follows:

| | |
|---|---|
| Iona flow | 70 MGD |
| Influent lead concentration | 0.2 mg/l |
| Effluent lead concentration (break through point) | 0.05 mg/l |
| Flow rate | 1 gpm/ft$^2$ |
| Contact time | 30 minutes |
| Estimated bed area | 1.1 acre |
| Estimated bed depth | 5 ft (152.4 cm) |
| Amount of coal in bed | $\simeq$ 5000 short tons (2273 metric tons) |
| Amount required for renewal per day | $\simeq$ 1 metric ton/day |
| Total lead removed | = 48 kgs/day |
| Efficiency of the bed | $\simeq$ 70% |

To obtain more reliable values for design purposes larger scale pilot experimentation is required. The larger scale would minimize the "scaling up" effect which is hazardous in forecasting the results of such large beds as that envisioned for 70 MGD based on small column results.

3.1.3.2  To remove dissolved organics from Iona sewage

The coal bed was operated continuously for 20 days (471 hours) although two interruptions occurred due to reversing the direction of the flow and to backwashing the bed respectively.

The throughput volume was approximately 1790 gallons of sewage flowing at an average rate of 315 ml/min which is equivalent to 1 gpm/ft$^2$ of area for an allowable contact time of 30 minutes.

All the obtained results are listed in Tables 1, 2, 3, 4, included in Appendix D-2, which show the effect of treatment on the sewage for the reduction of solids, $BOD_5$, COD and TOC respectively at three levels of 0, 0.5, 1 and 2 meters depth of coal.

The effects of the treatment on reducing the pollution parameters of the sewage are summarized as follows:

a.  pH

With the coal treatment, a substantial decrease in the pH value of the original sewage was noticed. The neutral pH value of 6.84 for the sewage was dropped to an acidic value of 5.1 at the 2 meter level in the bed.

b.  Solids

Solids include the total residue, volatile residue and fixed residue.  The results in Table 1, Appendix D-2 show no substantial reduction of the value of solids. Although during the first day of operation, an increase rather than a decrease in the total and volatile residue was obtained, this is likely due to the leaching of some water-soluble components from the coal.  After the first day, no further increase in the total or volatile residue was noticed. However a slight reduction of 39% in the volatile residue was obtained.

c.  $BOD_5$

The reduction of $BOD_5$ by treatment with coal is considered satisfactory.  The results included in Appendix D-2 Table 2 show that after the leaching of 976 gallons through the bed the efficiency of removal does not decrease and it remained at a high value of 88% at the 2 meter level under expanded-flow conditions.

After backwashing, the bed maintained an efficiency of 75% for the first 200 gallons of sewage application, after that the efficiency is decreasing to a value of 38% after the application of 1790 gallons.

The adsorptive capacity of the coal to remove $BOD_5$ was estimated from the analysis obtained from the effluent from the 0.5 meter level.  The results shown in Table 5 indicate that more than 1377 gallons of sewage were passed

through before reaching the break through point at 50 mg/1 $BOD_5$ in the effluent. A cumulative efficiency of removal of approximately 57% was calculated at this point. During this period more than 390 grams of $BOD_5$ was removed.

The adsorptive capacity, under these conditions, was found to be equivalent to 95 mgs $BOD_5$ removed per 1 gram of coal. During the running periods some grab samples exhibited unexpected very low removal of $BOD_5$. This can be explained as due to the leakage of $BOD_5$ (a sudden increase in the $BOD_5$ level due to the presence of bacterial slime), also due to a channeling effect through the coal particles. Therefore, it is difficult to utilize such data to scale up the coal bed to a larger size for the treatment of such a magnitude as 70 MGD of Iona effluent. Larger experiments should be conducted with deeper coal beds allowing longer contact time and a steady continuous flow would be advisable to obtain more reliable results and to reinforce the encouraging results obtained during this experiment.

d. COD

Table 3 Appendix D-2 shows that the COD removal follows the same pattern as the $BOD_5$ removal. At the 0.5 meter level, the average removal efficiency was 47% while it reached 63% and 79% at the 1 meter and 2 meter levels respectively.

Backwashing does not restore the original efficiency of the bed as happened in the case of $BOD_5$. An estimated adsorptive capacity was calculated after passing approximately 1790 gallons through the first 0.5 meter level and was found to equal approximately 130 mgs of COD removed, per gram of coal.

e.  TOC

A very poor efficiency was shown for the TOC removal as presented in Table 4 , Appendix D-2.

A range of 25 to 66% removal efficiency was obtained during the bed operation. Larger contact time may be required to improve the adsorption efficiency.

The poor efficiency can be attributed to the partial contribution of some soluble organic components of the coal with the measured TOC values causing an increase of the TOC concentration in the effluent. Additional research work is required to confirm this assumption.

3.2  Industrial sewage

This includes the treatment of an oil refinery wastewater effluent using contact and column methods to remove mainly phenol, cyanide, ammonia and other dissolved organics.

The results obtained with the oxidized surface coal, unoxidized core coal and activated carbon are compared.

## 3.2.1  Batch tests

The results of Table 1, included in Appendix D-3 indicate that phenols are reduced to satisfactory level with the core coal, a 77% removal was obtained when 1% w/w coal was contacted by shaking with the wastewater, while the oxidized surface coal showed a lesser efficiency of 49%. In comparison, 0.5% w/w activated carbon reduced the phenol level to non-detectable limits.

Regarding the cyanide, it was difficult to determine the effectiveness of either type of coal for removal because of the low level originally present in the sewage which does not exceed 0.01 mg/l $CN^-$. This level is considered quite low for detection purposes. Table 2, Appendix D-3 shows that no appreciable reduction in the ammonia or the Kjeldahl total nitrogen was achieved using either activated carbon or coal. Surface coal was the least effective. By increasing the quantity of coal applied to more than 1%, an increase in the level of both $NH_3$-N and K-N, even higher than the original, was observed. This may be due to the leaching out of some nitrogeneous components from the surface coal.

The total residue and volatile solids were removed to a certain extent when coal was used in small quantities. However, with higher quantities (2% and 4% w/w) the total residue level increased more than the original level as shown in Table 3 by the negative signs. This may be due to the

leaching of colloidal or dissolved components from the coal upon shaking with the effluent, which adds to the total and the volatile residue levels. In comparison, activated carbon is not very effective in the removal of solids as shown in Table 3, Appendix D-3.

The efficiencies of removal of organic matter represented by $BOD_5$, COD and TOC by coal, in comparison with activated carbon, are shown in Table 4, Appendix D-3. The activated carbon is the most effective for reduction of $BOD_5$ since 82% removal was obtained when 0.5% activated carbon was used, while 26% and 30% removal was obtained using the same quantity of the surface coal and the core coal respectively. Meanwhile, relatively better effectiveness of surface coal was noticed for the removal of $BOD_5$ than that of the core coal.

The non-oxidized coal was found to be the most effective for COD and TOC removal, with 0.5% coal added 60% removal of COD and 45% removal of TOC was obtained. The efficiencies in both cases increase by increasing the percentage of coal added, reaching an efficiency of removal more than 80% for COD and 50% for TOC.

Table 5, Appendix D-3 shows that oil and grease are effectively removed by both types of coal while a relatively high efficiency (up to 80%) is exhibited by the core coal.

Effect of treatment on pH:   Table 6  , Appendix D-3
shows that the original refinery effluent had a neutral to
a very slightly alkaline pH 7.62 to 8.2.   The treatment with
activated carbon does not change the pH of the effluent, but
a very slight change in the pH, on the acidic side, was
observed when non-oxidized coal was used.

The treatment with oxidized surface coal affects
greatly the pH of the effluent.   The pH decreased to decidely
acidic, up to 3.65 upon the addition of 4% w/w coal.   This
again confirms the presence of acidic compounds in the coal
which are leached out in the effluent, changing its colour
to dark yellow upon treatment with the coal.

3.2.2   Column tests

These experiments were conducted using a flow rate
of 165 ml/min which is equivalent to 1 gpm/ft$^2$ but provides
only 2-3 minutes of contact through the 20 cm depth of coal.
This short contact time does not seem to be suitable for
practical use, at least 25 - 30 minutes of time should be
allowed.

The results from column tests after running 10
liters of effluent through beds of surface coal and core
coal are listed in Table 7, Appendix D-3.

Generally, the removal of different pollutants seems
to follow the same pattern as in the case of batch tests.
The total residue does not reduce efficiently, although the
total suspended solids are removed to a high degree.   The

$BOD_5$ is also reduced with both types of coal, with a relative higher efficiency when oxidized coal is used as shown in Figure 39. Total carbon is reduced to less than one third of the original value. High efficiency for removal of phenol, oil and grease was also observed.

3.2.3  Design application

The synthetic waste mixture (phenol, cyanide and ammonia) was passed through the coal bed continuously for 17 days. During this period more than 950 gallons of the effluent were leached through the bed.

The results of monitoring from 3 sampling points on the bed and the calculated cumulative removal for the phenol, cyanide and ammonia are shown in Tables 1, 2 and 3 respectively included in Appendix D-4.

The bed continued operation until the break through concentrations of 0.2 mg/1 phenol, 0.1 mg/1 cyanide and 5 mg/1 ammonia were reached. The break through lines for phenol and cyanide are shown in Figures 1a and 1b, Appendix D-4 respectively.

Using the data obtained from the three levels on the coal bed, the Bohart Adams relationship, explained in Appendix D-1 was applied to obtain the design parameters of a coal bed to treat a refinery effluent at the rate of 8 gpm (Imp.)/1000 Bbl  of crude with an inflow rate of 1 gpm/ft$^2$. The details of the tentative calculations, based

BOD$_5$ ORIGINAL: 57 PPM

CORE COAL

SURFACE COAL

VOLUME PASSED THROUGH COLUMN(L)
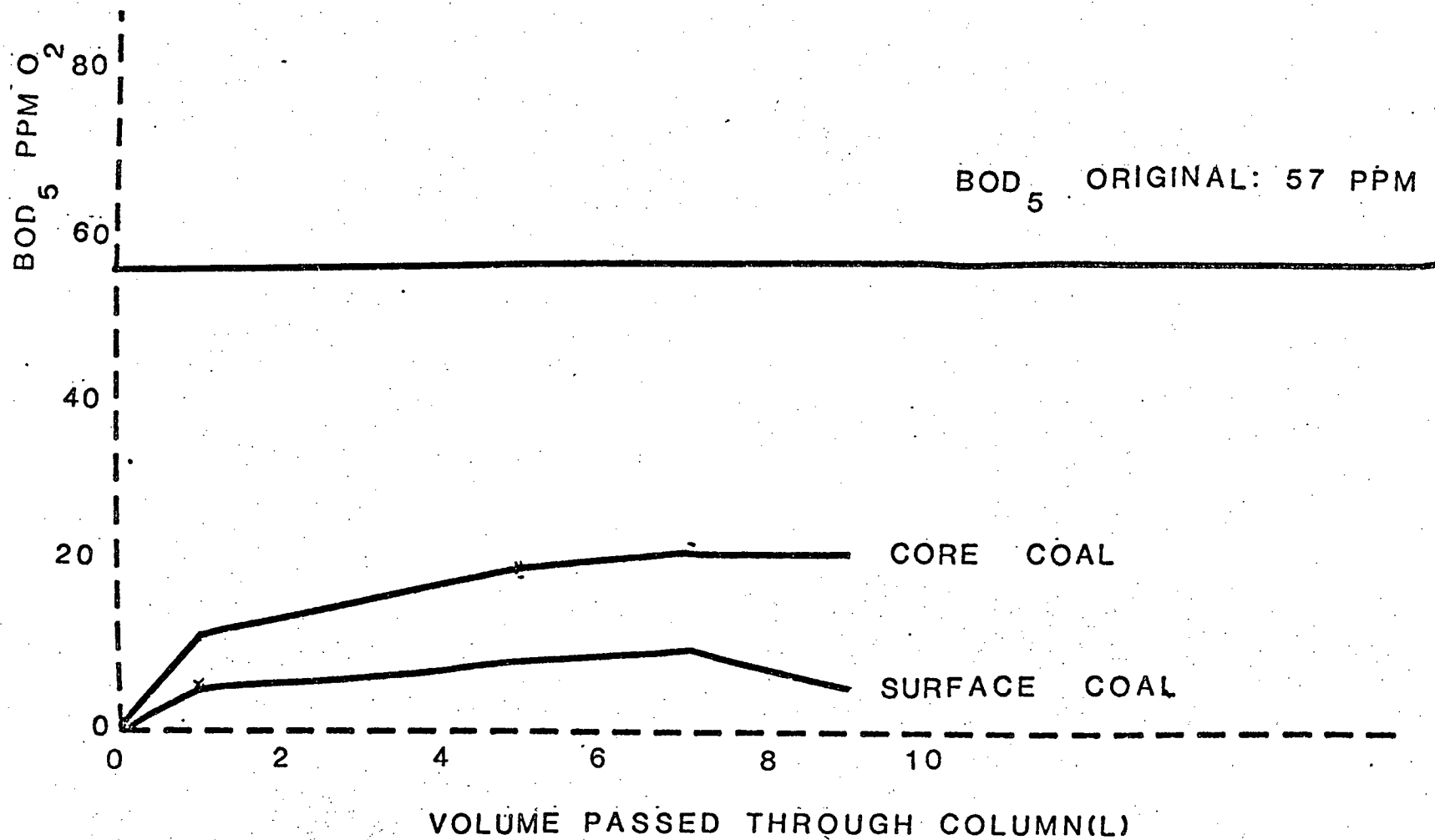
FIGURE 39 : LEACHING OF REFINERY WASTE EFFLUENT THROUGH COAL COLUMN, CHANGES IN BOD$_5$.

on phenol removal and cyanide removal are found in
Appendix D-4.

As a conclusion for both calculations, the suggested
bed size to treat refinery wastes, at a rate of 8 gpm/ft$^2$/1000
Bbl, to remove phenol and cyanide should be 29 X 49 X 5 ft
deep (7000 ft$^3$). This bed would serve for one year for
phenol and 1.5 years for cyanide to reach the determined
break through concentrations. A larger pilot experiment
should be conducted to confirm these encouraging results.

Also, the adsorptive capacities of the coal towards
phenol, cyanide and ammonia, calculated from the empirical
formula and those obtained from the applied research are
compared and found to be as follows:

| Material removed | Absorptive capacity of coal mgs material removed/gram of coal | |
| | Calculated from B.A.* formula | Obtained experimentally |
| --- | --- | --- |
| Phenol | 0.4139 | 0.3149 |
| Cyanide | 0.2333 | 0.2861 |
| Ammonia | N.A.** | 2.25 |

\*    Bohart Adams

\*\*   Not applied

# VIII. SUMMARY AND CONCLUSIONS

1) Hat Creek coal samples used in this work are ranked as lignite variety.

2) The coal has macroporous structure, the highest percentage of pore volume lay in the transitional and macropore range (60-300 $^O$A), while activated carbon has a microporous structure with pore diameters of range 50-70 $^O$A.

3) The coal has an iodine value equal to one-seventh of that of activated carbon but 60 times more than that of sand.

4) Oxidized surface coal has relatively more fractured surface, larger pore diameters and more available acid functional groups (carboxyl COOH and phenolic -OH) than in the case of the non oxidized core coal.

5) Coal possesses good sorptive quality towards the six heavy metals tested. Ninety-nine percent or more of the following heavy metals were removed from solution, namely mercury, lead, copper, zinc, cadmium and chromium. The coal is most selective to adsorb mercury followed by lead, while the least selectivity is exhibited towards chromium.

6) Eighty to ninety percent of the BOD and COD values can be reduced by coal. Phosphate was not removed effectively, but using powdered coal between 50-80% of the phosphate was removed by a contact process. The best results for phosphate removal were obtained with soil which exhibits a higher ability to hold phosphate. Hat Creek coal does not appear to have any value for the removal of nitrate and very little value for ammonia; meanwhile, phenol and cyanide are removed satisfactorily.

7) The adsorptive capacity of the coal increases by:

a. increasing the solute concentration in the solution.

b. increasing the contact time till approaching equilibrium state.

c. increasing the coal dosage.

d. decreasing the particle size of the coal, although granular coal is more efficient for use in continuous column contacting rather than batch processes.

8) Clay-minerals in coal consist mainly of kaolinite (6-9% d.w.b. of the coal), while bentonite is not detectable. Enough practical evidences are provided to show that the kaolinite doesn't significantly participate with the organic matter

in the interaction with the metal ions. Therefore
no interference in the adsorption mechanism
studied is expected due to clay minerals.

9)  The adsorption of metal ions by coal is likely taking
place through a chemisorption mechanism where
the carboxyl COOH and/or the phenolic hydroxyl -OH
groups of the coal interact with the adsorbed lead
ions to form metal complexes.

10)  There are proximate carboxyl groups in the coal
structure which can allow a complex formation by
the interaction of the two adjacent COOH with the
metal ion to form a compound similar to the acid
anhydride form.

11)  Coal removes dissolved organics through the combined
effect of physical adsorption and biological
oxidation of the organic substrate by the
micro-organisms available on the coal surface.

12)  Data obtained from the application of actual wastes are
in good agreement with those obtained from the
standard laboratory tests used with synthetic
wastes.

13)  Hat Creek coal can be evaluated as a satisfactory and
valuable material for the purification of sewage
wastewaters.

# IX. RECOMMENDATIONS FOR FUTURE RESEARCH

The results of this research indicate that much research is still needed to enable coal to be used efficiently for the removal of pollutants from wastewaters. Some suggested lines of study are:

1. A study to improve the capability of the coal surface to adsorb more efficiently phosphates, ammonia and nitrates.

2. Evaluation of the adsorptive capacity of the coal to remove pesticides.

3. Determination of the role of other functional groups in coals such as quinones and nitrogen containing groups in the mechanism of interaction with heavy metals.

4. Moisture-mineral matter-free coal is recommended for use in the future investigation of mechanisms. This will allow more accurate identification of the functional groups using infra-red spectroscopic as well as microscopic methods.

5. More investigation is required to determine quantitatively the number of carboxyl groups present in adjacent positions and the extent of their participation in forming metal complexes in the coal.

6.  More studies are recommended for the identification of
    the type of complexes formed with metal ions, and
    the nature of the chemical bonds formed.

7.  The possibility of using the powdered coal as a coagulant
    and sedimentation aid in addition to heavy metal
    removal in the primary treatment of raw sewage
    with the determination of the electrical surface
    charge of the coal surface (zeta potential).

8.  Determination of the technical and economic feasibility
    of procurement and disposal of the coal.  More
    research studies in the regeneration of the coal
    after use and the possibility of using the spent
    coal as a source of energy are strongly recommended.
    Incineration or landfill is a possibility requiring
    investigation, also backwashing with acidic and/or
    alkaline solutions holds some promises of removing
    respectively adsorbed metal ions and organic matter
    from the coal surface.

9.  Aerated, expanded-type coal beds are recommended to be
    used in future research studies to avoid develop-
    ment of anaerobic conditions and "fouling" of the
    bed due to the increase of the pressure drop
    along the bed.

10. Experimental pilot beds should be one of the early
    developments for treatment of sewage flows

emanating from small urban areas. These larger

size beds would minimize the "scaling-up" effect

which is hazardous in forecasting the design

parameters such as that envisioned for 70 MGD

based on data obtained from small columns.

11. Economic studies to compare the cost of a coal treatment

process to other tertiary processes commonly used

in advanced wastewater purification.

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APPENDICES

LIST OF APPENDICES                    i.

# A P P E N D I X   A

APPARATUS AND INSTRUMENTS

## LIST OF APPARATUS AND INSTRUMENTS

1. "BiCO" Jaw Crusher, capacity ≃ 400 lbs/hr, motor power 2 hp, 210 volt.

2. "BiCO" pulverizer, capacity 200 lbs/hr, motor power 1 hp, 210 volt, adjustable range of particle size 4 mesh to fine.

3. Full height U.S. standard screen fine mesh sieves, 8" diameter, made of brass. A series of sieves of mesh size 4, 8, 16, 20, 50, 60, 100, 140 and 325 were used.

4. Ro-Tap mechanical sieve shaker, which reproduces circular and tapping motion and accommodates six 8" diameter full height sieves, with receiving pan. Motor power 1/4 h.p. 1750 rpm.

## APPENDIX A, TABLE 1

### U.S. Sieve Series and Tyler Equivalents

| U.S. Number | SIEVE OPENINGS | | Tyler Screen Scale Equivalent Mesh |
| --- | --- | --- | --- |
| | Millimeters | Inches | |
| No.    4 | 4.76 | 0.187 | 4 |
| 12 | 1.68 | 0.0661 | 10 |
| 14 | 1.41 | 0.0555 | 12 |
| 16 | 1.19 | 0.0469 | 14 |
| 20 | 0.84 | 0.0331 | 20 |
| 50 | 0.297 | 0.0117 | 48 |
| 60 | 0.250 | 0.0098 | 60 |
| 100 | 0.149 | 0.0059 | 100 |
| 140 | 0.105 | 0.0041 | 150 |
| 200 | 0.074 | 0.0029 | 200 |
| 270 | 0.053 | 0.0021 | 270 |
| 325 | 0.044 | 0.0017 | 325 |

5. Digital pH/ion Fisher-Accumet pH meter, model 420, with a glass calomel electrode combination.

6. Reichert low power light microscope 4.5 X, model MeF.

7. Scanning Electron Microscope, model ETEC Autoscan , light resolution 10 nm (100 $^{O}$A) to 2.5 nm (25 $^{O}$A). Its basic components are: lens system, electron gun, electron collector, visual and recording cathode ray tubes (CRTS) and the electronics associated with them.

8. The JEOL Co. Electron Microprobe, model JXA-3A. Its main components are:

   a) Electron optics to produce a small diameter electron beam; it has an electron gun plus two electron lenses.

   b) X-ray spectrometer to measure the wave length and intensity of the characteristic X-ray radiation produced.

   c) Light microscope to locate the area in the specimen to be examined. The probe operates in vacuum and so all elements having atomic numbers > 4 can be detected.

9. Perkin-Elmer double beam grating infra-red spectrophotometers, model 621 and 521.

10. The Micromeritic Surface Area and Pore Volume Analyzer. This test was conducted by the Fuel Science Division, N.R.C., Edmonton, Alberta.

11. Jarrel Ash atomic absorption spectrophotometer, model MV-500 for mercury analysis.

12. Perkin-Elmer double beam, single channel atomic absorption spectrophotometer, model 306.

13. Technicon Industrial AutoAnalyser II.

14. High-low adjustable speed Eberbach mechanical shaker, 115 volts, 3.6 amp., 60 cycles A.C.

15. TXT American proportioning pump, adjustable capacity, series 100.

16. Beckman total organic carbon analyzer, model 915, equipped with Beckman infra-red analyzer unit, model 215A.

# A P P E N D I X    B

GENERAL TECHNIQUES

B-1   The Electron Microprobe Analysis

B-1-1   Preparation of coal sections for microscopic study

Coal specimen were prepared by mounting coal particles of average particle size of 1 mm in epoxy resin mounts.

Each specimen was then prepared by repeated grinding on a series of coarse and fine abrasive papers followed by polishing on diamond abrasive till a flat, smooth, scratch-free surface was obtained.  Any ridges or valleys on the surface cause variations in electron incidence and X-ray "take-off" angles.

No etching was applied because it may alter the topography or surface chemistry of the specimen.  The specimens were then coated with carbon to ensure electrical and thermal conductivity.  The coating material was applied very thinly to yield stable specimen currents and X-ray flux. Thickness in the range of 50-500 $^{\circ}$A is recommended.

B-1-2   Theory and technique

The electron microprobe is a powerful instrument which permits the characterization of heterogeneous materials and surfaces on such a micrometer (Um) or sub-micrometer scale.

The area to be examined is irradiated with a finely focussed electron beam which may be static or swept in a roster across the surface of the specimen.  The types of signals produced when the electron beam impinges on a specimen include

secondary electrons, back-scattered electrons, characteristic X-rays, auger electrons and various energy values are used to measure many characteristics of the sample, e.g. composition, surface topography, crystallography etc.

a)  Elemental identification

Most SEM's[*] and EMP's[**] are equipped with detector systems, an energy dispersive spectrometer (EDS) or crystal spectrometer. The EDS system is capable of identifying elements with an atomic number $Z > 11$ in a few minutes. With adjacent elements in the range $4 < Z < 11$, overlapping of the peaks may occur.

For elements present in trace amounts, longer counting times are necessary but instrument instability limits counting time to 10 to 15 minutes in practice. A 30 kilovolt accelerating potential is sufficient for non-ambiguous identification of all the elements.

b)  Elemental distribution

The amplified signal for the detector system is made to modulate the brightness of a cathode ray tube (CRT) scanned in synchronism with the electron probe. Thus, on the CRT a picture is obtained by the variation of X-ray emission from the surface. An X-ray area scan can show tones ranging from black to white, depending on the experimental conditions. In places of high concentration of the element in the scanned area, the picture will be nearly photographically white, it will be gray where the element concentration is lower and black where the element is absent. Care must be taken to ensure that no

[*]   Scanning Electron Microscope
[**]  Electron Microprobe

other peak interferes with the signal of the desired element.
The desired peak should be carefully isolated by means of a
single channel analyzer from which the amplified output is
displaced on a CRT and so provide the elemental distribution
desired.

c)   Absorption electron image (AEI)

Electron images are obtained for the different coal
particles.  The AEI is the exact converse of the back-
scattered image.  In this case, the specimen current (i.e.
the electrons remaining in the specimen and producing X-rays)
was used to control the spot intensity of the cathode ray tube
(CRT).

A set of electron images are also produced on the
CRT showing the elemental distribution across certain areas of
the specimen.  Each image gives the concentration of a particular
element in the given area.

d)   Display circuits

This gives a time trace across the given area which
shows the levels of concentration of particular elements across
that section.

This line shows the variation in X-ray intensity which
is called the Y-axis display.  Magnification up to 2500 X is
possible by the microprobe without exceeding the resolution
of the instrument.

B-2   Infra-red Absorption

B-2-1   Grinding

The size of the coal sample was first reduced to approximately 325 mesh to obtain reliable spectra.   Size reduction is accomplished by both grinding in an agate mortar and pestle for about 10 minutes for each sample, followed by a Spex 3" x 2" vibratory mixer mill for 30 minutes, the freshly prepared samples are then used in the preparation of the KBr pellets.

B-2-2   Preparation of the KBr pellets (Laury, 1963)

The KBr pellets were prepared by adding 1 mg from the coal (0.5 mg from activated carbon) to 300 mgs of dry KBr. The mixture was then ground using a mortar and pestle for 5 minutes.   The ground mixture was then placed in a Perkin Elmer pellet press, the press was evacuated for one minute and then loaded to 18,000 lbs for one minute to yield a 13 mm diameter KBr pellet.

The pellets were then stored in glass vials in a dessicator until required.

B-2-3   Calculation of the specific extinction coefficient K

For each main absorption band, K is calculated using the following relationship:

$$K \, m/A \; = \; D$$

where   K   =   the specific extinction coefficient $(cm^2/mg)$

      m   =   the weight of the coal in the disc in milligrams

      A   =   the area of the disc (disc diameter $\approx$ 13 mm)

      D   =   optical density (absorbance)

A linear relationship was established between the absorbance and the coal density (m/A), the gradient of this line is equal to K in $cm^2/mg$.

The absorption intensities were calculated by the base line method according to the method of R.A. Friedel as outlined in a paper by Fujii et al., 1970.

The K values for the main absorption bands for each type of coal as well as activated carbon, before and after adsorption of heavy metals, were calculated and compared.

B-2-4   Base line technique (Ewing, 1960)

Since the absorbance A = $\log \frac{Po}{P}$ at certain wave length $\lambda$

where   Po  =   the transmitted power from empty curvette

               called the background

and     P   =   the transmitted power through  the sample

if a base line drawn across the dip in the curve and designated $P_B$ the power level is where this line intersects the $\lambda$ wavelength line. Therefore, the base line absorbance can be defined as:

$$A_B = \log \frac{P_B}{P}$$

It is exactly so if the absorption curves of the other substances present are assumed to be linear over this short range.

B-3   BET Surface Area and Pore Structure of the Coal

The BET equation (Brunauer, et al. 1938)

$$\frac{P}{v(Po-P)} = \frac{1}{v_m \cdot C} + \frac{C-1}{v_m \cdot C} \cdot P/Po$$

where P  =  partial pressure of $N_2$ in the gas mixture

Po  =  saturation pressure of $N_2$ at the temperature

of the liquid coolant

v  =  volume of $N_2$ adsorbed on the sample at STP

$v_m$  =  volume of adsorbed $N_2$ due to monolayer coverage

C  =  constant.

When  $\frac{P}{v(Po-P)}$  is plotted as a function of P/Po and the slope

and intercept of the best straight line were evaluated by the

method of least squares.  $v_m$ can be evaluated as the

reciprocal of the sum of the slope and intercept, and converted

to the sample surface area by multiplying by F where

$$F = \frac{6.02 \times 10^{23} \times 16.2 \times 10^{-20} \times 10^{-6}}{22.414}$$

and 6.02 X $10^{23}$  =  Avogado's  No. (molecules/mole)

16.2 X $10^{-20}$  =  area covered by a $N_2$ molecule ($m^2$/molecule)

$10^{-6}$  =  liters/μ liter

22,414  =  Molar volume of $N_2$ at STP (liter/mole)

B-4-1                    SYNTHETIC WASTEWATERS CONTAINING
                                HEAVY METALS

Metal                                    Reagent used*

1.  Lead                 $Pb(NO_3)_2$ crystals, A.R., F.W. 331.23

2.  Cadmium              $Cd(NO_3)_2$ $4H_2O$ crystals, A.R., F.W. 308.47

3.  Mercury              $Hg(NO_3)_2$ granular, A.R., F.W. 324.60

4.  Copper               $Cu(NO_3)_2$ $3H_2O$ crystals, A.R., F.W. 241.60

5.  Zinc                 $Zn(NO_3)_2$ X $H_2O$ flakes, A.R.

6.  Chromium             $Cr(NO_3)_2$ $9H_2O$ crystals, A.R., F.W. 400.15

*  The above reagents were supplied by Mallinchrodt Inc.,

   St. Louis, Missouri, 63147, U.S.A.

B-4-2              PARTICLE SIZE OF COAL USED IN THE
                            ADSORPTION TESTS

| Sieve No. | Size of Opening mm | Mean Size of Particle | Fineness Modulus |
|---|---|---|---|
| 3 | 6.680 | 0.533 mm | 3.87 |
| 60 | 0.246 | 0.2965 mm | - |
| 150 | 0.104 | 0.1117 mm | - |
| Pan (fines) | - | 0.03414 mm | - |

B-4-3

        Certified atomic absorption standards, reference solution
of 100 ppm for cadmium,   mercury, copper, zinc, and chromium were supplied
by Fisher Scientific Company, Fairlawn, New Jersey, 07410, U.S.A.

## STANDARDIZED INSTRUMENT PARAMETERS FOR DIFFERENT METALS

| Metal | Lamp Current | Fuel | Support | Flame Starchiometry | Wave Length nm | Working Range | DETECTION LIMIT Absorption Scale | Concentration Scale (Expanded) |
|-------|--------------|------|---------|---------------------|----------------|---------------|----------------------------------|--------------------------------|
| Copper | 3 mA | Acetylene | Air | Oxidizing | 324.7 | $\leq$ 20 mg/1 | 0.1 mg/1 | 0.03 mg/1 |
|  | " | " | " | " | 218.2 | 10-100 mg/1 | - | - |
| Lead | 6 mA | " | " | " | 217.0 | $\leq$ 20 mg/1 | 0.2 mg/1 | 0.1 mg/1 |
|  | " | " | " | " | 283.3 | 10-100 mg/1 | - | - |
| Zinc | 5 mA | " | " | " | 213.9 | $\leq$ 20 mg/1 | 0.01 mg/1 | - |
|  | " | " | " | " | 307.6 | 10-100 mg/1 | - | - |
| Mercury | 3 mA | " | " | " | 253.7 | 5-100 mg/1 | - | - |
|  |  | Flameless or cold vapor method | | | 253.7 | $\leq$ 5 mg/1 | 0.5 µg/1 in a 100 mls sample | |
| Chromium | 3 mA | Acetylene | Air | Oxidizing | 357.9 | $\leq$ 20 mg/1 | - | 0.015 mg/1 |
|  |  |  |  |  | 425.4 | 10-100 mg/1 | | |
| Cadmium | 3 mA | " | " | Reducing | 228.8 | $\leq$ 20 mg/1 | - | 0.01 mg/1 |
|  |  |  |  |  | 326.1 | 10-100 mg/1 | | |

B-5    EXCHANGEABLE CATIONS AND TOTAL EXCHANGE CAPACITY (Black, 1965)

       (by Ammonium acetate method (pH 7.0)

Reagents:

A.     1.    IN $NH_4O$ AC:dissolve 77.08 gms of $NH_4O$ AC/1 of distilled

             water.   Adjust pH at 7 with $NH_4OH$ or HOAC.

       2.    ISO propanol

       3.    IN KCl:dissolve 74.6 gms of KCl/1 of distilled water.

Procedure

A.     For exchangeable cations

             Weigh out accurately 10 grams of coal, add 40 ml of

IN $NH_4O$ AC, stopper the tube and shake for 5 minutes.   Shake to

rinse down coal adhering to sides, let stand overnight, shake tube

again for 15 min.   Prepare Buchner funnels with Whatman No.42

filter paper and place above 500 ml filtering flasks.   Transfer

contents to funnel with suction applied.   Rinse the tube and

sopper with 1N $NH_4O$ AC from the wash bottle.   Wash the coal with

four 30 ml portions of 1N $NH_4O$ AC, let each portion drain com-

pletely before adding the next but do not allow coal to become

dry.   Transfer the leachate to a 250 ml volumetric flask.   Rinse

the filtering flask and make up to volume with 1N $NH_4O$ AC.   Mix

well and save a portion of the extract (in 60 ml plastic bottles)

of Na, Ca, Mg and K by A.A

B.     For total exchange capacity (CEC)

             Replace the funnels containing the ammonia saturated

coal onto filtering flasks.   Wash with three 40 ml portions of

ISO propanol, again letting each portion drain completely before

adding the next. Discard the washings and rinse out flasks well with tap water and finally with D.W. Replace the funnels and flasks and leach coal with four 50 ml portions of 1N KCl, again letting each portion drain completely before adding the next. Transfer the leachate to a 250 ml volumetric flask. Rinse the filtering flask and make up to volume with D.W.

## Calculations

A.  <u>For exchangeable cations</u>

Sample = x
Blank  = b

$$\frac{m.eq}{100\ gm} = [(\frac{mg}{1}x - \frac{mg}{1}b)(\frac{mg}{1000\ mls})]\ (\frac{250\ mls}{10\ gm})$$

$$(\frac{1}{1000\ ml})\ (100\ gms)\ (dilution\ factor\ for\ AA^*)$$

B.  <u>For total exchange capacity (CEC)</u>

$$CEC = [(mls\ KCl - mls\ Blank).\ N_{KCl}\ \frac{m.eq}{ml}]$$

$$[250\ ml \times \frac{1}{10\ gm} \times \frac{1}{20\ ml}]\ [100\ gm]$$

AA*  Atomic Absorption Spectrophotometer.

The Iodine Number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration of the residual filtrate is 0.02 normal.

### B.6.1  Reagents and Equipment

Hydrochloric Acid, 5 percent weight—To 550 ml of distilled water add 70 ml of reagent-grade concentrated hydrochloric acid (HCl).

Sodium Thiosulfate, 0.1 normal—Dissolve 25 grams of reagent-grade sodium thiosulfate ($Na_2S_2O_3$ $5H_2O$) in one (1) liter of freshly boiled distilled water. Add a few drops of chloroform to minimize bacterial decomposition of the thiosulfate solution. Standarize the thiosulfate solution against 0.100 normal potassium biniodate (KH $(IO_3)_2$). Prepare the 0.1000 normal KH $(IO_3)_2$ using primary standard quality KH $(IO_3)_2$ which has been dried overnight at 105 degrees C and cooled in a desiccator. Weigh 3.249 grams KH $(IO_3)_2$ and make-up to exactly one liter in a volumetric flask with distilled water. Store in a glass-stoppered bottle.

To 80 ml of distilled water add, with constant stirring, one ml of concentrated sulfuric acid ($H_2SO_4$), 10 ml of 0.1000 KH $(IO_3)_2$ solution and approximately one gram of potassium iodide (KI). Titrate the mixture immediately with the thiosulfate solution adding 2-3 drops of starch solution when the iodine fades to a light yellow color. Continue the titration by adding the thiosulfate dropwise until a drop produces a colorless solution. Record the volume of titrate used.

$$\text{Normality of sodium thiosulfate} = \frac{1.000}{\text{ml of } Na_2S_2O_3 \text{ consumed}}$$

Iodine Solution—Dissolve 12.7 grams of reagent-grade iodine ($I_2$) and 19.1 grams of potassium iodide in a small quantity, approximately 20 ml, of distilled water. (If excess water is used, materials will not go into solution.) Dilute to one (1) liter in a volumetric flask with distilled water. Store in a glass-stoppered bottle in a dark place or use in a dark bottle. To standarize the iodine solution, pipette 25.0 ml into a 250 ml Erlenmeyer flask and immediately titrate with the 0.1 normal thiosulfate solution. Add 2-3 drops of starch solution near the endpoint and continue titrating until solution is colorless. Record the volume of titrant used.

$$\text{Normality of iodine solution} = \frac{\text{ml of } Na_2S_2O_3 \text{ used} \times \text{normality } Na_2S_2O_3}{25}$$

Starch Solution—To 2.5 grams of starch (potato, arrowroot, or soluble), add a little cold water and grind in a mortar to a thin paste. Pour into one (1) liter of boiled distilled water, stir, and allow to settle. Use the clear supernatant. Preserve with 1.25 grams of salicylic acid per one (1) liter of starch solution.

Filter Paper—Whatman Folded No. 2V, 10.5 cm.

Spex-Mixer Mill—No. 8000 Spex-Mixer Mill and No. 8001 Grinding Vials, Spex Industries, Inc., 3800 Park Avenue, Metuchen, New Jersey.

### B.6.2  Procedure

Grind a representative sample of carbon in a Spex-Mixer Mill (usually 70 seconds) until $90 \pm 5$ percent will pass a 325 mesh sieve (by wet sieve analysis). Load the Spex-Mixer Mill with a $5.5 \pm 0.5$ gram sample and use 64 one-fourth inch diameter smooth steel balls. An adequate sample of the pulverized carbon should then be dried at 140 degrees C for one (1) hour, or 110 degrees C for three (3) hours. A moisture balance can also be used.

Weigh 1.000 gram of the dried pulverized carbon (see Note 1) and transfer the weighed sample into a dry, glass-stoppered, 250 ml Erlenmeyer flask. To the flask add 10 ml of 5 percent wt. HCl acid and swirl until the carbon is wetted. Place the flask on hot plate, bring contents to boil and allow to boil for only 30 seconds.

After allowing the flask and contents to cool to room temperature, add 100 ml of standarized 0.1 normal iodine solution to the flask. Immediately stopper flask and shake contents vigorously for 30 seconds. Filter by gravity immediately after the 30-second shaking period through Whatman No. 2V filter paper. Discard the first 20 or 30 ml of filtrate and collect the remainder in a clean beaker. Do not wash the residue on the filter paper.

Mix the filtrate in the beaker with a stirring rod and pipette, 50 ml of the filtrate into a 250 ml Erlenmeyer flask. Titrate the 50 ml sample with standarized 0.1 normal sodium thiosulfate until the yellow color has almost disappeared. Add about 1 ml of starch solution and continue titration until the blue indicator color just disappears. Record the volume of sodium thiosulfate solution used.

