

The Sorptive Behavior of Organic Compounds on Retorted Oil Shale

by

Adil Noshirwan Godrej

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APPROVED:

Gregory D. Boardman, Chairman

Daniel L. Gallagher

Robert C. Hoehn

William R. Knocke

John T. Novak

Lucian W. Zelazny

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(ABSTRACT)

Oil shale is a valuable natural resource of oil. The United States has only 5% of the known world reserves of recoverable crude oil and about 73% of the known world reserves of recoverable oil shale. Before there can be full-scale commercial development of oil shale, the problems associated with the large amounts of wastes generated by the processing of the shale must be solved. The wastes have a complex chemical matrix. It is felt that the spent shale can be used as a sorbent to either treat or pretreat the contaminated process waters or could be codisposed with the process waters. Quite extensive work has been done in exploring this alternative with respect to inorganic constituents, but that with organic constituents has been mainly restricted to the measurement of total organic carbon. This study was done to base the analysis of the suitability of the spent shale as a sorbent upon individual compounds so that a more fundamental understanding could be obtained as to how families of compounds behave.

Single- and multisolute batch sorption isotherm experiments performed on Antrim spent shale from Michigan indicated a consistent sorptive behavior by the shale with respect to the four sorbates used in the study — Phenol, 2-Hydroxynaphthalene (HN), 2,3,5-Trimethylphenol (TP) and 1,2,3,4-Tetrahydroquinoline (THQ). The sorptive capacity of the spent shale was least for Phenol and greatest for THQ, with the order being Phenol < TP < HN < THQ. Single-solute continuous-flow column experiments on shale could not be better analyzed because of a lack of proper kinetic data, but the order in which the compounds would reach a 50% breakthrough, as well as the sorptive order (from least to largest amounts sorbed) of the four study compounds in batch multi-component experiments, could be predicted based upon the single-solute experimental data. The

order of breakthrough at 10% of influent in the continuous-flow column experiments cannot be predicted with the same degree of clarity.

Averages of the ratios of the amount sorbed of any one component to the total sorbed amount of all components in multisolute systems were calculated and indicated the partitioning of the components as 11% (Phenol), 32% (HN), 37% (THQ), and 20% (TP) in a four-component system. Average ratios for bi- and trisolute systems computed from the tetrasolute system agreed to within 11% for those compounds that sorb to larger extents (HN and THQ) and to within 19% for those that sorb to a smaller degree (Phenol and TP).

A comparison with single-component batch isotherm experiments performed on Filtrasorb 300 granular activated carbon (GAC) showed that the shale had a sorptive capacity of about two orders of magnitude less than that of the GAC.

The multicomponent shale data could not be adequately modelled with any one of three models -- a multicomponent Freundlich type model, the multicomponent Langmuir model, and the simplified ideal adsorbed solution theory model.

Among the three phenolic compounds studied, the effects on sorption due to ascending a homologous series (from Phenol to HN) are more pronounced than those associated with branching (from Phenol to TP). No relationship was found to exist between the amounts sorbed and the octanol-water partition coefficient.

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List of Abbreviations

AEC	United States Atomic Energy Commission
ARCO	Atlantic Richfield Company
BET	Brunauer, Emmett, Teller (model)
C:H	Carbon:Hydrogen (ratio)
COD	Chemical oxygen demand
DOC	Dissolved organic carbon
DOE	United States Department of Energy
EPA	United States Environmental Protection Agency
ERD	Environmental Readiness Document
ERDA	United States Energy Research and Development Agency
GAC	Granular activated carbon
GPDM	General pore diffusion model
IAS	Ideal adsorbed solution (theory)
IGT	Institute of Gas Technology
IETC	Iaramic Energy Technology Center (currently Western Research Institute)
LRC	Loading ratio correlation (model)
MCL	Maximum contaminant level

MEIC	Morgantown Energy Technology Center
MGD	million gallons per day
MIS	Modified <i>in situ</i>
NPC	National Petroleum Council
OPEC	Organization of Petroleum Exporting Countries
OTA	United States Congress, Office of Technology Assessment
PAC	Powdered activated carbon
PSD	Prevention of significant deterioration
RCRA	Resource Conservation and Recovery Act of 1976
SEM	Scanning electron microscope/microscopy
SFC	United States Synthetic Fuels Corporation
SIAS	Simplified ideal adsorbed solution (theory and model)
SUNOCO	Sun Oil Company
TDS	Total dissolved solids
TKN	Total Kjeldahl nitrogen
TOC	Total organic carbon
TOSCO	The Oil Shale Corporation
USGS	United States Geological Survey

Symbols Used and Some Conversion Factors

a	Langmuir constant
b	Langmuir constant
C	equilibrium concentration of solute in solvent
C_s	saturation concentration of the solute in solution
i and j	(subscripts) components in mixtures of sorbates
k	Freundlich constant
k'	SIAS constant
M	mass of sorbent
N	total number of solutes in a multicomponent system
n	Freundlich constant
n'	SIAS constant
q	amount of solute sorbed per unit weight of sorbent
q_T	total of all values of q at one experimental condition
α_i	$\frac{q_i}{q_T}$
$\bar{\alpha}_i$	average of α_i values
β	constant in Freundlich type multicomponent model
ψ	constant in Freundlich type multicomponent model

Some Conversion Factors

bbl barrel, equal to 42 U. S. gallons (0.159 m³)

gal·ton⁻¹ equivalent to 4.17 ℓ·tonne⁻¹

quad equivalent to 10¹⁵ Btu.

Based on a heating value of 5.8×10^6 Btu/bbl,

1 quad = 172.4×10^6 bbl of crude oil equivalent

Chapter I

Introduction

The petroleum in the United States is a natural resource that is rapidly being consumed. The fact that the supply is not inexhaustible and the gravity of the situation that will result from the supply becoming so depleted as to be inadequate to meet demands have been generally appreciated only within the past few years. As a result, these years have seen widespread efforts to conserve petroleum and its products and to seek possible substitutes for it. [90]

Oil shale deposits have been found on all of the inhabited continents. The extent of the worldwide resources cannot be accurately determined, but it appears to be very large indeed. In 1965, the U.S. Geological Survey (USGS) estimated that the world's oil shale deposits comprised over 4 quadrillion tons, having a total potential shale oil yield of over 2 quadrillion bbl. If all of this oil were extracted and distributed among the world's residents, each person would receive about 600,000 bbl. However, the spent shale waste would cover the entire surface of the world, land areas and oceans included, to a depth of about 10 ft. [160]

A period of 56 years separates the statements given above. Besides the fact that the language of the first (made in 1924 by Martin J. Gavin of the U.S. Bureau of Mines) gives a clue as to when it might have been made, it is representative of the general feeling of the current times. Consider, though, that the U.S. has only about 5% of the known world reserves of recoverable crude oil and about 73% of the known world reserves of recoverable oil shale [185]. The estimated worldwide reserves of the rich oil shale (25-100 gal-ton⁻¹) alone are 17×10^{12} barrels (bbl), whereas the reserves of crude oil are estimated to be equal to only 4% of this figure [202]. In view of this, Gavin's statement of

1924 that “as sources of substitutes for petroleum oils, the reserves of oil shale in the United States stand out as most important” [90], takes on the aspects of prophecy.

It should be noted that in 1924, when Gavin wrote his monograph (actually, the 1924 version is a revision of an earlier one written in 1922), the estimated annual consumption of crude oil in the U.S. was 600×10^6 bbl, of which about 20% was imported [90]. At that time, however, Arabian oil was largely undiscovered. By 1978, the U.S. consumed 6×10^9 bbl of oil of which 45% was imported [160]. More importantly, “it is unlikely that sufficient U.S. reserves exist to provide secure supplies beyond the end of the 20th century” [160].