Notes on Procedure

1.   The capacity of a carbon for any adsorbate is dependent on the concentration of the adsorbate in the medium contacting the carbon. Thus, the concentration of the residual filtrate must be specified, or known, so that appropriate factors may be applied to correct the concentration to agree with the definition. The amount of sample to be used in the determination is governed by the activity of the carbon. If the residual filtrate normality (C) is not within the range 0.008N to 0.035N given in the Iodine Correction Table, the procedure should be repeated using a different weight of sample.

2. It is important to the test that the potassium iodide to iodine weight ratio is 1.5 to 1 in the standard iodine solution.

Calculation

$$\text{Iodine Number} = \frac{X}{m}D$$

$$\frac{X}{m} = \frac{A - (2.2B \times \text{ml of thiosulfate solution used})}{\text{Weight of sample (grams)}}$$

$$C = \frac{N_2 \times \text{ml of thiosulfate solution used}}{50}$$

$X/m$ = mg iodine adsorbed per gram of carbon

$N_1$ = Normality of iodine solution

$N_2$ = Normality of sodium thiosulfate solution

$A$ = $N_1 \times 12693.0$

$B$ = $N_2 \times 126.93$

$C$ = Residual filtrate normality

$D$ = Correction factor (obtained from Table B-1)

## IODINE CORRECTION FACTOR (D)

| Residual Filtrate Normality (C) | .0000 | .0001 | .0002 | .0003 | .0004 | .0005 | .0006 | .0007 | .0008 | .0009 |
|---|---|---|---|---|---|---|---|---|---|---|
| .0080 | 1.1625 | 1.1613 | 1.1600 | 1.1575 | 1.1550 | 1.1538 | 1.1513 | 1.1500 | 1.1475 | 1.1463 |
| .0090 | 1.1438 | 1.1425 | 1.1400 | 1.1375 | 1.1363 | 1.1350 | 1.1325 | 1.1300 | 1.1288 | 1.1275 |
| .0100 | 1.1250 | 1.1238 | 1.1225 | 1.1213 | 1.1200 | 1.1175 | 1.1163 | 1.1150 | 1.1138 | 1.1113 |
| .0110 | 1.1100 | 1.1088 | 1.1075 | 1.1063 | 1.1038 | 1.1025 | 1.1000 | 1.0988 | 1.0975 | 1.0963 |
| .0120 | 1.0950 | 1.0938 | 1.0925 | 1.0900 | 1.0888 | 1.0875 | 1.0863 | 1.0850 | 1.0838 | 1.0825 |
| .0130 | 1.0800 | 1.0788 | 1.0775 | 1.0763 | 1.0750 | 1.0738 | 1.0725 | 1.0713 | 1.0700 | 1.0688 |
| .0140 | 1.0675 | 1.0663 | 1.0650 | 1.0625 | 1.0613 | 1.0600 | 1.0588 | 1.0575 | 1.0563 | 1.0550 |
| .0150 | 1.0538 | 1.0525 | 1.0513 | 1.0500 | 1.0488 | 1.0475 | 1.0463 | 1.0450 | 1.0438 | 1.0425 |
| .0160 | 1.0413 | 1.0400 | 1.0388 | 1.0375 | 1.0375 | 1.0363 | 1.0350 | 1.0333 | 1.0325 | 1.0313 |
| .0170 | 1.0300 | 1.0288 | 1.0275 | 1.0263 | 1.0250 | 1.0245 | 1.0238 | 1.0225 | 1.0208 | 1.0200 |
| .0180 | 1.0200 | 1.0188 | 1.0175 | 1.0163 | 1.0150 | 1.0144 | 1.0138 | 1.0125 | 1.0125 | 1.0113 |
| .0190 | 1.0100 | 1.0088 | 1.0075 | 1.0075 | 1.0063 | 1.0050 | 1.0050 | 1.0038 | 1.0025 | 1.0025 |
| .0200 | 1.0013 | 1.0000 | 1.0000 | 0.9988 | 0.9975 | 0.9975 | 0.9963 | 0.9950 | 0.9950 | 0.9938 |
| .0210 | 0.9938 | 0.9925 | 0.9925 | 0.9913 | 0.9900 | 0.9900 | 0.9888 | 0.9875 | 0.9875 | 0.9863 |
| .0220 | 0.9863 | 0.9850 | 0.9850 | 0.9838 | 0.9825 | 0.9825 | 0.9813 | 0.9813 | 0.9800 | 0.9788 |
| .0230 | 0.9788 | 0.9775 | 0.9775 | 0.9763 | 0.9763 | 0.9750 | 0.9750 | 0.9738 | 0.9738 | 0.9725 |
| .0240 | 0.9725 | 0.9708 | 0.9700 | 0.9700 | 0.9688 | 0.9688 | 0.9675 | 0.9675 | 0.9663 | 0.9663 |
| .0250 | 0.9650 | 0.9650 | 0.9638 | 0.9638 | 0.9625 | 0.9625 | 0.9613 | 0.9613 | 0.9606 | 0.9600 |
| .0260 | 0.9600 | 0.9588 | 0.9588 | 0.9575 | 0.9575 | 0.9563 | 0.9563 | 0.9550 | 0.9550 | 0.9538 |
| .0270 | 0.9538 | 0.9525 | 0.9525 | 0.9519 | 0.9513 | 0.9513 | 0.9506 | 0.9500 | 0.9500 | 0.9488 |
| .0280 | 0.9488 | 0.9475 | 0.9475 | 0.9463 | 0.9463 | 0.9463 | 0.9450 | 0.9450 | 0.9438 | 0.9438 |
| .0290 | 0.9425 | 0.9425 | 0.9425 | 0.9413 | 0.9413 | 0.9400 | 0.9400 | 0.9394 | 0.9388 | 0.9388 |
| .0300 | 0.9375 | 0.9375 | 0.9375 | 0.9363 | 0.9363 | 0.9363 | 0.9363 | 0.9350 | 0.9350 | 0.9346 |
| .0310 | 0.9333 | 0.9333 | 0.9325 | 0.9325 | 0.9325 | 0.9319 | 0.9313 | 0.9313 | 0.9300 | 0.9300 |
| .0320 | 0.9300 | 0.9294 | 0.9288 | 0.9288 | 0.9280 | 0.9275 | 0.9275 | 0.9275 | 0.9270 | 0.9270 |
| .0330 | 0.9263 | 0.9263 | 0.9257 | 0.9250 | 0.9250 | | | | | |

# A P P E N D I X   C

## DATA RESULTS

C-1-1    TABLE 1.    PROXIMATE AND ULTIMATE ANALYSIS

DATE: 27 JUN 75    HAT CREEK COAL PROJECT  -  STATISTICAL ANALYSIS OF PROXIMATE TEST DATA    PAGE 1
DIAMOND DRILL HOLE 74-039

| LAB/DRL | HOL T/O # | FROM | TO | LENGTH | EQUIL | AS RECVD | ASH | V.M. | F.C. | GROSS BTU/LB | SULFR | SODA | POTAS | ASH | V.M. | F.C. | GROSS BTU/LB | SULFR | SODA | POTAS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 39-301 | 2.0 | 33.0 | 31.0 | 10.00 | 99.99 | | | | | | | | | | | | | | |
| CT | 39-001 | 33.0 | 53.0 | 20.0 | | 26.75 | 61.71 | 23.36 | 14.94 | 2800 | 0.31 | | | 49.37 | 18.69 | 11.95 | 2240 | 0.25 | | |
| CT | 39-002 | 53.0 | 73.0 | 20.0 | | 21.53 | 52.87 | 26.49 | 20.63 | 4342 | 0.37 | | | 42.30 | 21.20 | 16.51 | 3473 | 0.30 | | |
| CT | 39-003 | 73.0 | 93.0 | 20.0 | | 17.64 | 54.61 | 26.71 | 18.67 | 4305 | 1.03 | | | 43.69 | 21.37 | 14.94 | 3444 | 0.83 | | |
| | 39-302 | 93.0 | 98.0 | 5.0 | 10.00 | 99.99 | | | | | | | | | | | | | | |
| CT | 39-004 | 98.0 | 118.0 | 20.0 | | 11.85 | 41.41 | 34.68 | 23.71 | 6213 | 2.09 | | | 33.13 | 27.91 | 18.97 | 4971 | 1.67 | | |
| CT | 39-005 | 118.0 | 138.0 | 20.0 | 18.38 | 16.71 | 30.28 | 34.09 | 35.63 | 8538 | 0.62 | .124 | .148 | 24.22 | 27.27 | 28.51 | 6830 | 0.50 | .099 | .119 |
| CT | 39-006 | 138.0 | 158.0 | 20.0 | | 18.41 | 24.68 | 36.87 | 38.45 | 9360 | 0.54 | | | 19.75 | 29.49 | 30.76 | 7488 | 0.43 | | |
| CT | 39-007 | 158.0 | 178.0 | 20.0 | 20.94 | 20.40 | 34.31 | 32.09 | 33.61 | 7740 | 0.23 | .161 | .099 | 27.45 | 25.67 | 26.88 | 6192 | 0.18 | .129 | .080 |
| CT | 39-008 | 178.0 | 198.0 | 20.0 | | 22.84 | 20.55 | 36.31 | 43.13 | 9721 | 0.16 | | | 16.44 | 29.05 | 34.50 | 7777 | 0.12 | | |
| CT | 39-009 | 198.0 | 218.0 | 20.0 | | 21.47 | 23.80 | 34.53 | 41.67 | 9112 | 0.19 | | | 19.04 | 27.63 | 33.33 | 7290 | 0.15 | | |
| CT | 39-010 | 218.0 | 238.0 | 20.0 | | 23.11 | 26.78 | 34.91 | 38.31 | 8764 | 0.22 | | | 21.42 | 27.93 | 30.65 | 7012 | 0.18 | | |
| CT | 39-011 | 238.0 | 258.0 | 20.0 | | 20.47 | 23.61 | 37.68 | 38.70 | 9047 | 0.23 | | | 18.89 | 30.15 | 30.96 | 7238 | 0.18 | | |
| CT | 39-012 | 258.0 | 278.0 | 20.0 | | 22.24 | 16.08 | 37.76 | 46.17 | 10231 | 0.30 | | | 12.86 | 30.21 | 36.93 | 8185 | 0.24 | | |
| CT | 39-013 | 278.0 | 298.0 | 20.0 | | 22.25 | 15.32 | 38.01 | 45.67 | 10529 | 0.32 | | | 13.06 | 30.41 | 36.54 | 8423 | 0.26 | | |
| CT | 39-014 | 298.0 | 318.0 | 20.0 | | 23.73 | 20.61 | 36.16 | 43.23 | 9885 | 0.28 | | | 16.49 | 28.93 | 34.58 | 7908 | 0.22 | | |
| CT | 39-015 | 318.0 | 338.0 | 20.0 | | 21.66 | 14.02 | 36.92 | 49.07 | 10739 | 0.40 | | | 11.21 | 29.53 | 39.25 | 8591 | 0.32 | | |
| CT | 39-015 | 338.0 | 358.0 | 20.0 | | 23.58 | 15.26 | 36.59 | 48.15 | 10760 | 0.27 | | | 12.21 | 29.27 | 38.52 | 8608 | 0.22 | | |
| CT | 39-017 | 358.0 | 378.0 | 20.0 | 24.81 | 22.49 | 18.17 | 36.91 | 44.92 | 10061 | 0.28 | .289 | .049 | 14.53 | 29.53 | 35.94 | 8049 | 0.23 | .231 | .039 |
| CT | 39-018 | 378.0 | 398.0 | 20.0 | 24.58 | 22.33 | 21.20 | 34.54 | 44.25 | 9766 | 0.30 | .316 | .036 | 16.96 | 27.63 | 35.40 | 7813 | 0.24 | .253 | .029 |
| CT | 39-019 | 398.0 | 418.0 | 20.0 | | 23.10 | 16.94 | 37.19 | 45.86 | 10562 | 0.29 | | | 13.56 | 29.75 | 36.69 | 8449 | 0.23 | | |
| CT | 39-020 | 418.0 | 438.0 | 20.0 | | 19.56 | 27.49 | 33.42 | 39.10 | 8897 | 0.39 | | | 21.99 | 26.73 | 31.28 | 7118 | 0.31 | | |
| | 39-303 | 438.0 | 1441.0 | 1003.0 | 10.00 | 99.99 | | | | | | | | | | | | | | |

401

402

263.

|  | TOTAL LENGTH | COUNT | MOISTURES | | DRY BASIS | | | | | | | ESTIMATED IN-SITU MOISTURE OF 20.00% | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| SAMPLE TYPE | | | | | | | | | GROSS | | | | | | | GROSS | | | |
| SERIES 1-199 : | 4CC.0 | 20 | % | % | % | % | % | % | BTU | % | % | % | % | % | % | BTU | % | % | % |
| SERIES 201-299 : | 0.0 | 0 | | | AS | % | | % | | % | | % | | % | | % | | % | |
| SERIES 301-399 : | 1039.0 | 3 | EQUIL | RECVD | ASH | V.M. | F.C. | /LB. | SULFR | SCCA | PCTAS | ASH | V.M. | F.C. | /LB. | SULFR | SCDA | POTAS |
| SODA & POTASH TESTS: | | 4 | | | | | | | | | | | | | | | | |
| MAXIMUM | | | 26.75 | 61.71 | 38.C1 | 49.07 | 10760 | 2.09 | 0.316 | C.148 | 49.37 | 30.41 | 39.25 | 8608 | 1.57 | 0.253 | 0.115 | |
| MINIMUM | | | 11.85 | 14.02 | 23.36 | 14.94 | 2800 | 0.16 | 0.124 | 0.C36 | 11.21 | 18.69 | 11.95 | 2240 | C.12 | 0.099 | 0.029 | |
| RANGE | | | 14.90 | 47.69 | 14.65 | 34.13 | 7960 | 1.93 | 0.192 | 0.112 | 38.16 | 11.72 | 27.30 | 6368 | 1.55 | 0.154 | 0.090 | |
| WEIGHTED MEAN (EXCLUDING SERIES 301-399) | | 20 | 21.11 | 28.03 | 34.27 | 37.69 | 8568 | C.44 | | | 22.43 | 27.42 | 30.16 | 6855 | C.35 | | | |
| ARITHMETIC MEAN (SERIES 1-199) | | 20 | 21.11 | 28.04 | 34.27 | 37.69 | 8569 | 0.44 | 0.223 | 0.083 | 22.42 | 27.41 | 30.15 | 6855 | 0.35 | 0.178 | 0.C67 |
| STANDARD DEVIATION | | | 3.16 | 14.05 | 4.13 | 10.27 | 2336 | 0.43 | 0.C94 | C.C51 | 11.24 | 3.30 | 8.22 | 1869 | C.35 | 0.075 | 0.041 | |
| COEFF. OF VARIATION % | | | 14.99 | 50.10 | 12.04 | 27.24 | 27.26 | 98.19 | | | 50.11 | 12.05 | 27.25 | 27.26 | 0.00 | | | |

REGRESSION EQUATIONS (DRY BASIS):     Y = 80.16 - 0.00607X       WHERE Y = PERCENTAGE OF ASH,
                                  X = 13195.12 -164.60Y          X = GRCSS BTU PER POUND.

LINEAR CORRELATION COEFFICIENT =   -0.9956

<>< > NOTE:   IN DERIVING THE ABOVE REGRESSION EQUATIONS FROM THE 1-199 SERIES SAMPLES,
              ONLY THE 19 SAMPLES CONTAINING ASH VALUES < 55.00% HAVE BEEN USED.
              ( 55.00% DRY ASH = 44.00% ASH AT 20.00% MOISTURE )

C.1.1  TABLE 2      COMPOSITE DRILL HOLE SAMPLE

LOCATION: D.D.H. No. 74-39

SAMPLE NO. 39-401

FOOTAGE:    33' - 93'

WIDTH:      60'

Analysis report no.  67-9115

| PROXIMATE ANALYSIS | As received | Dry basis | ULTIMATE ANALYSIS | As received | Dry basis |
|---|---|---|---|---|---|
| | | | | % Weight | |
| % Moisture | 22.22 | xxxxx | Moisture | 22.22 | xxxxx |
| % Ash | 15.23 | 19.58 | Carbon | 44.82 | 57.62 |
| % Volatile | 30.22 | 38.85 | Hydrogen | 3.41 | 4.39 |
| % Fixed Carbon | 32.33 | 41.57 | Nitrogen | 0.84 | 1.08 |
| | 100.00 | 100.00 | Chlorine | 0.03 | 0.04 |
| | | | Sulfur | 0.24 | 0.31 |
| Btu | 7607 | 9780 | Ash | 15.23 | 19.58 |
| % Sulfur | 0.24 | 0.31 | Oxygen (diff) | 13.21 | 16.98 |
| % Alk. as Na₂O | 0.27 | 0.35 | | 100.00 | 100.00 |

| SULFUR FORMS | | | MINERAL ANALYSIS | % Wt. Ignited Basis |
|---|---|---|---|---|
| % Pyritic Sulfur | | 0.03 | Phos. pentoxide, P₂O₅ | 0.11 |
| % Sulfate Sulfur | | 0.01 | Silica; SiO₂ | 57.15 |
| % Organic Sulfur (diff.) | | 0.27 | Ferric oxide, Fe₂O₃ | 6.50 |
| % Total Sulfur | | 0.31 | Alumina, Al₂O₃ | 26.36 |
| | | | Titania, TiO₂ | 0.87 |
| WATER SOLUBLE ALKALIES | | | Lime, CaO | 4.40 |
| % Na₂O = | ND | | Magnesia, MgO | 0.31 |
| % K₂O = | | | Sulfur trioxide, SO₃ | 2.27 |
| | | | Potassium oxide, K₂O | 0.30 |
| | | | Sodium oxide, Na₂O | 1.59 |

| FUSION TEMPERATURE OF ASH | Reducing | Oxidizing | | |
|---|---|---|---|---|
| | | | Undetermined | 0.14 |
| Initial Deformation | 2660°F | 2700+°F | | 100.00 |
| Softening (H = W) | 2675°F | 2700+°F | | |
| Softening (H = ½W) | 2685°F | 2700+°F | SILICA VALUE = | |
| Fluid | 2700°F | 2700+°F | T250 = | °F |

H is Cone Height
W is Cone Width

% EQUILIBRIUM MOISTURE =  ND

HARDGROVE GRINDABILITY INDEX =  38

FREE SWELLING INDEX =  ND

ESTIMATED VISCOSITY  ND

at Critical Viscosity Temperature of     °F =     Poises

ND-Not determined

Respectfully submitted,

COMMERCIAL TESTING & ENGINEERING CO.

R. A. Houser,
District Manager

C.1.1.  TABLE 3      COMPOSITE DRILL HOLE SAMPLE

LOCATION:  D.D.H. No. 74-39
SAMPLE NO. 402
FOOTAGE:   178' - 438'
WIDTH:     260'

| | Analysis report no. | 67-9114 | | | % Weight | |
|---|---|---|---|---|---|---|
| PROXIMATE ANALYSIS | As received | Dry basis | ULTIMATE ANALYSIS | As received | Dry basis |
| % Moisture | 19.04 | xxxxx | Moisture | 19.04 | xxxxx |
| % Ash | 34.87 | 43.07 | Carbon | 30.47 | 37.64 |
| % Volatile | 23.58 | 29.12 | Hydrogen | 2.30 | 2.84 |
| % Fixed Carbon | 22.51 | 27.81 | Nitrogen | 1.01 | 1.25 |
| | 100.00 | 100.00 | Chlorine | 0.03 | 0.03 |
| | | | Sulfur | 0.63 | 0.78 |
| Btu | 4965 | 6133 | Ash | 34.87 | 43.07 |
| % Sulfur | 0.63 | 0.78 | Oxygen (diff) | 11.65 | 14.39 |
| % Alk. as Na$_2$O | 0.42 | 0.52 | | 100.00 | 100.00 |

| SULFUR FORMS | | MINERAL ANALYSIS | % Wt. Ignited Basis |
|---|---|---|---|
| % Pyritic Sulfur | 0.49 | Phos. pentoxide, P$_2$O$_5$ | 0.25 |
| % Sulfate Sulfur | 0.07 | Silica, SiO$_2$ | 49.93 |
| % Organic Sulfur (diff.) | 0.22 | Ferric oxide, Fe$_2$O$_3$ | 12.31 |
| % Total Sulfur | 0.78 | Alumina, Al$_2$O$_3$ | 26.84 |
| | | Titania, TiO$_2$ | 0.89 |
| WATER SOLUBLE ALKALIES | | Lime, CaO | 2.57 |
| % Na$_2$O = | | Magnesia, MgO | 2.01 |
| % K$_2$O = | ND | Sulfur trioxide, SO$_3$ | 3.48 |
| | | Potassium oxide, K$_2$O | 0.76 |
| | | Sodium oxide, Na$_2$O | 0.71 |
| | | Undetermined | 0.25 |
| | | | 100.00 |

| FUSION TEMPERATURE OF ASH | Reducing | | Oxidizing | |
|---|---|---|---|---|
| Initial Deformation | 2500 | °F | 2620 | °F |
| H is Cone Height    Softening (H = W) | 2530 | °F | 2650 | °F |
| W is Cone Width    Softening (H = ½ W) | 2540 | °F | 2670 | °F |
| Fluid | 2600 | °F | 2700 | °F |

% EQUILIBRIUM MOISTURE = ND
HARDGROVE GRINDABILITY INDEX = 54
FREE SWELLING INDEX = ND

SILICA VALUE =
T250 =                         °F
ESTIMATED VISCOSITY    ND
at Critical Viscosity Temperature of          °F =     Poises

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

ND-Not determined

R. A. Houser,
District Manager

C.1.1.   TABLE 4         OXIDIZED SURFACE COAL

COMPOSITE OF SAMPLES S.S.1 and S.S.2

| PROXIMATE ANALYSIS | Analysis report no. As received | 64-11737 Dry basis | ULTIMATE ANALYSIS | % Weight As received | Dry basis |
|---|---|---|---|---|---|
| % Moisture | 14.38 | xxxxx | Moisture | 14.38 | xxxxx |
| % Ash | 22.51 | 26.29 | Carbon | 41.92 | 48.96 |
| % Volatile | 32.19 | 37.60 | Hydrogen | 2.59 | 3.03 |
| % Fixed Carbon | 30.92 | 36.11 | Nitrogen | 0.68 | 0.80 |
| | 100.00 | 100.00 | Chlorine | 0.07 | 0.08 |
| | | | Sulfur | 0.38 | 0.44 |
| Btu | 6607 | 7717 | Ash | 22.51 | 26.29 |
| % Sulfur | 0.38 | 0.44 | Oxygen (diff) | 17.47 | 20.40 |
| % Alk. as Na₂O | 0.08 | 0.09 | | 100.00 | 100.00 |

% Wt.

| SULFUR FORMS | | MINERAL ANALYSIS | Ignited Basis |
|---|---|---|---|
| % Pyritic Sulfur | | Phos. pentoxide, $P_2O_5$ | 0.04 |
| % Sulfate Sulfur | | Silica; $SiO_2$ | 85.22 |
| % Organic Sulfur | ND | Ferric oxide, $Fe_2O_3$ | 0.81 |
| % Total Sulfur | | Alumina, $Al_2O_3$ | 8.27 |
| | | Titania, $TiO_2$ | 0.31 |
| WATER SOLUBLE ALKALIES | | Lime, CaO | 2.68 |
| % Na₂O = | ND | Magnesia, MgO | 0.48 |
| % K₂O = | | Sulfur trioxide, $SO_3$ | 1.62 |
| | | Potassium oxide, $K_2O$ | 0.08 |
| | | Sodium oxide, $Na_2O$ | 0.28 |
| | | Undetermined | 0.21 |
| | | | 100 0 |

| FUSION TEMPERATURE OF ASH | Reducing | Oxidizing |
|---|---|---|
| Initial Deformation | °F | °F |
| Softening (H = W) | ND  °F | ND  °F |
| Softening (H = ½W) | °F | °F |
| Fluid | °F | °F |

H is Cone Height
W is Cone Width

% EQUILIBRIUM MOISTURE = ND
HARDGROVE GRINDABILITY INDEX = ND
FREE SWELLING INDEX = ND

ND - Not Determined
% Moisture is Lab Basis

SILICA VALUE =
T250 =            °F
ESTIMATED VISCOSITY   ND
at Critical Viscosity Temperature of        °F =        Poises

Respectfully submitted,
COMMERCIAL TESTING & ENGINEERING CO.

/ R. A. Houser
District Manager

C-1-2    TABLE 1.        PORE SIZE DISTRIBUTION OF COALS AND ACTIVATED CARBON

| Pore Diameter $\overset{o}{A}$ (d) | Sample of Core Coal | | Sample of Surface Coal | | Activated Carbon | |
|---|---|---|---|---|---|---|
| | % Pore* Volume (V) | $\frac{\Delta V}{\Delta d} \times 10^3$ | % Pore* Volume (V) | $\frac{\Delta V}{\Delta d} \times 10^3$ | % Pore* Volume (V) | $\frac{\Delta V}{\Delta d} \times 10^3$ |
| 27.6 | - | - | - | - | - | - |
| 37.2 | 2.6 | 0.7 | 0.7 | 0.19 | 5.9 | 1.59 |
| 44.2 | 3.9 | 0.88 | 1.2 | 0.27 | 9.2 | 2.08 |
| 53.4 | 4.7 | 0.88 | 1.7 | 0.32 | 12.4 | 2.32 |
| 66.2 | 5.4 | 0.82 | 3.6 | 0.54 | 16.3 | 2.46 |
| 85.4 | 11.0 | 1.29 | 5.7 | 0.67 | 19.1 | 2.24 |
| 117.4 | 20.0 | 1.70 | 11.2 | 0.95 | 23.5 | 2.00 |
| 181.0 | 34.4 | 1.88 | 14.8 | 0.82 | 31.8 | 1.76 |
| 228.0 | 42.3 | 1.86 | 26.2 | 1.15 | 37.0 | 1.62 |
| 372.0 | 63.2 | 1.70 | 74.7 | 2.01 | 67.1 | 1.80 |

\*  % pore volume associated with pores of diameter

$\leq$  given in column 1

SURFACE AREA CALCULATIONS

C.1.2  TABLE 2    Core Coal (-60 + 100 mesh)

SAMPLE IDENTIFICATION NUMBER = 1

| | | | |
|---|---|---|---|
| W1= 25.3271 | H1= 512.100 | X1= 131.700 | PS= 751.000 |
| W2= 20.8713 | H2= 144.380 | X2= 529.000 | ALPHA= 0.66E-04 |
| ε 4.4558 | IS= 77.000 | VD= 27.220 | S= 16.2 |

B= 0.01820
C= 0.1100E-05
VS= 15.91368

| ITERATION | WHICH X | A | P1 | P2 | V | X | Y |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.04169 | 149.9900 | 60.3700 | 2.6340 | 0.0804 | 0.0332 |
| 2 | 0 | 0.00714 | 174.7700 | 84.6600 | 2.8316 | 0.1127 | 0.0449 |
| 3 | 0 | 0.00714 | 201.8600 | 109.8800 | 3.0242 | 0.1463 | 0.0567 |
| 4 | 0 | 0.00714 | 236.7400 | 137.3200 | 3.2274 | 0.1828 | 0.0693 |
| 5 | 0 | 0.00714 | 273.0500 | 166.9900 | 3.4350 | 0.2224 | 0.0832 |
| 6 | 0 | 0.00714 | 312.5000 | 198.3900 | 3.6658 | 0.2642 | 0.0979 |
| 7 | 1 | 0.04169 | 370.4200 | 303.2200 | 4.5022 | 0.4038 | 0.1504 |
| 8 | 1 | 0.04169 | 442.5000 | 385.6000 | 5.3131 | 0.5134 | 0.1986 |
| 9 | 1 | 0.04169 | 518.9000 | 461.6000 | 6.2484 | 0.6146 | 0.2553 |
| 10 | 1 | 0.04169 | 613.1000 | 540.8000 | 7.7343 | 0.7201 | 0.3326 |
| 11 | 1 | 0.04169 | 703.2000 | 607.8000 | 10.4080 | 0.8093 | 0.4078 |
| 12 | 1 | 0.04169 | 759.8000 | 652.6000 | 14.0002 | 0.8590 | 0.4737 |
| 13 | 1 | 0.04169 | 798.5000 | 678.4000 | 18.5003 | 0.9033 | 0.5051 |
| 14 | 1 | 0.04169 | 870.5000 | 710.1000 | 24.5627 | 0.9455 | 0.7068 |
| 15 | 1 | 0.04169 | 905.7000 | 717.2000 | 32.2816 | 0.9550 | 0.6573 |

SW= 11.065

$P_1$ = initial pressure, ton

$P_2$ = equilibrium pressure, ton

$V$ = vol. of $N_2$ absorbed, ml/g coal

$X$ = P1/P2 (relative vapour pressure)

$Y = \dfrac{X}{V(1 - X)}$

$S_W$ = surface area, $m^2/g$

C.1.2  TABLE 3 Surface  Coal  ( – 60 + 100 mesh )

SAMPLE IDENTIFICATION NUMBER = 2
N1= 24.9419        H1= 507.600        X1= 131.700        PS= 751.000
N2= 20.2280        H2= 140.980        X2= 529.600        ALPHA= 0.66E-04
 I= 4.7139         IS= 77.000         VD= 27.220         S= 16.2
                          B= 0.01756
                          C= 0.1064E-05
                          VS= 16.27952

| ITERATION | WHICH X | A | P1 | P2 | V | X | Y |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.03941 | 149.8600 | 90.0400 | 0.7676 | 0.1199 | 0.1775 |
| 2 | 0 | 0.00675 | 174.9700 | 111.5700 | 0.8128 | 0.1486 | 0.2147 |
| 3 | 0 | 0.00675 | 206.2400 | 135.3000 | 0.8687 | 0.1802 | 0.2530 |
| 4 | 0 | 0.00675 | 249.1300 | 164.6200 | 0.9149 | 0.2192 | 0.3069 |
| 5 | 0 | 0.00675 | 299.9900 | 199.2400 | 0.9735 | 0.2653 | 0.3709 |
| 6 | 1 | 0.03941 | 360.0700 | 305.7600 | 1.1859 | 0.4071 | 0.5791 |
| 7 | 1 | 0.03941 | 430.3000 | 387.2000 | 1.3942 | 0.5156 | 0.7634 |
| 8 | 1 | 0.03941 | 501.3000 | 459.7000 | 1.6951 | 0.6121 | 0.9310 |
| 9 | 1 | 0.03941 | 605.9000 | 549.1000 | 2.2676 | 0.7312 | 1.1994 |
| 10 | 1 | 0.03941 | 682.5000 | 620.7000 | 3.3566 | 0.8265 | 1.4192 |
| 11 | 1 | 0.03941 | 754.4000 | 668.5000 | 5.8369 | 0.8901 | 1.3882 |
| 12 | 1 | 0.03941 | 827.0000 | 695.7000 | 10.4943 | 0.9264 | 1.1988 |
| 13 | 1 | 0.03941 | 907.9000 | 709.2000 | 18.0680 | 0.9443 | 0.9390 |

IH= 3.132

.1.2  TABLE 4   Activated Carbon - Calgon ( -60 ◆ 100 mesh)

SAMPLE IDENTIFICATION NUMBER ▫ 3
| | | | |
|---|---|---|---|
| W1▫ 21.7717 | H1▫ 505.300 | X1▫ 131.700 | PS▫ 751.000 |
| W2▫ 21.5526 | H2▫ 128.410 | X2▫ 529.000 | ALPHA▫  0.66E-04 |
| ▫  0.2191 | IS▫  77.000 | VD▫  27.220 | S▫ 16.2 |

B▫  0.42647
C▫ 0.2609E-04
VS▫ 18.56200

| ITERATION | WHICH X | A | P1 | P2 | V | X | Y |
|---|---|---|---|---|---|---|---|
| 1 | 1 | 0.84791 | 150.0100 | 7.3720 | 117.7991 | 0.0098 | 0.0001 |
| 2 | 1 | 0.84791 | 175.2600 | 91.6000 | 152.5973 | 0.1220 | 0.0009 |
| 3 | 0 | 0.14523 | 206.1100 | 112.0200 | 157.4452 | 0.1492 | 0.0011 |
| 4 | 0 | 0.14523 | 242.1400 | 136.0100 | 162.4724 | 0.1811 | 0.0014 |
| 5 | 0 | 0.14523 | 287.4000 | 164.5600 | 167.9130 | 0.2191 | 0.0017 |
| 6 | 0 | 0.14523 | 300.6200 | 190.2400 | 172.7542 | 0.2533 | 0.0020 |
| 7 | 1 | 0.84791 | 356.8400 | 286.2700 | 190.4437 | 0.3812 | 0.0032 |
| 8 | 1 | 0.84791 | 416.4000 | 360.2700 | 205.2300 | 0.4797 | 0.0045 |
| 9 | 1 | 0.84791 | 494.7000 | 435.0000 | 222.4298 | 0.5792 | 0.0062 |
| 10 | 1 | 0.84791 | 585.9000 | 514.5000 | 247.0969 | 0.6851 | 0.0088 |
| 11 | 1 | 0.84791 | 654.2000 | 579.7000 | 280.5992 | 0.7719 | 0.0121 |
| 12 | 1 | 0.84791 | 726.1000 | 640.4000 | 325.4463 | 0.8527 | 0.0178 |
| 13 | 1 | 0.84791 | 809.9000 | 689.0000 | 405.5468 | 0.9174 | 0.0274 |
| 14 | 1 | 0.84791 | 901.8000 | 712.6000 | 555.0440 | 0.9489 | 0.0334 |

<u>CALGON ACTIVE CARBON</u>

The calgon active carbon did not exhibit a Type II isothem;
it more closely resembled that of a Type I isotherm.  Therefore, the
classical BET interpretation for surface area could not be used. The
specific surface area for this sample was determined using the isotherm
plot (see Figure 1).

$$S_W = 705.9 \ m^2/g,$$

APPENDIX C-2. SORPTIVE PROPERTIES OF COAL.

C-2-1 ADSORPTION OF METAL IONS.

BATCH TESTS.

TABLE 1. CONTACT PROCESS LEAD. TIME: 8 Hrs., % COAL: 1% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/1 | mg Pb Removed per gm Coal | % Detectable Removed | Effluent Conc. mg/1 | mg Pb Removed per gm Coal | % Detectable Removed | Effluent Conc. mg/1 | mg Pb Removed per gm Coal | % Dectectable Removed | Effluent Conc. mg/1 | mg Pb Removed per gm Coal | % Detectable Removed |
| 0.05 | <0.06 | >0.008* | >40-100 | <0.06 | >0.008* | >40-100 | <0.06 | >0.008* | >40-100 | <0.04 | >0.0012* | >60-100 |
| 0.1 | <0.06 | >0.028* | >70-100 | <0.06 | >0.028* | >70-100 | <0.06 | >0.028* | >70-100 | <0.04 | >0.0032* | >80-100 |
| 0.2 | <0.06 | >0.068* | >85-100 | <0.06 | >0.068* | >85-100 | 0.1 | 0.01 | 50 | <0.04 | >0.072* | >90-100 |
| 0.5 | <0.06 | >0.188* | >94-100 | <0.06 | >0.188* | >94-100 | <0.06 | >0.188* | >94-100 | <0.06 | >0.188* | >94-100 |
| 5 | 0.1 | 0.49 | 98 | 0.2 | 0.48 | 96 | 0.3 | 0.47 | 94 | <0.06 | >1.988* | >99.4-100 |
| 50 | 1.0 | 4.9 | 98 | 1.1 | 4.89 | 97.8 | 1.3 | 4.87 | 97.4 | 0.3 | 4.97 | 99.4 |
| 100 | 28 | 7.2 | 72 | - | - | - | - | - | - | 2.2 | 9.78 | 97.8 |
| 250 | 130 | 12.0 | 48 | - | - | - | - | - | - | 6.2 | 18.8 | 97.5 |
| 500 | 228 | 27.2 | 54.4 | 180 | 32.0 | 64 | 130 | 37.0 | 74 | 79.0 | 42.1 | 84.2 |

Blank: < 0.06

\* The above figures are calculated on the basis that since a blank is 0.06 then the effluent concentration will be $\frac{0.06}{2} = 0.03$ mg/1 as an average value.

Time: 8 hrs.      Coal: 5% w/w

| Solution Concentration mg/l | Mean particle size 0.533 mm (coarse) | | | Mean particle size 0.03414 mm (fine) | | |
|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg Pb removed per gm coal | % Removal | Effluent conc. mg/l | mg Pb removed per gm coal | % Removal |
| 0.05 | - | - | - | < 0.04 | > 0.0002 | > 20 |
| 0.1 | - | - | - | < 0.04 | > 0.0012 | > 60 |
| 0.2 | - | - | - | < 0.04 | > 0.0032 | > 80 |
| 0.5 | - | - | - | - | - | - |
| 5 | - | - | - | - | - | - |
| 50 | - | - | - | - | - | - |
| 100 | 2.4 | 1.95 | 97.6 | < 0.4 | > 1.99 | > 99.6 |
| 250 | 15 | 4.7 | 94 | 1.1 | 4.98 | 99.6 |
| 500 | 16 | 9.68 | 96.8 | 1.0 | 9.98 | 99.8 |

TABLE 3: CONTACT PROCESS MERCURY.    TIME: 8 HRS.    COAL: 1% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | 0.02 | 0.008 | 80 | 0.013 | 0.0087 | 87 | 0.018 | 0.0082 | 82 | 0.008 | 0.0092 | 92 |
| 0.5 | 0.0357 | 0.0464 | 92.9 | 0.0228 | 0.04770 | 95.4 | 0.035 | 0.0465 | 93 | - | - | - |
| 5 | 0.22 | 0.478 | 95.6 | 0.157 | 0.484 | 96.86 | 0.66 | 0.434 | 86.8 | 0.28 | 0.472 | 94.4 |
| 50 | 6.2 | 4.38 | 87.6 | 3.36 | 4.664 | 93.28 | 1.217 | 4.878 | 97.57 | 1.913 | 4.809 | 96.17 |
| 100 | 1.6 | 9.84 | 98.4 | 1.33 | 9.867 | 98.67 | 3.072 | 9.693 | 96.93 | 0.467 | 9.953 | 99.53 |
| 250 | 28.95 | 22.11 | 88.42 | 10.17 | 23.98 | 95.93 | 5.7 | 24.43 | 97.72 | 4 | 24.6 | 98.4 |
| 500 | 170.59 | 32.041 | 64.08 | 21.33 | 47.87 | 95.73 | 42.67 | 45.73 | 91.47 | 8 | 49.2 | 98.4 |

< Sensitivity 0.002 mg/l

TABLE 4 : CONTACT PROCESS MERCURY.  TIME: 8 HRS.  COAL: 5% w/w

| Solution Concentration ppm (mg/1) | Coal size 0.533 mm av. | | | Coal size 0.2905 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/1 | mg Removed per gm Coal | % Removal | Effluent Conc. mg/1 | mg Removed per gm Coal | % Removal | Effluent Conc. mg/1 | mg Removed per gm Coal | % Removal | Effluent Conc. mg/1 | mg Removed per gm Coal | % Removal |
| 0.1 | 0.0032 | 0.00193 | 96.8 | 0.0095 | 0.00181 | 90.5 | 0.028 | 0.00144 | 72 | 0.002 | 0.00196 | 98 |
| 0.5 | 0.116 | 0.00768 | 76.8 | 0.0143 | 0.00971 | 97.14 | 0.56 | 0.0012 | -12 | 0.0045 | 0.0099 | 99.1 |
| 5 | 0.0848 | 0.0983 | 98.3 | 0.0434 | 0.09913 | 99.13 | 0.075 | 0.0985 | 98.5 | 0.0375 | 0.09925 | 99.25 |
| 50 | 0.367 | 0.09927 | 99.27 | 1.224 | 0.9755 | 97.55 | 0.378 | 0.9924 | 99.24 | 1.96 | 0.9608 | 96.08 |
| 100 | 0.633 | 1.9873 | 99.37 | 0.391 | 1.9922 | 99.61 | 0.267 | 1.9947 | 99.73 | 0.96 | 1.9808 | 99.04 |
| 250 | 1.08? | 4.9783 | 99.57 | 0.8 | 4.984 | 99.68 | 12.45 | 4.751 | 95.02 | 2.4 | 4.952 | 99.04 |
| 500 | 8.57 | 9.829 | 98.29 | 2.933 | 9.9413 | 99.41 | 2.94 | 9.9412 | 99.41 | 1.57 | 9.9686 | 99.69 |

< Sensitivity 0.002 mg/1

TABLE 5. CONTACT PROCESS MERCURY.    TIME: 8 HRS.    COAL: 10% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | <0.002 | >0.00098 | >98 | <0.002 | >0.00098 | >98 | <0.0046 | >0.00095 | >95.4 | <0.0016 | >0.00098 | >98.4 |
| 0.5 | 0.0913 | 0.00408 | 81.74 | 0.01714 | 0.00482 | 96.57 | 0 | 0.005 | 100 | - | - | - |
| 5 | 0.015 | 0.04985 | 99.7 | 0.0435 | 0.04956 | 99.13 | 0.05 | 0.0495 | 99 | 0.0375 | 0.04952 | 99.25 |
| 50 | 0.252 | 0.4975 | 99.5 | 0.56 | 0.4944 | 98.88 | 0.694 | 0.4931 | 98.61 | 0.73 | 0.4927 | 98.54 |
| 100 | 0.522 | 0.9948 | 99.48 | 0.765 | 0.9924 | 99.24 | 0.264 | 0.9974 | 99.74 | 0.33 | 0.9967 | 99.67 |
| 250 | 2.29 | 2.477 | 99.08 | 1.265 | 2.4874 | 99.49 | 5.38 | 2.446 | 97.85 | 0.643 | 2.4936 | 99.74 |
| 500 | 3.0 | 4.37 | 99.4 | 2.44 | 4.9756 | 99.51 | 1.143 | 4.9886 | 99.77 | 1.84 | 4.9816 | 99.63 |

< Sensitivity 0.002 mg/l

TABLE 6. CONTACT PROCESS COPPER.  TIME: 8 HRS.  COAL: 1% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03419 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.5 | 0.042 | 0.0458 | 91.6 | 0.032 | 0.0468 | 93.6 | 0.009 | 0.0491 | 98.2 | 0.010 | 0.040 | 98 |
| 5.0 | 0.467 | 0.4533 | 90.6 | 0.334 | 0.4666 | 93.3 | 0.210 | 0.479 | 95.8 | 0.145 | 0.4855 | 97.1 |
| 50 | 8.392 | 4.1608 | 83.2 | 5.949 | 4.4051 | 88.1 | 5.147 | 4.4853 | 89.7 | 4.998 | 4.5002 | 90 |
| 100 | 33.753 | 6.6247 | 66.2 | 28.345 | 7.1655 | 71.7 | 14.545 | 8.5455 | 85.5 | 11.935 | 8.8065 | 88.1 |
| 250 | 160.997 | 8.9003 | 35.6 | 141.830 | 10.817 | 43.3 | 101.581 | 14.8419 | 59.4 | 95.831 | 15.4169 | 61.7 |
| 500 | 355.493 | 14.3507 | 28.7 | 335.410 | 16.459 | 32.9 | 316.243 | 18.3757 | 36.8 | 314.327 | 18.5673 | 37.1 |

Blank:  < 0.003 mg/l

TABLE 7. CONTACT PROCESS COPPER. TIME: 8 hrs. COAL: 5% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.177 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.5 | 0.021 | 0.00958 | 95.8 | 0.030 | 0.0094 | 94. | 0.013 | 0.0097 | 97.4 | 0.011 | 0.00958 | 95.8 |
| 5.0 | 0.340 | 0.0932 | 93.2 | 0.184 | 0.0963 | 96.3 | 0.83 | 0.0983 | 98.3 | 0.092 | 0.008 | 98.16 |
| 50 | 5.520 | 0.8896 | 88.96 | 4.513 | 0.9097 | 90.97 | 1.846 | 0.9631 | 96.31 | 1.566 | 0.9687 | 96.87 |
| 100 | 8.392 | 1.832 | 91.61 | 8.019 | 1.84 | 91.98 | 4.476 | 1.9105 | 95.52 | 4.848 | 1.903 | 95.15 |
| 250 | 36.61 | 4.268 | 85.36 | 21.85 | 4.563 | 91.26 | 15.525 | 4.6895 | 93.79 | 14.758 | 4.7048 | 94.10 |
| 500 | 166.747 | 6.665 | 66.65 | 93.915 | 8.1217 | 81.22 | 59.607 | 8.8079 | 88.08 | 50.982 | 8.9804 | 89.80 |

Blank: < 0.003 mg/l

TABLE 8. CONTACT PROCESS COPPER. TIME: 8 HRS. COAL: 10% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.5 | 0.022 | 0.00478 | 95.6 | 0.021 | 0.00479 | 95.8 | 0.012 | 0.00488 | 97.6 | 0.010 | 0.0049 | 98 |
| 5.0 | 0.227 | 0.0477 | 95.46 | 0.172 | 0.04828 | 96.56 | 0.059 | 0.0494 | 98.82 | 0.073 | 0.0493 | 98.54 |
| 50 | 3.730 | 0.4627 | 92.54 | 2.816 | 0.4718 | 94.37 | 0.839 | 0.4916 | 98.32 | 0.790 | 0.4931 | 98.62 |
| 100 | 7.27 | 0.9273 | 92.73 | 5.221 | 0.9478 | 94.78 | 2.350 | 0.9765 | 97.65 | 2.331 | 0.9767 | 97.67 |
| 250 | 17.058 | 2.3294 | 98.18 | 14.183 | 2.3582 | 94.33 | 7.858 | 2.4214 | 96.86 | 7.475 | 2.4252 | 97.01 |
| 500 | 53.67 | 4.4633 | 89.27 | 35.649 | 4.6435 | 92.87 | 22.233 | 4.7777 | 95.55 | 21.083 | 4.7892 | 95.78 |

Blank: < 0.003 mg/l

TABLE 9. CONTACT PROCESS ZINC. TIME: 8 HRS. COAL: 1% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.5 | 0.027 | 0.0473 | 94.6 | 0.025 | 0.0475 | 95.0 | 0.022 | 0.0478 | 95.6 | 0.095 | 0.0405 | 81 |
| 5.0 | 0.191 | 0.4809 | 96.18 | 0.119 | 0.4881 | 97.62 | 0.115 | 0.4885 | 97.7 | 0.125 | 0.4875 | 97.5 |
| 50 | 12.636 | 3.7364 | 74.73 | 10.306 | 3.9694 | 79.39 | 7.463 | 4.2537 | 85.07 | 7.660 | 4.234 | 84.68 |
| 125 | 60.512 | 6.4488 | 51.59 | 54.727 | 7.0273 | 56.22 | 44.049 | 8.0951 | 64.76 | 42.269 | 8.2731 | 66.19 |
| 250 | 165.072 | 8.492 | 33.97 | 146.385 | 10.3615 | 41.44 | 110.225 | 11.0225 | 44.09 | 121.023 | 12.898 | 51.59 |
| 500 | 327.739 | 17.2261 | 34.45 | 319.84 | 18.0158 | 36.03 | 323.79 | 17.6209 | 35.24 | 307.996 | 19.2004 | 38.40 |

Blank : < 0.01

TABLE 10. CONTACT PROCESS ZINC.  TIME: 8 HRS.  COAL: 5% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | gm Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.5 | 0.024 | 0.00952 | 95.2 | 0.018 | 0.00964 | 96.4 | 0.015 | 0.0097 | 97.0 | 0.023 | 0.00954 | 95.4 |
| 5.0 | 0.117 | 0.09766 | 97.66 | 0.119 | 0.4881 | 97.62 | 0.115 | 0.4885 | 97.7 | 0.056 | 0.09888 | 98.88 |
| 50 | 3.909 | 0.9218 | 92.18 | 2.725 | 0.9455 | 94.55 | 1.777 | 0.9645 | 96.45 | 1.777 | 0.9645 | 96.45 |
| 125 | 18.954 | 2.1209 | 84.84 | 13.615 | 2.2277 | 89.11 | 7.475 | 2.3505 | 94.02 | 7.875 | 2.3425 | 93.7 |
| 250 | 53.838 | 3.923 | 78.46 | 53.838 | 3.923 | 78.46 | 38.265 | 4.235 | 84.69 | 35.150 | 4.297 | 85.94 |
| 500 | 173.74 | 6.525 | 65.25 | 157.947 | 6.8410 | 68.41 | 132.675 | 7.346 | 73.46 | 128.727 | 7.4255 | 74.25 |

Blank:  < 0.01

TABLE 11. CONTACT PROCESS ZINC.   TIME: 8 hrs., % COAL: 10 w/w

| Solution Concentration ppm (mg/1) | Coal size 0.533 mm av. | | | Coal size 0.2969 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/1 | mg removed per gm coal | % Removal | Effluent conc. mg/1 | mg removed per gm coal | % Removal | Effluent conc. mg/1 | mg removed per gm coal | % Removal | Effluent conc. mg/1 | mg removed per gm coal | % Removal |
| 0.5 | 0.021 | 0.00479 | 95.8 | 0.087 | 0.00413 | 82.6 | 0.022 | 0.00478 | 95.6 | 0.016 | 0.00484 | 96.8 |
| 5.0 | 0.078 | 0.04922 | 98.44 | 0.115 | 0.04885 | 97.7 | 0.064 | 0.04936 | 98.72 | 0.047 | 0.04953 | 99.05 |
| 50 | 2.290 | 0.4771 | 95.42 | 1.461 | 0.4854 | 97.08 | 1.050 | 0.4895 | 97.9 | 1.003 | 0.48997 | 97.99 |
| 125 | 11.475 | 1.1352 | 90.82 | 9.522 | 1.1548 | 92.38 | 4.538 | 1.2046 | 96.37 | 5.028 | 1.1997 | 95.98 |
| 250 | 33.815 | 2.1618 | 86.47 | 34.705 | 2.152 | 86.12 | 27.141 | 2.2286 | 89.14 | 13.704 | 2.363 | 94.52 |
| 500 | 108.193 | 3.9181 | 78.36 | 88.450 | 4.1155 | 82.31 | 65.548 | 4.3445 | 86.89 | 52.912 | 4.471 | 89.42 |

Blank:  < 0.01

## TABLE 12. CONTACT PROCESS CADMIUM
### Coal: 1% w/w.  Time: 8 hours

| Mean Particle Size of coal mm | 0.533 mm | | | 0.2965 mm | | | 0.117 mm | | | 0.03414 mm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solution Concentration mg/l | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal |
| 0.1 | 0.007 | 0.0093 | 93 | 0.007 | 0.0093 | 93 | 0.006 | 0.0094 | 94 | <0.003 | >0.00985* | >98.5-100 |
| 0.2 | 0.01 | 0.019 | 95 | 0.01 | 0.019 | 95 | <0.003 | >0.0198* | >99.2-100 | 0.004 | 0.0196 | 98 |
| 0.5 | 0.023 | 0.0477 | 95.4 | 0.01 | 0.049 | 98 | 0.01 | 0.049 | 98 | 0.007 | 0.0195 | 98.6 |
| 5 | 0.043 | 0.4957 | 99.14 | 0.018 | 0.4982 | 99.64 | 0.004 | 0.4996 | 99.92 | 0.013 | 0.4987 | 99.74 |
| 50 | 0.865 | 4.9135 | 98.27 | 0.830 | 4.917 | 98.34 | 0.426 | 4.9574 | 99.15 | 0.140 | 4.996 | 99.92 |
| 100 | 70.417 | 2.9583 | 29.583 | 54.533 | 4.5467 | 45.47 | 47.651 | 5.2349 | 52.35 | 41.297 | 5.8703 | 58.70 |
| 250 | 133.358 | 11.6632 | 46.653 | 123.957 | 12.6043 | 50.42 | 120.891 | 12.911 | 51.64 | 109.166 | 14.083 | 56.33 |
| 500 | 405.057 | 9.494 | 18.989 | 311.627 | 18.837 | 37.674 | 400.969 | 9.903 | 19.8 | 322.396 | 16.761 | 33.5 |

\* Calculated on average of effluent basis.

## TABLE 13. CONTACT PROCESS CADMIUM
### Coal 5% w/w.  Time: 8 hours

| Mean Particle Size of Coal mm | 0.533 mm | | | 0.2965 mm | | | 0.117 mm | | | 0.03414 mm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solution Concentration mg/l | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal |
| 0.1 | 0.003 | 0.00194 | ~97 | <0.003 | >0.00197* | >92.5-100 | 0.004 | 0.00192 | 96 | 0.005 | 0.0019 | 95 |
| 0.2 | 0.003 | 0.00394 | 98.5 | 0.004 | 0.00392 | 98 | 0.024 | 0.00176 | 98 | <0.003 | >0.00397* | >98.2-100 |
| 0.5 | 0.009 | 0.00982 | 98.2 | 0.003 | 0.00994 | 99.4 | 0.008 | 0.00984 | 98.4 | 0.005 | 0.0099 | 99 |
| 5 | 0.069 | 0.09864 | 98.64 | 0.07 | 0.09986 | 99.86 | 0.1 | 0.098 | 98 | <0.003 | >0.09997* | >99.97 |
| 50 | 0.215 | 0.9957 | 99.57 | 0.118 | 0.93764 | 99.76 | 0.003 | 0.9999 | 99.99 | 0.076 | 0.99484 | 99.85 |
| 100 | 22.766 | 1.54468 | 77.23 | 14.507 | 1.70985 | 85.49 | 8.789 | 1.82422 | 91.21 | 5.718 | 1.8856 | 94.28 |
| 250 | 40.5 | 4.188 | 83.76 | 30.95 | 4.381 | 87.62 | 19.875 | 4.602 | 92.05 | 14.905 | 4.702 | 94.04 |
| 500 | 182.844 | 6.343 | 63.43 | 110.915 | 7.782 | 77.82 | 119.539 | 7.609 | 76.09 | 82.722 | 8.346 | 83.46 |

\* Calculated on average of effluent basis

## TABLE 14. CONTACT PROCESS CADMIUM
### Coal 10% w/w.  Time: 8 hours

| Mean Particle Size of Coal mm | 0.533 mm | | | 0.2965 mm | | | 0.117 mm | | | 0.03414 mm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solution Concentration mg/l | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal |
| 0.1 | 0.009 | 0.00091 | 91 | <0.003 | >0.00097 | >97 | 0.005 | 0.00095 | 95 | <0.003 | >0.00098* | >99.5-100 |
| 0.2 | 0.006 | 0.00194 | 97 | 0.003 | 0.00197 | 98.5 | <0.003 | >0.00196* | >99.2-100 | <0.003 | >0.00198 | >99.2-100 |
| 0.5 | 0.005 | 0.00495 | 99 | <0.003 | >0.00498* | >99.7-100 | 0.006 | 0.00494 | 98.8 | 0.010 | 0.0049 | 98 |
| 5 | 0.011 | 0.04980 | 99.78 | 0.004 | 0.04996 | 99.92 | <0.003 | >0.04998* | >99.97 | <0.003 | >0.04998* | >99.97 |
| 50 | 0.126 | 0.4987 | 99.75 | 0.076 | 0.49924 | 99.85 | 0.051 | 0.49948 | 99.898 | 0.038 | 0.49952 | 99.92 |
| 100 | 10.801 | 0.8920 | 89.190 | 6.030 | 0.93964 | 93.964 | 4.024 | 0.95976 | 95.976 | 2.647 | 0.9735 | 97.353 |
| 250 | 14.618 | 2.3538 | 94.153 | 12.481 | 2.375 | 95.00 | 9.223 | 2.408 | 96.31 | 5.679 | 2.443 | 97.73 |
| 500 | 85.300 | 4.1469 | 82.938 | 65.550 | 4.345 | 86.89 | 49.14 | 4.509 | 90.172 | 22.661 | 4.773 | 95.4678 |

* Calculated on average of effluent basis

TABLE 15. CONTACT PROCESS CADMIUM
Time: 4 hrs.   Coal 1%.
Size: 0.2965 mm (Medium)

| Solution conc. mg/l | Effluent conc. mg/l | mg Cd removed per gm coal | % Removal |
|---|---|---|---|
| 0.1 | 0.007 | 0.0093 | 93 |
| 0.5 | 0.014 | 0.0486 | 97.2 |
| 5 | 0.085 | 0.4915 | 98.3 |
| 50 | 9.645 | 4.0355 | 80.71 |
| 100 | 33.395 | 6.6605 | 65.805 |
| 250 | 155.948 | 9.4052 | 37.621 |
| 500 | 356.169 | 14.283 | 28.77 |

TABLE 16.  CONTACT PROCESS CADMIUM
EFFECT OF PARTICLE SIZE
Time: 4 hrs.  Coal 5%
Conc. of Cd = 500 ppm

| Particle Size | Solution conc. mg/l | Effluent conc. mg/l | mg Cd removed per gm coal | % Removal |
|---|---|---|---|---|
| 0.03414 | 500 | 88.972 | 8.221 | 82.21 |
| 0.117 | 500 | 124.093 | 7.518 | 75.18 |
| 0.2965 | 500 | 173.479 | 6.5304 | 65.30 |
| 0.533 | 500 | 231.205 | 5.376 | 53.76 |

TABLE 17. CONTACT PROCESS CHROMIUM.  TIME 8 HRS.  COAL: 1% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | <0.025 | >0.0075 | >75 | <0.019 | >0.0081 | >81 | <0.019 | >0.0081 | >81 | <0.017 | >0.0083 | >83 |
| 0.5 | <0.05 | >0.045 | >90 | <0.05 | >0.045 | >90 | <0.05 | >0.045 | >90 | <0.05 | >0.045 | >90 |
| 5 | 0.8 | 0.42 | 84 | 0.4 | 0.46 | 92 | 0.6 | 0.44 | 88 | 0.4 | 0.46 | 92 |
| 50 | 16.3 | 3.37 | 67.4 | 11.8 | 3.82 | 76.4 | 8.05 | 4.195 | 83.9 | 9.1 | 4.09 | 81.8 |
| 100 | 80 | 2.0 | 20 | 75 | 2.5 | 25 | 70 | 3.0 | 30 | 73 | 2.7 | 27 |
| 250 | 214 | 3.6 | 14.4 | 212 | 3.8 | 15.2 | 206 | 4.4 | 17.6 | 214 | 3.6 | 14.4 |
| 500 | 493 | 0.7 | 1.4 | 480 | 2.0 | 4 | 468 | 3.2 | 6.4 | 465 | 3.5 | 7 |

Blank:

TABLE 18. CONTACT PROCESS CHROMIUM.   TIME: 8 HRS.   COAL: 5% w/w

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | <0.025 | >0.0015 | >75 | <0.021 | >0.0016 | >79 | <0.005 | >0.0019 | >95 | <0.015 | >0.0017 | >85 |
| 0.5 | <0.024 | >0.0095 | >95.2 | <0.05 | >0.009 | >90 | <0.05 | >0.009 | >90 | <0.005 | >0.0099 | >99 |
| 5 | 0.4 | 0.092 | 92.0 | 0.3 | 0.094 | 94 | 0.2 | 0.096 | 96 | 0.17 | 0.0966 | 96.6 |
| 50 | 8.5 | 0.83 | 83.0 | 6.8 | 0.864 | 86.4 | 3.8 | 0.924 | 92.4 | 3.6 | 0.928 | 92.8 |
| 100 | 11.3 | 1.774 | 88.7 | 10 | 1.8 | 90 | 10 | 1.8 | 90 | 9.5 | 1.81 | 90.5 |
| 250 | 132 | 2.36 | 47.2 | 125 | 2.5 | 50 | 135 | 2.3 | 46 | 133 | 2.34 | 46.8 |
| 500 | 475 | 0.5 | 5 | 462 | 0.76 | 7.6 | 450 | 1.0 | 10 | 445 | 1.1 | 11 |

TABLE 19. CONTACT PROCESS CHROMIUM.   TIME 8 HRS.   COAL 10% w/w.

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal siz 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg Removed per gm Coal | % Removal | Effluent conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | <0.011 | >0.0008 | >89 | <0.05 | >0.0005 | >50 | <0.01 | >0.0009 | >90 | <0.028 | >0.0007 | >72 |
| 0.5 | <0.05 | >0.0045 | >90 | <0.033 | >0.0046 | >93.4 | <0.045 | >0.0045 | >91 | <0.05 | >0.0045 | >90 |
| 5 | 0.3 | 0.047 | 94.0 | 0.5 | 0.045 | 90 | 0.2 | 0.048 | 96 | 0.09 | 0.0491 | 98.2 |
| 50 | 4.5 | 0.455 | 91.0 | 5.2 | 0.448 | 89.6 | 3.2 | 0.468 | 93.6 | 2.9 | 0.471 | 94.2 |
| 100 | 9.1 | 0.909 | 90.9 | 10.8 | 0.896 | 89.6 | 12.6 | 0.874 | 87.4 | 6.2 | 0.938 | 93.8 |
| 250 | 68 | 1.82 | 72.8 | 84 | 1.66 | 66.4 | 95 | 1.55 | 62 | 61 | 1.89 | 75.6 |
| 500 | 365 | 1.35 | 27 | 330 | 1.7 | 34 | 405 | 0.95 | 19 | 400 | 1.0 | 20 |

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TABLE 20. CONTACT PROCESS CHROMIUM

Contact time: 4 hrs
Coal size : 0.2965 mm

| | Coal 1% w/w | | | | Coal 5% w/w | | | |
|---|---|---|---|---|---|---|---|---|
| Influent Solution Conc. mg/l | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | | Influent Solution Conc. mg/l | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | 0.04 | 0.005 | 60 | | 0.1 | <0.05 | >0.001 | >50 |
| 0.5 | 0.07 | 0.043 | 86 | | 0.5 | <0.05 | >0.009 | >90 |
| 5 | 0.7 | 0.43 | 86 | | 5 | 1.0 | 0.08 | 80 |
| 50 | 17.5 | 3.25 | 65 | | 50 | 7.1 | 0.858 | 85.8 |
| 100 | 64.6 | 3.54 | 35.4 | | 100 | 13.5 | 1.73 | 86.5 |
| 250 | 220 | 3.00 | 12 | | 250 | 130 | 2.4 | 48 |
| 500 | 470 | 3.00 | 6 | | 500 | 445 | 1.1 | 11.0 |

Blank < 0.05

C-2-2         REGRESSION ANALYSIS OF ADSORPTION ISOTHERM DATA

(1)   LEAD ADSORPTION

| DESCRIPTION OF THE ISOTHERM | | | LINEAR REGRESSION ANALYSES | | |
|---|---|---|---|---|---|
| % Coal | Particle Size mm (Contact time) | (x/m) Ci | k | n | $r^2$ |
| 1% | 0.533 (8 hrs) | 36.071 | 1.5587 | 1.9782 | 0.94493 |
| 1% | 0.2965 (4 hrs) | 40.0 | 6.93179 | 3.5405 | 0.97263 |
| 1% | 0.03414 (8 hrs) | 110.0 | 7.3757 | 2.365 | 0.98764 |

$$\frac{x}{m} = K\,C_e^{\frac{1}{n}}$$

(2)   CADMIUM ADSORPTION

| DESCRIPTION OF THE ISOTHERM | | | LINEAR REGRESSION ANALYSES | | |
|---|---|---|---|---|---|
| % Coal | Particle Size mm (Contact time) | (x/m) $C_i$ | k | n | $r^2$ |
| 1% | 0.533 (8 hrs) | 20.51262 | 0.59105 | 1.75212 | 0.8113 |
| 1% | 0.2965 (8 hrs) | 30.749 | 0.96444 | 1.79595 | 0.81083 |
| 1% | 0.117 (8 hrs) | 23.656 | 0.90342 | 1.90329 | 0.85189 |
| 1% | 0.03414 (8 hrs) | 18.744 | 3.2777 | 3.56397 | 0.79474 |
| 5% | 0.533 (8 hrs) | 18.89 | 0.36551 | 1.57520 | 0.89090 |
| 5% | 0.2965 (8 hrs) | 21.22 | 0.614036 | 1.75403 | 0.87872 |
| 5% | 0.117 (8 hrs) | 29.95 | 0.37969 | 1.42276 | 0.98669 |
| 5% | 0.03414 (8 hrs) | 16.92 | 1.4356 | 2.51907 | 0.93665 |
| 10% | 0.533 (8 hrs) | 14.55 | 0.401846 | 1.73146 | 0.86261 |
| 10% | 0.2965 (8 hrs) | 9.34 | 0.74568 | 2.45856 | 0.93274 |
| 10% | 0.117 (8 hrs) | 11.42 | 0.84994 | 2.39212 | 0.92601 |
| 10% | 0.03414 (8 hrs) | 17.15 | 1.04146 | 2.21855 | 0.91953 |
| 1% | 0.2965 (4 hrs) | 27.67 | 0.62748 | 1.64136 | 0.92654 |

(3) COPPER ADSORPTION

| DESCRIPTION OF THE ISOTHERM | | | LINEAR REGRESSION ANALYSES | | |
|---|---|---|---|---|---|
| % Coal | Particle Size mm (Contact time) | (x/m) Ci | k | n | $r^2$ |
| 1% | 0.533 (8 hrs) | 25.78 | 0.55460 | 1.61871 | 0.95036 |
| 1% | 0.2965 (8 hrs) | 31.91 | 0.694715 | 1.62379 | 0.94888 |
| 1% | 0.117 (8 hrs) | 41.534 | 1.10285 | 1.71267 | 0.96761 |
| 1% | 0.03414 (8 hrs) | 69.77 | 0.66324 | 1.33478 | 0.89472 |
| 5% | 0.533 (8 hrs) | 25.2 | 0.21845 | 1.30870 | 0.98186 |
| 5% | 0.2965 (8 hrs) | 49.2 | 0.26656 | 1.19054 | 0.98243 |
| 5% | 0.117 (8 hrs) | 72.05 | 0.34290 | 1.16212 | 0.94609 |
| 5% | 0.03414 (8 hrs) | 75.87 | 0.51385 | 1.24421 | 0.98967 |
| 10% | 0.533 (8 hrs) | 13.91 | 0.08470 | 1.21831 | ≈ 1.00 |
| 10% | 0.2965 (8 hrs) | 58.8 | 0.19509 | 1.08860 | 0.99709 |
| 10% | 0.117 (8 hrs) | 54.25 | 0.311675 | 1.20453 | 0.91311 |
| 10% | 0.03414 (8 hrs) | 108.83 | 0.419063 | 1.11782 | 0.98867 |

## (4)  ZINC ADSORPTION

| DESCRIPTION OF THE ISOTHERM | | | LINEAR REGRESSION ANALYSES | | |
|---|---|---|---|---|---|
| % Coal | Particle Size mm (Contact time) | (x/m) Ci | k | n | $r^2$ |
| 1% | 0.533 (8 hrs) | 22.01 | 0.65223 | 1.76598 | 0.96179 |
| 1% | 0.2965 (8 hrs) | 25.56 | 0.77173 | 1.77555 | 0.95237 |
| 1% | 0.117 (8 hrs) | 30.44 | 0.86905 | 1.74754 | 0.95154 |
| 1% | 0.03414 (8 hrs) | 36.14 | 0.65825 | 1.55154 | 0.88909 |
| 5% | 0.533 (8 hrs) | 19.33 | 0.24748 | 1.42607 | 0.96825 |
| 5% | 0.2965 (8 hrs) | 22.1 | 0.28698 | 1.43012 | 0.96955 |
| 5% | 0.117 (8 hrs) | 31.8 | 0.35961 | 1.38631 | 0.96302 |
| 5% | 0.03414 (8 hrs) | 31.69 | 0.37888 | 1.40395 | 0.93452 |
| 10% | 0.533 (8 hrs) | 16.83 | 0.17202 | 1.35587 | 0.96286 |
| 10% | 0.2965 (8 hrs) | 26.27 | 0.13423 | 1.1778 | 0.88812 |
| 10% | 0.117 (8 hrs) | 30.82 | 0.24067 | 1.28071 | 0.93774 |
| 10% | 0.03414 (8 hrs) | 40.76 | 0.29564 | 1.26147 | 0.95417 |
| 1% | 0.2965 (4 hrs) | 21.07 | 0.60051 | 1.74666 | 0.89521 |

(5)  CHROMIUM ADSORPTION

| % Coal | Particle Size mm (Contact time) | (x/m) Ci | k | n | r² |
|---|---|---|---|---|---|
| 1% | 0.533 (8 hrs) | 4.13 | 0.18031 | 1.98438 | 0.74904 |
| 1% | 0.2965 (8 hrs) | 6.69 | 0.23962 | 1.86705 | 0.81934 |
| 1% | 0.117 (8 hrs) | 9.28 | 0.25614 | 1.7311 | 0.85201 |
| 1% | 0.03414 (8 hrs) | 8.45 | 0.26405 | 1.79329 | 0.84776 |
| 5% | 0.533 (8 hrs) | 3.92 | 0.08182 | 1.60609 | 0.76578 |
| 5% | 0.2965 (8 hrs) | 5.29 | 0.08638 | 1.51048 | 0.79665 |
| 5% | 0.117 (8 hrs) | 5.44 | 0.11900 | 1.62508 | 0.83628 |
| 5% | 0.03414 (8 hrs) | 6.08 | 0.11001 | 1.54897 | 0.80208 |
| 10% | 0.533 (8 hrs) | 7.14 | 0.06176 | 1.30813 | 0.90841 |
| 10% | 0.2965 (8 hrs) | 8.53 | 0.04280 | 1.17363 | 0.89515 |
| 10% | 0.117 (8 hrs) | 4.70 | 0.06264 | 1.43892 | 0.87755 |
| 10% | 0.03414 (8 hrs) | 6.36 | 0.06827 | 1.37048 | 0.78332 |
| 1% | 0.2965 (4 hrs) | 8.34 | 0.170825 | 1.5985 | 0.84300 |
| 1% | 0.296 (4 hrs) | 6.47 | 0.05713 | 1.31396 | 0.81913 |

DESCRIPTION OF THE ISOTHERM — LINEAR REGRESSION ANALYSES

## (6)   MERCURY ADSORPTION

| % Coal | Particle Size mm (Contact time) | (x/m) Ci | k | n | $r^2$ |
|---|---|---|---|---|---|
| 1% | 0.533 (8 hrs) | 258.72 | 1.49243 | 1.20547 | 0.77304 |
| 1% | 0.2965 (8 hrs) | 1007.19 | 1.17190 | 0.91609 | 0.95645 |
| 1% | 0.117 (8 hrs) | 2116.51 | 1.60065 | 0.86469 | 0.94287 |
| 1% | 0.03414 (8 hrs) | 6123.00 | 2.9508 | 0.81367 | 0.980608 |
| 5% | 0.533 (8 hrs) | 3061.60 | 1.50744 | 0.81596 | 0.84065 |
| 5% | 0.2965 (8 hrs) | 1037.95 | 1.931190 | 0.72352 | 0.87219 |
| 5% | 0.117 (8 hrs) | 1160.47 | 0.72156 | 0.84175 | 0.56056 |
| 5% | 0.03414 (8 hrs) | 1361.06 | 1.93099 | 0.94764 | 0.94849 |
| 10% | 0.533 (8 hrs) | 1120.11 | 1.11197 | 0.89871 | 0.81218 |
| 10% | 0.2965 (8 hrs) | 2951.26 | 1.45626 | 0.81620 | 0.98332 |
| 10% | 0.117 (8 hrs) | 2047.03 | 1.31187 | 0.84521 | 0.87939 |
| 10% | 0.03414 (8 hrs) | 3618.69 | 2.26493 | 0.84251 | 0.960397 |
| 1% | 0.2965 (4 hrs) | 1373.41 | 2.43744 | 0.98113 | 0.767318 |
| 5% | 0.2965 (4 hrs) | 1299.76 | 3.47967 | 0.59028 | 0.95303 |

Appendix C-2-3.    Comparison of adsorption of metal ions by coal and activated carbon.

Initial Conc. $C_i$ = 50 p.p.m. Pb++                          Particle size of materials = 48/100 Mesh Tyler.

Contact time = 8 hours

Solution = 100 c.c.

| Coal/Carbon Dosage % | Oxidized Surface Coal | | | Unoxidized Core Coal | | | Calgon Activated Carbon | | |
|---|---|---|---|---|---|---|---|---|---|
| | Ce mg/l | x/m mg/gm coal | % efficiency $\dfrac{C_i-C_o}{C_i}$ x 100 | Ce mg/l | x/m mg/gm coal | % efficiency $\dfrac{C_i-C_o}{C_i}$ x 100 | Ce mg/l | x/m mg/gm coal | % efficiency $\dfrac{C_i-C_o}{C_i}$ x 100 |
| 0 | 50 | 217* | ----- | 50 | 125* | ----- | 50 | 19.3* | ----- |
| 0.025 | 26 | 96 | 48.0 | 35 | 60 | 30 | 46 | 16 | 8 |
| 0.05 | 15 | 70 | 70.0 | 14 | 72 | 72 | 42 | 16 | 16 |
| 0.1 | 3 | 47 | 94.0 | 6 | 44 | 88 | 36 | 14 | 28 |
| 0.2 | 2.330 | 24.79 | 99.1 | 0.286 | 24.86 | 99.4 | 18 | 16 | 64 |
| 0.5 | 0.285 | 9.94 | 99.4 | 0.286 | 9.940 | 99.4 | 2 | 9.6 | 96 |
| 1 | 0.286 | 4.97 | 99.4 | 0.143 | 4.990 | 99.7 | 0.286 | 4.97 | 99.4 |
| 2 | 0.143 | 2.49 | 99.7 | 0.143 | 2.490 | 99.7 | 0.286 | 2.49 | 99.4 |
| 5 | 0.143 | 0.997 | 99.7 | 0.143 | 0.997 | 99.7 | 0.143 | 0.997 | 99.7 |

* Obtained by extrapolation of the isotherm line to the initial concentration 50 p.p.m. and this value represents the maximum adsorptive capacity.

Appendix C-2-4.    FACTORS INFLUENCING THE ADSORPTION PROCESS.

C-2-4-1 Table 1.  Effect of contact time

        Type of Coal: Oxidized Hat Creek coal

        Initial Conc.  = 50 mg/1 Pb

        Particle size of coal = 0.533 mn av.

        Coal weight = 1% W/W

| Contact Time (hours) | Equilibrium Concentration (mg/1) |
|:---:|:---:|
| 0 | 50.00 |
| 1 | 9.00 |
| 2 | 4.85 |
| 3 | 2.63 |
| 4 | 0.4 |
| 8 | 0.03 |
| 16 | 0.03 |
| 24 | 0.03 |

## C.2.4.1 TABLE 2

### EFFECT OF TIME ON THE EFFICIENCY OF REMOVAL OF LEAD IN CONTACT WITH COAL.
Coal % w/w: 1%.   Mean particle size: 0.2965
Solution concentration 0.1 mg/l.

| Contact time hrs. | Solution conc. mg/l | Effluent conc. mg/l | mg Pb removed per gm coal | % Removal |
|---|---|---|---|---|
| 1 | 0.1 | 0.7 | 0.003 | 30 |
| 2 | 0.1 | 0.07 | 0.003 | 30 |
| 3 | 0.1 | < 0.06 | > 0.007* | 70-100 |
| 4 | 0.1 | < 0.06 | > 0.007* | 70-100 |
| 8 | 0.1 | < 0.06 | > 0.007* | 70-100 |

Blank:   < 0.06

* Calculated on the basis $\frac{0.06}{2}$ = 0.03 as an average value

300.