Currently, from the point of view of the consumer — meaning usually the owner of a vehicle, since most petroleum is used for transportation purposes (almost all the rest being used as fuel oil) — the situation is quite pleasant compared to that of a few years ago. Oil prices (and hence the price of gasoline at the local service station) are fairly stable, and, in fact, have fallen over the last three to four years. The oil embargo of 1973 raised the prices of petroleum tremendously and even caused shortages, but for the most part the consumer has adjusted to this by now. Indeed, the vast majority of those who are less than thirty years of age have very little appreciation of the price increase that took place then.

In the late 1970s and early 1980s, however, prices of crude oil were so high and supplies so unreliable (as far as long-term stability was concerned) that serious consideration was once more given to the development of the oil shale industry. The United States Department of Energy (DOE), in an Environmental Readiness Document (ERD) on the commercialization of oil shale, stated that “there is a high probability that commercial scale aboveground retorting will be found environmentally acceptable” [212]. That document prudently did not state *when* this might happen because the very next statement in it said that “the primary unresolved problems that this technology faces are (1) stringent air quality regulations, (2) management of solid wastes, and (3) lack of data regarding the environmental, health, and safety impacts of the total fuel cycle” [212]. In fact, the problem of environmentally responsible waste management *vis-à-vis* oil shale is perhaps the only

major stumbling block to the development of an oil shale industry. It was felt then that in terms of price of production oil shale would be competitive by 1990 (and, indeed, by 1985), but that it would cost between \$5-15 bbl⁻¹ of production for waste management [212].

Similarly, the Office of Technology Assessment (OTA) of the U.S. Congress felt that by 1990 there would be few impediments to a production target of up to 200,000 bbl·d⁻¹; one concern being that of the marketability of the shale oil, but certainly no problems in complying with environmental regulations [160]. These statements were made when there were little data available pertaining to the treatment of oil shale wastes — whether treatment would be feasible using current technology, and what would be the added expense of the treatment if it were possible. One thing was clear: the amount of research related to oil shale, and especially the environmental aspects, was at a peak in the late 1970s and early 1980s. And then, surprisingly, the unity of the Organization of Petroleum Exporting Countries (OPEC) toward keeping the price of crude oil elevated suffered a setback — oil prices went down and the supply went up to the point that the subsequent glut had serious consequences for the economy of the state of Texas (which depends to a great extent upon revenues derived from petroleum). Unfortunately, this circumstance also brought all interest in oil shale to a veritable halt — when this author contacted one of the leading researchers in oil shale about some technical aspect of his work she expressed the sentiment that she was glad to hear about someone doing research in oil shale and that the fate of the industry was bound to look up in a few years [79].

It is indeed a time of waiting because, inevitably, the prospects for the commercialization of oil shale will be good in the future. It is equally important, however, to not lose whatever momentum was gained and continue the research already begun. This is specially true with respect to the environmental problems concerning the safe disposal of wastes from oil shale processing — public awareness of the necessity of preserving the environment is rising, and, although, if given the choice of financial ruin due to the high price of obtaining oil or pollution of the environment due to oil shale processing, the public *may* choose the latter, it is more constructive to prevent both from occurring if possible.

Two major fractions of wastes generated from oil shale processing are the spent shale and the process waters (or retort waters). A third major fraction consists of waste gases evolved during processing. The main concerns with respect to the spent shale are the sheer volume of the material and the relatively high levels of residual inorganic and organic materials (some of which are readily leached). The retort waters contain high levels of both inorganic and organic materials, some of which are toxic. Both, the spent shale and the retort waters, are considered to be hazardous wastes.

In a full-scale facility that produces oil from oil shale by mining and extracting, the large amounts of spent shale generated would be disposed of in a canyon or basin fill [226]. To facilitate compaction of the shale a considerable quantity of water would be used for moistening [143]. Some of the richest deposits of shale (containing up to 80 gallons of oil per ton of shale) occur in the Green River formation area in Colorado, Utah and Wyoming [157]. This area has limited water resources. Treatment costs for the retort waters are projected to be high [160], and, indeed, some people do not believe that they can be adequately treated by conventional wastewater treatment technology [162]. All the compounds present in the retort waters would have been originally present or derived from those present in the shale. A 13% moisture content (by weight) is considered optimum for compaction of the shale for disposal [23]. This has led researchers to the conclusion that co-disposal of the spent shale with the retort water would be an economically and environmentally attractive option for waste disposal [23, 114]. This conclusion would hold true for Eastern shales, also, although the scarcity of water is not a problem in the East.

This author has been involved in a study with other researchers in the past that has attempted to address the complex issue of co-disposal [18, 19]. Others involved in the study have addressed the kinetics of the sorption of inorganic materials on raw and retorted shales [44, 45], and of organic compounds on raw and spent shales and of various materials (both inorganic and organic) on a Western soil [91, 135]. From these studies it was determined that, of the shales studied, a spent shale called Antrim (which is an Eastern shale from Michigan) was the most promising adsorbent.

One of the earliest studies to evaluate the properties of spent shale as a sorbent indicated that “spent shales are effective in removing color, odor, inorganic carbon, and certain classes of organic compounds and in elevating the pH of retort waters so that NH_3 may be readily stripped” [82]. That study was performed in 1979. It should be noted that under current Resource Conservation and Recovery Act of 1979 (RCRA) regulations, the United States Environmental Protection Agency (EPA) does not allow co-disposal, principally due to a lack of data [114]. Perhaps, though, the use of spent shale as a pretreatment for retort waters may be more acceptable [82]. Most work to date on the related subjects has focused on the sorptive behavior of inorganic agents present in retort waters. Due to the complex nature of the organic matrix, work with organic compounds has either used the actual retort waters, with total organic carbon (TOC) being the parameter usually measured, or classes of organic compounds present in retort waters. Work with the retort waters is essential, but retort waters derived from different processes vary significantly in composition, as do the spent shales. It would be more instructive to study the behavior of individual compounds, alone and in combinations, in a controlled manner, and, at a later date, use the results of such studies to extrapolate to and better understand the behavior of classes of organic compounds and retort waters themselves. It is not possible to reduce the complexity of spent shale, but it is possible to use solutions of typical compounds to better characterize the sorptive properties of spent shale. Once a better understanding of the properties of the spent shale is achieved, it would be possible to further increase the complexity of the synthetic solutions and work toward using the actual retort waters. It is felt that this approach would enable a fundamental understanding of the interactions involved, and lead to a more solid foundation for predictive efforts. A policy of *festina lente* — hasten slowly — is thought to be most productive in such matters.

Research Objectives

It was with these issues in mind that the study reported upon here was undertaken. The objectives of this study were:

1. To characterize the sorptive behavior of Antrim spent shale with respect to 2-Hydroxynaphthalene, Phenol, 1,2,3,4-Tetrahydroquinoline, and 2,3,5-Trimethylphenol, in single- and multicomponent batch systems and single-component column systems;
2. To characterize the sorptive behavior of Filtrasorb 300 granular activated carbon with respect to the same organic compounds in single-component batch systems, and to compare the behavior of the shale and the activated carbon;
3. To determine the applicability of an equilibrium adsorption model towards predicting the multicomponent sorptive behavior of the shale based on single-component information; and,
4. To determine the extent of the relationship between the physicochemical characteristics of the study compounds and their sorption on to shale.

Chapter II

Literature Review — Oil Shale

Most of the literature available on oil shale is not easily accessible, residing as it does in specialty conference proceedings, government documents and project reports. A lot of the research on the technology has been done by oil companies, and except for that reported in public forums is not available for public review. Moreover, some studies have been reported in more than two forums, and this can be disconcerting for the researcher.

This chapter, therefore, is perhaps more extensive than normally found in a document of this kind. The selection of the information presented here, however, is not by any means exhaustive and indeed is somewhat eclectic. For the most part this author has attempted to provide pertinent information yet keep the reference list short. Normally, if one reference would do for presenting a fact, one has been used, unless the addition of others would lead to further useful information not presented in this document.

In order to understand why the development of an oil shale industry has been so haphazard in spite of the fact that oil shale has been considered a valuable natural resource for decades, it is necessary to delve into the history of the industry as well as appreciate the technical problems involved in the

processing of the shale. When compared to the production of crude oil from conventional sources, obtaining oil from shale involves a much higher investment in terms of time, manpower and capital. Although the production of oil from shale predates that from oil wells, the oil shale industry has not yet reached sustained commercial production. One strong reason for this are the considerably complicated problems associated with responsible environmental management. The following historical note should make clear another reason — large initial investments are needed over a fairly long period of time before the production becomes profitable, and this, understandably, has led to lukewarm enthusiasm among private developers.

History of the Development of Oil Shale

“A way to extract and make great quantities of pitch tarr and oyle out of a sort of stone” was the title of British Crown Patent No. 330, granted in 1694 [229]. Even earlier, in mid-14th century England, the word “petroleum” was used to describe oil extracted from oil shale [145]. However, it is uncertain when the extraction of oil from shale was first performed.

In the U.S. the richest deposit of oil shale is to be found in the area known as the Green River Formation — an area of about 17,000 square miles situated where the states of Colorado, Utah and Wyoming meet. A tributary of the Colorado River, the Green River, flows through the area. Most of the oil shale of the Green River Formation is located in a northwestern portion of Colorado called the Piceance (pronounced pe'-ance) Creek Basin.

The fact of the Piceance Creek Basin shale deposit, if not its overwhelming extent, has been known for centuries. The Ute Indians, who once inhabited the area, were often startled when bolts of lightning during summer storms caused flames to shoot from shale outcrops, and they called the shale “the rock that burns”. Early pioneers were even more ignorant, and the probably apocryphal tale is told — and retold in virtually every article ever written about oil shale — about an individual named Mike Callahan who settled near Rifle and built himself an impressive house whose *pièce de résistance* was a giant fireplace built from the black rock he had found in the nearby cliffs. At a glorious housewarming party, Callahan proudly lit the fireplace's inaugural fire which quickly escalated into a roaring conflagration, leveling both house and fireplace, and perhaps even Callahan. [223]

Mike Callahan's housewarming apparently took place in 1882 in Rio Blanco County in Colorado [185]. Maybe Mike Callahan was attracted to the coloration of the rich shale of the Mahogany Zone in the Piceance Creek Basin: the shale from this zone, when polished, resembles mahogany. Whatever the antecedents, the first recorded use in the U.S. of oil from shales was when "during the early 1800s, and possibly as early as Revolutionary times, lamp oil, lubricants, and medicinal substances were produced from the rather lean shales around the Appalachians" [223].

Across the Atlantic, the first commercial processing of oil shale started in France in 1838 [190, 223], although the year 1830 is also mentioned in this context [90]. The oil shales of France were of poor quality. The most successful oil shale industry to date has been that which operated in Scotland from 1850 to 1962 [39]. A list of countries where deposits of oil shales have been found is given in Table 1. Countries that had a commercial industry are indicated, as are those that have a currently-functioning industry.

In order to gain a proper perspective of the "ups and downs" that oil shale development has faced, it is instructive to study the history of the Australian, Scottish and U.S. oil shale industries.

The Scottish Industry

In 1850, James Young had a refinery that produced lubricants that were used, replacing sperm oil from whales, by the cotton mills in Manchester. The refinery had been operating for two to three years and used oil that seeped out of a coal mine at a flow rate of 360 gal·d⁻¹. In 1850 this seepage stopped, and James Young conceived the idea of using coal to produce oil. He tried retorting various coals at different temperatures and then condensing the vapors, but with little success. His oil refinery operations were located in Bathgate in the Lothian region of Scotland (see Figures 1 and 2). A friend of his provided him with a coal obtained from Boghead, situated on the outskirts of Bathgate. When Young retorted this coal he obtained a yield of 129 gal·ton⁻¹ at the lowest re-

Table 1. List of countries where deposits of oil shale have been found

<u>Continent</u>	<u>Country</u>
Africa	Angola Morocco † South Africa ‡ Zaire Zimbabwe
America	Argentina Brazil § Canada † Chile Uruguay United States ‡
Asia	China (Manchuria) § Israel † Jordan † Mongolia Syria Thailand Turkey U.S.S.R. (Estonia) §
Australia	Australia ‡ New Zealand
Europe	Austria Bulgaria France ‡ Germany ‡ Italy Luxembourg Portugal Romania Spain ‡ Sweden Switzerland U.K. (England, Scotland ‡ and Wales) Yugoslavia

† Performing research and development or contemplating development

‡ Oil shale industry existed in the past

§ Current oil production from oil shale

Sources: Compiled from [9, 90, 113, 160, 223]

torting temperature to facilitate decomposition. When retorted optimally, the coal was capable of yielding more than 135 gal·ton⁻¹. [39, 90]

This Boghead coal had a high bitumen content and was also called torbanite or cannel coal. “It was called ‘cannel’ because it burned with a long luminous flame like a candle and ‘cannel’ is the Old Scots word for a candle or literally ‘candle coal’.” [39] The oil condensed from retorting of this coal produced naphtha, burning oil and lubricants, as well as other products. Young patented his process: Patent No. 13292 of October 17, 1850. Once Young had a contract for the supply of Boghead coal, he began full-scale production of oil at Whiteside in 1851 (see Figure 2). [39, 90]

By 1860 the Bathgate Works was retorting 10,000 tons of coal per year [39]. However, by 1862 the seam of Boghead coal had been exhausted [90]. Young had turned his attention to the production of oil from true oil shale in 1856. Young’s competitors had been experimenting with shale that was plentiful in the West Lothian region of Scotland (see Figure 2). In order to forestall his competitors from infringing on his patent (which they thought applied only to the production of oil from coal), Young took legal action against them, both in the United Kingdom and in the United States. He usually won his cases, and even succeeded in having his patent in the U.S. extended to 1871 because the companies there were not paying him adequate royalties. [39]

Since 1856, Young, along with his son James, had been buying land in the West Calder and Midcalder area south of Bathgate. In the meantime, Colonel E. L. Drake had struck oil in Pennsylvania in 1859 and the prices of oil products dropped drastically. Young’s patent in the United Kingdom expired in 1864, and at this time he bought over the oil business from his two partners, Binney and Meldrum, for £50,000. In 1865 he built the Addiewell Oil Works near West Calder (see Figure 2). These Works were at the time the largest in the world and had a maximum processing capacity of 9.6 million gallons of oil per annum. The Addiewell and Bathgate Works were formally named the Young’s Paraffin Light and Mineral Oil Co. Ltd. in 1866. [39]



Figure 1. Scotland, showing the location of Bathgate: From [39].