## C.2.4.1  TABLE 3

### EFFECT OF CONTACT TIME ON ADSORPTION OF LEAD BY CONTACT PROCESS.  Solution conc. 500 ppm.  Coal 5% w/w

| Contact time hrs. | 4 HOURS | | | 8 HOURS | | |
|---|---|---|---|---|---|---|
| Mean Particle Size mm | Effluent conc. mg/l | mg Pb removed per gm coal | % Removal | Effluent conc. mg/l | mg Pb removed per gm coal | % Removal |
| 0.03414 | 1.5 | 9.97 | 99.7 | 1.0 | 9.98 | 99.8 |
| 0.117 | 2.1 | 9.96 | 99.6 | 3.3 | 9.93 | 99.3 |
| 0.2965 | 10 | 9.8 | 98.0 | 8.2 | 9.84 | 98.4 |
| 0.533 | 26 | 9.48 | 94.8 | 16 | 9.68 | 96.8 |

C.2.4.1 TABLE 4. CONTACT PROCESS LEAD. TIME: 24 hrs, MEAN PARTICLE SIZE 0.533 mm*

| Solution Concentration mg/l | Coal 1% w/w | | | Coal 5% w/w | | | Coal 10% w/w | | |
|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Pb Removed per gm Coal | % Detectable Removed | Effluent Conc. mg/l | mg Pb Removed per gm Coal | % Dectectable Removed | Effluent Conc. mg/l | mg Pb Removed per gm Coal | % Dectectable Removed |
| 0.05 | <0.03 | >0.0035 | >70-100 | <0.03 | >0.007 | >70-100 | <0.03 | >0.00035 | >70-100 |
| 0.1 | <0.03 | >0.0085 | >85-100 | <0.03 | >0.0017 | >85-100 | <0.03 | >0.00085 | >85-100 |
| 0.2 | <0.03 | >0.0185 | >92.5-100 | <0.03 | >0.0037 | >92.5-100 | <0.03 | >0.00185 | >92.5-100 |

Blank: < 0.03

\* The above figures are calculated on the basis that since a blank is 0.03 then

the effluent concentration will be $\frac{0.03}{2}$ = 0.015 mg/l as an average value

APPENDIX C-2-4-2    EFFECT OF COAL DOSAGE

TABLE 1    CONTACT PROCESS MERCURY

COAL SIZE: 0.2965 mm av.    TIME: 8 HRS.

| Influent Conc. mg/l | Coal 1% w/w | | | Coal 5% w/w | | | Coal 10% w/w | | |
|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Hg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Hg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Hg Removed per gm Coal | % Removal |
| 0.1 | 0.013 | 0.0087 | 87 | 0.0095 | 0.00181 | 90.5 | <0.002 | >0.00098 | >98 |
| 0.5 | 0.0228 | 0.0477 | 95.4 | 0.01431 | 0.00971 | 97.14 | 0.01714 | 0.00482 | 96.57 |
| 5 | 0.157 | 0.484 | 96.86 | 0.0434 | 0.09913 | 99.13 | 0.0435 | 0.04946 | 99.13 |
| 50 | 3.36 | 4.664 | 93.28 | 1.224 | 0.9755 | 97.55 | 0.56 | 0.4944 | 98.88 |
| 100 | 1.33 | 9.867 | 98.67 | 0.391 | 1.9922 | 99.61 | 0.765 | 0.9924 | 99.24 |
| 250 | 10.17 | 23.98 | 95.93 | 0.8 | 4.984 | 99.68 | 1.265 | 2.4874 | 99.49 |
| 500 | 21.33 | 47.87 | 95.73 | 2.933 | 9.9413 | 99.41 | 2.44 | 4.9756 | 99.51 |

C-2-4-2  TABLE 2. CONTACT PROCESS CADMIUM.  TIME 8 hrs. MEAN PARTICLE SIZE: 0.2965 mm

| Solution Concentration mg/l | Coal 1% w/w | | | Coal 5% w/w | | | Coal 10% w/w | | |
|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal | % Removal |
| 0.1 | 0.007 | 0.0093 | 93 | <0.003 | >0.00197* | >98.5-100 | <0.003 | >0.00098* | >98.5-100 |
| 0.2 | 0.010 | 0.019 | 95 | 0.004 | 0.00392 | 98 | 0.003 | 0.00197 | 98.5 |
| 0.5 | 0.010 | 0.049 | .98 | 0.003 | 0.00994 | 99.4 | <0.003 | >0.00493* | >99.7-100 |
| 5 | 0.018 | 0.4982 | 99.64 | 0.007 | 0.09986 | 99.86 | 0.004 | 0.04996 | 99.92 |
| 50 | 0.83 | 4.917 | 98.34 | 0.118 | 0.99764 | 99.76 | 0.076 | 0.49924 | 99.85 |
| 100 | 54.533 | 4.5467 | 45.467 | 14.507 | 1.70986 | 85.49 | 6.036 | 0.93964 | 93.964 |
| 250 | 123.957 | 12.6043 | 50.42 | 30.95 | 4.381 | 87.62 | 12.481 | 2.375 | 95.00 |
| 500 | 400.969 | 9.903 | 19.8 | 110.915 | 7.782 | 77.82 | 65.550 | 4.345 | 86.89 |

*  Calculated on average of effluent basis

C-2-4-2 TABLE 3. CONTACT PROCESS COPPER. TIME: 8 HRS. MEAN PARTICLE SIZE 0.2965 mm

| Solution Concentration mg/l | Coal 1% w/w | | | Coal 5% w/w | | | Coal 10% w/w | | |
|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg cu Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg cu Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg cu Removed per gm Coal | % Removel |
| 0.5 | 0.032 | .0468 | 93.6 | 0.030 | 0.0094 | 94 | 0.021 | 0.0048 | 95.8 |
| 5.0 | 0.334 | 0.4666 | 93.3 | 0.184 | 0.0963 | 96.3 | 0.172 | 0.0483 | 96.5 |
| 50 | 5.949 | 4.4051 | 88.1 | 4.513 | 0.9097 | 90.97 | 2.816 | 0.4718 | 94.4 |
| 100 | 28.345 | 7.1655 | 71.7 | 8.019 | 1.84 | 91.98 | 5.221 | 0.948 | 94.8 |
| 250 | 141.83 | 10.817 | 43.3 | 21.85 | 4.563 | 91.26 | 14.18 | 2.358 | 94.3 |
| 500 | 335.41 | 16.46 | 32.9 | 93.915 | 8.1217 | 81.22 | 35.65 | 4.643 | 92.9 |

C-2-4-2 TABLE 4. CONTACT   PROCESS ZINC.   TIME 8 HRS. MEAN PARTICLE SIZE .2965 mm

| Solution Concentration mg/l | Coal 1% w/w | | | Coal 5% w/w | | | Coal 10% w/w | | |
|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Zn Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Zn Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Zn Removed per gm Coal | % Removal |
| .5 | 0.025 | 0.0475 | 95.0 | 0.018 | 0.00964 | 96.4 | 0.087 | 0.00413 | 82.6 |
| 5.0 | 0.119 | 0.4881 | 7.62 | 0.119 | 0.4881 | 97.62 | 0.115 | 0.04885 | 97.7 |
| 50 | 10.306 | 3.9694 | 79.39 | 2.725 | 0.9455 | 94.55 | 1.461 | 0.4854 | 97.08 |
| 125 | 54.727 | 7.0273 | 6.22 | 13.615 | 2.2277 | 89.11 | 9.522 | 1.1543 | 92.38 |
| 250 | 146.385 | 10.3615 | 41.44 | 53.838 | 3.923 | 78.46 | 34.705 | 2.152 | 86.12 |
| 500 | 319.84 | 18.0158 | 36.03 | 157.947 | 6.8410 | 68.41 | 88.450 | 4.1155 | 82.31 |

C-2-4-2 TABLE 5. CONTACT PROCESS CHROMIUM

MEAN PARTICLE SIZE: 0.2965 mm. TIME: 8 HRS.
EFFECT OF PERCENTAGE COAL

| Influent Solution Conc. mg/l | Coal 1% w/w | | | Coal 5% w/w | | | Coal 10% w/w | | |
|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | <0.019 | >0.0081 | >81 | <0.021 | >0.0016 | >79 | <0.05 | >0.0005 | >50 |
| 0.5 | <0.05 | >0.045 | >90 | <0.05 | >0.009 | >90 | <0.033 | >0.0046 | >93.4 |
| 5 | 0.4 | 0.46 | 92 | 0.3 | 0.094 | 94.0 | 0.5 | 0.45 | 90 |
| 50 | 11.8 | 3.82 | 76.4 | 6.8 | 0.864 | 86.4 | 5.2 | 0.448 | 89.6 |
| 100 | 75 | 2.5 | 25 | 10 | 1.8 | 90 | 10.8 | 0.896 | 89.6 |
| 250 | 212 | 3.8 | 15.2 | 125 | 2.5 | 50 | 84 | 1.66 | 66.4 |
| 500 | 480 | 2.0 | 4.0 | 462 | 0.76 | 7.6 | 330 | 1.7 | 34 |

APPENDIX C-2-4-3 EFFECT OF SOLUTION CONCENTRATION

C-2-4-3
TABLE 1. CONTACT PROCESS ZINC
EFFECT OF CONCENTRATION AT 4 HRS. CONTACT
MEAN COAL SIZE 0.2965 mm.    COAL 1% w/w

| Solution conc. mg/l | Effluent conc. mg/l | mg Zn removed per gm Coal | % Removal |
|---|---|---|---|
| 0.5 | 0.069 | 0.0431 | 86.2 |
| 5 | 0.130 | 0.487 | 97.4 |
| 50 | 12.117 | 3.7883 | 75.77 |
| 100 | 37.736 | 6.2264 | 62.26 |
| 250 | 159.329 | 9.0671 | 36.27 |
| 500 | 373.166 | 12.6834 | 25.37 |

C-2-4-3
TABLE 2. CONTACT PROCESS COPPER
EFFECT OF CONCENTRATION AT 4 HRS. CONTACT
MEAN COAL SIZE 0.2965 mm
COAL 1% w/w

| Solution conc. mg/l | Effluent conc. mg/l | mg. Cu removed per gm coal | % Removal |
|---|---|---|---|
| 0.5 | 0.017 | 0.0483 | 96.6 |
| 5.0 | 0.775 | 0.4225 | 84.5 |
| 50 | 7.218 | 4.2782 | 85.56 |
| 100 | 30.634 | 6.9336 | 69.37 |
| 250 | 147.887 | 10.2113 | 40.85 |
| 500 | 359.155 | 14.0845 | 28.17 |

C-2-4-4          TABLE 1. CONTACT PROCESS MERCURY
                    EFFECT OF TIME OF CONTACT
              MEAN COAL SIZE 0.2965 mm.   COAL 5% w/w

| Particle Size mm | Influent Conc, mg/l | Effluent Conc. mg/l | mg Hg Removed per gm Coal | % Removal |
|---|---|---|---|---|
| 0.03414 | 50 | 0.36 | 0.9928 | 99.28 |
| 0.117 | 50 | 0.63 | 0.9874 | 98.74 |
| 0.2965 | 50 | 0.77 | 0.9846 | 98.46 |
| 0.533 | 50 | 0.9 | 0.982 | 98.2 |

C-2-4-4                    TABLE 2. CONTACT PROCESS CHROMIUM
                                TIME 4 HRS 5% w/w   COAL

| Particle Size mm | Influent Solution Conc. mg/l | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
|---|---|---|---|---|
| 0.03414 | 50 | 4.3 | 0.914 | 91.4 |
| 0.117 | 50 | 5.6 | 0.888 | 88.8 |
| 0.2965 | 50 | 7.1 | 0.858 | 85.8 |
| 0.533 | 50 | 7.6 | 0.848 | 84.8 |

C-2-4-4        TABLE 3.  CONTACT PROCESS ZINC
         COAL PARTICLE SIZE EFFECT AT 4 HRS. CONTACT
                   WITH 5% COAL w/w

| Solution conc. mg/l | Particle size   mm | Effluent conc. mg/l | mg Zn removed per gm Coal | % Removal |
|---|---|---|---|---|
| 100 | 0.533 (> ¼ in) | 16.897 | 1.662 | 83.1 |
| 100 | 0.2965(> 60  ) | 11.8 | 1.764 | 88.2 |
| 100 | 0.117 (> 150 ) | 9.644 | 1.807 | 90.4 |
| 100 | 0.03414 (< 150) | 7.044 | 1.859 | 93.0 |

C-2-4-4        TABLE 4.  CONTACT PROCESS COPPER
         COAL PARTICLE SIZE EFFECT AT 4 HRS CONTACT
                   WITH 5% COAL w/w

| Solution Conc. mg/l | Particle size | Effluent conc. mg/l | mg. Cu removed per gm coal | % Removal |
|---|---|---|---|---|
| 500 | 1/4" mesh (0.533 mm) | 207.746 | 5.845 | 58.45 |
| 500 | > 60 mesh (0.2965 mm) | 142.606 | 7.1478 | 71.48 |
| 500 | > 150 mesh (0.117 mm) | 70.423 | 8.5915 | 85.92 |
| 500 | < 150 mesh (0.03414 mm) | 63.204 | 8.7359 | 87.36 |

Appendix C-2-5.    Analysis of Variance for data from
the batch tests with heavy metal.

| Square of Variation | Degree of Freedom | Sum Square | Mean Square | F-Value |
|---|---|---|---|---|
| Coal Dosage (C) | 2 | 2104.9 | 1052.5 | 341.14** |
| Particle size (P) | 3 | 16.727 | 5.5757 | 1.8072(N.S.) |
| Solution Conc (N) | 8 | 7914.7 | 989.34 | 320.67** |
| Type of Metal Ion (E) | 5 | 531.26 | 106.25 | 34.439** |
| C x P | 6 | 28.544 | 4.7573 | 1.5420(N.S.) |
| C x N | 16 | 3601.6 | 225.10 | 72.961** |
| P x N | 24 | 70.369 | 2.9320 | 0.95034(N.S.) |
| C x E | 10 | 538.46 | 53.846 | 17.453** |
| P x E | 15 | 57.696 | 3.8464 | 1.2467(N.S.) |
| N x E | 40 | 1744.0 | 43.599 | 14.132** |
| C x P x N | 48 | 117.71 | 2.4522 | 0.79482(N.S.) |
| C x P x E | 30 | 103.46 | 3.4485 | 1.1178(N.S.) |
| C x N x E | 80 | 1474.2 | 18.428 | 5.9729** |
| P x N x E | 120 | 385.05 | 3.2087 | 1.0400(N.S.) |
| Error | 240 | 740.46 | 3.0852 | |
| Total | 647 | 19429.0 | | |

**    highly significant at the 1% level.

N.S.    Non significant

APPENDIX C-2-6 . DATA OF COLUMN ADSORPTION TESTS.

C-2-6  TABLE 1 .  COLUMN ADSORPTION PROCESS - LEAD
Volume of Solution = 500 ml. Rate of Flow - 0.3 gpm/ft$^2$
Depth of Column = $\frac{9''(20cm.)}{600 \text{ gms coal}}$ , contact time = 30 min.

| Solution Concentration mg/l | Mean Particle Size 0.5-3 mm | | | Mean Particle Size 0.2965 mm | | | Mean Particle Size 0.117 mm | | | Mean Particle Size 0.3414 mm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Pb Removed per gm coal X 10$^{-4}$ | % Removal | Effluent Conc. mg/l | mg Pb Removed per gm coal X 10$^{-4}$ | % Removal | Effluent Conc. mg/l | mg Pb Removed per gm coal X 10$^{-4}$ | % Removal | Effluent Conc. mg/l | mg Pb Removed per gm coal X 10$^{-4}$ | % Removal |
| 0.1 | <0.018 | >0.76* | >91-100 | <0.018 | >0.76* | >91-100 | <0.01 | >0.79* | >95-100 | <0.01 | >0.79* | >95-100 |
| 0.2 | <0.018 | >1.59* | >95.5-100 | <0.018 | >1.59* | >95.5-100 | <0.031 | >1.53* | >92-100 | <0.03 | >1.54* | >92.5-100 |
| 0.5 | <0.02 | >4.08* | >98-100 | <0.02 | >4.08* | >98-100 | <0.01 | >4.12* | >99-100 | <0.02 | >4.08* | >98-100 |
| 5 | 0.028 | 41.43 | 99.44 | <0.02 | >41.6* | >99.8-100 | <0.02 | >41.6* | >99.8-100 | 0.034 | 41.38 | 99.32 |
| 50 | 0.08 | 416.0 | 99.8 | <0.02 | >416.6* | >99.98 | 0.037 | 416.36 | 99.93 | <0.02 | >416.6* | >99.98 |
| 500 | 0.17 | 4160.0 | 99.97 | <0.02 | >4166.6* | >99.998 | <0.01 | >4166.6* | >99.999 | 0.035 | 4166.4 | 99.99 |

* Calculated on average of effluent basis.

C-2-6

TABLE 2  COLUMN ADSORPTION PROCESS MERCURY
VOLUME OF SOLUTION = 500 ml.  RATE OF FLOW = 0.3 gpm/ft$^2$
DEPTH OF COLUMN = 9"   600 gms OF COAL
CONTACT TIME = 30 min.

| Solution Concentration ppm (mg/1) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | 0.003 | $0.8 \times 10^{-4}$ | 97.0 | 0 | $0.8 \times 10^{-4}$ | 100 | 0 | $0.8 \times 10^{-4}$ | 100 | 0 | $0.8 \times 10^{-4}$ | 100 |
| 0.5 | 0.0062 | $4.1 \times 10^{-4}$ | 98.76 | 0.0055 | $4.1 \times 10^{-4}$ | 98.9 | 0.0018 | $4.1 \times 10^{-4}$ | 99.64 | 0.00455 | $4.1 \times 10^{-4}$ | 99.09 |
| 5 | 0.0062 | $41.6 \times 10^{-4}$ | 99.88 | 0 | $41.6 \times 10^{-4}$ | 100 | 0.0023 | $41.6 \times 10^{-4}$ | 99.95 | 0.00295 | $41.6 \times 10^{-4}$ | 99.94 |
| 50 | 0.0048 | $416.6 \times 10^{-4}$ | 99.99 | 0.008 | $416.6 \times 10^{-4}$ | 99.98 | 0.0016 | $416.6 \times 10^{-4}$ | 99.996 | 0.00182 | $416.6 \times 10^{-4}$ | 99.996 |
| 100 | 0.0152 | $833.2 \times 10^{-4}$ | 99.98 | 0.0088 | $833.2 \times 10^{-4}$ | 99.991 | 0.014 | $833.2 \times 10^{-4}$ | 99.986 | 0.00273 | $833.2 \times 10^{-4}$ | 99.997 |
| 250 | 0.0038 | $2083.3 \times 10^{-4}$ | 99.998 | 0.011 | $2083.2 \times 10^{-4}$ | 99.995 | 0.00455 | $2083.2 \times 10^{-4}$ | 99.998 | 0.00455 | $2083.2 \times 10^{-4}$ | 99.998 |
| 500 | 0.032 | $4166.4 \times 10^{-4}$ | 99.993 | 0.0045 | $4166.6 \times 10^{-4}$ | 99.999 | 0.0023 | $4166.6 \times 10^{-4}$ | 99.999 | 0.0023 | $4166.6 \times 10^{-4}$ | 99.999 |

< Sensitivity 0.002 mg/1

313.

C-2-6    TABLE 3    COLUMN ADSORPTION PROCESS -- COPPER.

Volume of Solution = 500 ml.    Rate of Flow = 0.3 gpm.
Depth of Column = 9 ins.    Wt. of Coal = 600 gms.
contact time = 30 min.

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal |
| 0.5 | 0.053 | 3.725 | 89.4 | 0.048 | 3.766 | 90.4 | 0.039 | 3.841 | 92.2 | 0.143 | 2.975 | 71.4 |
| 5.0 | 0.053 | 41.225 | 98.94 | 0.056 | 41.20 | 98.88 | 0.025 | 41.46 | 99.5 | 0.075 | 410.41 | 98.5 |
| 50 | 0.070 | 416.083 | 99.86 | 0.087 | 415.94 | 99.83 | 0.104 | 415.8 | 99.79 | 0.382 | 413.48 | 99.24 |
| 100 | 0.141 | 832.15 | 99.86 | 0.156 | 832.033 | 99.84 | 0.052 | 832.9 | 99.95 | 0.069 | 832.76 | 99.93 |
| 250 | 0.141 | 2082.158 | 99.94 | 0.139 | 2082.18 | 99.94 | 0.052 | 2082.9 | 99.98 | 0.087 | 2082.61 | 99.97 |
| 500 | 1.426 | 4154.783 | 99.71 | 3.401 | 4138.32 | 99.34 | 1.701 | 4152.49 | 99.66 | 3.089 | 4140.92 | 99.38 |

TABLE 4.  COLUMN ADSORPTION PROCESS CADMIUM

| Mean Particle Size of Coal mm | 0.533 mm | | | 0.2965 mm | | | 0.117 mm | | | 0.03414 mm | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Solution Concentration mg/l | Effluent Conc. mg/l | mg Cd Removed per gm Coal $X~10^{-4}$ | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal $X~10^{-4}$ | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal $X~10^{-4}$ | % Removal | Effluent Conc. mg/l | mg Cd Removed per gm Coal $X~10^{-4}$ | % Removal |
| 0.1 | 0.007 | 0.775 | 93 | <0.003 | >0.821* | >98.5 | <0.002 | >0.825* | >98-100 | <0.002 | >0.825* | >99-100 |
| 0.2 | 0.007 | 1.6 | 96.5 | 0.003 | 1.641 | 98.5 | 0.009 | 1.59 | 95.5 | <0.002 | >1.66* | >99.5-100 |
| 0.5 | 0.007 | 4.11 | 98.6 | 0.004 | 4.133 | 99.2 | 0.006 | 4.12 | 98.8 | <0.002 | >4.16* | >99.8-100 |
| 5 | 0.008 | 41.6 | 99.84 | <0.03 | >41.54* | >99.7-100 | <0.002 | >41.66* | >99.98 | 0.005 | 4.625 | 99.9 |
| 50 | 0.012 | 416.033 | 99.75 | <0.03 | >416.54* | >99.97 | <0.002 | >416.66* | >99.98 | <0.002 | >416.66* | >99.98 |
| 500 | <0.03 | >4166.54* | >99.997 | <0.03 | >4166.54* | >99.997 | <0.03 | >4166.54* | >00.997 | <0.03 | >4166.54* | >99.997 |

Volume of Solution 500 c.c.
Flow Rate 0.3 gpm/ft².

Depth of Column 9" (20cm.)
Coal 600 gms

* Calculated on average of effluent basis.

contact time = 30 min.

C-2-6    TABLE 5    COLUMN ADSORPTION PROCESS -- ZINC.

Volume of Solution = 500 ml.    Rate of Flow = 0.3 gpm/ft$^2$.
Depth of Column      = 9" (20cm.)  Wt. of Coal  = 600 gms.
contact time          = 30 min.

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal | Effluent conc. mg/l | mg removed per gm coalX10$^{-4}$ | % Removal |
| 0.5 | 0.044 | 3.800 | 91.2 | 0.057 | 3.691 | 88.6 | 0.034 | 3.883 | 93.2 | 0.028 | 3.933 | 94.4 |
| 5.0 | 0.044 | 41.30 | 99.12 | 0.067 | 41.108 | 98.66 | 0.043 | 41.308 | 99.14 | 0.038 | 41.35 | 99.24 |
| 50 | 0.078 | 416.02 | 99.84 | 0.050 | 416.25 | 99.9 | 0.074 | 416.05 | 99.85 | 0.039 | 416.34 | 99.92 |
| 100 | 0.055 | 832.875 | 99.95 | 0.059 | 832.84 | 99.94 | 0.079 | 832.68 | 99.92 | 0.039 | 833.01 | 99.96 |
| 250 | 0.066 | 2082.78 | 99.97 | 0.075 | 2082.71 | 99.97 | 0.16 | 2082.0 | 99.94 | 0.039 | 2083.1 | 99.98 |
| 500 | 3.194 | 4140.05 | 99.36 | 2.39 | 4146.75 | 99.52 | 1.56 | 4153.67 | 99.69 | 3.03 | 4141.42 | 99.39 |

C-2-6

TABLE 6 . COLUMN ADSORPTION CHROMIUM

volume of solution = 500 ml. , rate of flow = 0.3 gpm/ft$^2$.
depth of column = 9" (20cm.) , wt. of coal = 600 gms.
contact time = 30 min.

| Solution Concentration ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal | Effluent Conc. mg/l | mg Removed per gm Coal | % Removal |
| 0.1 | <0.03 | >0.58X10$^{-4}$ | >70 | <0.02 | >0.67X10$^{-4}$ | >80 | <0.03 | >0.58X10$^{-4}$ | >70 | <0.034 | >0.55X10$^{-4}$ | >66· |
| 0.5 | <0.02 | >4.0X10$^{-4}$ | >96 | <0.02 | >4.0X10$^{-4}$ | >96 | <0.008 | >4.0X10$^{-4}$ | >98.4 | <0.052 | >3.7X10$^{-4}$ | >89.6 |
| 5 | 0.104 | 40X10$^{-4}$ | 97.92 | <0.045 | > 41X10$^{-4}$ | >99.1 | <0.115 | > 40X10$^{-4}$ | >97.7 | <0.052 | > 11X10$^{-4}$ | >99.96 |
| 50 | 0.10 | 415X10$^{-4}$ | 99.8 | 0.08 | 416X10$^{-4}$ | 99.84 | 0.09 | 415X10$^{-4}$ | 99.82 | 0.08 | 416X10$^{-4}$ | 99.8 |
| 100 | 0.11 | 832X10$^{-4}$ | 99.9 | 0.16 | 832X10$^{-4}$ | 99.84 | 0.08 | 832X10$^{-4}$ | 99.92 | 0.03 | 832X10$^{-4}$ | 99.92 |
| 250 | 0.4 | 2082X10$^{-4}$ | 99.84 | 0.08 | 2082X10$^{-4}$ | 99.96 | 0.07 | 2082X10$^{-4}$ | 99.97 | 0.18 | 2081X10$^{-4}$ | 99.92 |
| 500 | 0.98 | 4158X10$^{-4}$ | 99.8 | 0.27 | 4164.4X10$^{-4}$ | 99.95 | 0.09 | 4165X10$^{-4}$ | 99.93 | 0.26 | 4164X10$^{-4}$ | 99.94 |

APPENDIX C-2-7    LONG TERM ADSORPTION OF LEAD THROUGH A COAL COLUMN

C-2-7                    TABLE 1 . BREAK-THROUGH DATA DURING 32 DAYS.

DAYS OF OPERATION

| Sampling Point | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Influent | 4.97 | 4.97 | 4.2 | 4.42 | 4.64 | 4.885 | 5.13 | 2.29 | 2.29 | 4.45 | 5.23 | 5.23 | 5.72 | 5.72 | 5.2 | 5.33 | 3.24 | 3.24 |
| 6" Level | 0.08 | 0.335 | 0.245 | 0.325 | 0.27 | 0.465 | 0.505 | 0.28 | 0.55 | 0.65 | 0.66 | 0.605 | 0.66 | 0.65 | 0.728 | 0.715 | 0.687 | 0.388 |
| 1 1/2' " | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 |
| 2 1/2' " | <0.02 | <0.02 | <0.02 | <0.02 | | | | | | | | | <0.03 | | | | | |
| 3 1/2' " | <0.02 | <0.02 | <0.02 | <0.02 | | | | | | | | | | | | | | |
| 4 1/2' " | <0.02 | <0.02 | <0.02 | <0.02 | | | | | | | | | | | | | | |
| 5 1/1' " | <0.02 | <0.02 | <0.02 | <0.02 | | | | | | | | | | | | | | |
| 6 1/2' " | <0.02 | <0.02 | <0.02 | <0.02 | | | | | | | | | | | | | | |
| 7 Effluent | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.04 | <0.02 | <0.62 | <0.02 | <0.02 | <0.02 |

column dimensions : 6" (15.24cm.) diam.   , 2 m. depth.
coal particle size = 0.533 mm.

DAYS OF OPERATION

| 19 | 20 | 21 | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 5.15 | 5.76 | 5.76 | 5.71 | 4.906 | 4.906 | 4.96 | 4.96 | 5.077 | 5.077 | 4.6 | 4.6 | 4.5 | 4.5 |
| 0.7205 | 0.6 | 0.68 | 0.55 | 0.66 | 0.622 | 0.61 | 0.544 | 0.439 | 0.3365 | 0.573 | 0.555 | 0.441 | 0.539 |
| <0.02 | <0.02 | <0.02 | <0.02 | 0.047 | <0.02 | <0.02 | 0.01 | 0.03 | 0.005 | 0.02 | 0.19 | 0.0245 | 0.206 |
| | | | 0.035 | <0.02 | <0.02 | | 0.223 | 0.045 | | 0.03 | | 0.107 | 0.039 |
| <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | <0.02 | 0.025 | 0.03 | 0.045 | 0.02 | 0.047 |

318a.

TABLE 2 .CONTINUOUS ADSORPTION OF LEAD

ADSORPTIVE CAPACITY OF COAL

column dimensions 6"(15.24cm.) ,2 m.depth.

coal particle size = 0.533 mm.

| Batch No. | Rate of Flow l/hr | Influent Conc. mg/l Pb. | Total mg of Lead Applied | Average Effluent from 6" Level | mgs of Lead in Effluent | mgs of Lead Adsorbed | mgs Removed per gm Coal | % Removal |
|---|---|---|---|---|---|---|---|---|
| 1 | 8.21 | 4.94 | 1346.67 | 0.25 | 67.74 | 1278.93 | 0.676 | 94.97 |
| 2 | 5.65 | 4.2 | 948.4 | 0.26 | 68.71 | 889.69 | 0.470 | 93.81 |
| 3 | 4.70 | 4.64 | 1047.8 | 0.34 | 76.78 | 971.02 | 0.513 | 92.67 |
| 4 | 6.35 | 5.13 | 1042.42 | 0.49 | 99.57 | 942.85 | 0.498 | 90.45 |
| 5 | 7.78 | 2.5 | 700 | 0.46 | 128.8 | 571.2 | 0.302 | 81.6 |
| 6 | 5.93 | 4.45 | 844.16 | 0.38 | 72.08 | 772.08 | 0.408 | 91.46 |
| 7 | 5.65 | 5.23 | 1180.99 | 0.63 | 142.26 | 1038.73 | 0.549 | 87.95 |
| 8 | 5.36 | 5.77 | 1485.2 | 0.65 | 167.3 | 1317.9 | 0.696 | 88.74 |
| 9 | 9.41 | 5.20 | 1174.2 | 0.73 | 164.38 | 1009.82 | 0.533 | 86.00 |
| 10 | 6.35 | 5.33 | 1083.06 | 0.75 | 151.99 | 931.07 | 0.492 | 85.97 |
| 11 | 5.91 | 3.24 | 804.82 | 0.67 | 166.43 | 638.39 | 0.340 | 79.32 |
| 12 | 6.02 | 5.15 | 930.1 | 0.72 | 130.21 | 799.89 | 0.423 | 86.0 |
| 13 | 7.34 | 5.76 | 1690.56 | 0.64 | 187.84 | 1502.72 | 0.794 | 88.89 |
| 14 | 8.09 | 5.71 | 1108.88 | 0.60 | 116.5 | 992.38 | 0.524 | 89.49 |
| 15 | 6.21 | 4.91 | 1218.65 | 0.65 | 161.46 | 1057.19 | 0.559 | 86.75 |
| 16 | 4.70 | 4.96 | 1119.97 | 0.61 | 137.74 | 982.23 | 0.519 | 87.7 |
| 17 | 4.70 | 5.08 | 1146.39 | 0.43 | 97.32 | 1049.07 | 0.0670 | 91.51 |
| 13 | 4.70 | 4.60 | 1038.68 | 0.61 | 137.74 | 900.94 | 0.4760 | 86.74 |
| 19 | 5.51 | 4.50 | 1016.10 | 0.49 | 110.64 | 905.46 | 0.4780 | 89.11 |
| 20 | 5.72 | 4.45 | 763.66 | 0.67 | 115.32 | 648.34 | 0.3425 / 9.66 | 84.9 |

APPENDIX C-2-8    SELECTIVITY IN ADSORPTION OF MIXED METALS BY COAL.

C-2-3    TABLE 1 .   CONTINUOUS ADSORPTION OF MERCURY.
column dimensions :6"(15.24cm.) , 2m. depth.
coal particle size 0.533mm.

DAYS OF OPERATION

| Sampling Point | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Influent | 6.2 | 6.79 | 6.08 | 7.448 | 7.448 | 5.7 | 6.14 | 6.14 | 5.75 | 5.65 |
| 6" Level | 0.36 | 1.63 | 1.26 | 1.8 | 1.24 | 1.5 | 1.78 | 1.75 | 2.4 | 2.62 |
| 1 1/2' " | 0.0215 | 0.0085 | 0.0118 | 0.0104 | 0.0146 | 0.02 | 0.0325 | 0.02 | 0.062 | 0.096 |
| 2 1/2' " | 0.0236 | 0 | 0 | 0.0063 | 0.0083 | 0.0035 | 0.0123 | 0.0073 | 0.01 | 0.016 |
| 3 1/2' " | 0.005 | 0.0055 | 0.003 | 0.00341 | 0.0034 | 0.0031 | 0.00928 | 0.0055 | 0.0071 | 0.0053 |
| 4 1/2' " | 0.0075 | 0.0345 | 0.005 | 0.007 | 0.00156 | 0.0021 | 0.0057 | 0.005 | 0.005 | 0.0086 |
| 5 1/2' " | 0.0075 | 0.002 | 0.015 | 0.0031 | 0.0018 | 0.0018 | 0.005 | 0.0043 | 0.0037 | 0.0123 |
| 6 1/2' " | 0.0051 | 0.002 | 0.011 | 0.007 | 0.0021 | 0.00135 | 0.01 | 0.0028 | 0.0037 | 0.0058 |
| 7' Effluent | - | 0.003 | 0.004 | 0.0021 | 0.001 | 0.0016 | 0.005 | 0.0028 | 0.0025 | 0.0083 |

| 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|
| 5.65 | 5.8 | 5.8 | 8.2 | 8.6 | 8.6 | 8.6 | 8.6 | 6.0 |
| 1.7 | 1.43 | 1.56 | 1.92 | 1.8 | 1.16 | 1.35 | 1.54 | 1.78 |
| 0.0515 | 0.026 | 0.0624 | 0.045 | 0.0685 | 0.076 | 0.06 | 0.086 | 0.08 |
| 0.0186 | 0.0106 | 0.016 | 0.0148 | 0.018 | 0.0136 | 0.0126 | 0.0186 | 0.023 |
| 0.0063 | 0.0036 | 0.0083 | 0.0077 | 0.0088 | 0.01 | 0.0063 | 0.005 | 0.0124 |
| 0.006 | 0.0058 | 0.0062 | 0.0075 | 0.0077 | 0.0075 | 0.0057 | 0.0067 | 0.0094 |
| 0.0054 | 0.0054 | 0.006 | 0.0125 | 0.0074 | 0.0057 | 0.0045 | 0.0058 | 0.0068 |
| 0.0056 | 0.0052 | 0.0063 | 0.007 | 0.0078 | 0.0068 | 0.005 | 0.0053 | 0.0062 |
| - | 0.0051 | 0.0062 | 0.004 | 0.0074 | 0.0075 | 0.003 | 0.0058 | 0.0066 |

C-2-8  TABLE 2.  CONTINUOUS ADSORPTION THROUGH COLUMN 6" DIAM., 2 M LENGTH, COAL SIZE: 0.533 mm

LEAD

DAYS OF OPERATION

| Sampling Point | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Influent | 4.81 | 6.46 | 5.91 | 6.12 | 6.12 | 6.45 | 5.97 | 5.97 | 4.21 | 4.64 |
| 6" Level | 3.98 | 6.10 | 6.68 | 7.38 | 7.32 | 6.23 | 5.99 | 6.58 | 4.24 | 5.76 |
| 1 1/2' " | 0.0195 | 0.0370 | 0 | 0.0278 | 0.019 | 0.0254 | 0.092 | 0.142 | 0.181 | 0.467 |
| 2 1/2' " | 0.0116 | 0 | 0.0845 | 0 | 0.0215 | 0 | 0.022 | 0 | 0.0215 | 0.0215 |
| 3 1/2' " | 0.074 | 0.0179 | 0 | 0 | 0 | 0 | 0.016 | 0 | 0 | 0.0278 |
| 4 1/2' " | 0.0122 | 0.023 | 0.0179 | 0 | 0 | 0.0298 | 0.0157 | 0 | 0 | 0.0254 |
| 5 1/2' " | 0.023 | 0.0191 | 0.0195 | 0 | 0.019 | 0 | 0.0256 | 0.0255 | 0 | 0 |
| 6 1/2' " | 0.032 | 0.039 | 0.0285 | 0 | 0 | 0.0132 | 0 | 0.0197 | 0 | 0 |
| 7' Effluent | 0 | 0.0179 | 0.023 | 0 | 0 | 0 | 0 | 0.0175 | 0 | 0 |

| 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|----|----|----|----|----|----|----|----|----|
| 4.64 | 5.87 | 5.87 | 6.37 | 5.97 | 5.97 | 5.97 | 5.65 | 5.79 |
| 6.23 | 5.05 | 6.14 | 6.09 | 6.03 | 6.23 | 6.47 | 6.29 | 6.20 |
| 0.153 | 0.116 | 0.205 | 0.133 | 0.278 | 0.205 | 0.159 | 0.385 | 0.306 |
| 0 | 0.0273 | 0.0168 | 0.0107 | 0 | 0.0175 | 0.0187 | 0 | 0.0234 |
| 0 | 0.00813 | 0.0124 | 0.0083 | 0 | – | 0.0526 | 0 | 0.0127 |
| 0.0274 | 0 | 0 | 0 | 0 | 0.0187 | 0.01244 | 0 | 0 |
| 0 | 0 | 0 | 0.0493 | 0.0107 | 0.00813 | 0 | 0 | 0 |
| 0 | 0 | 0 | 0.0107 | 0.0473 | 0.0062 | 0 | 0 | 0 |
| – | 0 | 0 | 0.0151 | 0.0278 | 0 | 0.0378 | 0 | 0.0151 |

C-2-8    TABLE 3 .    CONTINUOUS ADSORPTION THROUGH COLUMN 6" DIAM., 2 M LENGTH, COAL SIZE: 0.533 mm

COPPER

| Sampling Point | DAYS OF OPERATION | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Influent | 5.84 | 6.27 | 5.75 | 6.187 | 6.187 | 5.89 | 5.51 | 5.51 | 3.75 | 4.44 |
| 6" Level | 2.0 | 3.13 | 3.62 | 4.087 | 5.28 | 4.79 | 4.98 | 5.34 | 3.84 | 5.12 |
| 1 1/2' " | 0.061 | 0.13 | 0.014 | 0.064 | 0.052 | 0.089 | 0.188 | 0.236 | 0.427 | 1.27 |
| 2 1/2' " | 0.0596 | 0.009 | 0.067 | 0.039 | 0.075 | 0.0054 | 0.024 | 0.048 | 0.037 | 0.035 |
| 3 1/2' " | 0.034 | 0.039 | 0.018 | 0.036 | 0.027 | 0.036 | 0.0185 | 0.033 | 0.0463 | 0.049 |
| 4 1/2' " | 0.057 | 0.115 | 0.067 | 0.029 | 0.027 | 0.063 | 0.022 | 0.052 | 0.0463 | 0.0392 |
| 5 1/2' " | 0.111 | 0.058 | 0.05 | 0.036 | 0.054 | 0.045 | 0.0389 | 0.0463 | 0.044 | 0.0294 |
| 6 1/2' " | 0.096 | 0.261 | 0.05 | 0.036 | 0.018 | 0.11 | 0.011 | 0.0462 | 0.0426 | 0.0294 |
| 7' Effluent | 0.0143 | 0.058 | 0.07 | 0.061 | 0.05 | 0.054 | 0.063 | 0.0393 | 0.037 | 0.0392 |

| 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|
| 4.44 | 2.14 | 2.14 | 5.97 | 5.59 | 5.59 | 5.59 | 6.8 | 5.986 |
| 4.35 | 2.86 | 2.92 | 4.99 | 4.85 | 5.14 | 5.32 | 6.57 | 6.204 |
| 0.562 | 0.497 | 0.75 | 0.653 | 0.304 | 0.836 | 0.79 | 1.68 | 1.59 |
| 0.0431 | 0.024 | 0.087 | 0.032 | 0.044 | 0.0618 | 0.0718 | 0.0235 | 0.0717 |
| 0.0294 | 0.043 | 0.046 | 0.058 | 0.04 | 0.131 | 0.051 | 0.0235 | 0.0431 |
| 0.0679 | 0.013 | 0.044 | 0.03 | 0.085 | 0.226 | 0.182 | 0.0353 | 0.0528 |
| 0.0255 | 0.044 | 0.048 | 0.083 | 0.036 | 0.033 | 0.055 | 0.0294 | 0.0604 |
| 0.0255 | 0.0296 | 0.041 | 0.041 | 0.03 | 0.109 | 0.109 | 0.0431 | 0.085 |
| - | 0.1182 | 0.048 | 0.04 | 0.09 | 0.1182 | 0.091 | 0.066 | 0.066 |

C-2-8 TABLE 4 . CONTINUOUS ADSORPTION THROUGH COLUMN 6" DIAM., 2 M LENGTH, COAL SIZE: 0.533

CADMIUM

DAYS OF OPERATION

| Sampling Point | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Influent | 5.104 | 5.625 | 5.21 | 5.47 | 5.47 | 5.76 | 5.64 | 5.64 | ?.67 | 4.07 |
| 6" Level | 3.125 | 5.417 | 5.16 | 6.69 | 6.061 | 3.065 | 5.2 | 5.56 | 3.88 | 5.279 |
| 1 1/2' " | 0.04 | 0.117 | 0.0042 | 0.0552 | 0.173 | 0.638 | 1.43 | 1.6 | 2.21 | 4.28 |
| 2 1/2' " | 0.0615 | 0.012 | 0.0094 | 0.0167 | 0.0158 | 0 | 0.0062 | 0.037 | 0.0062 | 0.0455 |
| 3 1/2' " | 0.0068 | 0.0146 | 0 | 0.0203 | 0 | 0.0356 | 0.0014 | 0 | 0 | 0.0105 |
| 4 1/2' " | 0.018 | 0.0083 | 0.0031 | 0.00682 | 0 | 0.035 | 0.0026 | 0 | 0 | 0 |
| 5 1/2' " | 0.0375 | 0.0396 | 0.0042 | 0.0065 | 0 | 0 | 0.0016 | 0.0083 | 0 | 0 |
| 6 1/2' " | 0.0104 | 0.0156 | 0.0052 | 0.0072 | 0 | 0.079 | 0.0014 | 0.0048 | 0.0079 | 0 |
| 7' Effluent | 0.0083 | 0.0073 | 0.0188 | 0 | 0 | 0.0396 | 0 | 0.0122 | 0 | 0.00406 |

| 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|
| 4.07 | 5.0 | 5.0 | 5.175 | 5.35 | 5.35 | 5.35 | 5.22 | 5.48 |
| 5.221 | 4.38 | 5.71 | 5.14 | 5.18 | 5.45 | 5.42 | 5.77 | 5.73 |
| 2.75 | 3.28 | 3.95 | 3.64 | 3.48 | 4.52 | 4.5 | 5.65 | 5.42 |
| 0.0374 | 0.0279 | 0.0638 | 0.03 | 0.0269 | 0.0241 | 0.0243 | 0.1057 | 0.220 |
| 0.0018 | 0.0122 | 0.0029 | 0.002 | 0.002 | – | 0.035 | 0.0029 | 0.0016 |
| 0.0181 | 0.0085 | 0.0033 | 0.0011 | 0 | 0.002 | 0.0055 | 0.0052 | 0.0013 |
| 0.0031 | 0.0024 | 0.0013 | 0.022 | 0.014 | 0.0011 | 0.0078 | 0 | 0.00087 |
| 0 | 0 | 0.0011 | 0.0081 | 0 | 0.0074 | 0.0065 | 0.0011 | 0 |
| – | 0.0098 | 0 | 0.002 | 0.00293 | 0.0069 | 0.0145 | 0.0013 | 0 |

C-2-8   TABLE 5 .   CONTINUOUS ADSORPTION THROUGH COLUMN 6" DIAM., 2 M LENGTH, COAL SIZE: 0.533 mm

ZINC

DAYS OF OPERATION

| Sampling Point | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|
| Influent | 5.35 | 5.5 | 6.6 | 7.52 | 7.52 | 7.00 | 6.56 | 6.56 | 3.5 | 5.0 |
| 6" Level | 4.33 | 6.198 | 7.02 | 7.05 | 7.58 | 8.13 | 6.64 | 6.81 | 4.33 | 6.38 |
| 1 1/2' " | 0.097 | 0.145 | 0.03 | 0.169 | 0.717 | 1.276 | 2.29 | 2.71 | 3.54 | 6.379 |
| 2 1/2' " | 0.077 | 0.04 | 0.05 | 0.046 | 0.048 | 0.0343 | 0.052 | 0.113 | 0.035 | 0.133 |
| 3 1/2' " | 0.052 | 0.033 | 0.017 | 0.068 | 0.015 | 0.066 | 0.041 | 0.033 | 0.033 | 0.027 |
| 4 1/2' " | 0.0395 | 0.1074 | 0.082 | 0.254 | 0.0135 | 0.101 | 0.022 | 0.038 | 0.0375 | 0.01025 |
| 5 1/2' " | .0868 | 0.054 | 0.076 | 0.046 | 0.034 | 0.025 | 0.042 | 0.048 | 0.035 | 0.0102 |
| 6 1/2' " | 0.0395 | 0.023 | 0.081 | 0.076 | 0.062 | · 0.184 | 0.019 | 0.04 | 0.053 | 0.032 |
| 7' Effluent | 0.0063 | 0.0034 | 0.101 | 0.046 | 0.037 | 0.074 | 0.048 | 0.091 | 0.0163 | 0.01311 |

| 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|----|----|----|----|----|----|----|----|----|
| ·5.0 | ·4.34 | 4.34 | 5.39 | 5.39 | 5.39 | 5.39 | 5.35 | 5.56 |
| 6.58 | 4.63 | 6.38 | 5.6 | 5.39 | 5.43 | 5.56 | 5.97 | .5.97 |
| 4.34 | 4.96 | 5.84 | 5.39 | 5.19 | 6.26 | 6.17 | 7.41 | 6.58 |
| 0.0803 | 0.0421 | 0.2049 | 0.134 | 0.1211 | 0.1088 | 0.159 | 0.514 | 0.761 |
| 0.01025 | 0.0475 | 0.031 | 0.043 | 0.0298 | 1.138 | 0.0434 | 0.0102 | 0.033 |
| 0.1227 | 0.0123 | 0.0556 | 0.0225 | 0.0127 | 0.0205 | 0.0597 | 0.0281 | 0.072 |
| 0.0184 | 0.0184 | 0.0246 | 0.0809 | 0.033 | 0.0289 | 0.0679 | 0.0086 | 0.0475 |
| 0.01148 | 0.0172 | 0.0254 | 0.033 | 0.0705 | 0.351 | 0.0372 | 0.0413 | 0.072 |
| No Eff. | 0.0496 | 0.0225 | 0.0372 | 0.0664 | 0.0597 | 0.1046 | 0.0708 | 0.129 |

C-2-8  TABLE  6 .  CONTINUOUS ADSORPTION THROUGH COLUMN 6" DIAM., 2 M LENGTH.  COAL SIZE: 0.533 mm

CHROMIUM

| Sampling Point | DAYS OF OPERATION | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
| Influent | 5.2 | 6.13 | 5.13 | 5.4 | 5.4 | 3.42 | 4.5 | 4.5 | 1.94 | 2.75 |
| 5" Level | 1.31 | 2.16 | 2.3 | 2.5 | 4.08 | 0.98 | 0.617 | 3.44 | 2.0 | 3.92 |
| 1 1/2' " | 0.031 | 0.042 | 0.014 | 0.054 | 0.057 | 0.065 | 0.1 | 0.188 | 0.109 | 0.957 |
| 2 1/2' " | 0.022 | 0 | 0.018 | 0.026 | 0.038 | 0.003 | 0.033 | 0.032 | 0.037 | 0.0485 |
| 3 1/1' " | 0.0155 | 0.011 | 0.007 | 0.02 | 0.021 | 0.024 | 0.026 | 0.026 | 0.0069 | 0.0387 |
| 4 1/1' " | 0.023 | 0.011 | 0.012 | 0.021 | 0.016 | 0.157 | 0.0194 | 0.02 | 0.029 | 0.0813 |
| 5 1/1' " | 0.0088 | 0.012 | 0.018 | 0.037 | 0.024 | 0.018 | 0.0156 | 0.02 | 0.017 | 0.0253 |
| 6 1/2' " | 0.014 | 0.0088 | 0.0095 | 0.016 | 0.006 | 0.459 | 0.0013 | 0.0106 | 0.014 | 0.0197 |
| 7' Effluent | 0 | 0.0088 | 0.0108 | 0.018 | 0.021 | 0.016 | 0.015 | 0.0181 | 0.0075 | 0.0314 |

| 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|
| 2.75 | 4.0 | 4.0 | 5.06 | 5.89 | 5.89 | 5.89 | 4.98 | 6.04 |
| 2.33 | 1.33 | 4.23 | 3.61 | 3.42 | 3.75 | 4.08 | 4.23 | 3.87 |
| 0.2732 | 0.098 | 0.46 | 0.237 | 0.156 | 0.282 | 0.2 | 0.479 | 0.443 |
| 0.0904 | 0.03 | 0.159 | 0.77 | 0.060 | 0.079 | 0.077 | 0.084 | 0.098 |
| 0.0207 | 0.029 | 0.082 | 0.039 | 0.039 | - | 0.067 | 0.045 | 0.057 |
| 0.479 | 0.015 | 0.042 | 0.033 | 0.031 | 0.052 | 0.042 | 0.045 | 0.037 |
| 0.01436 | 0.012 | 0.05 | 0.042 | 0.017 | 0.033 | 0.016 | 0.034 | 0.034 |
| 0.021 | 0.015 | 0.043 | 0.04 | 0.014 | 0.044 | 0.04 | 0.008 | 0.032 |
| - | 0.019 | 0.033 | 0.024 | 0.031 | 0.033 | - | 0.0186 | 0.0304 |

## C-3-1 - BATCH TESTS

### C-3-1 TABLE 1 ADSORPTION ISOTHERMS FOR $BOD_5$
### REMOVAL WITH COAL AND ACTIVATED CARBON

CONTACT TIME = 4 hrs

| Carbon Dosage (M) gm Per Litre | Active Carbon 4/8 Columbia | | | H.C. Coal Size 150 Mesh (0.03414 mm) | | | H.C. Coal Size 1/4" (0.533 mm) | | |
|---|---|---|---|---|---|---|---|---|---|
| | $C_f$ | $X = C_o - C_f$ | $\frac{X}{M}$ | $C_f$ mg/l | $X = C_o - C_f$ | $\frac{X}{M}$ | $C_f$ mg/l | $X = C_o - C_f$ | $\frac{X}{M}$ |
| 0 | 366 | | | | | | | | |
| 1 gram | 270 | 96 | 96 | 258 | 108 | 318 | 48 | 48 | 48 |
| 2 grams | 282 | 84 | 42 | 246 | 120 | 60 | 306 | 60 | 30 |
| 3 grams | 168 | 198 | 66 | 240 | 126 | 42 | 282 | 84 | 28 |
| 4 grams | - | - | - | 228 | 138 | 34.5 | 258 | 108 | 27 |
| 5 grams | 174 | 192 | 38.4 | 234 | 132 | 26.4 | 258 | 108 | 21.6 |
| 8 grams | - | - | - | 228 | 138 | 17.3 | 234 | 132 | 16.5 |
| 10 grams | - | - | - | 216 | 150 | 15 | 234 | 132 | 13.2 |

### C-3-1 TABLE 2 ADSORPTION ISOTHERMS FOR COD
### REMOVAL WITH COAL AND ACTIVATED CARBON

CONTACT TIME = 4 hrs

| Carbon Dosage (M) gm Per Liter | Active Carbon 4/8 Columbia | | | H.C. Coal Size 150 Mesh. | | | H.C. Coal Size 1/4" (0.533 mm) | | |
|---|---|---|---|---|---|---|---|---|---|
| | $C_f$ mg/l | $X = C_o - C_f$ | $\frac{X}{M}$ | $C_f$ mg/l | $X = C_o - C_f$ | $\frac{X}{M}$ | $C_f$ mg/l | $X = C_o - C_f$ | $\frac{X}{M}$ |
| 0 | 733 | | | | | | | | |
| 1 | 480 | 253 | 253 | 462 | 271 | 271 | 684 | 149 | 149 |
| 2 | 443 | 290 | 145 | 446 | 287 | 143.5 | 554 | 179 | 39.5 |
| 3 | 381 | 352 | 117.3 | 440 | 293 | 97.7 | 532 | 201 | 67 |
| 4 | - | - | - | 428 | 305 | 76.2 | 502 | 231 | 57.8 |
| 5 | 335 | 398 | 79.6 | 335 | 398 | 79.6 | 441 | 292 | 58.4 |
| 8 | - | - | - | 320 | 413 | 51.6 | 418 | 315 | 39.4 |
| 10 | - | - | - | 304 | 429 | 42.9 | 382 | 351 | 35.1 |

APPENDIX C-3-2. COLUMN ABSORPTION TESTS.

C-3-2. TABLE 1. REDUCTION OF BOD$_5$ and COD
LEIF EXTRACT AEROBIC LEACHING
COLUMN 20 cm X 7 cm I.D.
Particle size 0.533 mm
Flow = 5-7 ml/min.

| Run Number | Throughput Volume Liters | Service Time (hrs) | BOD of Influent mg/l | BOD of Effluent mg/l | BOD Removed mg/l | Removal Efficiency % | COD of Influent mg/l | COD of Effluent mg/l | COD Removed mg/l | Removal Efficiency % | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 1 | 3 hrs | 267 | 257 / 260 / 252 | 10 / 7 / 15 | 3.7 / 2.6 / 5.6 | 520 | 522 / 512 / 496 | - / 8 / 24 | - / 1.5 / 4.6 | This period considered as inoculation period for the column |
| Wash H$_2$O | 1 | | - | 50 | - | - | | 176 | | | The column washed and dried |
| 2 | 2 | 6 hrs | 276 | 72 / 42 | 204 / 234 | 74 / 85 | 640 | 208 / 168 | 432 / 472 | 68 / 74 | Removal efficiency increases due to bacterial action |
| 3 | 2 | 6 hrs | 325 | 120 / 85 / 77 / 98 / 10 | 205 / 240 / 248 / 227 / 315 | 63 / 74 / 76 / 70 / 97 | 680 | 280 / 200 / 200 / 232 / 120 | 400 / 480 / 480 / 448 / 560 | 59 / 71 / 71 / 66 / 82 | Samples withdrawn for analysis every 1 hr. |
| 4 | 2 | 6 hrs | 585 | 167 / 120 / 133 / 136 / 46 / 13 | 418 / 465 / 452 / 449 / 539 / 572 | 72 / 80 / 77 / 77 / 92 / 98 | 1110 | 320 / 300 / 290 / 340 / 256 / 296 | 790 / 810 / 820 / 770 / 854 / 814 | 71 / 73 / 74 / 69 / 77 / 73 | Samples withdrawn for analysis every 1 hr. |
| 5 | 2 | 6 hrs | 310 | 85 / 179 / 196 / 201 / 106 | 225 / 131 / 114 / 109 / 204 | 73 / 42 / 47 / 35 / 66 | 624 | 192 / 306 / 325 / 202 / 306 | 433 / 318 / 299 / 422 / 318 | 69 / 51 / 48 / 68 / 51 | Samples are taken for analysis every 1 hr. |
| Back Wash | 2 | | | < 20 / < 20 / < 20 / 18.18 | | | | 149 / 211 / 165 / 298 | | | Backwashing with city tap water did not improve or regenerate the surface properties of the coal |
| 6 | 2.5 | 6 hrs | 360 | 184 / 114 / 77 | 176 / 246 / 283 | 49 / 68 / 79 | 681 | 388 / 356 / 253 | 293 / 525 / 428 | 43 / 48 / 63 | |
| 7 | 4 | 12 hrs | 257 | 135 / 84 / 84 / 111 | 122 / 173 / 173 / 146 | 48 / 67 / 67 / 57 | 626 | 277 / 152 / 208 / 264 | 349 / 474 / 418 / 362 | 56 / 76 / 67 / 58 | |
| 8 | 4 | 12 hrs | 275 | 117 / 50 / 97 | 158 / 225 / 178 | 58 / 82 / 65 | 648 | 344 / 160 / 224 | 304 / 488 / 424 | 47 / 75 / 65 | |
| 9 | 7 | 20 hrs | 297 | 93 / 71 / 71 | 204 / 226 / 226 | 69 / 76 / 76 | 655 | 216 / 247 / 223 | 439 / 408 / 432 | 67 / 62 / 66 | |
| 10 | 2.5 | 6 hrs | 418 | 180 / 141 / 90 | 238 / 277 / 328 | 57 / 66 / 78 | 712 | 480 / 336 / 240 | 232 / 376 / 472 | 33 / 53 / 66 | |
| Washing | | | | | | | | | | | The coal washed with warm water then dried |
| TESTS WITH HIGH FLOW RATE 50 ml/min AVERAGE: | 0.5 ℓ / 0.5 ℓ / 1 ℓ / 0.5 ℓ | 50 min | 468 | 302 / 352 / 352 / 359 | 166 / 116 / 116 / 109 | 36 / 25 / 25 / 23 | 710 | 539 / 548 / 608 / 608 | 171 / 162 / 102 / 102 | 24 / 23 / 14 / 14 | The efficiency of removal drops greatly with faster flow rate because of insufficient contact time. |

C-3-2.  TABLE 2.  REDUCTION OF BOD$_5$ and COD

BEEF EXTRACT ANIONIC LEACHING

COLUMN 20 cm X 7 cm I.D.

Particle size 0.2965 mm

Flow  =  5-7 ml/min.

| Run Number | Throughput Volume Liters | Service Time (hrs) | BOD of Influent mg/l | BOD REMOVAL | | | COD of Influent mg/l | COD REMOVAL | | | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | BOD of Effluent mg/l | BOD Removed mg/l | Removal Efficiency % | | COD of Effluent mg/l | COD Removed mg/l | Removal Efficiency % | |
| 1 | 1 | 3 hrs | 310 | 300 | 10 | 3.2 | 640 | 554 | 86 | 13.4 | Bacterial inoculation |
| | | | | 340 | – | – | | 544 | 96 | 15 | period. No appreciable |
| | | | | 190 | 120 | 38.7 | | 384 | 256 | 40 | reduction |
| Wash H$_2$O | 1 | – | | 68 | – | – | | 32 | | | The column washed and dried |
| 2 | 2 | 6 hrs | 326 | 52 | 274 | 84 | 620 | 176 | 444 | 72 | Appreciable increase in |
| | | | | 44 | 282 | 87 | | 150 | 470 | 76 | the reduction efficiency |
| | | | | 22 | 304 | 93 | | 120 | 500 | 81 | due to bacterial action |
| 3 | 2 | 6 hrs | 322 | 90 | 232 | 72 | 627 | 214 | 413 | 66 | |
| | | | | 0 | 322 | =100 | | 159 | 468 | 75 | Samples withdrawn for |
| | | | | 30 | 292 | 91 | | 151 | 476 | 76 | analysis every 1 hr. |
| | | | | 84 | 238 | 74 | | 126 | 501 | 80 | |
| | | | | 66 | 256 | 80 | | 111 | 516 | 82 | |
| 4 | 2 | 6 hrs | 510 | 81 | 429 | 84 | 1019 | 188 | 831 | 82 | |
| | | | | 133 | 377 | 74 | | 251 | 768 | 75 | Samples withdrawn for |
| | | | | 185 | 325 | 64 | | 451 | 568 | 56 | analysis every 1 hr. |
| | | | | 175 | 336 | 66 | | 480 | 539 | 53 | |
| Back Wash | | | | 76 | | | | 251 | | | Backwashing with city |
| | | | | 18 | | | | 79 | | | tap water did not improve |
| | | | | 30 | | | | 39 | | | or regenerate the surface |
| | | | | 10 | | | | 32 | | | properties of the coal |
| 5 | 2.5 | 6 hrs | 360 | 117 | 243 | 68 | 681 | 230 | 451 | 66 | |
| | | | | 119 | 241 | 67 | | 245 | 436 | 64 | |
| | | | | 125 | 235 | 65 | | 204 | 477 | 70 | |
| 6 | 4 | 12 hrs | 257 | 125 | 132 | 51 | 626 | 237 | 389 | 62 | |
| | | | | 145 | 112 | 44 | | 240 | 386 | 62 | |
| | | | | 114 | 143 | 56 | | 240 | 386 | 62 | |
| | | | | 140 | 117 | 46 | | 344 | 282 | 45 | |
| 7 | 4 | 12 hrs | 275 | 180 | 95 | 35 | 648 | 384 | 264 | 41 | |
| | | | | 177 | 98 | 36 | | 336 | 312 | 48 | |
| | | | | 190 | 85 | 31 | | 344 | 304 | 47 | |
| 8 | 7 | 20 hrs | 297 | 129 | 168 | 57 | 655 | 333 | 322 | 49 | |
| | | | | 148 | 149 | 50 | | 327 | 328 | 50 | |
| | | | | 147 | 150 | 51 | | 325 | 330 | 50 | |
| 9 | 2.5 | 6 hrs | 418 | 177 | 241 | 58 | 712 | 488 | 224 | 32 | |
| | | | | 191 | 227 | 54 | | 392 | 320 | 45 | |
| | | | | 190 | 228 | 55 | | 376 | 336 | 47 | |

...ashing

TESTS WITH HIGH FLOW RATE 50 ml/min AVERAGE:

| | 2.5 | 50 min | 468 | 125 | 343 | 73 | 710 | 280 | 430 | 61 | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 204 | 264 | 56 | | 339 | 371 | 52 | |
| | | | | 150 | 318 | 68 | | 382 | 328 | 46 | |

C-3-2.   TABLE 3.   CUMULATIVE REDUCTION OF BOD & COD
LEACHING OF BEEF EXTRACT THROUGH
HAT CREEK COAL 9" BED

| Service Volumes Liters | Coal Size 0.533 mm | | | | | | Coal Size 0.2965 mm | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $BOD_5$ | | | COD | | | $BOD_5$ | | | COD | | |
| | Total BOD Applied | Total BOD Removed | % Removal | Total COD Applied | Total COD Removed | % Removal | Total BOD Applied | Total BOD Removed | % Removal | Total COD Applied | Total COD Removed | % Removal |
| | gm | gm | % | gm | gm | % | gm | gm | % | gm | gm | % |
| 2 | 0.552 | 0.438 | 79 | 1.280 | 0.904 | 71 | 0.652 | 0.573 | 88 | 1.240 | 0.942 | 76 |
| 4 | 1.202 | 0.932 | 78 | 2.640 | 1.851 | 70 | 1.296 | 1.109 | 86 | 2.494 | 1.892 | 76 |
| 6 | 2.372 | 1.897 | 80 | 4.860 | 3.470 | 71 | 2.316 | 1.843 | 80 | 4.532 | 3.245 | 72 |
| 8 | 2.992 | 2.210 | 74 | 6.108 | 4.186 | 69 | 3.216 | 2.442 | 76 | 6.235 | 4.392 | 70 |
| 10.5 | 3.892 | 2.798 | 72 | 7.811 | 5.058 | 65 | 4.244 | 2.946 | 69 | 8.739 | 5.825 | 67 |
| 14.5 | 4.920 | 3.412 | 69 | 10.315 | 6.661 | 65 | 5.344 | 3.317 | 62 | 11.331 | 6.998 | 62 |
| 18.5 | 6.020 | 4.160 | 69 | 12.907 | 8.282 | 64 | 7.423 | 4.407 | 59 | 15.916 | 9.285 | 58 |
| 25.5 | 8.099 | 5.691 | 70 | 17.492 | 11.266 | 64 | 8.463 | 4.987 | 59 | 17.696 | 10.018 | 57 |
| 28 | 9.144 | 6.394 | 70 | 19.272 | 12.166 | 63 | 9.638 | 5.758 | 60 | 19.471 | 10.959 | 56 |
| 30.5 | 10.314 | 6.711 | 65 | 21.047 | 12.502 | 59 | - | - | - | - | - | - |

APPENDIX   C-4     ADSORPTION  OF  PHOSPHATES   .

C-4-1.     BATCH     TESTS .

C-4-1.                        TABLE 1.    CONTACT PROCESS

PHOSPHATE REMOVAL

Time  =    1 hr.
Coal  =    1% w/w

| Solution Conc. ppm (mg/l) | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal |
| 2 | 2.14 | – | – | 2.21 | – | – | 2.42 | – | – | 1.32 | 0.068 | 24 |
| 5 | 4.96 | 0.004 | 0.8 | 5.1 | – | – | 4.9 | 0.01 | 2.0 | 2.42 | 0.258 | 51.6 |
| 10 | 10.08 | – | – | 9.77 | 0.023 | 2.3 | 9.65 | 0.035 | 3.5 | 6.28 | 0.372 | 37.2 |
| 50 | 50.02 | – | – | 49.34 | 0.066 | 1.32 | 49.5 | 0.05 | 1 | 41.37 | 0.863 | 17.26 |
| 100 | | | | | | | | | | 95 | 0.5 | 5 |
| 250 | | | | | | | | | | 239.03 | 1.097 | 4.4 |
| 500 | | | | | | | | | | 478 | 2.2 | 4.4 |

TABLE 2 . CONTACT PROCESS
REMOVAL OF PHOSPHATE

Contact time: 3 hrs.
Coal : 1% w/w

| Solution Conc. ppm mg/l | Coal size 0.533 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal |
| 2 | 2.42 | – | – | 2.14 | – | – | 1.93 | 0.007 | 3.5 | 1.20 | 0.081 | 40.5 |
| 5 | 4.75 | 0.025 | 5.0 | 4.63 | 0.037 | 7.4 | 4.41 | 0.059 | 11.8 | 2.51 | 0.249 | 49.8 |
| 10 | 9.59 | 0.041 | 4.1 | 9.1 | 0.09 | 9 | 9.81 | 0.019 | 1.9 | 5.64 | 0.436 | 43.6 |
| 50 | 49.34 | 0.066 | 1.32 | 44.74 | 0.526 | 10.52 | 45.35 | 0.465 | 9.3 | 38.92 | 1.108 | 22.2 |
| 100 | | | | | | | | | | 63.74 | 3.626 | 36.26 |
| 250 | | | | | | | | | | 196.13 | 5.387 | 21.55 |
| 500 | | | | | | | | | | 410.65 | 8.935 | 17.87 |

TABLE 3. CONTACT PROCESS
REMOVAL OF PHOSPHATE

Contact time: 6 hrs.
Coal        : 1% w/w

| Solution Conc. ppm mg/l | Coal size 0.5331 mm av. | | | Coal size 0.2965 mm av. | | | Coal size 0.117 mm av. | | | Coal size 0.03414 mm av. | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal |
| 2 | 1.99 | 0.001 | 0.5 | 2.05 | — | — | 1.84 | 0.016 | 8 | 0.858 | 0.1142 | 57.1 |
| 5 | 5.15 | — | — | 4.9 | 0.01 | 2.0 | 4.2 | 0.08 | 16 | 1.56 | 0.344 | 68.8 |
| 10 | 9.56 | 0.044 | 4.4 | 9.6 | 0.04 | 4 | 9.07 | 0.093 | 9.3 | 3.46 | 0.654 | 65.4 |
| 50 | 47.5 | 0.25 | 5 | 49.5 | 0.05 | 1 | 48.11 | 0.189 | 3.78 | 38 | 1.2 | 24 |

TABLE 4. CONTACT PROCESS

REMOVAL OF PHOSPHATE

Time = 3 hours
Coal size = 0.03414 mm

| Influent Solution Conc. mg/l | Coal % → w/w 0.5 % w/w | | | 1% w/w | | | 5% w/w | | |
|---|---|---|---|---|---|---|---|---|---|
| | Equilibrium conc. mg/l | mg Removed per gm coal | % Removal | Equilibrium conc. mg/l | mg Removed per gm coal | % Removal | Equilibrium conc. mg/l | mg Removed per gm coal | % Removal |
| 2 | 1.41 | 0.12 | 29.5 | 1.2 | 0.081 | 40.5 | 0.613 | 0.0278 | 69.5 |
| 5 | 3.25 | 0.35 | 35 | 2.51 | 0.249 | 49.8 | 0.73 | 0.0854 | 85.4 |
| 10 | 7.38 | 0.524 | 26.2 | 5.64 | 0.436 | 43.6 | 0.858 | 0.1823 | 91.42 |
| 50 | 41.37 | 1.726 | 17.26 | 38.92 | 1.108 | 22.2 | 8.99 | 0.8232 | 82.02 |
| 100 | 73.55 | 5.29 | 26.5 | 63.74 | 3.626 | 36.26 | 18.99 | 1.6202 | 81.01 |
| 250 | 199.19 | 10.16 | 20.32 | 196.13 | 5.387 | 21.55 | 98.58 | 3.028 | 60.57 |
| 500 | 367.74 | 26.45 | 26.45 | 410.65 | 8.935 | 17.87 | 306.45 | 3.871 | 38.7 |

C-4-1.

TABLE 5. CONTACT PROCESS
EFFECT OF CONTACT TIME
PHOSPHATE REMOVAL

Coal Size = 0.03414 mm
Coal = 1% w/w

| Influent Solution Conc. mg/l | Contact Time Hrs. → | 1 HR. | | | 3 HR. | | | 6 HR. | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal |
| 2 | | 1.32 | 0.068 | 34 | 1.2 | 0.081 | 40.5 | 0.859 | 0.1142 | 57.1 |
| 5 | | 2.42 | 0.258 | 52 | 2.51 | 0.249 | 49.8 | 1.56 | 0.344 | 68.8 |
| 10 | | 6.28 | 0.372 | 37 | 5.64 | 0.436 | 43.6 | 3.46 | 0.654 | 65.4 |
| 50 | | 41.37 | 0.863 | 17 | 38.92 | 1.108 | 22.2 | 38 | 1.2 | 24 |
| 100 | | 95 | 0.5 | 5 | 63.74 | 3.626 | 36.26 | | | |
| 250 | | 239.03 | 1.07 | 4.4 | 196.13 | 5.387 | 21.55 | | | |
| 500 | | 478 | 2.2 | 4.4 | 410.65 | 8.935 | 17.87 | | | |

C-4-1 .

TABLE 6. EFFECT OF PERCENTAGE COAL ON THE
REMOVAL CAPACITY FOR PHOSPHATE

Time: 6 hrs
Coal size: 0.03414 mm av.

| % Coal Added | Influent conc. mg/l → 2 mg/l | | | 5 mg/l | | | 10 mg/l | | | 50 mg/l | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal | Effluent conc. mg/l | mg Removed per gm coal | % Removal |
| 0.5 | 0.92 | 0.216 | 54 | 2.94 | 0.412 | 41.2 | 6.25 | 0.75 | 37.5 | 39.53 | 2.094 | 20.94 |
| 1 | 0.853 | 0.1142 | 57.1 | 1.56 | 0.344 | 68.8 | 3.46 | 0.654 | 65.4 | 38 | 1.2 | 24 |
| 5 | 0.46 | 0.0308 | 77 | 0.43 | 0.0914 | 91.4 | 0.64 | 0.1872 | 93.6 | 13.45 | 0.731 | 73.1 |

C-4-2.     TABLE 1.     COLUMN ADSORPTION PROCESS
PHOSPHATE REMOVAL

Wt. of coal = 600 gms;   bed depth = 20 cm;   influent conc. = 10 mg/l

| Throughput Volume Liters | Total $PO_4^{-3}$ Applied mgs. | Coal size 0.533 mm | | | Coal size 0.2965 mm | | | Coal size 0.117 mm | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Equilibrium Soln. Conc. mg/l | % Removal Efficiency | Cumulative Removal mgs. | Equilibrium Soln. Conc. mg/l | % Removal Efficiency | Cumulative Removal mgs. | Equilibrium Soln. Conc. mg/l | % Removal Efficiency | Cumulative Removal mgs. |
| 1/2 | 5 | 2.14 | 78.6 | 3.93 | 0.46 | 95.4 | 4.77 | 0.306 | 97 | 4.85 |
| 1 | 10 | - | - | - | 1.5 | 85 | 9.02 | 0.37 | 96 | 9.67 |
| 1 1/2 | 15 | - | - | - | 3.5 | 65 | 12.27 | 1.26 | 87 | 13.17 |
| 2 | 20 | 6.45 | 35.5 | 9.255 | - | - | - | 2.1 | 79 | 17.12 |
| 2 1/2 | 25 | 8.0 | 20 | 10.255 | 3.34 | 66.6 | 18.93 | 2.1 | 79 | 21.07 |
| 3 | 30 | 8.1 | 19 | 11.205 | 4.93 | 50.7 | 21.47 | 2.4 | 76 | 24.87 |
| 3 1/2 | 35 | - | - | - | 6.2 | 38 | 23.37 | - | - | - |
| 4 | 40 | - | - | - | - | - | - | 3.46 | 65 | 29.78 |

C-4-2.     TABLE 2.     COLUMN ADSORPTION PROCESS
PHOSPHATE REMOVAL

Coal size less than 150 mesh (0.03414)
Influent Conc. = 247 mg/l $PO_4^{-3}$
Max. flow rate = 7-9 ml/min.

| Throughput Volume Liters | Cumulative Applied Phosphate mgs. | Equilibrium Solution Conc. mg/l | Phosphate Removed mg/l | % Efficiency of Removal | Cumulative Removal of $PO_4^{-3}$ mgs. |
|---|---|---|---|---|---|
| 0.2 | 49.4 | 0.735 | 245.96 | 99.7 | 49.2 |
| 0.42 | 103.7 | 0.46 | 246.23 | 99.8 | 103.4 |
| 0.59 | 145.7 | <0.306 | 246.38 | 99.9 | 145.2 |
| 1.39 | 343.3 | 18.7 | 228.3 | 92.4 | 327.9 |
| 1.64 | 405.1 | 52.1 | 194.59 | 78.9 | 376.5 |
| 2.14 | 528.6 | 70.5 | 176.5 | 71.4 | 464.8 |
| 2.34 | 578.0 | 127.2 | 119.8 | 48.5 | 488.7 |
| 2.54 | 627.4 | 213.3 | 33.7 | 13.6 | 495.5 |

N.B.   Very poor permeability av.  3 ml/min.

C-4-2.     TABLE 3.    COLUMN ADSORPTION PROCESS
PHOSPHATE REMOVAL

Using Abbotsford sandy loam

Sand size less than 150 mesh (0.03414)

Influent Conc. = 247 mg/l

Max. flow rate = 7-9 ml/min.

| Throughput Volume Liters | Cumulative Applied $PO_4^{-3}$ mgs. | Equilibrium Solution Conc. mg/l | Phosphate Removed mg/l | % Efficiency of Removal | Cumulative Removal of $PO_4^{-3}$ mgs. |
|---|---|---|---|---|---|
| 1 | 247 | <0.306 | >246.4 | >99.9 | 246.4 |
| 2 | 494 | <0.306 | >246.4 | >99.9 | 492.8 |
| 3 | 741 | <0.306 | >246.4 | >99.9 | 739.2 |
| 6.5 | 1606 | 0.644 | 246.05 | 99.7 | 1600.4 |
| 7 | 1729 | <0.306 | >246.4 | >99.9 | 1723.6 |
| 7.5 | 1853 | 2.298 | 244.7 | 99.1 | 1846 |
| 8.0 | 1976 | 25.190 | 221.8 | 89.8 | 1956.9 |
| 8.5 | 2100 | 73.860 | 173.14 | 70.1 | 2043.5 |

N.B.   Detectable limit for $PO_4^{-3}$ is 0.306 mg/l.

Appendix C-5.  Absorbance and Specific Extinction Coefficient of assigned infra red bands.

A:  Absorbance,  K Specific extinction coefficient in $cm^2/mg$.

| Type of Treatment | 1000 cm-1 | | Band Assignment 1600 cm-1 | | 1720 cm-1 | | 3000 cm-1 | |
|---|---|---|---|---|---|---|---|---|
| | A | K | A | K | A | K | A | K |
| **1  Water Washed Surface Coal** | | | | | | | | |
| Wahsed sample | 0.31 | 0.42 | 0.32 | 0.43 | 0.24 | 0.31 | ---- | ---- |
| Treated with lead | 0.19 | 0.25 | 0.49 | 0.65 | 0.08 | 0.11 | ---- | ---- |
| Treated with barium | 0.12 | 0.17 | 0.62 | 0.82 | 0.05 | 0.07 | ---- | ---- |
| Acid anlydride | 0.33 | 0.44 | 0.37 | 0.49 | 0.33 | 0.44 | ---- | ---- |
| **2  Acid Washed Surface Coal** | | | | | | | | |
| Washed sample | 0.53 | 0.70 | 0.37 | 0.50 | 0.31 | 0.41 | ---- | ---- |
| Treated with lead | 0.23 | 0.30 | 0.34 | 0.45 | 0.25 | 0.33 | ---- | ---- |
| Treated with barium | 0.23 | 0.30 | 0.41 | 0.54 | 0 | 0 | ---- | ---- |
| Acid anlydride* | 0.54 | 0.72 | 0.36 | 0.48 | 0.36 | 0.48 | ---- | ---- |

\* Two shoulders appeared at 1775 and 1765 which are assigned for acid anlydride formation.

| Type of Treatment | 1000 cm-1 | | 1600 cm-1 | | 1720 cm-1 | | 3000 cm-1 | |
|---|---|---|---|---|---|---|---|---|
| **3  Water Washed Core Coal** | | | | | | | | |
| Washed sample | 0.61 | 0.81 | 0.45 | 0.60 | ------ | ------ | 0.47 | 0.63 |
| Treated with lead | 0.57 | 0.76 | 0.18 | 0.23 | 0.10 | 0.13 | 0.19 | 0.25 |
| Acid anlydride | 0.52 | 0.69 | 0.26 | 0.34 | 0.2 | 0.26 | 0.2 | 0.27 |
| **4  Acid Washed Core Coal** | | | | | | | | |
| Washed sample | 0.57 | 0.76 | 0.38 | 0.51 | 0.19 | 0.25 | ---- | ---- |
| Treated with lead | 0.54 | 0.72 | 0.24 | 0.32 | 0.10 | 0.13 | ---- | ---- |
| Treated with barium | 0.45 | 0.60 | 0.42 | 0.55 | ---- | ---- | ---- | ---- |
| Acid Anlydride | 0.63 | 0.84 | 0.20 | 0.27 | 0.15 | 0.20 | ---- | ---- |

Appendix C-6.    Molar ratio between adsorbed lead and released hydrogen.

C-6-1.    Adsorption of lead ions and the pH drop.

| Coal Samples | Effluent Conc. mg/l | % Efficiency of removal | mgs removed per gram coal | PH Measure | PH drop from Original | No. of H+ displaced per gram coal A | No. Pb++ ions absorbed/ gram coal B | $\frac{Pb++}{H+}$ $\frac{(B)}{(A)}$ * |
|---|---|---|---|---|---|---|---|---|
| | initial 530 | ------ | ----- | 4.235 | ----- | ------ | ----- | ----- |
| **A- Surface Coal** | | | | | | | | |
| Water-washed 1 | 86 | 83.8 | 44.4 | 2.70 | | | | |
| 2 | 88 | 83.4 | 44.2 | 2.70 | | | | |
| Mean | 87 | 44.3 | 44.3 | 2.70 | 1.535 | $1.90 \times 10^{-4}$ | $2.14 \times 10^{-4}$ | 1:0.89 |
| Std.dev. | ±1 | | | | | | | (1:1) |
| % error | 1.15% | | | | | | | |
| Acid-washed 1 | 120 | 77.4 | 41.0 | 2.42 | | | | |
| 2 | 125 | 76.4 | 40.5 | 2.43 | | | | |
| Mean | 122.5 | 76.9 | 40.75 | 2.425 | 1.810 | $3.66 \times 10^{-4}$ | $1.97 \times 10^{-4}$ | 1.07:2.0 |
| Std.dev. | ±2.5 | | | | | | | (1:2) |
| % error | 2.04% | | | | | | | |
| **B- Core Coal** | | | | | | | | |
| Water-washed 1 | 122 | 77.0 | 40.8 | 3.70 | | | | |
| 2 | 120 | 77.4 | 41.0 | 3.66 | | | | |
| Mean | 121 | 77.2 | 40.9 | 3.68 | 0.555 | $0.11 \times 10^{-4}$ | $2 \times 10^{-4}$ | 1:0.055 |
| Std.dev. | +1 | | | | | | | |
| % error | 0.83% | | | | | | | |
| Acid-washed 1 | 367 | 30.8 | 16.3 | 2.71 | | | | |
| 2 | 364 | 31.3 | 16.6 | 2.70 | | | | |
| Mean | 365.5 | 31.0 | 16.45 | 2.705 | 1.530 | $2 \times 10^{-4}$ | $0.795 \times 10^{-4}$ | 0.8:2.0 |
| Std.dev. | ±1.5 | | | | | | | (1:2) |
| % error | 0.41% | | | | | | | |

(  )  approximate values.        * see sample calculation Appendix C-6-2.