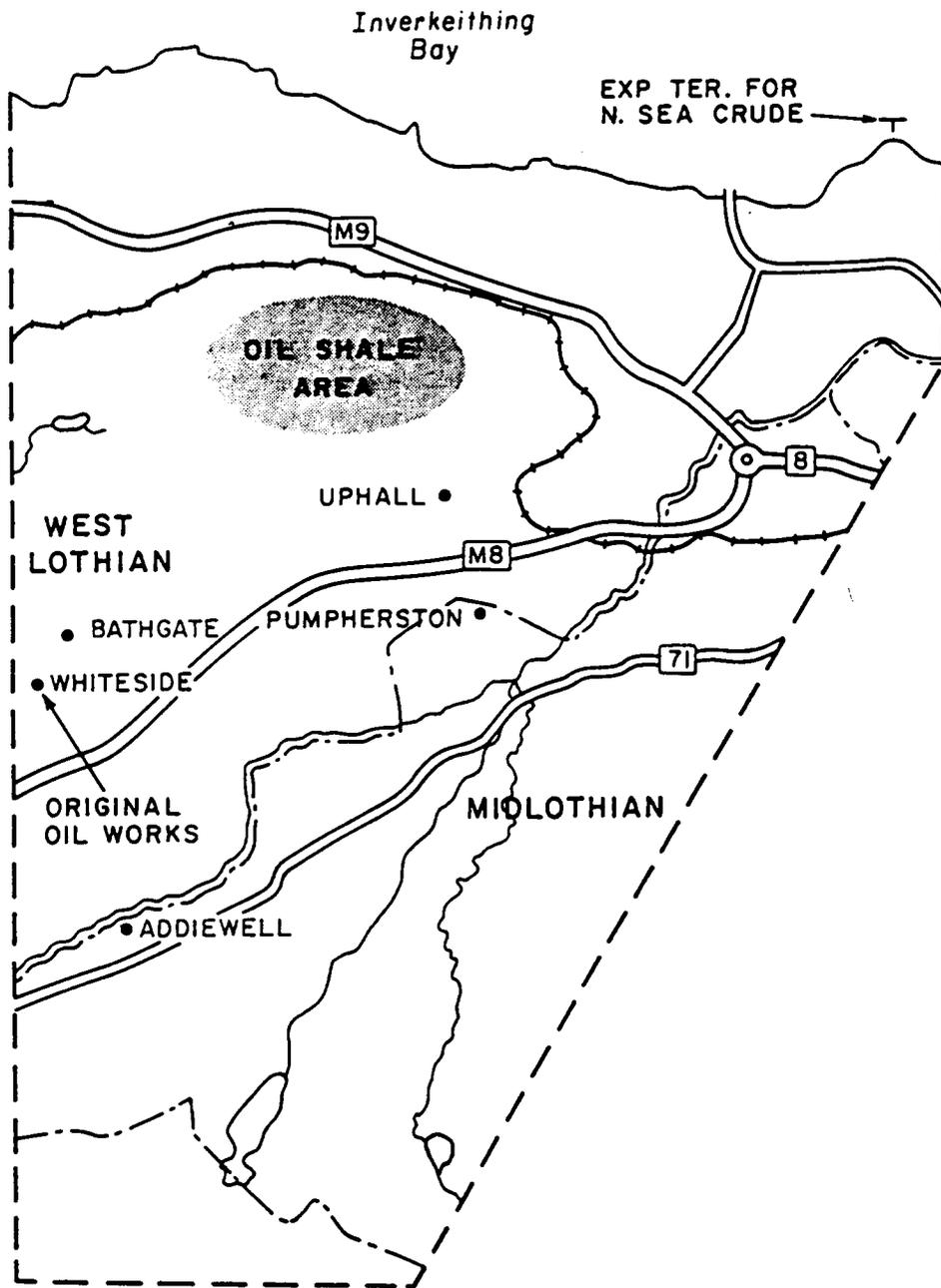


Figure 2. The Lothian region of Scotland: From [39].

In 1864, the year Young's patent expired, the effects of the oil find in Pennsylvania were felt in Scotland as that year was the first that the cheap petroleum oils were imported. Between 1851 and 1922 over 140 individuals or companies had "entered the oil shale industry in Scotland. In 1871 there were 51 active companies, but of these the number in existence in 1910 was only 6. In 1919 the 4 largest companies ... consolidated under one company, Scottish Oils (Ltd.)." [90] One of these was Young's Paraffin Light and Mineral Oil Co. Ltd., and another was the Pumpherston Oil Co. Ltd. located in Pumpherston in the Midlothian region (see Figure 2). The introduction of cheap petroleum oils had caused the failure of numerous companies and the consolidation of others. Retorting, mining methods, refining and marketing were streamlined so as to keep the Scottish oil shale industry in competition with the imported oil. [90]

The processing of oil shale reached a peak of 3,673,760 tons in 1913 and declined thenceforth. The richest shales were used early and the production of oil fell. In 1890, the shales were producing an average of 41.6 gal-ton⁻¹ of oil, whereas by 1918 this had fallen to 27.6 gal-ton⁻¹. The production of ammonium sulfate rose accordingly. Ammonium sulfate was a by-product of the shale processing and the low oil yielding shales produced more ammonium sulfate because of their higher nitrogen content. [90]

The retorting process involved using steam for converting the residual carbon in the shale to oil, but it also combined with the nitrogen in the shale to form ammonia. At first the odoriferous ammonia water, which condensed along with the oil, was thought to be a nuisance and was separated from the oil and pumped to waste. It was noticed the grass grew longer in the areas affected by this water, and then realized that a valuable fertilizer was being wasted. Most Shale Oil Works, therefore, built Sulphate of Ammonia plants in which ammonia gas was released from the crude ammonia water and bubbled into lead-lined vats containing sulphuric acid to form crystals of ammonium sulphate. The production of Sulphate of Ammonia made it possible for many Oil Shale Companies to stay in business. In fact, the financial justification for starting the Pumpherston Oil Company in 1883 was based on the price of Sulphate of Ammonia at that time, and on the quality of the oil shale in the Pumpherston area for its production. [39]

Young retired from the oil shale business in 1870. Retorting costs were reduced with the introduction of the Pumpherston retort. Scottish Oils Ltd. eventually ended up as a subsidiary of the current British Petroleum Co. Ltd. Winston Churchill, then Chancellor of the Exchequer, exempted indigenous oil companies (all producing oil from shale) from paying gasoline taxes starting

in 1928. This, however, only slowed the decline, and by the 1950s only 12 mines, four Works (that produced crude oil from shale), and one refinery (at Pumpherston) were left. The industry had to pay half the tax, and when the tax concessions were stopped in 1962, the oil shale industry in Scotland shut down. Even if it hadn't shut down by then it would have by now because the raw material would have been exhausted. Only 75 million tons of low grade oil shale are left in central Scotland. [39]

About 10,000 people were directly employed, and about 40,000 indirectly employed, by the Scottish oil shale industry at its peak. The companies owned whole villages that were constructed adjacent to the mines or Works to house the workers and their families. The spent shale and ash piles (called "bings" in Scotland) were in proximity to these villages, and often the liquid effluent from retorting was pumped onto these piles and allowed to filter through the spent shale. The spent shale piles are still evident in the Lothian region. The material from these is being used to build roads. The Pumpherston Works in the 1930s started producing bricks from spent shale by pulverizing it and then mixing it with hydrated lime and lime slurry. The production rate was 20 million bricks per annum. The bricks had a wet crushing strength of over 3,000 lb-in⁻². [39]

The acme of design in Scottish oil shale retorts was achieved when the 52 retorts were constructed at Westwood in 1942. The Westwood retort is illustrated in cross-section in Figure 3.

The Westwood retort was a vertical retort designed for continuous operation and was 34 ft tall. The shale was fed from the top and heated on its way down. Once they were brought on stream the retorts were thermally self-sufficient. Air and steam flowed countercurrent to the shale and were introduced from the bottom. These stripped the oil from the shale (which reached a maximum temperature of 785 °C) and the oil was subsequently condensed for further processing. The steam also reacted with the carbon in the shale to form water gas and with the nitrogen to form ammonia. The 52 retorts together could process 1,200 tons of shale per day and produce 600 to 700 bbl·d⁻¹ of oil. In 1948 a synthetic detergent producing plant was constructed that used the olefin content