C-6-2.    Sample calculation of the ion ratio  $\dfrac{Pb^{++}}{H^+}$

pH of the original solution = 4.235

   $pH = - \log (H^+)$

   $(H^+) = 0.0001$ per liter

   since the volume of the solution = 0.2 liter

   $(H^+)/100$ c.c. (1 gm coal) $= 0.0001 \times 0.1 = 0.1 \times 10^{-4}$

pH after absorption of lead = 2.7 = 0.002 ions/liter

   $(H^+)$ after reaction/100 c.c. (1 gm coal)$= 0.002 \times 0.1 = 2 \times 10^{-4}$

   $H^+$ released $= 2 \times 10^{-4} - 0.1 \times 10^{-4} = 1.9 \times 10^{-4}$

$Pb^{++}$ interact $= \dfrac{\text{mgs Pb removed/gm coal}}{\text{ml Wt} \times 1000} = \dfrac{\dfrac{H^+ \text{ ions } /\text{gram coal}}{44.3}}{207 \times 103}$

   $= 2.14 \times 10^{-4}$

Molar ratio of $Pb^{++}/H^+ = \dfrac{2.1 \times 10^{-4}}{2 \times 10^{-4}} = \dfrac{1}{0.89}$

# Appendix C-7. Acidic Groups in Coal.

## C-7-1. Carboxyl and hydroxyl groups in Coal.

| Coal/Carbon | Total Acidity (A) | | Carboxyl groups (B) | | Phenolics (A-B) | | % Carboxyl | % Phenolics |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | m.equi/gm | m.equiv/ BET surface area | m.equi/gm | m.equiv/ BET surface area | m.equiv/gm | m.equiv/ BET surface area | | |
| S.W. | 7.895 | 2.547 | 2.288 | 0.738 | 5.607 | 1.809 | 28.1 | 71.9 |
| | 7.895 | 2.547 | 2.156 | 0.696 | 5.739 | 1.851 | | |
| S.W.Pb | 8.9471 | 2.886 | 2.104 | 0.679 | 6.843 | 2.207 | 23.3 | 76.7 |
| | 8.6840 | 2.801 | 1.999 | 0.645 | 6.685 | 2.156 | | |
| S.A. | 8.684 | 2.801 | 2.630 | 0.848 | 6.054 | 1.953 | 30.7 | 69.3 |
| | 8.684 | 2.801 | 2.709 | 0.874 | 5.975 | 1.927 | | |
| S.A.Pb | 7.895 | 2.547 | 2.209 | 0.713 | 5.686 | 1.834 | 27.1 | 72.9 |
| | 8.421 | 2.716 | 2.209 | 0.713 | 6.212 | 2.003 | | |
| C.W. | 5.263 | 0.446 | 0.934 | 0.0792 | 4.329 | 0.367 | 17.0 | 83.0 |
| | 4.370 | 0.370 | 0.708 | 0.0600 | 3.662 | 0.310 | | |
| C.W.Pb | 4.265 | 0.361 | 1.092 | 0.0925 | 3.173 | 0.269 | 23.6 | 76.4 |
| | 4.265 | 0.361 | 0.923 | 0.0782 | 3.342 | 0.283 | | |
| C.A. | 4.737 | 0.401 | 1.275 | 0.1081 | 3.462 | 0.293 | 28.5 | 71.5 |
| | 4.2104 | 0.357 | 1.275 | 0.1081 | 2.935 | 0.249 | | |
| C.A.Pb | 5.526 | 0.468 | 1.086 | 0.0920 | 4.440 | 0.376 | 19.8 | 80.2 |
| | 5.526 | 0.468 | 1.105 | 0.0936 | 4.421 | 0.374 | | |
| Ac.W | 0.47 | 0.0007 | 0.09 | 0.0001 | 0.38 | 0.0006 | 9.5 | 80.8 |
| | 0.47 | 0.0007 | 0.09 | 0.0001 | 0.38 | 0.0006 | | |
| Ac.A | 1.47 | 0.0021 | 0.11 | 0.0002 | 1.36 | 0.0019 | 9.5 | 90.5 |
| | 1.05 | 0.0015 | 0.13 | 0.0002 | 0.92 | 0.0013 | | |

S.W. = water-washed surface coal
S.W.Pb= "     "     "      "Treated with Lead
S.A. = acid-washed surface coal
S.A.Pb= "     "     "      "Treated with Lead

C.W. = water-washed core coal
C.W.Pb= "     "     "      "Treated with Lead
C.A. = acid-washed core coal
C.A.Pb= "     "     "      "Treated with Lead

Ac.W = water-washed activated carbon
Ac.A = acid-washed activated carbon

Appendix C-7-2.       Analysis of variance of the acidic groups.

Table 1(a)       Carboxyl groups of various coal samples (m.eq./
                 unit surface area), effect of washing & treatment with

| Type of Wash | Treatment With Lead | Surface Coal | | Core Coal | |
|---|---|---|---|---|---|
| | | Replicate (1) | Replicate (2) | Replicate (1) | Replicate (2) |
| Water Washing | Untreated | 0.738 | 0.696 | 0.0792 | 0.060 |
| | Treated | 0.679 | 0.645 | 0.0925 | 0.0782 |
| Acid Washing | Untreated | 0.848 | 0.874 | 0.1081 | 0.1081 |
| | Treated | 0.713 | 0.713 | 0.0920 | 0.0936 |

Table 1(b)       Analysis of variance for data in table 1(a)

| Source of Variation | Degree of Freedom | Sums of squares | Mean squares | F |
|---|---|---|---|---|
| Washing (A) | 1 | 0.0145 | 0.0145 | 55.7** |
| Coal type (B) | 1 | 1.6863 | 1.6863 | 6467.6** |
| Treatment (C) | 1 | 0.0103 | 0.0103 | 39.3** |
| A x B | 1 | 0.0056 | 0.0056 | 21.3** |
| B x C | 1 | 0.0103 | 0.0103 | 39.7** |
| A x C | 1 | 0.0038 | 0.0038 | 14.8** |
| A x B x C | 1 | ------ | ------ | 3.7(N.S.) |
| Error | 8 | 0.0021 | 0.0003 | |
| Total: | 15 | 1.7339 | | |

**   Significant at 1% level.

N.S. Not significant.

Table 2(a).     Carboxyl groups of coals and activated carbon
                (m. eq/unit surface are), effect of acid washing.

| Type of Washing | Surface Coal | | Core Coal | | Activated Carbon | |
|---|---|---|---|---|---|---|
| | Replicate (1) | Replicate (2) | Replicate (1) | Replicate(2) | Replicate(1) | Replicate(2 |
| Water Washing | 0.738 | 0.696 | 0.0792 | 0.060 | 0.0001 | 0.0001 |
| Acid Washing | 0.848 | 0.874 | 0.1081 | 0.1081 | 0.0002 | 0.0002 |

Table 2(b).     Analysis of variance of data in Table 2(a).

| Source of Variation | Degree of Freedom | Sums of squares | Mean squares | F |
|---|---|---|---|---|
| Washing (A) | 1 | 0.0111 | 0.0111 | 47.5** |
| Type of coal/carbon (B) | 2 | 1.4938 | 0.7469 | 3191.2** |
| A x B | 2 | 0.0111 | 0.0056 | 23.7** |
| Error | 6 | 0.0014 | 0.0002 | ------ |
| Total: | 11 | 1.5174 | | |

**     Significant at 1% level.

Table 3(a).    Phenolic OH groups of various coal samples
(m. eq/unit surface area). Effect of washing
and treatment with lead.

| Type of Washing | Treatment with Lead | Surface coal Replicate (1) | Replicate (2) | Core Coal Replicate (1) | Replicate (2) |
|---|---|---|---|---|---|
| Water Washing | Untreated | 1.809 | 1.851 | 0.367 | 0.310 |
| | Treated | 2.207 | 2.156 | 0.269 | 0.283 |
| Acid Washing | Untreated | 1.953 | 1.927 | 0.293 | 0.249 |
| | Treated | 1.834 | 2.003 | 0.376 | 0.374 |

Table 3(b).    Analysis of Variance of data in Table 3(a).

| Source of Variation | Degrees of Freedom | Sums of squares | Mean squares | F |
|---|---|---|---|---|
| Washing (A) | 1 | 0.0037 | 0.0037 | 1.5 (N.S.) |
| Coal type (B) | 1 | 10.9214 | 10.9214 | 4482.1** |
| Treatment (C) | 1 | 0.0345 | 0.0345 | 14.2** |
| A x B | 1 | 0.0085 | 0.0085 | 3.5 (N.S.) |
| B x C | 1 | 0.0107 | 0.0107 | 4.4 (N.S.) |
| A x C | 1 | 0.0208 | 0.0208 | 8.5* |
| A x B x C | 1 | 0.0728 | 0.0728 | 29.9** |
| Error | 8 | 0.0195 | 0.0024 | |
| Total: | 15 | 11.0918 | | |

**   significant at the 1% level

*    significant at the 5% level

N.S. not significant.

Table 4(a).    Phenolic OH groups of coals and activated carbon (m.eq/unit surface area). Effect of acid-washing.

| Type of Washing | Surface coal | | Core coal | | Activated coal | |
|---|---|---|---|---|---|---|
| | Replicate (1) | Replicate (2) | Replicate (1) | Replicate (2) | Replicate (1) | Replicate (2) |
| Water Washing | 1.809 | 1.851 | 0.367 | 0.310 | 0.0006 | 0.0006 |
| Acid Washing | 1.953 | 1.927 | 0.293 | 0.249 | 0.0019 | 0.0013 |

Table 4(b).    Analysis of variance of data in Table 4(a).

| Source of Variation | Degrees of Freedom | Sums of squares | Mean squares | F |
|---|---|---|---|---|
| Washing (A) | 1 | 0.0006 | 0.-006 | 1.0 (N.S.) |
| Type of Coal/Carbon(B) | 2 | 8.1846 | 4.0923 | 6440.0** |
| A x B | 2 | 0.0160 | 0.0080 | 12.6** |
| Error | 6 | 0.0038 | 0.0006 | |
| Total: | 11 | 8.2051 | | |

** significant at 1% level

N.S. not significant.

Table 5(a).    Total acidity of various coal samples
               (m.eq/gm) Effect of washing and
               treatment with lead.

| Type of Washing | Treatment with Lead | Surface coal | | Core Coal | |
|---|---|---|---|---|---|
| | | Replicate (1) | Replicate (2) | Replicate (1) | Replicate (2) |
| Water Washing | Untreated | 7.895 | 7.895 | 5.263 | 4.370 |
| | Treated | 8.947 | 8.684 | 4.265 | 4.265 |
| Acid Washing | Untreated | 8.684 | 8.684 | 5.263 | 4.210 |
| | Treated | 7.895 | 8.721 | 5.526 | 5.526 |

Table 5(b).    Analysis of variance of data in Table 5(a).

| Source of Variation | Degrees of Freedom | Sums of squares | Mean squares | F |
|---|---|---|---|---|
| Washing (A) | 1 | 0.5346 | 0.5346 | 3.2(N.S.) |
| Coal type (B) | 1 | 51.5380 | 51.5380 | 310.3** |
| Treatment (C) | 1 | 0.1529 | 0.1529 | 0.9 (N.S.) |
| A x B | 1 | 0.2025 | 0.2025 | 1.2 (N.S.) |
| B x C | 1 | 0.0005 | 0.0005 | 0.0 (N.S.) |
| A x C | 1 | 0.0235 | 0.0235 | 0.1 (N.S.) |
| A x B x C | 1 | 1.7394 | 1.7394 | 10.5* |
| Error | 8 | 1.3287 | 0.1661 | |
| Total: | 15 | 55.5200 | | |

**    significant at the 1% level
*     significant at the 5% level
N.S.  not significant

Table 6(a).    Total acidity of coals and activated carbon
(m.eq/gm). Effect of acid washing.

| Type of Washing | Surface coal | | Core coal | | Activated carbon | |
|---|---|---|---|---|---|---|
| | Replicate (1) | Replicate (2) | Replicate (1) | Replicate (2) | Replicate (1) | Replicate (2) |
| Water Washing | 7.895 | 7.895 | 5.263 | 4.370 | 0.47 | 0.47 |
| Acid Washing | 8.684 | 8.684 | 5.263 | 4.210 | 1.47 | 1.05 |

Table 6(b).    Analysis of variance of data in Table 6(a).

| Source of Variation | Degrees of Freedom | Sums of squares | Mean squares | F |
|---|---|---|---|---|
| Washing (A) | 1 | 0.7517 | 0.7517 | 4.3 (N.S.) |
| Type of coal/ carbon (B) | 2 | 110.3159 | 55.1580 | 317.9** |
| A x B | 2 | 0.5052 | 0.2526 | 1.5 (N.S.) |
| Error | 6 | 1.0409 | 0.1735 | |
| Total: | 11 | 112.6137 | | |

**    significant at 1% level

N.S.    not significant.

Appendix C-7-3.   Released lead ions during the total acidity and carboxy group measurements.

| Coal Samples | Total Acidity Using Ba(OH)₂ Lead Released | | | Carboxyl Groups Using Barium Acetate Lead Released | | | Using Calcium Acetate Lead Released | | |
|---|---|---|---|---|---|---|---|---|---|
| | mg/l | mg/gm coal | % | mg/l | mg/gm coal | % | mg/l | mg/gm coal | % |
| Blank (no coal added) | 1 | N.D. | – | 3.5 | N.D. | – | 0.5 | N.D. | – |
| 1 Water-washed coal | | | | | | | | | |
| Original | 1 | N.D. | – | 3.5 | N.D. | – | 0.5 | – | – |
| Treated with Lead | 25 | 3.07 | 6.93 | 30 | 7.76 | 17.52 | 12 | 3.05 | 6.89 |
| 2 Acid-washed coal | | | | | | | | | |
| Original | 0.5 | N.D. | – | N.D. | N.D. | – | 1 | N.D. | – |
| Treated with Lead | 29 | 3.54 | 8.69 | 36.0 | 9.59 | 23.53 | 6 | 1.32 | 3.24 |

* The percentage of lead released = $\dfrac{\text{lead released (mg/gm coal)}}{\text{lead absorbed (mg/gm coal)}}$ x 100

APPENDIX C-8 .BIOLOGICAL OXIDATION OF DISSOLVED ORGANICS BY COAL.

C-8.   TABLE 1.        CUMULATIVE REMOVAL OF DISSOLVED ORGANICS USING INOCULATED COAL BED
Flow Rate = 50 ml/min
Mean Particle Size of Coal = 0.2965 mm

| Run Number | Volume Throughput liters | TOC (mgs) | | | BOD$_5$ (mgs) | | | COD (mgs) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Applied | Removed | % Removal | Applied | Removed | % Removal | Applied | Removed | % Removal |
| 1 | 20 | 1640 | 940 | 57.3 | 3140 | 1640 | 52.2 | 4420 | 2360 | 53.5 |
| 2 | 20 | 1640 | 740 | 45.1 | 3140 | 2000 | 63.7 | 4420 | 2120 | 48.0 |
| TOTAL | 40 | 3280 | 1680 | 51.2 ==== | 6280 | 3640 | 58.0 ==== | 8840 | 4480 | 51.0 ==== |

NOTE:    Three (3) grab samples were obtained during running of the first 20 liters
and found to have about the same analysis.  Therefore, the average of these
three results were considered as the average analysis of the whole batch.

C-8.

TABLE 2(a)           BACKWASHING WITH NaOH SOLUTION

pH = 11

|            | TOC mg/l | Total TOC Washed mgs | BOD Removed mg/l | BOD5 Washed mgs | COD mg/l | COD Washed mgs. |
|------------|----------|----------------------|------------------|-----------------|----------|------------------|
| Wash 1 (5 1) | 93     | 465                  | 135              | 675             | 234.3    | 1171.5           |
| Wash 2 (5 1) | 37     | 185                  | 42               | 210             | 70.7     | 353.5            |
| Wash 3 (5 1) | 33     | 165                  | 30               | 150             | 60.0     | 300.0            |
| Wash 4 (5 1) | 40     | 200                  | 36               | 180             | 66.0     | 330.0            |
|            |          | 1015                 |                  | 1215            |          | 2155.0           |
|            |          | =====                |                  | =====           |          | ========         |

C-8.

TABLE 2(b)       CONTROL EXPERIMENTS USING $H_2O$ and NaOH SOLUTION
                 LEACHED   THROUGH  FRESH  COAL

|            | TC mg/l | TIC mg/l | TOC mg/l |              |
|------------|---------|----------|----------|--------------|
| $H_2O$     | 8-10    | 4        | 4-6      |              |
| NaOH       |         |          |          | Total mgs    |
| Wash 1/ℓ   | 60      | 8        | 52       | 52           |
| Wash 1/ℓ   | 50      | 7        | 43       | 43           |
| Wash 1/ℓ   | 15      | 7        | 8        | 8            |
|            |         |          |          | 103 mgs      |
|            |         |          |          | ====         |

C-8.

TABLE 3.   CUMULATIVE REDUCTION OF TOC, COD, AND $BOD_5$ BY LEACHING OF OXO BEEF SOLUTION

THROUGH HAT CREEK COAL 9" BED

INOCULATED COLUMN
Average Particle Size of Coal = 0.533 mm

| Service Volume Liters | TOC | | | COD | | | $BOD_5$ | | |
|---|---|---|---|---|---|---|---|---|---|
| | Total TOC Applied mgs | Total TOC Removed mgs | % Removal | Total COD Applied mgs | Total COD Removed mgs | % Removal | Total BOD Applied mgs | Total BOD Removed mgs | % Removal |
| 1 | 148 | 51 | 34 | 580 | 392 | 68 | 350 | 180 | 50 |
| 2 | 296 | 102 | 34 | 1160 | 708 | 61 | 720 | 318 | 44 |
| 3 | 444 | 148 | 33 | 1740 | 972 | 56 | 1080 | 456 | 42 |
| 4 | 592 | 189 | 32 | 2320 | 1288 | 56 | 1440 | 588 | 41 |
| 5 | 740 | 235 | 32 | 2900 | 1664 | 57 | 1800 | 732 | 41 |
| 6 | 888 | 297 | 33 | 3480 | 2056 | 59 | 2160 | 906 | 45 |
| 7 | 1036 | 348 | 34 | 4060 | 2436 | 60 | 2520 | 1062 | 42 |
| 8 | 1184 | 399 | 34 | 4640 | 2800 | 60 | 2880 | 1236 | 43 |
| 9 | 1332 | 461 | 35 | 5220 | 3160 | 61 | 3240 | 1446 | 45 |
| | ==== | === | | ==== | ==== | | ==== | ==== | |

# APPENDIX C-9 . APPLICATIONS IN SEWAGE TREATMENT .

## C-9-1. TABLE 1. CONTACT PROCESS REMOVAL OF POLLUTANTS FROM IONA SEWAGE.

Coal size = 0.2965 mm

| Coal % Added | Contact Time Hrs. | BOD₅ Effl. Conc. mg/l | BOD₅ mg adsorbed per gm coal | BOD₅ % Removal | COD Effl. Conc. mg/l | COD mg adsorbed per gm coal | COD % Removal | TOTAL NITROGEN Effl. Conc. mg/l | TOTAL NITROGEN mg adsorbed per gm coal | TOTAL NITROGEN % Removal | TOTAL PHOSPHORUS Effl. Conc. mg/l | TOTAL PHOSPHORUS mg adsorbed per gm coal | TOTAL PHOSPHORUS % Removal | LEAD Effl. Conc. mg/l | LEAD mg adsorbed per gm coal | LEAD % Removal | % Detectable Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | O(orig. Iona) 96-111 | | | | 213.5 | | | 18.4 | | | 2.9 | | | 0.05 | | | |
| | 1 | 11 | 9.3 | >89 | 36 | 17.75 | 83 | 14.3 | 0.41 | 22 | 1.85 | 0.105 | 38 | 0.03 | 0.002 | 60 | 80 |
| | 4 | 11 | 9.3 | >89 | 41.8 | 17.17 | 80 | 12.3 | 0.61 | 33 | 1.8 | 0.110 | 34 | <0.02 | >0.003 | >80 | 100 |
| 1% | 16 | 11 | 9.3 | >89 | 45.6 | 16.79 | 79 | 10.6 | 0.78 | 42 | 1.9 | 0.099 | 34 | <0.02 | >0.003 | >80 | 100 |
| | 24 | 6 | 9.8 | >94 | 40.8 | 17.27 | 81 | 10.3 | 0.81 | 44 | | | | 0.03 | 0.002 | >80 | 100 |
| | 80 | 6 | 9.8 | >94 | 20 | 19.40 | 91 | 9.7 | 0.87 | 47 | 1.9 | 0.099 | 34 | <0.02 | >0.003 | >80 | 100 |
| | (orig. Iona) 96-111 | | | | 213.5 | | | 18.4 | | | 2.9 | | | 0.05 | | | |
| | 1 | 11 | 1.86 | >89 | 42 | 3.43 | 80 | 9.15 | 0.185 | 50 | 1.99 | 0.0182 | 30 | <0.02 | >0.0006 | >80 | 100 |
| | 4 | 11 | 1.86 | >89 | 35.9 | 3.55 | 83 | 8.25 | 0.203 | 55 | 1.7 | 0.024 | 41 | <0.02 | >0.0006 | >80 | 100 |
| 5% | 16 | 11 | 1.86 | >89 | 49.6 | 3.28 | 77 | 7.00 | 0.228 | 62 | 1.53 | 0.0274 | 47 | <0.02 | >0.0006 | >80 | 100 |
| | 24 | 5 | 1.98 | >95 | 35.2 | 3.57 | 84 | 7.68 | 0.214 | 58 | 1.22 | 0.0336 | 58 | <0.02 | >0.0006 | >80 | 100 |
| | 80 | < 5 | >1.98 | >95 | 17.2 | 3.93 | 92 | 9.75 | 0.173 | 47 | 0.64 | 0.0452 | 78 | | | | |

N.B. The sensitivity of instrument used in the lead analysis is < 0.02

TABLE 2. CONTACT PROCESS
REMOVAL OF POLLUTANTS
FROM IONA SEWAGE

Coal size = Fines less than 0.03414 mm

| Coal % Added | Contact Time Hrs. | BOD$_5$ Effl. Conc. mg.l | mg ad-sorbed per gm coal | % Removal | COD Effl. Conc. mg/1 | mg ad-sorbed per gm coal | % Removal | TOTAL NITROGEN Effl. Conc. mg/1 | mg ad-sorbed per gm coal | % Removal | TOTAL PHOSPHORUS Effl. Conc. mg/1 | mg ad-sorbed per gm coal | % Removal | LEAD Effl. Conc. mg/1 | mg ad-sorbed per gm coal | % Removal | % Detectable Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | O(orig. Iona)96-111 | | | | 213.5 | | | 18.4 | | | 2.9 | | | 0.05 | | | |
| | 1 | 12 | 9.2 | >89 | 35.9 | 17.8 | 83 | 11.9 | 0.65 | 35 | 1.06 | 0.184 | 63 | 0.03 | 0.002 | 60 | 80 |
| | 4 | 12 | 9.2 | >89 | 35.9 | 17.8 | 83 | 11.8 | 0.66 | 36 | 0.7 | 0.22 | 76 | <0.02 | >0.003 | >80 | 100 |
| 1% | 16 | 11 | 9.3 | >89 | 47.6 | 16.6 | 78 | 8.12 | 1.028 | 56 | - | - | - | <0.02 | >0.003 | >80 | 100 |
| | 24 | 6 | 9.8 | >94 | 22 | 19.2 | 90 | 10.8 | 0.76 | 41 | 0.59 | 0.231 | 80 | <0.02 | >0.003 | >80 | 100 |
| | 80 | < 5 | >9.9 | >95 | 7.2 | 20.6 | 97 | 6.55 | 1.185 | 64 | 0.4 | 0.25 | 86 | <0.02 | >0.003 | >80 | 100 |
| | O(orig. Iona)96-111 | | | | 213.5 | | | 18.4 | | | | | | 0.05 | | | |
| | 1 | 12 | 1.84 | >89 | 39.8 | 3.474 | 81 | 7.8 | 0.212 | 58 | 1.45 | 0.029 | 50 | <0.02 | >0.0006 | >80 | 100 |
| | 4 | 15 | 1.78 | >86 | 55.2 | 3.166 | 74 | 8.54 | 0.197 | 54 | 1.45 | 0.029 | 50 | <0.02 | >0.0006 | >80 | 100 |
| 5% | 16 | 6 | 1.96 | >94 | 24.4 | 3.782 | 89 | 12 | 0.128 | 35 | 0.71 | 0.044 | 76 | <0.02 | >0.0006 | >80 | 100 |
| | 24 | 5 | 1.98 | >95 | 7.2 | 4.126 | 97 | 6.76 | 0.233 | 63 | 0.59 | 0.0462 | 78 | 0.03 | 0.0004 | 60 | 80 |
| | 80 | < 5 | >1.93 | >95 | 6.8 | 4.134 | 97 | 8.04 | 0.207 | 56 | 1.0 | 0.038 | 66 | <0.02 | >0.0006 | >80 | 100 |

TABLE 1. COLUMN ADSORPTION TESTS.
REMOVAL OF POLLUTANTS
FROM IONA SEWAGE BY COAL

Flow rate = 10 - 12 ml/min

| Cumulative Throughput Volumes Liters | BOD5 | | | | COD | | | | TOTAL NITROGEN | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Effluent conc. mg/l | Removal of BOD5 mg/l | % Removal | Cumulative Removal mgs | Effluent conc. mg/l | Removal of COD mg/l | % Removal | Cumulative Removal mgs | Effluent conc. mg/l | Removal of T-N mg/l | % Removal | Cumulativ Removal mgs |
| Original Iona | 111 | | | | 213.5 | | | | 18.4 | | | |
| 0.5 | 111 | 0 | 0 | 0 | 213 | ≈0 | 0 | 0 | | | | |
| 1.0 | 78 | 33 | 30 | 16.5 | 154.8 | 58.7 | 28 | 29.35 | 6.05 | 12.35 | 67 | 6.175 |
| 1.5 | 75 | 36 | 32 | 34.5 | 126.8 | 86.7 | 41 | 72.70 | 4.55 | 13.85 | 75 | 13.1 |
| 2.0 | 62 | 49 | 44 | 59.0 | 119.6 | 93.9 | 44 | 119.65 | 3.80 | 14.6 | 79 | 20.4 |
| 2.5 | 54 | 57 | 51 | 87.5 | 96.8 | 116.7 | 55 | 178.0 | 3.80 | 14.6 | 79 | 27.7 |
| 3.0 | 28 | 83 | 75 | 129 | 82.2 | 130.7 | 61 | 243.35 | 3.83 | 14.57 | 79 | 34.99 |
| 3.5 | 27 | 84 | 76 | 171 | 80.8 | 132.7 | 62 | 309.7 | 2.98 | 15.42 | 84 | 42.70 |
| 4.0 | 30 | 81 | 73 | 211.5 | 76.0 | 137.5 | 64 | 378.45 | 3.10 | 15.30 | 83 | 50.35 |
| 4.5 | 30 | 81 | 73 | 252 | 74.2 | 139.3 | 65 | 448.1 | 3.12 | 15.28 | 83 | 57.99 |
| 5.0 | 28 | 83 | 75 | 293.5 | 76.0 | 137.3 | 64 | 516.85 | 3.50 | 14.9 | 81 | 65.44 |
| 5.5 | 31 | 80 | 72 | 333.5 | 63.6 | 149.9 | 70 | 591.8 | 4.18 | 14.22 | 77 | 72.55 |
| 6.0 | 24 | 87 | 78 | 377 | 55.6 | 157.9 | 74 | 670.75 | 4.3 | 14.10 | 77 | 79.60 |
| 8.0 | 24 | 87 | 78 | 533.6 | 48.0 | 165.5 | 77 | 968.65 | 3.8 | 14.6 | 79 | 112.93 |

Coal size = 0.5331 mm = 1/4"

| | TOTAL PHOSPHATE | | | | ORTHOPHOSPHATE | | | | LEAD | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Influent conc. mg/l | Removal of T-P mg/l | % Removal | Cumulative Removal mgs | Effluent conc. mg/l | Removal of $PO_4^{-3}$ mg/l | % Removal | Cumulative Removal mgs | Effluent conc. mg/l | Cumulative Removal mgs | % Removal | % Detectable Removal |
| 2.9 | | | | 1.83 | | | | 0.05 | | | |
| 2.00 | 0.9 | 31 | 0.45 | 0.53 | 1.3 | 71 | 0.65 | <0.02 | >0.015 | >80 | 100 |
| 2.00 | 0.9 | 31 | 0.90 | 0.6 | 1.23 | 67 | 1.27 | <0.02 | 0.03 | >80 | 100 |
| 2.00 | 0.9 | 31 | 1.35 | 0.9 | 0.93 | 51 | 1.73 | <0.02 | 0.045 | >80 | 100 |
| 1.90 | 1.0 | 35 | 1.85 | 0.82 | 1.01 | 55 | 2.24 | <0.02 | 0.06 | >80 | 100 |
| 1.62 | 1.28 | 44 | 2.49 | 0.92 | 0.91 | 50 | 2.69 | <0.02 | 0.075 | >80 | 100 |
| 1.75 | 1.15 | 40 | 3.070 | 1.19 | 0.64 | 35 | 3.01 | <0.02 | 0.09 | >80 | 100 |
| 1.86 | 1.04 | 36 | 3.59 | 1.29 | 0.54 | 30 | 3.28 | <0.02 | 0.105 | >80 | 100 |
| 1.90 | 1.0 | 35 | 4.09 | 1.26 | 0.57 | 31 | 3.57 | <0.02 | 0.12 | >80 | 100 |
| 2.05 | 0.85 | 29 | 4.51 | 1.28 | 0.55 | 30 | 3.84 | <0.02 | 0.135 | >80 | 100 |
| 2.11 | 0.79 | 27 | 4.91 | 1.25 | 0.58 | 32 | 4.13 | <0.02 | 0.15 | >80 | 100 |
| 2.14 | 0.76 | 26 | 5.29 | 1.25 | 0.58 | 32 | 4.42 | <0.02 | 0.165 | >80 | 100 |
| 2.15 | 0.75 | 26 | 5.66 | 1.30 | 0.53 | 29 | 4.69 | <0.02 | 0.18 | >80 | 100 |
| 2.05 | 0.85 | 29 | 7.19 | 1.24 | 0.59 | 32 | 4.98 | <0.02 | 0.234 | >80 | 100 |

APPENDIX D

DATA RESULTS OF DESIGN APPLICATIONS.

## TENTATIVE CALCULATION OF A COAL BED FOR
## IONA (VANCOUVER) SEWAGE TREATMENT

### 1.  Laboratory Experiment

Three vertical cylindrical columns of 1 1/2 in. I.D. with 1 ft, 2 ft, and 4 ft lengths were filled with Hat Creek coal of 0.533 mm mean particle size.

A solution of lead (5 mg/l) was applied continually at the rate of 1 gpm/ft$^2$. The data from this experiment is shown in Table 23. The "break-through" point was determined when the effluent solution reached a strength of 0.5 mg/l of lead.

### Theory

The performance of a coal bed may be evaluated by the use of the Bohart and Adams relationship (8) as shown in the following equation:

$$t = \frac{N_o}{C_o V} [D - \frac{V}{KN_o} \ln (\frac{C_o}{C_B} - 1)]$$

in which

$t$ = service time (hours)

$V$ = linear flow rate (ft/hr)

$D$ = depth of carbon bed (ft)

$D_o$ = critical depth of carbon bed (ft)

$K$ = rate constant (ft$^3$/lb/hr)

$N_o$ = adsorptive capacity (lb/ft$^3$)

$C_o$ = influent solute concentration (mg/l)

$C_B$ = allowable effluent solute concentration (mg/l)

If $t$ (time hrs) is plotted vs. $D$ (depth of bed ft) for the three columns a straight line is obtained as shown in Figure D - 1 - 1. From the experimental data obtained the mathematical relationship is applied in the above equation.

1.  Calculation of the Critical Depth, e.g. the theoretical depth of coal carbon which is sufficient to prevent the effluent solute concentration to exceed $C_B$ at zero time:

$$D_O = \frac{V}{KN_O} \ln \left(\frac{C_O}{C_B} - 1\right)$$

$$N_O = \text{(slope of the line) } C_O V$$

From the graph Figure 76 slope = 538.

$$C_O = \frac{5 \text{ mg/l}}{10^6} (62.4 \text{ ft}^3) = 3.12 \times 10^{-4} \text{ lb/ft}^3$$

$$V = 10 \text{ ft/hr (based on a contact time of 30 minutes and 1 gpm/ft}^2)$$

$$N_O = 538 \times 3.12 \times 10^{-4} \times 10 = 1.679 \text{ lb/ft}^3$$

$$\ln = \left(\frac{C_O}{C_B} - 1\right) = \ln \left(\frac{5}{.5} - 1\right) = 2.197$$

where
$$C_O = 5 \text{ mg/l}$$
$$C_B = 0.5 \text{ mg/l}$$

K may be calculated from the intercept of the line  graph:

b the intercept from Figure 76 is $\simeq$ 100.

$$b = \frac{1}{C_O K} \ln \left(\frac{C_O}{C_B} - 1\right)$$

OR
$$K = \frac{\ln \left(\frac{C_O}{C_B} - 1\right)}{C_O (b)} = \frac{2.197}{3.12 \times 10^{-4} \times 100} = 70.42 \text{ ft}^3/\text{lb/hr}$$

Then $D_O$ (critical depth) $= \dfrac{V}{KN_O} \ln \left(\dfrac{C_O}{C_B} - 1\right) =$

$$\frac{10}{70.42 \times 1.679} \times 2.197 \qquad = 0.186 \text{ ft}$$

With a 1 ft bed depth and the above values calculated, the service life would be:

$$t = \frac{N_o}{C_o V} \left[ D - \frac{V}{KN_o} \ln \left( \frac{C_o}{C_B} - 1 \right) \right]$$

$$= \frac{1.679}{3.12 \times 10^{-4} \times 10} \left[ 1 - \frac{10}{70.42 \times 1.679} \times 2.197 \right]$$

$$= 438 \text{ hrs}$$

$$= 18.25 \text{ days}$$

An application to Iona values where:

Flow rate = 70 M.G.D.

Lead content ≈ 0.2 mg/l

At 70 M.G.D. = 48,611.1 gpm

At an inflow (applied to bed) rate

$$= 1 \text{ gpm/ft}^2$$

Area of bed = 48,611.1 $ft^2$ (1.1 acres)

$V_o$ = 10 ft/hr

$N_o$ = 1.679 lbs/$ft^3$

K = 70.416 $ft^3$/lb/hr

$C_o$ = 0.2 mg/l = 0.1248 $\times 10^{-5}$ lb/$ft^3$

$C_B$ (required) = 0.05 mg/l (max. drinking water standard for lead).

$$\ln \left( \frac{C_o}{C_B} - 1 \right) = \ln \left( \frac{0.2}{0.05} - 1 \right) = 1.0986$$

Contact time required is 30 minutes, and

Flow rate = 1 gpm/$ft^2$

$$= 0.16 \text{ ft}^3/\text{ft}^2/\text{min}$$

$$= 0.16 \text{ f.p.m.}$$

∴ Required depth for 30 minutes contact time is 0.16 × 30

$$= 4.8 \text{ ft (say 5 ft bed depth)}$$

Service Life would be:

$$t = \frac{N_o}{C_o V} [D - \frac{V}{KN_o} \ln (\frac{C_o}{C_B} - 1)$$

$$= \frac{1.679}{0.1248 \times 10^{-5} \times 10} (5 - \frac{10}{70.42 \times 1.679} \times 1.0986$$

$$= 66,017.5 \text{ hrs}$$

$$= 2750 \text{ days}$$

$$= 7.5 \text{ years}$$

Total Volume of Wastewater Handled:

70 M.G.D. X 2750 = $1.925 \times 10^{11}$ gals

Annual Volume $70 \times 10^6 \times 365 = 2.555 \times 10^{10}$ gals

Life of Bed $= \dfrac{1.925 \times 10^{11}}{2.555 \times 10^{10}} = 7.5$ years

Changes (renewal) per year $= \dfrac{2.555 \times 10^{10}}{1.925 \times 10^{11}} = 0.1327$ of total bed

Total Volume of Coal:

| | | |
|---|---|---|
| Surface area | = | $48,611 \text{ ft}^2$ |
| Volume | = | $48,611 \times 5 = 243,055 \text{ ft}^3$ |
| Density of coal | $\approx$ | $42.7 \text{ lbs/ft}^3$ |
| ∴ Weight of coal | = | $42.7 \times 243,055$ |
| | = | 5189.2 tons |

Quantity required/year = $5189.2 \times .1327 = 688.6$ tons

Quantity required/day = 1.89 (say 2 tons)

Total Lead removed daily = 0.2 - 0.05 = 0.15 mg/l

$$= \frac{0.15 \times 70 \times 10^6}{\text{day}} \times \frac{10 \text{ lb/gal}}{10^6} = 105 \text{ lb.}$$

Efficiency of Coal Carbon Bed:

$$\text{Total lead removed} = 105 \times 365 = 38,325 \text{ lbs}$$

$$\text{Total capacity/year} = 1.679 \times \frac{243,055}{7.5} = 54,;23.25$$

$$\text{Efficiency} = \frac{38,325}{54,123.25} \times 100 = 70.8\%$$

Additional laboratory experiments are necessary to fortify the above calculations and estimates. The experimental work requires additional time to complete the 0.5 effluent value for the 4 ft column. Application rates of the lead solution at 2 gpm/ft$^2$ and 5 gpm/ft$^2$ would give additional reliable values for calculation purposes.

D - 1.  TABLE 1.  CONTINUOUS COLUMN ADSRPTION. PROCESS

Coal Size: 0.533 mm
Column dia: 1 7/8" (4.76 cm.)   REMOVAL OF LEAD—EFFECT OF BED DEPTH

| Day | Volume throughput per column Liters | gals. | Column service time hrs. | Influent conc. mg/l | Total of lead applied to each column mgs. | COAL BED 1 FT. DEPTH Effl. conc. mg/l | Removal of Pb mg/l | % Removal efficiency | Cumulative Pb removed mgs. | COAL BED 2 FT. DEPTH Effl. conc. mg/l | Removal of Pb mg/l | % Removal efficiency | Cumulative Pb removed mgs. | COAL BED 4 FT. DEPTH Effl. conc. mg/l | Removal of Pb mg/l | % Removal efficiency | Cumulative Pb removed mgs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 13.1 | 4.0 | 3 | 4.26 | 76.60 | <0.014 | >4.246 | >99.7 | 76.60 | <0.01 | >4.25 | 99.76 | 76.66 | <0.01 | >4.25 | 99.8 | 76.77 |
| 2 | 87.2 | 19.3 | 24 | 4.76 | 491.83 | 0.037 | 4.723 | 99.2 | 483.35 | <0.01 | >4.75 | 99.79 | 490.77 | <0.01 | >4.75 | 99.8 | 491.65 |
| 3 | 82.6 | 18.3 | 20 | 5.14 | 916.61 | 0.081 | 5.059 | 98.4 | 906.44 | <0.01 | >5.13 | 99.80 | 914.73 | <0.01 | >5.13 | 99.8 | 915.61 |
| 4 | 109.7 | 24.3 | 22 | 4.66 | 1427.99 | 0.091 | 4.569 | 98.0 | 1407.84 | <0.01 | >4.65 | 99.78 | 1425.01 | <0.01 | >4.65 | 99.8 | 1425.96 |
| 5 | 75.4 | 16.7 | 23 | 5.28 | 1826.19 | 0.126 | 5.154 | 97.6 | 1796.54 | <0.01 | >5.27 | 99.3 | 1822.46 | <0.01 | >5.27 | 99.8 | 1823.35 |
| 6 | 79.9 | 17.7 | 22 | 5.16 | 2238.65 | 0.162 | 4.998 | 96.9 | 2196.05 | 0.027 | 5.13 | 99.48 | 2232.46 | <0.01 | >5.15 | 99.8 | 2235.01 |
| 7 | 79.9 | 17.7 | 20 | 5.24 | 2657.5 | 0.183 | 5.057 | 96.5 | 2600.27 | <0.01 | >5.23 | 99.8 | 2650.51 | <0.01 | >5.23 | 99.8 | 2653.06 |
| 8 | 58.7 | 13.0 | 18 | 4.96 | 2948.69 | 0.212 | 4.748 | 95.7 | 2869.01 | <0.01 | >4.95 | 99.8 | 2941.11 | <0.01 | >4.95 | 99.8 | 2943.66 |
| 9 | 45.2 | 10.0 | 18 | 4.95 | 3172.23 | 0.236 | 4.714 | 95.2 | 3091.89 | <0.01 | >4.94 | 99.8 | 3164.20 | <0.01 | >4.94 | 99.8 | 3166.75 |
| 10 | 45.2 | 10.0 | 17 | 5.73 | 3431.00 | 0.273 | 5.457 | 95.2 | 3338.33 | <0.01 | >5.74 | 99.8 | 3393.42 | <0.01 | >5.72 | 99.8 | 3425.07 |
| 11 | 45.2 | 10.0 | 17 | 4.89 | 3651.81 | 0.244 | 4.645 | 95.0 | 3548.14 | 0.02 | 4.87 | 99.6 | 3613.35 | <0.01 | >4.88 | 99.8 | 3645.45 |
| 12 | 60.1 | 13.3 | 20 | 4.42 | 3917.29 | 0.22 | 4.200 | 95.0 | 3800.40 | 0.02 | 4.40 | 99.5 | 3877.63 | <0.01 | >4.41 | 99.8 | 3910.33 |
| 13 | 52.3 | 11.7 | 20 | 4.32 | 4145.55 | 0.22 | 4.100 | 94.9 | 4017.03 | 0.03 | 4.29 | 99.3 | 4104.30 | <0.01 | >4.31 | 99.8 | 4168.06 |
| 14 | 54.2 | 12.0 | 24 | 4.35 | 4381.29 | 0.22 | 4.130 | 94.9 | 4240.84 | 0.03 | 4.32 | 99.3 | 4338.41 | <0.01 | >4.34 | 99.8 | 4403.25 |
| 15 | 45.2 | 10.0 | 16 | 4.30 | 4575.48 | 0.22 | 4.08 | 94.88 | 4425.09 | 0.03 | 4.27 | 99.3 | 4531.24 | <0.01 | >4.31 | 99.8 | 4596.99 |
| 16 | 67.7 | 15.0 | 20 | 4.18 | 4858.63 | 0.258 | 3.922 | 93.8 | 4691.77 | 0.03 | 4.15 | 99.28 | 4812.36 | <0.01 | >4.34 | 99.8 | 4879.47 |
| 17 | 85.5 | 19.0 | 18 | 4.06 | 5206.99 | 0.466 | 3.594 | 88.5 | 5000.15 | 0.04 | 4.02 | 99.0 | 5157.29 | <0.01 | >4.17 | 99.9 | 5226.93 |
| 18 | 67.7 | 15.0 | 18 | 4.14 | 5487.43 | 0.159 | 3.981 | 96.1 | 5269.82 | 0.048 | 4.092 | 98.8 | 5434.48 | <0.01 | >4.05 | 99.8 | 5506.75 |
| 19 | 45.2 | 12.0 | 16 | 4.38 | 5724.79 | 0.167 | 4.213 | 96.1 | 5498.13 | 0.057 | 4.323 | 98.7 | 5667.75 | <0.01 | >4.13 | 99.8 | 5743.57 |
| 20 | 72.2 | 16.0 | 20 | 4.36 | 6039.83 | 0.214 | 4.146 | 95.1 | 5797.70 | 0.067 | 4.29 | 98.5 | 5978.73 | <0.01 | >4.37 | 99.8 | 6057.83 |
| 21 | 45.2 | 10.0 | 16 | 4.47 | 6241.7 | 0.238 | 4.232 | 94.7 | 5988.82 | 0.071 | 4.4 | 98.4 | 6177.43 | <0.01 | >4.35 | 99.8 | 6259.29 |
| 22 | 76.8 | 17.0 | 18 | 4.71 | 6603.3 | 0.470 | 4.24 | 90.0 | 6314.33 | 0.167 | 4.54 | 96.4 | 6525.97 | <0.01 | >4.46 | 99.8 | 6517.05 |
| 23 | 81.3 | 18.0 | 20 | 4.48 | 6967.47 | 0.500 | 3.98 | 88.8 | 6637.86 | 0.30 | 4.18 | 93.3 | 6865.75 | 0.048 | 4.66 | 98.9 | 6577.16 |
| 24 | 67.7 | 15.0 | 20 | 4.72 | 7287.2 | 0.530 | 4.19 | 88.7 | 6921.69 | 0.33 | 4.39 | 93.0 | 7163.13 | 0.048 | 4.43 | 98.9 | 7290.12 |
| 25 | 63.2 | 14.0 | 18 | 4.67 | 7582.46 | 0.556 | 4.114 | 88.1 | 7181.79 | 0.324 | 4.346 | 93.0 | 7437.9 | 0.105 | 4.62 | 97.9 | 7579.69 |
| | | | | | | | | | | | | | | 0.0925 | 4.58 | 98.0 | |

TABLE 1. (Continued)

| Day | Volume throughput per column Liters | gals. | Column Service time hrs. | Influent conc. mg/l | Total of lead applied to each column mgs. | COAL BED 1 FT. DEPTH Effl. conc. mg/l | Removal of Pb mg/l | % Removal efficiency | Cumulative Pb removed mgs. | COAL BED 2 FT. DEPTH Effl. conc. mg/l | Removal of Pb mg/l | % Removal Efficiency | Cumulative Pb removed mgs. | COAL BED 4 FT. DEPTH Effl. conc. mg/l | Removal of Pb mg/l | % Removal Efficiency | Cumulative Pb removed mgs. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 26 | 49.7 | 11.0 | 16 | 4.71 | 7816.43 | 0.510 | 4.200 | 89.0 | 7390.43 | 0.331 | 4.379 | 92.97 | 7655.43 | 0.070 | 4.64 | 93.5 | 7810.19 |
| 27 | 63.2 | 14.0 | 17 | 4.71 | 8114.72 | 0.602 | 4.103 | 87.2 | 7650.15 | 0.331 | 4.379 | 92.97 | 7932.29 | 0.070 | 4.64 | 98.5 | 8103.55 |
| 28 | 63.2 | 14.0 | 20 | 5.04 | 8432.87 | 0.648 | 4.392 | 87.1 | 7927.83 | 0.331 | 4.709 | 93.43 | 8230.01 | 0.070 | 4.97 | 98.6 | 8417.77 |
| 29 | 63.2 | 14.0 | 18 | 4.76 | 8733.82 | 0.701 | 4.059 | 85.3 | 8194.46 | 0.324 | 4.436 | 93.19 | 8510.47 | 0.0925 | 4.67 | 98.1 | 8713.03 |
| 30 | 87.2 | 19.3 | 24 | 4.6 | 9134.75 | 0.710 | 3.890 | 84.6 | 8523.51 | 0.285 | 4.315 | 93.80 | 8886.56 | 0.0925 | 4.51 | 93.0 | 9106.04 |
| 31 | 70.0 | 15.5 | 20 | 4.86 | 9474.94 | 0.740 | 4.120 | 84.7 | 8811.90 | 0.324 | 4.536 | 93.30 | 9204.04 | 0.162 | 4.7 | 96.7 | 9475.03 |
| 32 | 76.8 | 17.0 | 24 | 5.05 | 9862.64 | 0.765 | 4.285 | 84.8 | 9140.87 | 0.357 | 4.693 | 92.93 | 9564.36 | 0.102 | 4.95 | 98.0 | 9815.05 |
| 33 | 45.2 | 10.0 | 16 | 5.3 | 10101.99 | 0.867 | 4.433 | 83.6 | 9341.06 | 0.357 | 4.943 | 93.20 | 9787.58 | 0.127 | 5.17 | 97.5 | 10049.53 |
| 34 | 103.9 | 23.0 | 24 | 4.86 | 10606.79 | 0.775 | 4.085 | 84.0 | 9765.36 | 0.306 | 4.554 | 93.70 | 10260.59 | 0.128 | 5.35 | 97.3 | 10539.83 |
| 35 | 58.7 | 13.0 | 18 | 5.53 | 10931.45 | 0.918 | 4.612 | 83.3 | 10036.12 | 0.383 | 5.147 | 93.00 | 10562.76 | 0.178 | 5.35 | 96.7 | 10852.92 |
| 36 | 67.7 | 15.0 | 24 | 4.46 | 11233.57 | 0.765 | 3.695 | 82.8 | 10286.42 | 0.306 | 4.893 | 93.10 | 10844.15 | 0.153 | 4.31 | 96.7 | 11145.88 |
| 37 | 63.2 | 14.0 | 24 | 5.25 | 11565.50 | 0.918 | 4.332 | 82.5 | 10560.31 | 0.357 | 4.442 | 93.20 | 11153.51 | 0.204 | 5.05 | 96.2 | 11465.16 |
| 38 | 90.3 | 20.0 | 24 | 4.85 | 12003.55 | 0.714 | 4.136 | 85.2 | 10933.87 | 0.408 | 4.474 | 91.60 | 11554.71 | 0.204 | 4.65 | 95.9 | 11885.15 |
| 39 | 49.7 | 11.0 | 24 | 4.88 | 12245.97 | 0.794 | 4.086 | 83.7 | 11136.85 | 0.406 | 4.803 | 91.60 | 11776.96 | 0.203 | 4.68 | 95.9 | 12117.63 |
| 40 | 4.2 | 9.3 | 16 | 5.12 | 12461.00 | 0.754 | 4.366 | 85.2 | 11320.22 | 0.317 | 4.076 | 93.80 | 11978.68 | 0.210 | 4.91 | 93.8 | 12323.84 |
| 41 | 76.8 | 17.0 | 20 | 4.48 | 12804.94 | 0.771 | 3.709 | 82.7 | 11604.97 | 0.404 | 4.635 | 90.98 | 12291.60 | 0.278 | 4.20 | 97.4 | 12646.28 |
| 42 | 51.0 | 11.3 | 16 | 5.04 | 13062.14 | 0.848 | 4.192 | 83.1 | 11818.89 | 0.405 | 4.601 | 91.96 | 12528.13 | 0.134 | 4.91 | 96.0 | 12896.84 |
| 43 | 51.0 | 11.3 | 10 | 5.00 | 13317.29 | 0.869 | 4.131 | 82.6 | 12029.7 | 0.399 | 4.726 | 92.02 | 12762.92 | 0.197 | 4.8 | 97.2 | 13141.79 |
| 44 | 45.2 | 10.0 | 18 | 5.05 | 13545.35 | 0.887 | 4.163 | 82.4 | 12217.70 | 0.324 | 4.378 | 93.5 | 12976.35 | 0.138 | 4.91 | 95.1 | 13363.74 |
| 45 | 67.7 | 15.0 | 22 | 4.77 | 13868.47 | 0.803 | 3.967 | 83.2 | 12485.99 | 0.370 | 4.518 | 91.78 | 13272.91 | 0.231 | 4.54 | 95.1 | 13671.28 |
| 46 | 64.6 | 14.3 | 20 | 4.91 | 14185.55 | 0.833 | 4.077 | 83.0 | 12754.71 | 0.392 | 4.527 | 92.01 | 13564.68 | 0.245 | 4.67 | 95.7 | 13972.86 |
| 47 | 76.8 | 17.0 | 24 | 4.87 | 14559.43 | 0.884 | 3.986 | 81.8 | 13060.72 | 0.343 | 4.484 | 92.95 | 13912.23 | 0.215 | 4.66 | 96.8 | 14330.62 |
| 48 | 72.2 | 16.0 | 24 | 4.78 | 14904.81 | 0.880 | 3.900 | 81.5 | 13342.52 | 0.296 | 4.186 | 93.8 | 14236.22 | 0.147 | 4.63 | 96.6 | 14665.17 |
| 49 | 63.2 | 14.0 | 23 | 4.48 | 15188.05 | 0.863 | 3.617 | 80.7 | 13571.20 | 0.294 | 4.157 | 93.4 | 14500.87 | 0.147 | 4.33 | 96.4 | 14933.93 |
| 50 | 31.6 | 7.0 | 8 | 4.45 | 15328.72 | 0.881 | 3.569 | 80.2 | 13684.02 | 0.323 | 4.02 | 92.70 | 14632.28 | 0.162 | 4.29 | 94.0 | 15074.55 |
| 51 | 67.7 | 15.0 | 20 | 4.45 | 15630.16 | 0.908 | 3.482 | 78.2 | 13919.89 | 0.430 | 3.859 | 90.30 | 14904.59 | 0.269 | 4.21 | 93.0 | 15359.74 |
| 52 | 67.7 | 15.0 | 18 | 4.6 | 15941.76 | 1.452 | 3.148 | 68.4 | 14133.13 | 0.591 | 4.012 | 86.72 | 15166.00 | 0.325 | 4.28 | 92.4 | 15649.67 |
| 53 | 67.7 | 15.0 | 20 | 4.5 | 16246.59 | 1.430 | 3.070 | 68.2 | 14341.09 | 0.588 | | 87.21 | 15437.77 | 0.343 | 4.16 | | 15931.47 |
| 54 | - | - | - | - | - | | | | | - | | - | | - | | - | - |
| 55 | 117.4 | 26.0 | 35 | 4.28 | 16749.13 | 1.350 | 2.930 | 63.4 | 14625.12 | 0.721 | 3.779 | 83.98 | 15881.48 | 0.241 | 4.04 | 94.3 | 16405.83 |
| 56 | 63.2 | 14.0 | 20 | 4.28 | 17019.73 | 1.400 | 2.880 | 67.3 | 14867.21 | 0.700 | 3.580 | 83.6 | 16107.82 | 0.400 | 3.88 | 90.6 | 16651.14 |
| 57 | 45.2 | 10.0 | 24 | 4.00 | 17200.37 | 1.290 | 2.710 | 67.7 | 14989.59 | 0.600 | 2.400 | 85.0 | 16261.36 | 0.350 | 3.65 | 91.2 | 16815.97 |
| 58 | 67.7 | 15.0 | 20 | 4.00 | 17471.33 | 1.300 | 2.700 | 67.5 | 15172.49 | 0.700 | 3.300 | 82.5 | 16484.90 | 0.400 | 3.60 | 90.0 | 17059.83 |
| | | 826.0 | 1129 | | 17471.33 | | | | 15172.49 | | | | 16484.90 | | | | 17059.83 |

FIGURE D-1-1. ADSORPTION OF LEAD ON COAL LABORATORY COLUMNS.

Relationship of Time vs.Column Depth for Break-Through at 0.5 mg/1, Influent Concentration 5 mg/1.
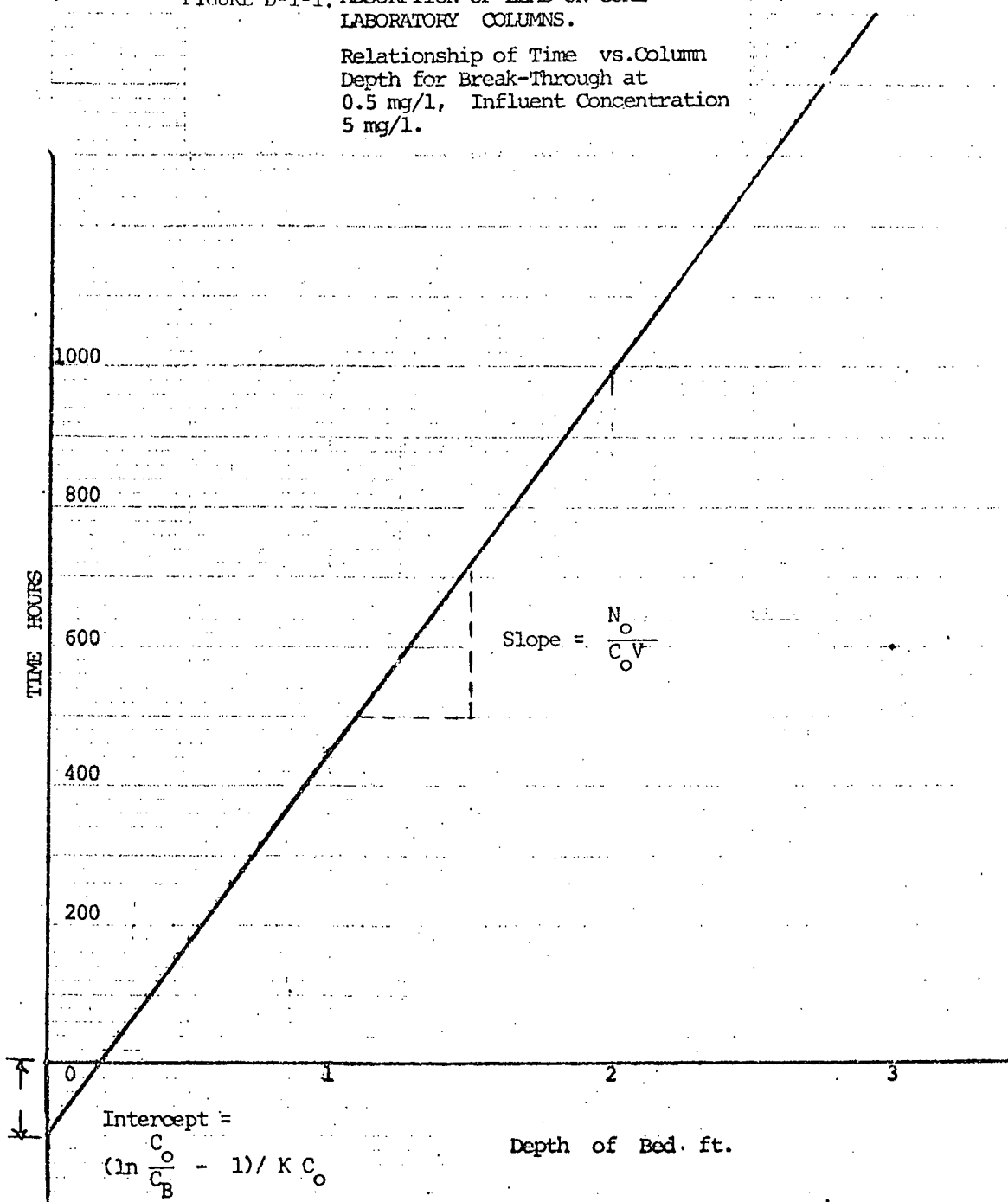
## D-2 TABLE 1 - REDUCTION OF TOTAL AND VOLATILE RESIDUE
## BY HAT CREEK COAL

| Throughput Volume Gallons | Samples | Total Residue mg/l | Volatile Residue mg/l | Fixed Residue mg/l |
|---|---|---|---|---|
| 85 | Original sewage | 500 | 128 | 346 |
|  | Effluent at 1 metre level | 500 | 236* ↑ | 264 (24%) |
|  | Effluent at 2 metre level | 520* ↑ | 230* ↑ | 290 (16%) |
| 34.0 | Original sewage | 544 | 176 | 368 |
|  | Effluent at 2 metre level | 450 (17%) | 108 (39%) | 342 (7%) |

*↑   Increasing of the levels more than the original

(  )   The percentage removal efficiency

D-2 TABLE 2 - TREATMENT OF IONA SEWAGE WITH COAL

REDUCTION OF $BOD_5$

| Volume Throughput gals. | Influent $BOD_5$ mg/l | 0.5 metre level | | | 1 metre level | | | 2 metre level | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Effluent $BOD_5$ mg/l | Removed $BOD_5$ mg/l | % Removal | Effluent $BOD_5$ mg/l | Removed $BOD_5$ mg/l | % Removal | Effluent $BOD_5$ mg/l | Removed $BOD_5$ mg/l | % Removal |
| Down flow: | | | | | | | | | | |
| 129.2 | 151.0 | 25.0 | 126.0 | 83.4 | 22.0 | 129.0 | 85.4 | 19.5 | 131.5 | 87.1 |
| 157.6 | - | - | - | - | - | - | - | - | - | - |
| Up flow: | | | | | | | | | | |
| 89.0 | 95.0 | 50.5 | 44.5 | 46.8 | 41.2 | 53.8 | 56.6 | 38.3 | 56.7 | 59.7 |
| 105.8 | 41.5 | <10 | 36.5 | 88.0 | <10 | 36.5 | 88.0 | <10 | 36.5 | 88.0 |
| 311.8 | 122.5 | 78.5 | 44 | 35.9 | 80.0 | 42.5 | 34.7 | 86.0 | 36.5 | 29.8 |
| 182.1 | 85.5 | 21.7 | 63.8 | 74.6 | 15.0 | 70.5 | 82.5 | 10.0 | 75.5 | 88.3 |
| After Backwashing: | | | | | | | | | | |
| 192.5 | 86.3 | 35.3 | 51.0 | 59.1 | 25.0 | 61.3 | 71.0 | 21.7 | 64.6 | 74.9 |
| 209.3 | 150.8 | 59.2 | 91.6 | 60.7 | 66.0 | 84.8 | 56.2 | 76.4 | 74.4 | 49.3 |
| 412.2 | 152.3 | 97.2 | 55.1 | 36.2 | 97.6 | 54.7 | 35.9 | 94.5 | 57.8 | 38.0 |
| 1789.5 (total) | 110.6 (average) | 46.5 | 64.1 | 58.0 | 44.0 | 66.6 | 60.2 | 43.9 | 66.7 | 60.3 |

Total $BOD_5$ applied = 893800 mgs.

Total $BOD_5$ removed at 0.5 metre level = 518017 mgs.

Average capacity of the coal = 95 mgs $BOD_5$ per gram of coal.

## D-2 TABLE 3 - TREATMENT OF IONA SEWAGE WITH COAL
## REMOVAL OF COD

| Volume Throughput gals | Influent COD mg/l | 0.5 metre level | | | 1 metre level | | | 2 metre level | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Effluent COD mg/l | Removed COD mg/l | % Removal | Effluent COD mg/l | Removed COD mg/l | % Removal | Effluent COD mg/l | Removed COD mg/l | % Removal |
| Down flow: | | | | | | | | | | |
| 129.2 | 166.0 | 79.0 | 87.0 | 54.4 | 71.1 | 94.9 | 57.2 | 3.5 | 16.25 | 97.9 |
| 157.6 | - | - | - | - | - | - | - | - | - | - |
| Up flow: | | | | | | | | | | |
| 89.0 | 200.7 | 83.8 | 111.9 | 55.8 | 92.6 | 108.1 | 53.9 | 46.3 | 154.4 | 76.9 |
| 105.8 | 154.4 | 92.6 | 61.8 | 40.0 | 61.8 | 92.6 | 60.0 | 46.0 | 108.4 | 70.2 |
| 311.8 | 381.9 | 129.7 | 34.0 | - | - | - | - | - | - | - |
| 182.1 | 126.5 | 55.3 | 71.1 | 56.3 | - | - | - | - | - | - |
| After Backwashing: | | | | | | | | | | |
| 192.5 | 110.7 | 47.4 | 63.3 | 57.2 | 43.4 | 67.3 | 60.8 | 39.5 | 71.2 | 64.3 |
| 209.3 | 200.1 | - | - | - | - | - | - | 50.0 | 150.1 | 75.0 |
| 412.2 | 177.0 | 96.3 | 80.8 | 45.7 | 84.7 | 92.3 | 52.2 | 61.7 | 115.3 | 65.1 |
| 1789.5 (total) | 189.6 (average) | 101.6 | 88.0 | 46.6 | 70.7 | 118.9 | 62.7 | 41.6 | 148.0 | 78.0 |

Total COD applied = 1,532,200 mgs.
Total COD removed at 0.5 metre level = 711,160 mgs.
Capacity of the coal = 130.4 mgs COD per gram coal

## D-2 TABLE 4 - TREATMENT OF IONA SEWAGE WITH COAL

### REMOVAL OF TOC

| Volume Throughput gals. | Influent TOC mg/1 | 0.5 metre level | | | 1 metre level | | | 2 metre level | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Effluent TOC mg/1 | Removed TOC mg/1 | % Removal | Effluent TOC mg/1 | Removed TOC mg/1 | % Removal | Effluent TOC mg/1 | Removed TOC mg/1 | % Removal |
| Down flow: | | | | | | | | | | |
| 129.2 | 47.5 | 16.0 | 31.5 | 66.3 | 17.0 | 30.5 | 64.2 | 14.0 | 33.5 | 70.5 |
| 157.6 | - | - | - | - | - | - | - | - | - | - |
| Up flow: | | | | | | | | | | |
| 89.0 | 52.5 | 31.0 | 21.5 | 41.0 | 35.0 | 17.5 | 33.3 | 33.0 | 19.5 | 37.1 |
| 105.8 | 49.0 | 36.0 | 13.0 | 26.5 | 34.0 | 15.0 | 30.6 | 28.5 | 20.5 | 41.8 |
| 311.8 | 77.6 | 48.8 | 28.8 | 37.1 | 50.1 | 27.5 | 35.4 | 47.6 | 30.0 | 38.7 |
| 182.1 | 52.6 | 39.2 | 13.4 | 25.5 | 40.8 | 11.8 | 22.4 | 39.2 | 13.4 | 25.4 |
| After Backwashing: | | | | | | | | | | |
| 192.5 | 50.8 | 36.2 | 14.6 | 29.1 | 41.9 | 8.9 | 17.5 | 36.1 | 14.7 | 28.9 |
| 209.3 | - | - | - | - | - | - | - | - | - | - |
| 412.2 | - | - | - | - | - | - | - | - | - | - |

1789.5
(Total)

-2 TABLE 5 - FIELD STUDY ON THE SEWAGE TREATMENT WITH HAT CREEK COAL

REMOVAL OF $BOD_5$

| Date | Hours Elapsed per Interval | Cumulative Service Time Hours | Flow Rate ml/min | Gallons Charged | Cumulative Gallons Charged | $BOD_5$ in influent Conc. mg/l | $BOD_5$ in influent Cumulative Applied Grams | 0.5 metre level Cumulative Removed Grams | % Removal | 1 metre level Effluent $BOD_5$ mg/l | 1 metre level Cumulative Removed Grams | % Removal | 2 metre level Effluent $BOD_5$ mg/l | 2 metre level Cumulative Removed | % Removal |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Start down flow 8/6/77 | | | | | | | | | | | | | | | |
| 9/6/77 | 23.2 | 23.2 | 275 | 84.6 | 84.6 | 151.0 | 57.7 | 48.1 | 83.4 | 22.0 | 49.3 | 85.4 | 19.5 | 50.2 | 87.1 |
| 10/6/77 | 24.0 | 47.2 | 140 | 44.6 | 129.2 | 82.5 | 74.3 | 56.1 | 75.4 | 41.5 | 57.6 | 77.5 | 38.3 | 59.1 | 79.5 |
| 11/6/77 | 28.5 | 75.7 | 290 | 109.8 | 239.0 | 117.0 | 132.3 | 91.3 | 69.0 | 44.0 | 93.8 | 70.9 | 41.0 | 96.8 | 73.2 |
| 12/6/77 | 24.0 | 99.7 | 150 | 47.8 | 286.8 | 117.0 | 157.6 | 105.8 | 67.1 | 48.0 | 108.7 | 69.0 | 41.0 | 113.2 | 71.3 |
| Start up flow 16/6/77 | | | | | | | | | | | | | | | |
| 17/6/77 | 31.0 | 130.7 | 215 | 89.0 | 375.8 | 95.0 | 195.8 | 127.4 | 65.1 | 41.2 | 130.3 | 66.6 | 40.5 | 135.1 | 69.0 |
| 18/6/77 | 27.0 | 157.7 | 295 | 105.8 | 481.6 | 41.5 | 215.6 | 144.8 | 67.2 | 10 | 147.7 | 68.5 | 10 | 152.5 | 70.8 |
| 21/6/77 | 74.5 | 232.2 | 315 | 311.8 | 793.4 | 122.5 | 388.1 | 206.8 | 53.3 | 80.0 | 207.5 | 53.5 | 86.0 | 203.9 | 52.5 |
| 23/6/77 | 43.5 | 275.7 | 315 | 182.1 | 975.5 | 85.5 | 458.4 | 259.3 | 56.6 | 15.0 | 265.5 | 57.9 | 10.0 | 266.0 | 58.0 |
| 24/6/77 | 26.0 | 301.7 | 315 | 108.8 | 1084.3 | 85.5 | 500.4 | 290.7 | 58.1 | 15.0 | 300.1 | 60.0 | 10.0 | 303.1 | 60.6 |
| After Backwashing | | | | | | | | | | | | | | | |
| 28/6/77 | 20 | 321.7 | 315 | 83.7 | 1168.0 | 86.3 | 533.0 | 304.8 | 57.2 | 35.0 | 319.5 | 59.9 | 33.5 | 323.1 | 63.6 |
| 30/6/77 | 50 | 371.7 | 315 | 209.3 | 1377.3 | 150.8 | 675.5 | 391.4 | 57.9 | 66.0 | 399.7 | 59.2 | 76.4 | 393.4 | 58.2 |
| 4/7/77 | 98.5 | 470.2 | 315 | 412.2 | 1789.5 | 152.3 | 959.0 | 493.2 | 51.4 | 97.6 | 501.5 | 52.3 | 94.5 | 501.0 | 52.2 |

Total $BOD_5$ removed at 0.5 metre level
capacity of coal $= \dfrac{493200}{5454}$

in 70 MGD flow at $BOD_5$ level of 150 mg/1.
load of $BOD_5$ daily
Therefore, quantity of coal required

= 493200 mgs

= 90.4 mgs $BOD_5$ removed per gram of coal

= 47418 kgs = 47.42 tons/day

= 526 tons

367.

TREATMENT OF REFINERY EFFLUENT WITH COAL.

D - 3      TABLE 1

REMOVAL OF PHENOL AND CYANIDE

Particle size of coal 48/100

Contact process

Contact time 24 hrs

| Analyses | Sample code | Effluent conc mg/l | Removed mg/l | % Removed | mgs Removed/ gm Coal |
|---|---|---|---|---|---|
| | $0 - F_1$ | 0.326 | | | |
| | 0.5% cc | 0.075 | 0.251 | 77.0 | 0.0502 |
| | 1.0% cc | 0.08 | 0.246 | 75.5 | 0.0246 |
| Phenol | | | | | |
| | 0.5% sc | 0.266 | 0.06 | 18.4 | 0.012 |
| | 1.0% sc | 0.167 | 0.159 | 48.8 | 0.0159 |
| | 0.5% ac | ± 0.005 N.D. | 0.321 | 98.5 | 0.0642 to 0.0652 |

Detectable limit      0.002 mg/l

Sensitivity      ± 0.005 mg/l

D - 3      TABLE 1 (cont)

ADSORPTION OF CYANIDE

| Analyses | Sample Code | Effluent conc mg/l | REMARKS |
|---|---|---|---|
| | $0 - F_1$ | 0.01 (N.D.) | The initial $CN^-$ concentration was very close to the detectable limit |
| | 0.5 ac | N.D. | $\simeq 0.01$, which makes it difficult to know the effectiveness of the coal |
| Cyanide | 0.5 cc | N.D. | for adsorption of cyanide, running contact experiments with standard |
| | 0.5 sc | N.D. | cyanide solutions of higher concentration will be more helpful to give isotherms. |

D - 3      TABLE 2. Contact Process

AMMONIA NITROGEN $NH_3$-N AND KJELDAHL TOTAL NITROGEN K-N

|  | $NH_3$-N mg/l | K-N |
|---|---|---|
| 0 - $F_1$ | 2.7 | 6.6 |
| 0.5% ac | 3.0 | 5.1 |
| 0.5% sc | 3.3 | 5.9 |
| 1.0% sc | 4.0 | 7.3 |
| 2.0% sc | 5.3 | 8.0 |
| 4.0% sc | 7.7 | 9.5 |
| 0.5% cc | 2.5 | 4.4 |
| 1.0% cc | 2.6 | 5.9 |
| 2.0% cc | 2.1 | 5.8 |
| 4.0% cc | 1.8 | 5.1 |

TABLE  3. Contact process

REMOVAL OF SOLIDS

A.   Total Residue

| Analyses | Sample Code | Effluent Conc mg/l | Removed mg/l | % Removed | mgs Removed/ gm Coal |
|---|---|---|---|---|---|
| | $0 - F_1$ | 3490.0 | | | |
| | 0.5% ac | 3200.0 | 290 | 8.3 | 58 |
| | 0.5% sc | 3180.0 | 310 | 8.9 | 62 |
| | 1.0% sc | 3440.0 | 50 | 1.4 | 5 |
| Total Residue | 2.0% sc | 3740.0 | -250 | - | - |
| | 4.0% sc | 3730.0 | -240 | - | - |
| | 0.5% cc | 3120.0 | 370 | 10.6 | 74 |
| | 1.0% cc | 3080.0 | 410 | 11.75 | 41 |
| | 2.0% cc | 3560 | - 70 | - | - |
| | 4.0% cc | 3650 | -160 | - | - |

D - 3     TABLE  3 (Cont)

REMOVAL OF SOLIDS

B. Volatile Solids

| | Sample Code | Effluent Conc mg/l | Removed mg/l | % Removed | mgs Removed/ gm Coal |
|---|---|---|---|---|---|
| | $0 - F_1$ | 301 | | | |
| Volatile Solids | 0.5% ac | 120 | 181 | 60.1 | 36.2 |
| | 0.5% sc | 200 | 101 | 33.6 | 20.2 |
| | 1.0% sc | 230 | 71 | 23.6 | 7.1 |
| | 2.0% sc | 270 | 31 | 10.3 | 1.55 |
| | 4.0% sc | 450 | - | - | - |
| | 0.5% cc | 240 | 61 | 20.3 | 12.2 |
| | 1.0% cc | 130 | 171 | 56.8 | 17.1 |
| | 2.0% cc | 250 | 51 | 16.9 | 2.55 |
| | 4.0% cc | 565 | - | - | - |

| Analyses | Sample Code | $BOD_5$ Av. | $BOD_5$ Removed | % Removal | mgs Removed/ gm Coal |
|---|---|---|---|---|---|
| | 0 - $F_1$ | 26.10 | | | |
| | o.5% ac | 4.80 | 21.3 | 82 | 4.26 |
| $BOD_5$ Removal | o.5% sc | 19.20 | 6.9 | 26 | 1.38 |
| | 1.0% sc | 18.00 | 8.1 | 31 | 0.81 |
| | 2.0% sc | 11.70 | 14.4 | 55 | 0.72 |
| | 4.0% sc | 5.70 | 20.4 | 78 | 0.51 |
| | 0.5% cc | 18.30 | 7.8 | 30 | 1.56 |
| | 1.0% cc | 17.70 | 8.4 | 32 | 0.84 |
| | 2.0% cc | 14.40 | 11.7 | 45 | 0.59 |
| | 4.0% cc | 12.90 | 13.2 | 51 | 0.33 |

D-3     TABLE 4   (Cont)

| Analyses | Sample Code | COD | COD Removed | % Removal | mgs Removed/ gm Coal |
|---|---|---|---|---|---|
| | 0 - $F_1$ | 234 | | | |
| | 0.5% ac | 181 | 53 | 23 | 10.6 |
| COD Removal | 0.5% sc | 181 | 53 | 23 | 10.6 |
| | 1.0% sc | 170 | 64 | 27 | 6.4 |
| | 2.0% sc | 275 | — | — | — |
| | 4.0% sc | 294 | — | — | — |
| | 0.5% cc | 94.3 | 140 | 60 | 28 |
| | 1.0% cc | 89.9 | 144 | 62 | 14.4 |
| | 2.0% cc | 43 | 191 | 82 | 9.5 |
| | 4.0% cc | 45 | 189 | 81 | 4.7 |

D-3    TABLE 4    (Cont)

| Analyses | Sample Code | FIRST EXPERIMENTS | | | | SECOND EXPERIMENTS | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | TOC | I.C. | TOC Removal | % Removal | TOC | I.C. | TOC Removal | % Removal |
| | | ppm | ppm | ppm | | ppm | ppm | ppm | |
| Total Organic Carbon | $0 - F_1$ | 87 (unfiltered) | 40 | | | 70 (filtered) | 55 | . | |
| | 0.5% ac | 55 | 46 | 32 | 37 | 68 | 50 | 2 | 3 |
| | 0.5% sc | 50 | <10 | 37 | 43 | 64 | 12 | 6 | 9 |
| | 1.0% sc | 55 | <10 | 32 | 38 | 73 | 10 | – | – |
| | 2.0% sc | 60 | <10 | 27 | 31 | 81 | <10 | – | – |
| | 4.0% sc | 90 | <10 | – | – | 108 | <10 | – | – |
| | 0.5% cc | 48 | 23 | 39 | 45 | 57 | <10 | 13 | 19 |
| | 1.0% cc | 48 | 23 | 39 | 45 | 58 | 40 | 12 | 17 |
| | 2.0% cc | 40 | 20 | 47 | 54 | 42 | 28 | 28 | 40 |
| | 4.0% cc | 41 | <10 | 46 | 53 | 43 | 28 | 27 | 39 |

NOTE:        TOC  =  Total organic carbon

I.C. =  Inorganic carbon.

D-3    TABLE 5

## REMOVAL OF OIL AND GREASE

| Sample Code | Effluent Conc mg/1 | Removed mg/1 | % Removed | mgs Removed/ gm Coal |
|---|---|---|---|---|
| 0 - $F_1$ | 100.0 | | | |
| 0.5% cc | 16.5 | 83.5 | 83.5 | 16.7 |
| 0.5% sc | 30.0 | 70.0 | 70.0 | 14.0 |

D-3    TABLE 6    Contact Process

## EFFECT OF TREATMENT ON pH

| Sample Code | Batch Exp. (1) pH | Batch Exp. (2) pH |
|---|---|---|
| 0 - $F_1$ (origin) | 8.20 | 7.62 |
| 0.5% ac | 8.35 | 7.50 |
| 0.5% cc | 7.35 | 6.95 |
| 1.0% cc | 7.30 | 6.85 |
| 2.0% cc | 6.80 | 6.85 |
| 4.0% cc | 7.18 | 6.75 |
| o.5% sc | 5.6 | 5.05 |
| 1.0% sc | 4.48 | 4.25 |
| 2.0% sc | 3.90 | 3.72 |
| 4.0% sc | 3.65 | 3.41 |

FIG.(1): CHANGE OF pH ON TREATMENT WITH COAL

ORIGINAL pH

NON-OXIDIZED COAL(CORE COAL)

pH

OXIDIZED COAL(SURFACE COAL)

AMOUNT OF COAL USED %W/W

374.
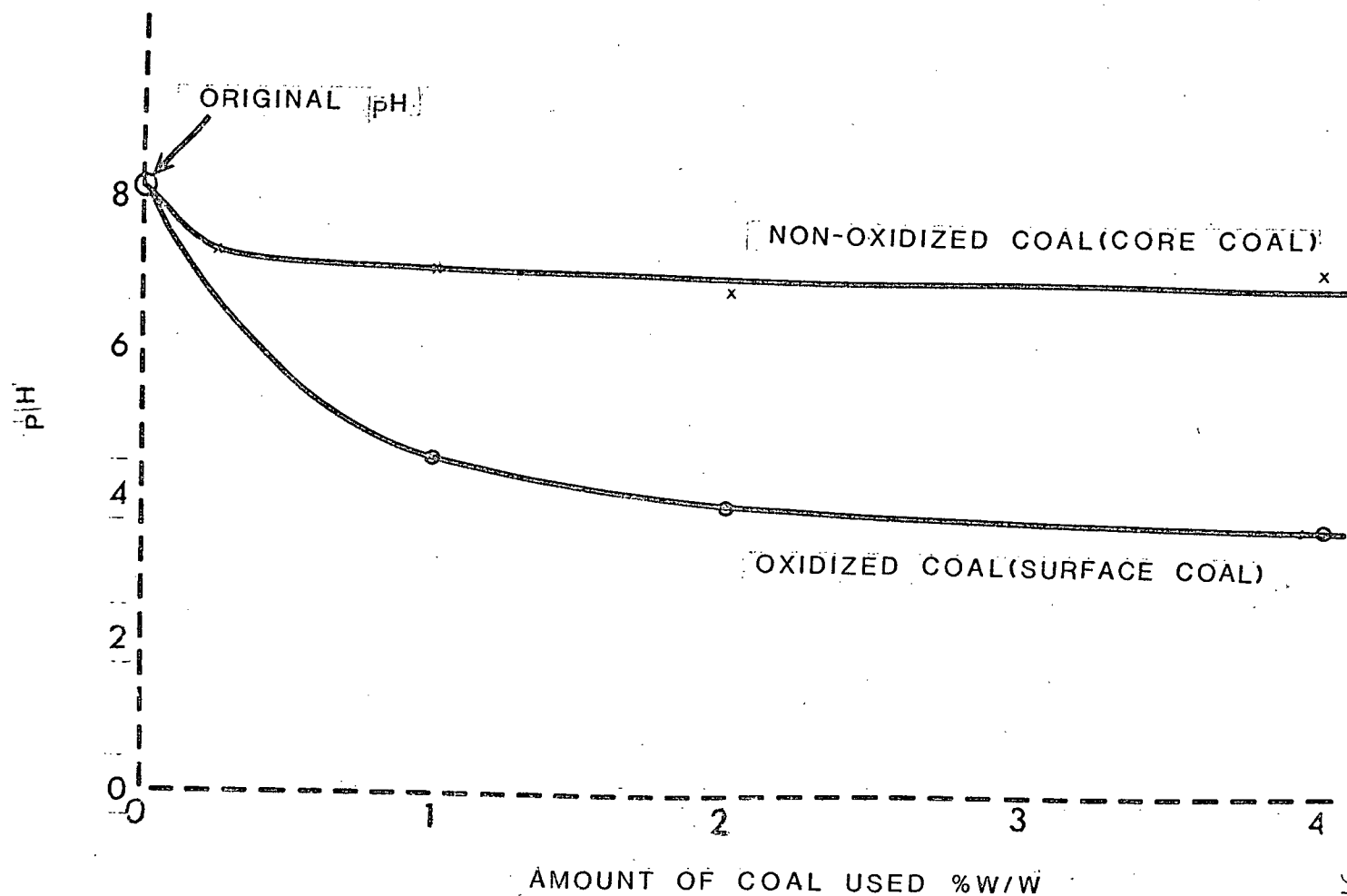
## TABLE 7. REFINERY WASTES COLUMN LEACHING

| Sample Code | Volume Throughput Liters | T.R. | V.S. | T.S.S. | SOLIDS ORGANIC MATTER BOD₅ | COD | TOC | TIC | Phenol | Oil & Grease | pH |
|---|---|---|---|---|---|---|---|---|---|---|---|
| O-F₁ | | | | | | | | | | | |
| SURFACE COAL OXIDIZED 14/20 MESH | | | | | | | | | | | |
| 0 | 3310 | 164 | 71 | 57 | 235 | 85 | 30 | 0.81 | 69.6 | – | |
| 1 | 2718 | 426 | 2.0 | 5.1 | -331 | 28 | 10 | 0.068 | – | 3.02 | |
| 2 | – | – | – | – | 52 | 34 | 13 | – | 8.7 | 3.03 | |
| 3 | 3212 | 250 | 2.5 | 7.0 | 134 | 38 | 10 | – | – | 3.05 | |
| 4 | 3192 | 238 | – | – | – | 56 | 18 | – | – | 3.09 | |
| 5 | 3232 | 240 | – | 8.6 | 81 | 47 | 12 | 0.12 | – | 3.19 | |
| 6 | 3206 | 168 | 1.5 | – | – | 52 | 13 | – | – | 3.15 | |
| 7 | 2618 | 138 | – | 10.0 | -690 | 47 | 10 | – | – | 3.19 | |
| 8 | 3006 | 256 | – | – | – | 64 | 17 | – | – | 3.18 | |
| 9 | 3200 | 230 | – | 5.3 | -197 | 52 | 10 | – | 11.2 | 3.18 | |
| 10 | – | – | 3.0 | – | – | 50 | 12 | 0.29 | – | 3.2 | |
| CORE COAL NON-OXIDIZED 14/20 MESH | | | | | | | | | | | |
| 1 | 2938 | 120 | 4.0 | 11.8 | 56 | 35 | 10 | 0.013 | – | 5.9 | |
| 2 | 3150 | 212 | – | – | 70 | 55 | 15 | – | 7.25 | 5.9 | |
| 3 | 3308 | 182 | 7.5 | 17.2 | 67 | 48 | 18 | – | – | 6.08 | |
| 4 | 3226 | 176 | – | – | – | 73 | 35 | – | – | 6.15 | |
| 5 | 3192 | 170 | – | 20.1 | – | 68 | 21 | 0.12 | – | 6.10 | |
| 6 | 2296 | 158 | 2.5 | – | – | 68 | 22 | – | – | 6.15 | |
| 7 | 3110 | – | – | 21.5 | 120 | 58 | 22 | – | – | 6.05 | |
| 8 | 3286 | 188 | – | – | – | 66 | 20 | – | – | 6.22 | |
| 9 | 3240 | 164 | – | 21.3 | – | 70 | 23 | – | 7.46 | 6.13 | |
| 10 | 3334 | 140 | 2.5 | – | 155 | 68 | 23 | 0.11 | – | – | |

APPENDIX D-4 :  DESIGN OF A COAL BED FOR REMOVAL OF PHENOL, CYANIDE, AND AMMONIA.