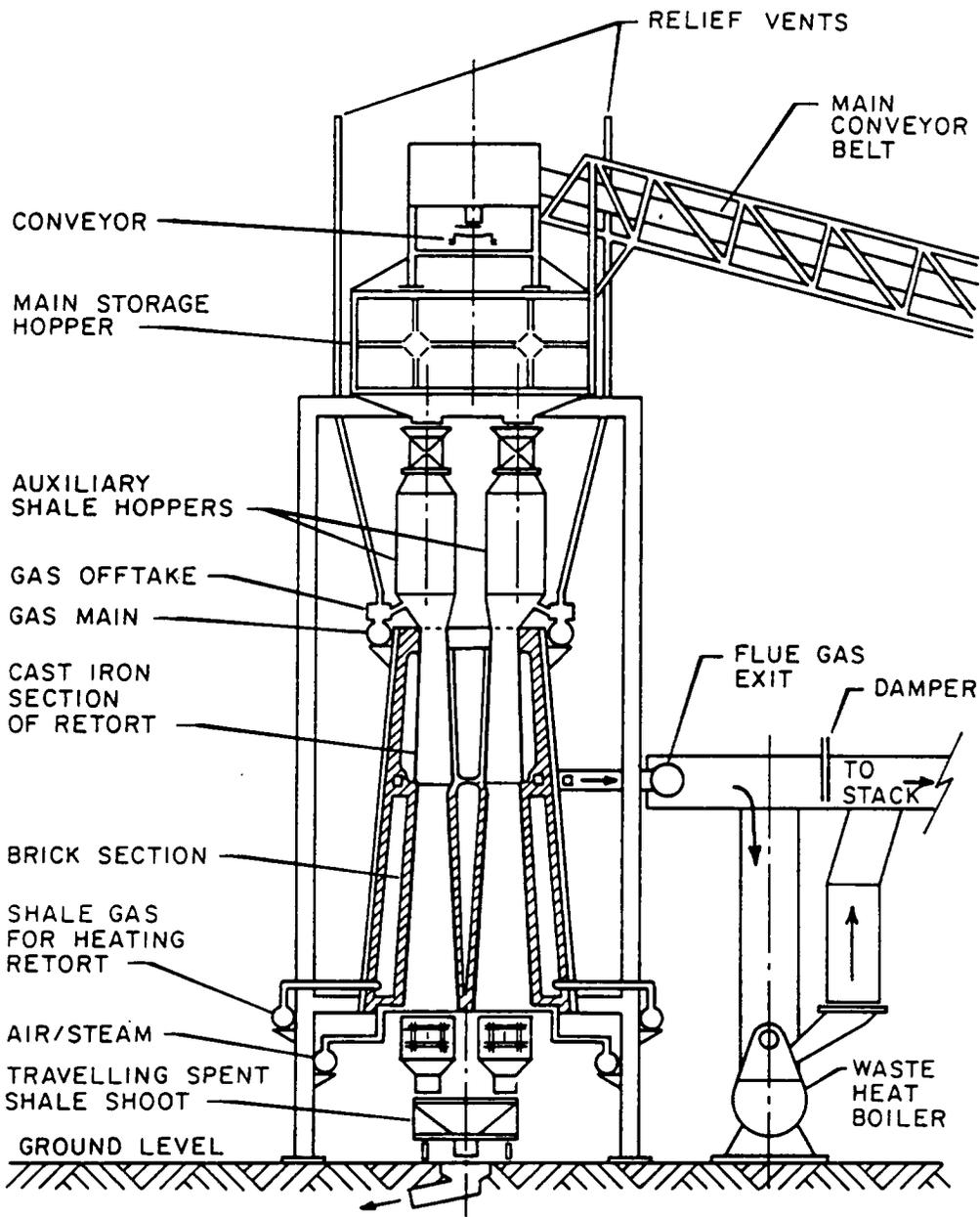


Figure 3. Scottish oil shale retort type erected at Westwood Works: From [39].

of the oil gas. Even though the Scottish oil shale industry ceased operations in 1962, the detergent plant is still being operated as Young's Paraffin Light and Mineral Oil Co. Ltd. [90]

The Australian Industry

Oil shale was first discovered in Australia by a French expedition that visited the Blue Mountains west of Sydney in New South Wales. The expedition discovered that river flow had brought down "large blocks of a black flammable non-coal rock" [28]. The records of the expedition were published in 1807, and stated: "We have discovered ... at the foot of a mountain, considerable masses of a bituminous schist which burns with a very lively flame, giving off thick smoke and an extremely pronounced odour of bitumen" [168]. What they had discovered was torbanite that had been washed down the valleys by floods [28].

It was reported by another French expedition in 1824 that the deposits had been mined for fuel by the early settlers. The Pioneer Kerosene Company built the first commercial oil shale works in 1865 near the city of Wollongong at the American Creek deposit on Mount Kembla. Operations there ceased in 1880 when the resources dwindled. Also in 1865, shortly after the Mount Kembla operation started, some retorts were established at Hartley Vale, west of Sydney. The Hartley Vale deposits proved to be one of the largest and richest in New South Wales, with oil yields of 60-70 gal-ton⁻¹ and gas yields of 50,000 m³-ton⁻¹. These deposits — over a quarter of a million tons of oil shale — were essentially mined out by 1903. [186]

New South Wales had over 100 retorts operating by 1877. However, many oil shale operations had ceased by the turn of the century, and in 1906 the Commonwealth Oil Corporation took over the operations of most of the remaining oil shale companies. The Corporation established the town of Newnes (named for its founder Sir George Newnes) about 90 miles northwest of Sydney. Sixty-four Pumphreton-type (Scottish) retorts were processing 76,160 tons of shale per annum by

1911. But by 1912 the Corporation was bankrupt because the Pumpherstons retorts could not handle the high grade of shale which had a yield of about 120 gal·ton⁻¹. [186] “Intumescence of the shale fractured the retorts and prevented the gradual descent of the spent material. Explosions were frequent.” [90] At the beginning of World War I, John Fell restarted the Newnes retorts after suitably modifying them. These again ceased production in 1922 due to high post-war production costs. “It was during this year that Fell, in an effort to curb production costs, attempted *in situ* retorting. Horizontal tunnels and flues were driven into the torbanite beds with air being drawn through the oil shale by an induced draft fan. However, shortly after initial ignition, the tunnels collapsed, prompting Fell to give up his attempts at *in situ* retorting.” [186]

Due to the economic depression of the early 1930s, the Australian government formed a committee in 1933 to determine if the Newnes deposits could be exploited again. By 1940, the Newnes plant had been shifted a short distance to Glen Davis, another town built at the eastern end of the deposits. The plant was kept going during World War II because Australia's imported oil supply was threatened. However, Glen Davis closed in 1952 due to post-war economic conditions and the availability of cheap petroleum from the Middle East. In 12 years of operation, the plant had retorted 1.46 million tons of shale and produced 61 million gallons of oil. [186]

In the early 1900s oil shale was discovered in northern Tasmania, and the first four retorts were started in 1910. Many companies started operations in the next 24 years and a total of 0.42 million gallons of oil was produced in this time. Also, in 1939 three retorts were opened at Marangaroo (southwest of Newnes and west of Sydney) and these produced 2.4 million gallons of oil between 1942 and 1945. The Australian oil shale industry entered what many hope is a dormant phase in 1952, with the closing of the plants at Glen Davis. [186]

The United States Industry

The history of the oil shale industry in the U.S. is principally the history of Western oil shale, since the oil shales in the west — particularly those in the Green River Formation — being richer shales than those in the east, have received the most attention in the past.

As stated earlier, the Ute Indians were aware of oil shale and called it “the rock that burns”. And Mike Callahan’s adventure of 1882 is probably apocryphal. But, a ruined old retort exists on a tributary of Chriss Creek in Juab County, Utah. Called the “Mormon” retort, it was believed to have been used by Mormons to produce oil from oil shale (to be used as dressing for leather, as axle grease and in lamps) sometime prior to 1859 [190].

By 1860, various bituminous substances were being retorted to produce oil. Fifty-three companies were involved in these ventures, and most of them were located in the east. Most operated under a license from the Young company of Scotland (Young’s Paraffin Light and Mineral Oil Co. Ltd.). The raw materials used were both cannel coals and some true oil shales. “The desired product was kerosene or ‘coal oil’ — the term still surviving from the time when most of the kerosene used in this country was really derived from coal and the like.” But the discovery of petroleum as a cheap source of oil drove these companies out of the oil shale business. Some survived by converting to the refining of petroleum. [90]

In Colorado, Roane Rowley and T. E. Bailey are reported to have experimented with shale as a smudge for Palisade peach orchards some time prior to 1905. James Doyle, discoverer and developer of the famous Portland gold mine at Cripple Creek, Colorado, entered the Mount Logan and Parachute Creek areas in about 1908 and is credited as having been the first to propose recovering commercial oil from oil shales. Doyle, with the assistance of C. A. Fisher, a Midwest geologist, J. C. Sparks, a New York chemist, and Ralph Arnold, is credited with bringing the immense deposits of bituminous rock in Colorado and Utah to the attention of the United States Government. [190]

In December 1916, President Wilson established “a 45,444 acre Naval Oil Shale Reserve in Colorado and an 86,584 acre Naval Oil Shale Reserve in Utah”. President Coolidge added to both these in 1924 — 23,000 acres to the Reserve in Colorado and 4,880 acres to the one in Utah. [190]

Dean Winchester of the USGS estimated the reserves of oil shale in 1915 to be equal to 20 billion barrels of oil, “three times the then estimated national petroleum reserves” [190]. Winchester was ordered to recheck his figures, since they sounded unbelievable. He found that he had been in error – the reserves were not 20 billion barrels but 40 billion barrels [223]! When *The National Geographic Magazine* published a report in 1918 entitled “Billions of Barrels Locked up in Rocks”, interest in oil shale reached a peak [190, 223]. The Oil Placer Act of 1872 allowed citizens to stake claims of up to 160 acres each, each claim to be in the name of eight people [190]. Estimates put the number of claims filed in Colorado anywhere from 10,000 to 30,000 and those filed in Utah and Wyoming anywhere from 25,000 to 120,000, although a firm number is not available since many claims were staked atop each other [190, 223].

On February 25, 1920, President Wilson signed the Oil Leasing Act of 1920 [190]. This act stopped the filing of further claims and authorized only the Secretary of the Interior to lease public lands to any person or corporation, the size of any one lease not to exceed 5,120 acres, with an annual rent of 50 cents per acre, but with a lease duration of indeterminate length to be determined by the Secretary [210]. This did not stop the rush, merely slowed it. More than 200 companies, many fraudulent ones that bilked stockholders upon the basis of minimal acreage of holdings, were formed [223]. Boom towns sprang up over Colorado. The Chamber of Commerce of DeBeque, Colorado, one of these boom towns and home to the retorts of the Monarch Oil Shale Company, advertised free train trips for Denver citizens to “Visit DeBeque the Oil Shale Center” and promised them “barbequed venison and free lunch” [190].

Before all this, however, at Elko, Nevada, the Catlin Shale Products Company had been operating the “first and only continuously operating commercial shale corporation” in the United States from the late 1890s [223]. Robert M. Catlin, a mining engineer from Burlington, Vermont, discovered the paraffin shales (a lighter form of oil shale) of Elko in 1875. He invested half a million dollars of his own money in three retorts, and he never sold stock. The last retort was built in 1921, was a continuously operating one, and could process 250 ton·d⁻¹ of shale and yield 50 barrels of oil. The company was never profitable and Catlin shut down operations in 1924. Oil prices had fallen

drastically, Catlin was in his 70s and the deposits of the Piceance Creek Basin had been established. Catlin Shale Products Company was dissolved on December 23, 1930, at which time it had less than \$3,800 in assets. [223]

By the time the Oil Leasing Act of 1920 was signed, “virtually every available acre of cliff outcrops had been claimed in Colorado, Utah and Wyoming. There was no knowledge of the rich, deep, basin center in Colorado and claims were not filed in this area.” [190] Around 1924, though, petroleum became cheaper, and interest in oil shale declined. The boom era of 1915-1930 ended. During the Second World War oil consumption increased, domestic reserves decreased, and interest in oil shale rose again.

On April 5, 1944, the 78th Congress passed Public Law 290 – the Synthetic Liquid Fuels Act. The Act authorized the production of synthetic fuels (synfuels) from “coal, oil shale, agricultural and forestry products and other substances” [190]. Consequently, construction began in 1945 on a demonstration plant in the Anvil Points area some miles west of Rifle, Colorado, on Naval Reserve land. Completed in 1947, the retort processed its first batch of oil shale that year. An on-site refinery opened in 1949. Underground mining using the room-and-pillar method was used to mine the shale. As a demonstration project it worked well in showing that gasoline diesel and fuel oils could be produced from shale oil. However, costs of production were too high compared to natural petroleum to generate any interest from the oil industry. Congress stopped funding for the Anvil Points site in 1955, and since then it has been kept in a standby state and has been used by industry on various occasions for research. [190]

Between 1940 and 1969 there was considerable improvement in mining and retorting on a large scale. *In situ* techniques for retorting were also developed. About 75,000 bbl of oil were produced during this time of pilot testing. Some of the principal organizations involved were the Sinclair Oil and Gas Company (now a part of Atlantic Richfield Oil Company, now ARCO), Union Oil Company of California, Inc., The Oil Shale Corporation (now TOSCO), Shell Oil Company, Inc., and the Colorado School of Mines Research Foundation, Inc. (which was acting as a contractor

for Mobil Oil Company, Continental Oil Company, Humble Oil and Refining Company, Pan American Petroleum Company, Phillips Petroleum Company, and Atlantic Richfield Company). [190]

Among the more *outré* methods tried was Project Bronco, set up in 1967 by the U.S. Atomic Energy Commission (AEC), the U.S. Department of the Interior, CER Geonuclear Corporation (consisting of Continental Oil, Edgerton, Germeshauser & Grier, Inc. — now called EG&G, and Reynolds Electrical and Engineering Company, Inc.), and the Lawrence Radiation Laboratory. The objective of this project was to develop a commercial scale nuclear *in situ* retort, using a 50 kiloton nuclear device to rubblize a chimney 520 feet high and 230 feet in diameter. Upto 26 other oil companies evinced an interest in the project. A project engineer from the AEC created a sensation at the Third Annual Oil Shale Symposium (held a year before the project was formed) by announcing that the nuclear method would produce oil at a cost of 29 cents per barrel, at a time when natural petroleum prices were \$3.00 per barrel! The figures were questionable and so was the feasibility of the project and it was essentially abandoned in 1970 without a single explosion. [190, 223]

In early 1967, in an attempt to gain control of the shale lands (which had been withdrawn from further leasing by President Hoover in 1930) by using the minerals present in the shale as the primary objective, a prospector named Merle I. Zweifel filed 20,000 claims, totalling 4,000,000 acres of land, for mining dawsonite. Oil shale in the Piceance Creek Basin — prime oil shale land — contains up to 20% nahcolite (NaHCO_3 — sodium bicarbonate, or baking soda) and some dawsonite ($\text{NaAl}(\text{OH})_2\text{CO}_3$ — sodium aluminum dihydroxy carbonate, or the active ingredient in Roloids® antacid). Studies showed that “a single square mile might contain, in addition to nearly a billion barrels of shale oil, 126 million tons of soda ash from nahcolite, 100 million tons of sodium chloride and 42 million tons of alumina (Al_2O_3), from which aluminum is easily extracted, which would equal more than one and a half times the United States’ entire supply of bauxite, the present source of commercial aluminum”. However, shale has only 4% of alumina whereas bauxite has

50%, and moreover it cannot be separately mined and removed without disturbing the oil. Zweifel's scheme, therefore, did not go too far. [223]

"It is estimated that 72 percent of oil shale lands containing nearly 80 percent of the shale oil is Federally owned. Of the higher grade resources, about 81 percent is in Federal ownership" [190]. In 1968 the Federal Government had offered to lease public oil shale lands for development. There were three tracts. For some reason, the total bid for the three tracts amounted to only \$500,000 [190]. One bid was by a drilling operator in the amount of \$625 [161]. Among charges of another Teapot Dome scandal and the giveaway of public lands, the lease offering was withdrawn [223]. (The Teapot Dome scandal of the 1920s involved charges of bribery and corruption concerning the leasing of the Naval Oil Reserve near Caspar, Wyoming — known as the Teapot Dome for a sandstone formation — to Pan-American Petroleum and Transport Company for a very low amount.) In early 1974 the Government again offered six experimental sites for lease. Each site was about 5,100 acres and there were two each in the states of Colorado, Utah and Wyoming (designated C-a, C-b, U-a, U-b, W-a, W-b, respectively). The Colorado sites were in the Piceance Creek Basin where the richest oil shale is to be found. Eight bids were received for tract C-a, and the high bid was by Standard Oil Company of Indiana and Gulf Oil Corporation for \$210 million. The oil embargo of 1973 had had its effects! Table 2 provides the amounts bid. As can be seen, the oil shale resources were finally being taken seriously. Bids for the other tracts were considerably less (ranging between \$4 million and \$118 million) and there were no bids for the two Wyoming tracts. [190] But, another spurt in oil shale activity was on the way.