D-4   · TABLE 1.  CONTINUOUS COLUMN ADSORPTION PROCESS.

HAT CREEK SURFACE COAL SIZE 4/14 TYLER MESH                                    PHENOL REMOVAL                                    BREAK-THROUGH 0.2 mg./1

| Run No. | Volume Throughput Liters | Volume Throughput Gals | Service Time Hours | Influent PhoH Conc. mg/1 | Cumulative Total Phenol Applied mgs | 1 FOOT DEPTH Effl. Conc. mg/1 | Removal PhoH mg/1 | Cumulative Phenol Removed mgs | % Removal Efficiency | 3 FEET DEPTH Effl. Conc. mg/1 | Removal PhoH mg/1 | Cumulative Phenol Removed mgs | % Removal Efficiency | 5 1/2 FEET DEPTH Effl. Conc. mg/1 | Removal PhoH mg/1 | Cumulative Phenol Removed mgs | % Removal Efficiency |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 45 | 10 | 1 | 1.87 | 84 | 0.84 | 1.03 | 46 | 54.8 | 0.138 | 1.732 | 78 | 92.9 | 0.08 | 1.79 | 80.6 | 95.9 |
| 2 | 1059 | 250 | 22 | 2.38 | 2450 | 0.98 | 1.40 | 1438 | 58.7 | 0.138 | 2.242 | 2307 | 94.2 | 0.03 | 2.30 | 2367 | 96.6 |
| 3 | 1084 | 240 | 24 | 2.38 | 2557 | 1.73 | 0.65 | 1467 | 57.4 | 0.180 | 2.200 | 2406 | 94.1 | 0.08 | 2.30 | 2471 | 96.6 |
| 4 | 1555 | 300 | 29 | 2.38 | 3202 | 1.85 | 0.53 | 1611 | 50.3 | 0.74 | 1.640 | 2850 | 89.0 | 0.11 | 2.27 | 3086 | 96.4 |
| 5 | 1649 | 365 | 36 | 2.26 | 3866 | 1.26 | 1.00 | 1904 | 49.3 | 0.75 | 1.51 | 3294 | 85.2 | 0.14 | 2.12 | 3709 | 96.0 |
| 6 | 1943 | 450 | 43 | 2.14 | 4496 | 1.24 | 0.90 | 2170 | 48.3 | 0.76 | 1.38 | 3700 | 82.3 | 0.17 | 1.97 | 4288 | 95.4 |
| 7 | 2499 | 555 | 55 | 2.58 | 5950 | - | - | - | - | 0.78 | 1.80 | 4701 | 79.3 | 0.24 | 2.34 | 5589 | 94.5 |
| 8 | 3574 | 791 | 79 | 2.58 | 8703 | - | - | - | - | - | - | - | - | 0.42 | 2.16 | 7911 | 91.0 |
| 9 | 3980 | 881 | 88 | 2.58 | 9751 | - | - | - | - | - | - | - | - | 0.82 | 1.76 | 8626 | 88.5 |

- Flow rate      = 1 gpm/ft$^2$
- Contact time   = 30 minutes
- Bed size       = 6" diam., 5 1/2 ft. depth.

TABLE 2. CONTINUOUS COLUMN ADSORPTION PROCESS.

HAT CREEK SURFACE COAL SIZE 4/14 TYLER MESH                    CYANIDE REMOVAL

| Run No. | Volume Throughput Liters | Gals | Service Time Hours | Influent CN Conc. mg/1 | Cumulative Total CN Applied mgs | 1 FOOT DEPTH Effl. Conc. mg/1 | Removal CN mg/1 | Cumulative Removal mgs | % Removal Efficiency | 3 FEET DEPTH Effl. Conc. mg/1 | Removal CN mg/1 | Cumulative Removal mgs | % Removal Efficiency | 5 1/2 FEET DEPTH Effl. Conc. mg/1 | Removal CN mg/1 | Cumulative Removal mgs | % Removal Efficiency |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 45 | 10 | 1 | 1.42 | 64 | N.D. | 1.42 | 64 | 100.0 | 0.01 | 1.41 | 64 | 100.00 | N.D. | 1.42 | 63.4 | ≈100.00 |
| 2 | 1039 | 230 | 22 | 1.42 | 1476 | N.D. | 1.42 | 1476 | 100.00 | N.D. | 1.42 | 1476 | 100.00 | N.D. | 1.42 | 1476 | ≈100.00 |
| 3 | 1084 | 240 | 24 | 1.42 | 1540 | 0.62 | 0.80 | 1512 | 98.2 | N.D. | 1.42 | 1540 | 100.00 | N.D. | 1.42 | 1540 | ≈100.00 |
| 4 | 1355 | 300 | 29 | 1.42 | 1925 | 0.58 | 0.84 | 1740 | 90.4 | N.D. | 1.42 | 1925 | 100.00 | N.D. | 1.42 | 1924 | ≈100.00 |
| 5 | 1649 | 365 | 36 | 1.51 | 2369 | 0.10 | 1.41 | 2155 | 91.0 | N.D. | 1.42 | 2342 | 98.9 | N.D. | 1.51 | 2369 | ≈100.00 |
| 6 | 1945 | 430 | 43 | 1.45 | 2795 | 0.4 | 1.05 | 2464 | 88.2 | 0.12 | 1.33 | 2733 | 97.8 | N.D. | 1.45 | 2795 | ≈100.00 |
| 7 | 2499 | 555 | 55 | 1.53 | 3646 | - | - | - | - | 0.34 | 1.19 | 3395 | 93.1 | N.D. | 1.53 | 3646 | ≈100.00 |
| 8 | 3574 | 791 | 79 | 1.52 | 5280 | - | - | - | - | - | - | - | - | 0.17 | 1.35 | 5097 | 96.5 |
| 9 | 3980 | 881 | 88 | 1.52 | 5897 | - | - | - | - | - | - | - | - | 0.64 | 0.88 | 5454 | 92.5 |

- Flow rate = 1 gpm/ft$^2$
- Contact time = 30 minutes
- Bed size = 6" diam., 5 1/2 ft. depth

D-4   TABLE 3.   CONTINUOUS COLUMN ADSORPTION PROCESS
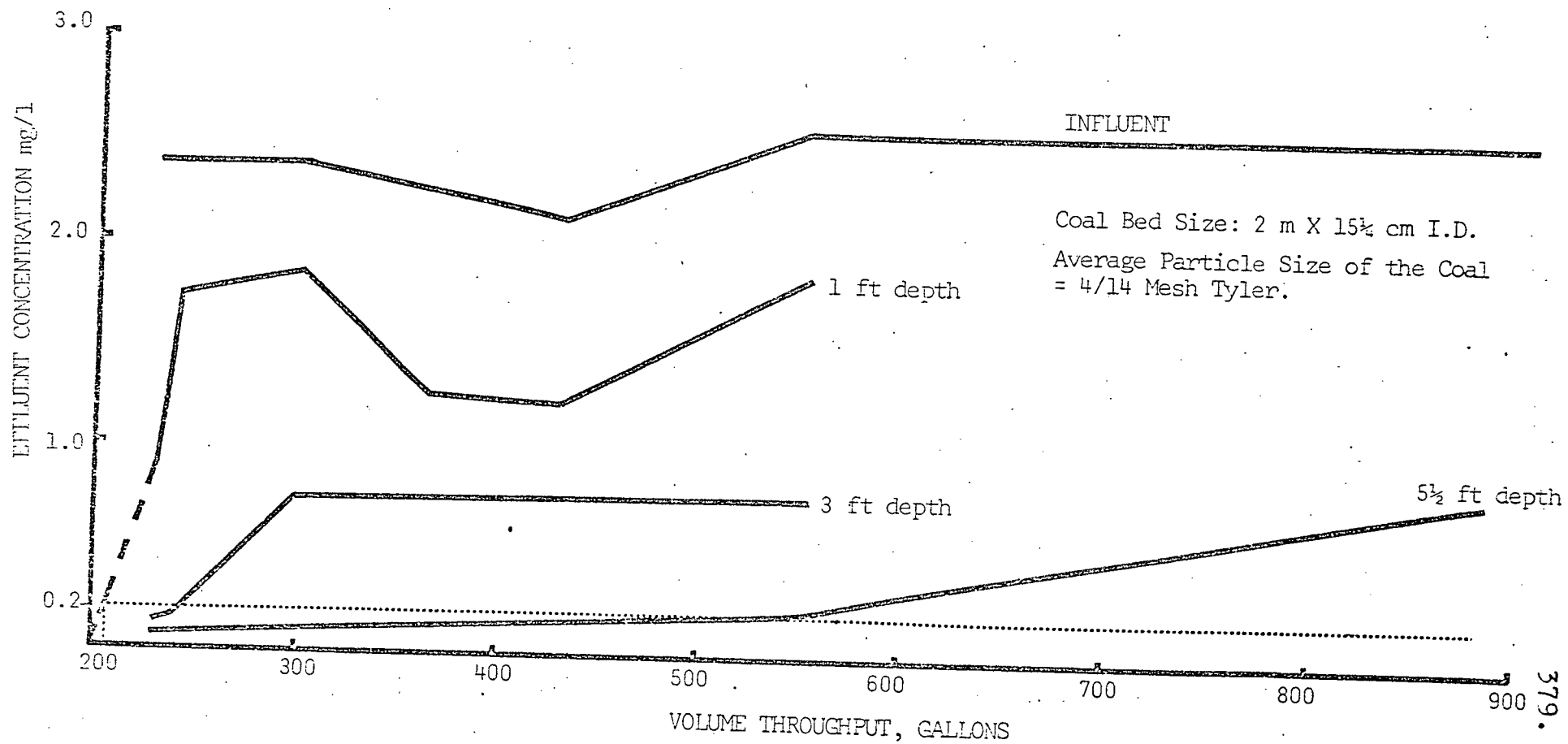
HAT CREEK SURFACE COAL SIZE 4/14 TYLER MESH                    AMMONIA REMOVAL

| Run No. | Volume Throughput Liters | Gals | Service Time Hours | Influent $NH_3$ Conc. mg/l | Cumulative Total $NH_3$ Applied gm | 1 FOOT DEPTH Effl. Conc. mg/l | Removal $NH_3$ mg/l | Cumulative Removal gm | % Removal Efficiency | 3 FEET DEPTH Effl. Conc. mg/l | Removal $NH_3$ mg/l | Cumulative Removal gm | % Removal Efficiency | 5 1/2 FEET DEPTH Effl. Conc. mg/l | Removal $NH_3$ mg/l | Cumulative Removal gm | % Removal Efficiency |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 45 | 10 | 1 | 43.61 | 1.96 | 37.32 | 6.29 | 0.28 | 14.4 | 31.89 | 11.72 | 0.53 | 26.9 | 25.04 | 18.57 | 0.34 | 42.6 |
| 2 | 1039 | 230 | 22 | 43.61 | 45.31 | 37.32 | 6.29 | 6.53 | 14.4 | 31.89 | 11.72 | 12.18 | 26.9 | 25.04 | 18.57 | 19.30 | 42.6 |
| 3 | 1084 | 240 | 24 | 45.00 | 47.54 | 33.54 | 11.46 | 7.05 | 14.9 | 28.11 | 16.89 | 12.94 | 27.3 | 22.68 | 22.32 | 20.30 | 42.9 |
| 4 | 1355 | 300 | 29 | 45.00 | 59.54 | 35.67 | 9.33 | 9.58 | 16.1 | 32.13 | 12.87 | 16.43 | 27.6 | 25.75 | 19.25 | 25.52 | 42.9 |
| 5 | 1649 | 365 | 36 | 45.00 | 72.77 | 40.59 | 4.41 | 10.88 | 15.0 | - | - | - | - | 37.56 | 7.44 | 27.71 | 38.1 |
| 6 | 1943 | 430 | 43 | 43.84 | 85.66 | 43.38 | 0.46 | 11.27 | 10.24 | - | - | - | - | 36.14 | 7.7 | 54.26 | 51.1 |
| 7 | 2499 | 553 | 55 | 43.84 | 110.04 | | | | | | | | | | | | |
| 8 | 3574 | 791 | 79 | 45.00 | 158.42 | - | - | - | - | 41.68 | 3.32 | - | - | 41.80 | 3.2 | 37.7 | 23.8 |
| 9 | 3930 | 881 | 88 | 39.79 | 174.57 | - | - | - | - | 37.42 | 2.37 | - | - | 36.47 | 3.32 | 39.05 | 22.4 |
| 10 | 4296 | 951 | 95 | 39.79 | 187.14 | - | - | - | - | 37.42 | 2.37 | | | 36.47 | 3.08 | 40.02 | 21.4 |

- Initial conc                  50 ppm
- Allowable break-through   =   5 ppm
- Bed size                   =   6" diam., 5 1/2 ft. depth

D-4     FIGURE 1(a)   BREAK THROUGH CURVE FOR ADSORPTION OF PHENOL BY HAT CREEK COAL

INFLUENT

Coal Bed Size: 2 m X 15¼ cm I.D.

Average Particle Size of the Coal = 4/14 Mesh Tyler.

1 ft depth

3 ft depth

5½ ft depth

EFFLUENT CONCENTRATION mg/l

VOLUME THROUGHPUT, GALLONS

379.

D-4    FIGURE 2 (b)   BREAK THROUGH CURVE FOR ADSORPTION OF CYANIDE BY HAT CREEK COAL

INFLUENT

Coal Bed Size: 2 m X 15¼ cm I.D.

Average Particle Size of the Coal = 4/14 Mesh Tyler.

5 ft depth

1 ft depth

3 ft depth

Break through point

EFFLUENT CONCENTRATION mg/l

1.5

1.0

0.5

0.1

200    300    400    500    600    700    800    900

VOLUME THROUGHPUT, GALLONS

380.
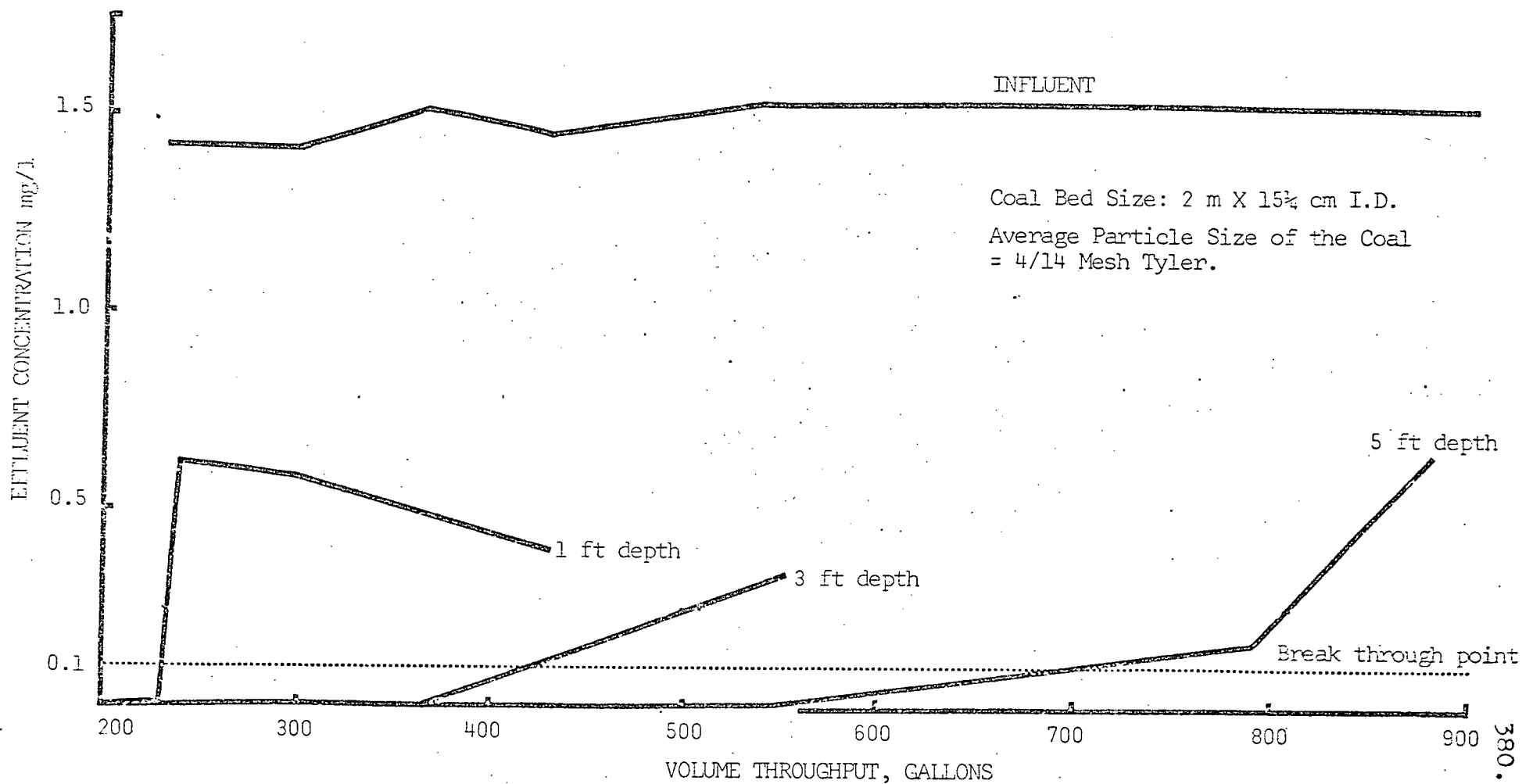
The Bohart Adams relationship was applied in this work to obtain the design parameters of a coal bed to treat such effluent with respect to the adsorptive capacity of the coal.

The equations are as follows:

$$t = \frac{N_o}{C_o V} [D - \frac{V}{KN_o} \ln (\frac{C_o}{C_B} - 1)]$$

The theoretical depth $D_o$ at $t = 0$

$$D_o = \frac{V}{KN_o} \ln (\frac{C_o}{C_B} - 1)$$

where

$t$ = service time (hours)

$V$ = linear flow rate (ft/hr)

$D$ = depth of carbon bed (ft)

$D_o$ = critical depth of carbon bed (ft)

$K$ = rate constant $(ft^3/lb/hr)$

$N_o$ = adsorptive capacity $(lb/ft^3)$

$C_o$ = influent solution concentration (mg/l)

$C_B$ = allowable effluent solution concentration (mg/l).

If $t$ is plotted vs. $D$ for the different levels along the bed, a straight line is obtained as shown in Figures 1 and 2, the slope of the line would be equal to $\frac{N_o}{C_o V}$ and the intercept b.

$$b = \frac{1}{C_o K} \ln(\frac{C_o}{C_B} - 1) \quad \text{or}$$

$$K = \frac{\ln (\frac{C_o}{C_B} - 1)}{C_o (b)}$$

1. Calculation of Design Parameters to Remove Phenol

$$C_o = 2 \text{ mg/l}$$

$$C_B = 0.2 \text{ mg/l}$$

$$V = 9.6 \text{ ft/hr (based on contact time 30 min and 1 gpm/ft2)}$$

From the straight line shown in Figure 1, slope = 12.5 and intercept b = 13.

$$C_o = \frac{2 \text{ mg/l}}{10^6} (62.4 \text{ ft}^3) = 1.248 \times 10^{-4} \text{ lb/ft}^3$$

$$\therefore \quad N_o = (12.5) \times 1.248 \times 10^{-4} \times 9.6 = 0.015 \text{ lb/ft}^3$$

$$\ln \left(\frac{C_o}{C_B} - 1\right) = \ln \left(\frac{2}{0.2} - 1\right) = 2.1972$$

$$K = \frac{\ln \left(\frac{C_o}{C_B} - 1\right)}{C_o(b)} = \frac{2.197}{1.248 \times 10^{-4} \times 13} = 1354.3 \text{ ft}^3/\text{lb/hr}$$

Then

$$D_o = \frac{V}{KN_o} \ln \left(\frac{C_o}{C_B} - 1\right)$$

$$D_o = \frac{9.6}{1354.3 \times 0.015} \times 2.1972 = 1.0382 \text{ ft.}$$

For treatment of a refinery effluent at the rate of 8 I gpm/1000 Bbl of crude with an inflow rate of 1 gpm/ft$^2$ an 8 ft$^2$ area for the coal bed is required; and to apply contact time of 30 minutes, the linear velocity of the flow would be 0.16 ft/min, i.e. 9.6 ft/hr. Therefore, the required depth for 30 minutes contact

$$= 0.16 \times 30 = 4.8 \text{ ft (say 5 ft).}$$

To calculate the service life for this bed to remove phenol:

$$t = \frac{N_o}{C_o V} [D - D_o]$$

The quantity of flow per day = 11,520 gals/day based on a 24 hr operation.

∴      The flow per week = 80,640 gals, based on 7 days per week operation.

∴      $t = \dfrac{0.015}{1.248 \times 10^{-4} \times 9.6} [5 - \dfrac{9.6}{1354.3 \ (0.015)} \times 2.197]$

∴      t = <u>50 hours</u>

∴      Total volume of flow within this period

= 8(60) (50) = 24,000 gals

Annual volume   = 8 X 60 X 24 X 365

= <u>4,204,800 gals/year</u>

∴      No. of coal changes = $\dfrac{4,204,800}{24,000}$ = 175.2 times/year

Volume of coal per change = <u>5 X 8</u> = 40 ft$^3$

∴      Total coal volume required = 175.2 X 175.2 X 40

= 7,008 ft$^3$/year

Since th e depth of the bed = 5 ft; therefore the area of the bed required = 1,402 ft$^2$, and weight of the coal = 7,000 X 36.24

= 127 tons coal/year.

Accordingly, the suggested dimensions for the coal bed based on phenol removal would be

<u>30 X 50 ft$^2$ area and 5 ft depth</u>

Quantity of coal required per day to treat 8 gpm/ 1,000 barrel effluent = 0.35 ton/day = 700 lbs. Total phenol (2 - 0.2 mg) removed from this effluent daily = <u>0.2107 lbs.</u>

Calculation of the Efficiency of the Bed

Total phenol to be adsorbed = 75.5 lbs/year

$$\left[\frac{8.34 \text{ lbs} \times 1.2 \left(\frac{\text{Imp.gal}}{\text{U.S.}}\right)}{10^6 \text{ gals/mg/l}}\right] = 75.5 \text{ lbs/year for each 1,000 barrel crude}$$

Total capacity $= 0.015 \ (\text{lb/ft}^3) \times 7,000$

$= 105$ lbs/year

Experimental Efficiency $= \dfrac{75.5}{105} \times 100 = \underline{72\%}$

Computed from $D_o$

Theoretical Efficiency $= \dfrac{D - D_o}{D} \times 100 = 5 - \dfrac{1.0385}{5} \times 100$

$= \underline{79\%}$

## 2. Removal of Cyanide

$$t = \frac{N_o}{C_o V}\left[D - \frac{V}{KN_o} \ln \left(\frac{C_o}{C_B} - 1\right)\right].$$

For cyanide, $C_o = 1$ mg/l

$C_B = 0.1$ mg/l

$C_o = \dfrac{1}{10^6}(62.4) = 0.624 \times 10^{-4} \text{ lb/ft}^3$

$V = 9.6$ ft/hr

Slope $= 14.8$

$N_o = (14.8) \times 0.624 \times 10^{-4} \times 9.6 = 0.00887 \text{ lb/ft}^3$

$\ln = \left(\dfrac{C_o}{C_B} - 1\right) = \ln\left(\dfrac{1}{0.1} - 1\right) = 2.1972$

$K = \dfrac{2.1972}{0.624 \times 10^{-4} \times 1.0} = 35,212$

Then $D_o = \dfrac{9.6}{35,212 \times 0.00887} \times 2.1972 = \underline{0.06753 \text{ ft}}$

Required depth for the refinery effluent for 1 gpm/ft$^2$ flow rate and velocity = 0.16 ft/min, for 30 minute contact time. The required depth = 0.16 X 30 = <u>4.8 ft (say 5 ft)</u>

<u>The Service Life</u>

$$t = \frac{N_o}{C_o V} [D - D_o]$$

$$t = \frac{0.00887}{0.624 \times 10^{-4} \times 9.6} [5 - 0.06753] = \underline{73.0 \text{ hours}}$$

Total Volume = 8(60) X 73      = <u>35040 gals</u>

Volume of Coal = 8 ft$^2$ X 5      = 40 ft$^3$

Annual volume = 8 x 60 x 24 x 7 x 52      = 4,193,280 gals

No. of changes per year = $\frac{4,193,280}{35,040}$      = 119.7 per year

Volume of coal per change      = 40 ft$^3$

Annual coal volume = 119.7 X 40      = 4,787 ft$^3$

Total cyanide removed = (0.9 mg/l) X $\left(\frac{4,193,280 \text{ gals}}{\text{year}}\right)$

$$\left(\frac{8.34 \text{ lbs} \times 1.2 \text{ Imp/U.S.}}{10^6 \text{ gals/mg/l}}\right)$$

= <u>37 lbs/year from each 1,000 barrel</u>

<u>Efficiency</u>

Total cyanide adsorbed = 37 lbs/year

Total capacity = 0.00887 X 4787 = 42.46 lbs

Efficiency = $\frac{37}{42.46}$ X 100      = <u>87.1%</u>

Computed from $D_o$,

Efficiency $\frac{5 - 0.06753}{5}$      = <u>98.6%</u>

Consumption per day      = 0.238

Consumption of coal per year      = <u>87 tons</u>

From earlier calculation

For phenol, coal required/year = 127 tons (0.35 tons/day).

∴      The suggested bed to treat refinery wastes containing

both phenol and cyanide is 29 X 49 X 5 ft (7,000 ft$^3$).

It will serve 1 year to remove phenol and 1.5 years

for cyanide.

3.   Comparison Between the Adsorptive Capacities of Coal Towards
     Phenol and Cyanide in the Mixture

(a)   Adsorption of Phenol

   (i)   Adsorptive capacity calculated from the Bohart

         Adams relationship (as before)

         =   0.015 lb/ft$^3$

         =   0.4139 mgs PhoH/gm coal

   (ii)  Computed from the applied research:

         Total phenol removed during the service period at

         the 5 1/2 feet level (bottom of the bed)

         =   5,589 milligrams.   Total grams of coal = 17,750 gms

∴        Adsorptive capacity at break-through of 0.2 mg/l

         phenol $= \frac{5,589}{17,750}$ =   0.3149 mg/gm coal

(b)   Adsorption of Cyanide

   (i)   Computed from the Bohart Adams relationship:

         Capacity - 0.00845 lb/ft$^3$ = 0.2333 mgs/gm/coal

   (ii)  Computed from the applied research:

         Total cyanide removed during the service period at

         the 5 1/2 feet level        = 5,079

         Capacity $= \frac{5,079}{17,750}$ =   0.28614 mgs/gm coal

FIGURE 2   THE EFFECT OF THE DEPTH OF THE COAL BED ON THE SERVICE LIFE, FOR BREAK THROUGH AT 0.1 mg/l CYANIDE, AND INFLUENT CONCENTRATION 1 mg/l CYANIDE.
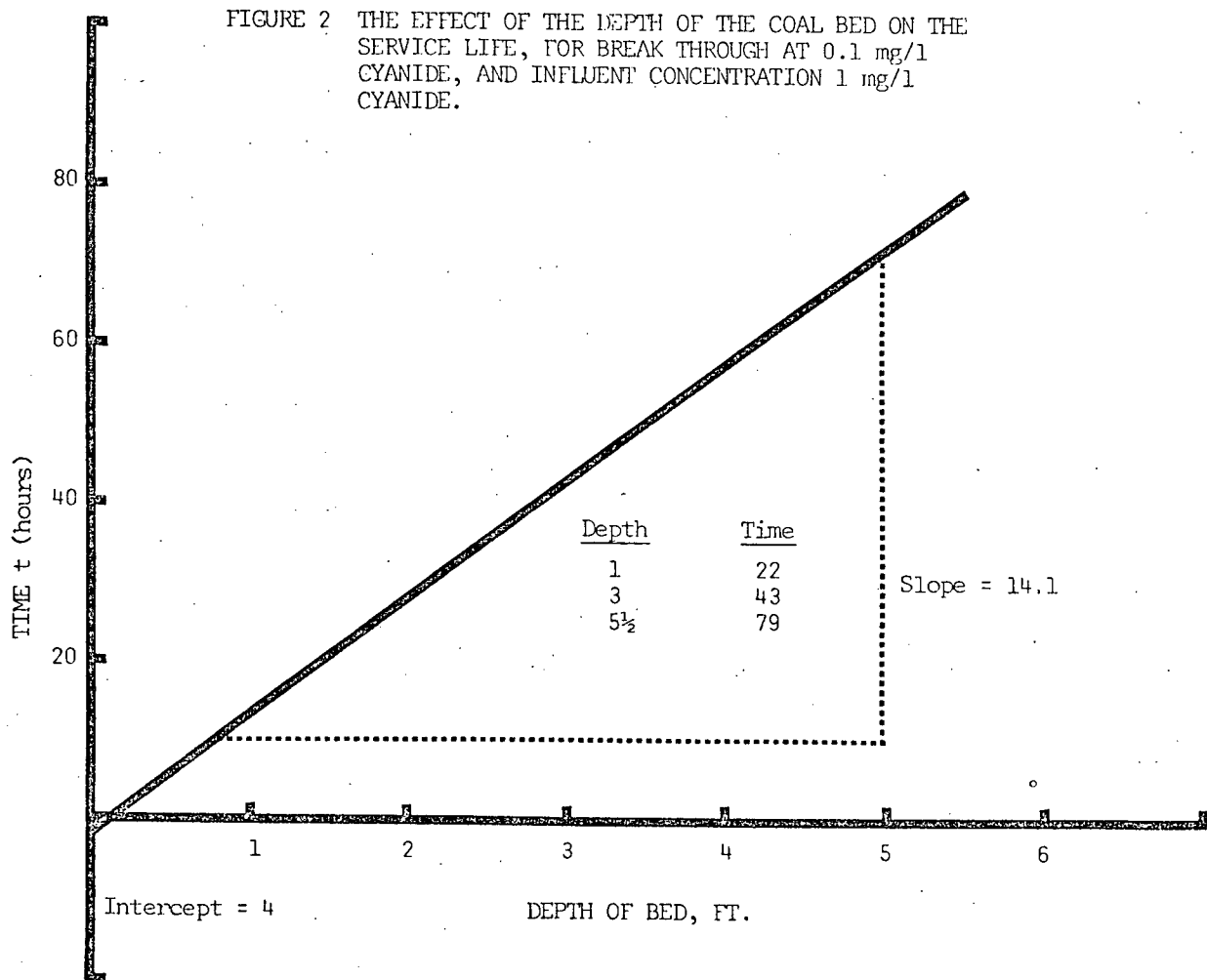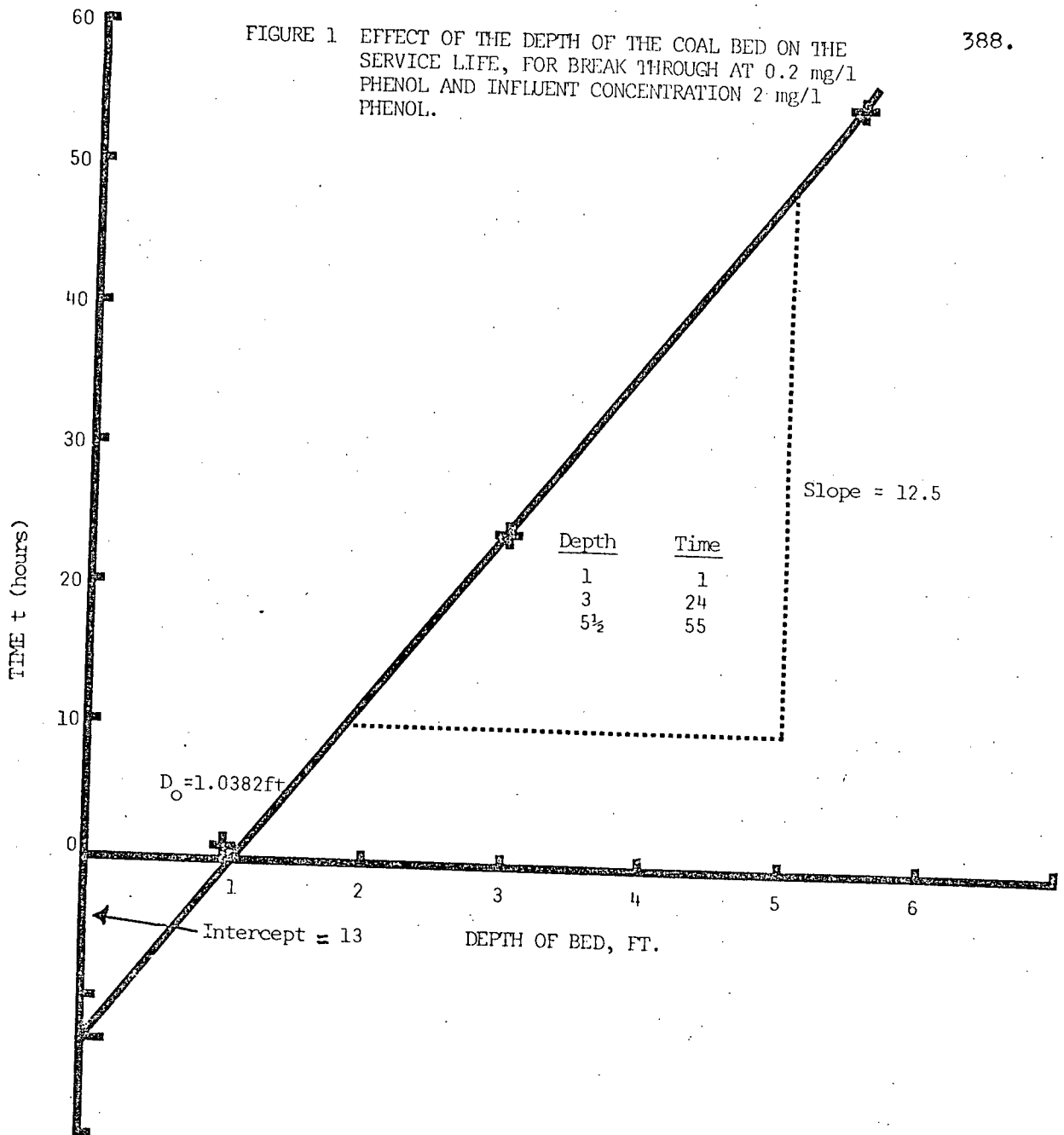
FIGURE 1  EFFECT OF THE DEPTH OF THE COAL BED ON THE
SERVICE LIFE, FOR BREAK THROUGH AT 0.2 mg/l
PHENOL AND INFLUENT CONCENTRATION 2 mg/l
PHENOL.

388.

| Depth | Time |
|-------|------|
| 1     | 1    |
| 3     | 24   |
| 5½    | 55   |

Slope = 12.5

$D_o$=1.0382ft

Intercept = 13

DEPTH OF BED, FT.

TIME t (hours)

3.  Removal of Ammonia

By applying an influent of 40-45 mg/l range concentration, the effluent concentration never decreased to the allowable level of 5 ppm $NH_3$.

A maximum efficiency of 42.9% removal was obtained at the 5 1/2 feet level and throughput volume of 300 gallons, after that, the efficiency dropped rapidly to 21%.

A very small value of 14.4% efficiency was obtained from the first foot level.

The data show that Hat Creek coal is a very poor adsorbent for ammonia and therefore is not recommended to be used for that purpose.

Total volume run-through    = 951 gals

Total applied ammonia    = 187.14 grams

Total ammonia removed in
the 5 1/2 feet level    = 40.02  grams

Capacity of coal = $\frac{40,020}{17,750}$    = 2.25 mgs $NH_3$/gram coal

Efficiency = $\frac{40.02}{187.14}$ X 100    = 21.4%