From 1970 to about 1984, various projects have been operated in the oil shale lands in the west. One of these is Paraho Corporation. Paraho is a contraction of the Portuguese words "para homem" meaning "for mankind" [160]. The Corporation consists of 17 companies, among them are Sohio Petroleum Corporation, Gulf Oil Corporation, Shell Development Corporation, Standard Oil Co. of Indiana, Sun Oil Company (SUNOCO), Chevron Research Company, Marathon Oil Company, Mobil Research and Development Corp., Atlantic Richfield Co. (ARCO), Texaco, Inc., and Phillips Petroleum Co. Other ventures during the same years were by Superior Oil

Table 2. Bids for leasing of Colorado tract C-a, January 8, 1974

Bidder	Bid
1. Standard Oil Company of Indiana & Gulf Oil Corporation	\$210,305,600.00
2. Sun Oil Company	175,001,190.98
3. American Petrofina Co., Marathon Oil Co., & Phelps Dodge Corp.	80,000,000.00
4. Atlantic Richfield Co., Ashland Oil Co., Inc., & The Oil Shale Corp.	63,333,333.36
5. Shell Oil Company	63,000,000.00
6. The Carter Oil Company	33,125,294.51
7. Occidental Oil Shale, Inc.	<u>16,361,044.24</u>
<i>Total</i>	\$641,126,463.09
<i>Average</i>	\$ 91,589,494.72
8. Lawrence S. Shaw, San Diego, California, bid "Forty-nine percent of net profits per acre after production costs. Enclosed find a token payment in the amount of \$1 for the bonus bid. If you know the exact amount of this bid I will put up one-fifth of this amount."	

Source: [190]

Company, Occidental Petroleum Corporation, Geokinetics, Inc., Equity Oil Co., Inc., and Union Oil Co. TOSCO, SOHIO, and The Cleveland-Cliffs Iron company started the Colony Development Company in 1964 and operated a TOSCO II retort at Parachute Creek near Rifle, Colorado. [190] Later, ARCO, Ashland Oil, Inc., and Exxon Co. participated in the operations at one time or another. Exxon's decision in 1982 to pull out of Parachute Creek was quite widely reported. [190, 214]

In 1980, the Energy Security Act was passed and the United States Synthetic Fuels Corporation (SFC) was established to promote development of synfuels [21]. In the year prior to that, though, one prediction was that synfuels would not be developed “until the year 2000, if indeed then” [7].

The Laramie Energy Technology Center

The Bureau of Mines started a station on the present University of Wyoming campus in Laramie, Wyoming, in 1924, and in 1935 it received the formal name of U.S. Bureau of Mines Petroleum Experiment Station. The name was changed to Petroleum and Oil Shale Experiment Station in 1944 when the Anvil Points project terminated operations. It conducted basic research on the lithology and oil yields of shales of the Green River Formation, and on the chemistry of conversion. *In situ* tests were begun in 1964 near Rock Springs, Wyoming. Two batch surface retorts — one of 10 ton and one of 150 ton capacity — were also constructed and operated at Laramie. The Center was transferred to the Energy Research and Development Agency (ERDA) in 1974, and to the DOE in 1977 (when ERDA was converted to DOE). It received the new name of the Laramie Energy Technology Center (LETC). It was made the lead laboratory for the Fossil Energy Oil Shale Program in 1979. [214] In 1982 it was transferred to the University of Wyoming and set up separately as the University of Wyoming Research Corporation. Currently, it operates under the Western Research Institute name. The DOE has a Laramie Projects Office at the Center that is attached to the DOE's Morgantown Energy Technology Center (METC) in Morgantown, West

Virginia. In this document, it shall be referred to by its former name of LETC, since a lot of the pioneering work done there was performed when it was called by that name.

Operations in the Eastern United States

During the 1970s and 1980s, interest has been paid to the shales of the eastern United States. These shales, although not as rich as those in the west, are spread over a much larger area. The Dow Chemical Co. has studied the Antrim shales of Michigan since the mid-1950s [112, 146, 156, 167 208]. Most work on eastern shales has been done by research laboratories, mainly governmental and university. Thus, among others, work has been done by the University of Michigan [118, 119], LETC [139, 144, 151, 152], METC [121, 183, 194], the University of Kentucky [13, 14, 35, 188, 193], the Institute of Gas Technology [142, 204], the University of Louisville [13, 29, 37, 38, 180, 187, 209], and the Stone and Webster Engineering Corporation [2, 64, 170] (which did work with the Petrosix process developed by Petrobrás of Brazil).

The East has not seen the extent of larger-scale experimentation as has the West, principally because the West had an earlier start. However, research does continue.

Oil Shale Developments in Other Countries

France, Spain, Sweden and Germany had oil shale industries that operated for some time in the 19th century. France's industry operated sporadically until 1957, whereas Sweden's closed in 1964. Germany extracted some shale oil in the Second World War, but merely on a short-term basis due to fuel shortages. South Africa started small-scale production from its rich (100 gal-ton⁻¹) shales in the early 1900s and stopped in 1964 due to depletion of resources. [113]

The only countries that have currently operating commercial industries are China, the U.S.S.R. and Brazil. China's industry started in the 19th century, but received boosts due to the Japanese occupation of World War II, and the Korean War. The industry is based in Manchuria with an estimated production rate of 1.5 million barrels per year. China also has resources in the Kwangtung province which have not been developed yet. The U.S.S.R.'s industry essentially started in 1920 in Estonia, where 80% of the reserves lie. Most of the oil is used for the generation of electricity, and recent expansion goals were set at 200,000 bbl·d⁻¹. [10, 113]

Brazil's industry has operated intermittently since 1862. Its deposits are estimated to be 3 trillion barrels of oil. The industry was nationalized in 1950. Petrobrás, the national oil company, developed the Petrosix process and has operated a demonstration retorting plant at São Mateus do Sul since 1970. [113] The plant processes 1,600 ton·d⁻¹ of 20 gal·ton⁻¹ shale and produces 800 gal·d⁻¹ of shale oil. Since 1980, it has been operating as a commercial plant. [116] The Brazilian shales are very similar to the Devonian-Mississippian shales of the eastern U.S., and the Petrosix process is being tried out on the eastern U.S. shales [64, 170]. The only other countries attempting to develop oil shale are Canada, Morocco, Jordan and Israel. The status of shale oil projects worldwide as of early 1983 is shown in Table 3.

Formation, Composition and Extent of Deposits

Genesis and Composition of Oil Shale

Oil shale and petroleum both had their genesis in inland seas and lakes. Both started with the mixing of sediments from inland bodies of water with dead plant and animal matter that settled to the bottom, and was then subjected to heat and pressure. Whereas in some areas the organic matter

Table 3. Status of oil shale development projects worldwide

Country/location	Company/owner	Capacity (bbl-d ⁻¹)
UNDER CONSTRUCTION		
USA		
Parachute Creek	Union Oil of California	50 000
DESIGN ENGINEERING		
Brazil		
São Mateus do Sul	Petrobrás	25 000
<i>World Total</i>		75 000
PLANNED		
USA		
Garfield County	Mobil	...
Wolf Den	Geokinetics	3 000
Agency Draw	Geokinetics	20 000
Salt Lake	Phillips, Sohio, Sun Oil	15 000
Rangely	Rio Blanco Oil Shale	20 000
Bonanza	Paraho Development	39 500
Rifle	Superior Oil, Sohio, Cleveland	15 000
Uinta County	Magic Circle Energy	31 500
West Slope	Shale Energy Corporation of America	5 800
Total (excluding Mobil)		149 800
<i>World Total</i>		149 800
CANCELLED, DELAYED INDEFINITELY OR STATUS UNCERTAIN		
USA		
Rio Blanco	Occidental	94 000
Piceance Creek	Multimineral Corp.	50 000
DeBeque	Cities Service	...
Garfield	Chevron Oil Shale	50 000
Rifle	Exxon, TOSCO	50 000
Vernal	TOSCO	50 000
Total		294 000
Australia		
Queensland	Esso Exploration	20 000
Morocco		
...	Onarep	...
<i>World Total (excluding Cities Service, Onarep)</i>		314 000
World total, identified projects		538 800

Source: [113]

was subjected to sufficient heat and pressure to be converted (by distillation) to petroleum, in other areas there was insufficient heat and pressure to cause distillation and the organic matter remained in its pre-distilled form, known as kerogen. The following extract indicates the difference between kerogen and petroleum:

The chief chemical difference between kerogen and petroleum is geometric: unlike petroleum the kerogen molecules are connected with elaborate chains. To convert kerogen to a close equivalent of petroleum, one need only apply the heat it did not receive from the earth. At a temperature between 850 and 900 degrees F. "retorting" occurs. The molecular chains break, and the kerogen is distilled into, by weight, about 66 percent shale oil (which is usually released as a vapor), 25 percent coke-like solid matter, and 9 percent combustible gas. Thin layers of shale with a high kerogen content can be retorted with a match, which creates a sooty flame and an acrid odor. The amount of shale oil produced varies, of course, with the percentage of kerogen, ranging from less than five gallons per ton of shale rock to nearly 100 gallons per ton. One cubic foot of reasonably rich shale will yield about three gallons of shale oil. The biggest residue from retorting is "spent shale" which weighs only slightly less than the original shale rock and expands during retorting to a volume between 20 and 40 percent greater, meaning that more space is required to dispose of these tailings than the hole from which the shale rock was dug. [223]

Kerogen "resembles a very old, dry leaf mold" [90], and usually occurs scattered in the rock as "small globules or irregular streaks" [90]. Almost all oil shale occurring worldwide is either fine or very fine grained and is uniform laterally [202]. Some oil shales, like those from the Green River Formation in the U.S., have very thin pairs of layers, one dark and the other light, that are called varves. These are about 30 μm thick per pair, and probably indicate seasonal differences in deposition when the oil shale was being formed [202]. These layers can be likened to the growth rings in trees. The chemical composition of any one deposit is usually very uniform. The kerogen globules range in color from yellow to brown to black [90, 230]. Kerogen is not soluble in organic solvents [39]. The Mahogany Zone (a particularly rich zone) in the Green River Formation is called that because if the shale is polished it resembles aged mahogany [223].

In reality then, oil shale is neither oil nor shale. It is a precursor of oil — kerogen — dispersed in a fine grained rock. To distinguish it from coal, it is generally accepted that the ash content of oil shale must be at least 33% [90, 230]. Such definitions, however, do not work when applied to the rich oil shales of Australia which yield low amounts of ash [230]. One definition of oil shale states that "oil shale is a compact, laminated rock of sedimentary origin, yielding over 33 per cent of ash and containing organic matter that yields oil when distilled but not appreciably when extracted with

the ordinary solvents for petroleum” [90]. Another description (that also contains a useful list of alternate names by which oil shale has been called) is:

Oil shale is a sedimentary rock containing solid, combustible organic matter in a mineral matrix. The organic matter, often called kerogen, is largely insoluble in petroleum solvents, but decomposes to yield oil when heated. Oil shale as defined is used as a lithologic term but is further interpreted as an economic term referring to the rock's ability to yield oil. ... Additional names given to oil shales include black shale, bituminous shale, carbonaceous shale, coaly shale, cancell shale, cancell coal, lignitic shale, stellarite, torbanite, tasmanite, gas shale, organic shale, kerosene shale, coorongite, maharahu, kukersite, kerogen shale, algal shale and “the rock that burns”. [49]

Perhaps a good working definition would be that oil shale is an “organic-rich shale that can yield substantial quantities of oil when subjected to destructive distillation by low confining pressure in a closed retort system. The oil shale deposit which yields at least 10 gallons (3.8 wt. %) of oil per short ton of shale by such extraction method is considered the lowest boundary of oil shale. For the upper boundary, certain Australian shale reaches 90 + %.” [230] This is not to say that the Australian shales literally drip with oil. Far from it; kerogen is a solid and the oil it yields typically has a high pour point [16]. The essential difference between kerogen and bitumen (another more familiar precursor of oil) is that kerogen is insoluble in solvents whereas bitumen is. Depending on the heteroatom used, the stoichiometric formulæ given for kerogen are: $C_{18}H_{28}O$ (molecular weight ≈ 260), $C_{39}H_{60}O_3N$ (mol. wt. ≈ 590), or $C_{215}H_{330}O_{12}N_5S$ (mol. wt. ≈ 3204) [16]. The rock part of the oil shale consists predominantly of quartz and clays, principally illite and smectite (montmorillonite). Pyrite is almost always present. The quartz is found as uncemented discrete particles. The structure is derived from the clay layers and the kerogen. [202]

In the following discussion, and indeed in the rest of this document, western shale will refer to shale from the western part of the U.S., and eastern shale will refer to shale from the eastern part of the U.S.

Tables 4 and 5 give the mineral constitution of western and eastern shales, respectively. The eastern shales typically have a simpler matrix than do the western shales. Western shales contain a fairly

Table 4. Typical mineral composition of western shales

Dominant Minerals	
<i>Mineral</i>	<i>Percentage</i>
Dolomite (ankeritic)	40 - 60
Quartz	10 - 20
Feldspar: orthoclase, albite	10 - 20
Carbonates: calcite, siderite	5 - 10
Clays	< 1 - 30
Sulfides: pyrites, etc.	< 1 - 5

Location Dependent	
<i>Mineral</i>	<i>Percentage</i>
Micas: biotite, muscovite, phlogopite	< 1 - 5
Complex carbonates: trona, shortite, nahcolite	≪1 - 15
Zeolites: analcime	< 1 - 5
Miscellaneous, up to 50	≪1 - 2

Source: [49]

Table 5. Typical mineral composition of eastern shales

Mineral	Percentage
Clays: illite, kaolinite	25 - 35
Quartz	20 - 30
Feldspar: orthoclase, albite	10
Sulfides: pyrite, marcasite, etc.	3 - 8
Iron oxides	2
Miscellaneous: zircon, apatite, etc.	1

Source: [49]

high percentage of dolomite — $(\text{Mg,Fe})\text{Ca}(\text{CO}_3)_2$ — whereas eastern shales have a higher percentage of clays and quartz.

The elemental composition of the organic matter in western and eastern shales is compared in Table 6. The major difference is in the carbon:hydrogen (C:H) ratio. the C:H ratios of shales are compared with those of other organic fuel sources in Table 7. Shales have C:H ratios close to those of petroleum, although lignitic coal has a C:H ratio close to that of eastern shales.

The relative mix of constituents changes depending upon the grade of shale (Table 8). For example, leaner shales contain a higher percentage of quartz (SiO_2). Shales also contain soluble chemicals that are removed upon retorting (a process that frequently involves steam stripping). For example, nahcolite (NaHCO_3) is easily removed.

The variation of inorganic and organic constituents in oil shale with respect to oil yields is given in Table 9. As is to be expected, the lesser grade shales contain a higher percentage of inorganic materials and a lower percentage of organic materials. The oil content is shown as being determined by the “Fischer assay”. This is a standard laboratory procedure for determining the oil content of oil shale, and a few words about it are in order at this time.

The Fischer Assay and the TOSCO Modified Fischer Assay

The Fischer assay is a laboratory-scale retort. It is a dry retorting technique (i.e., it does not use steam to help remove the oil from the shale). Originally developed by the U.S. Bureau of Mines in 1949 [108], it uses an air-sealed aluminum retorting vessel in which crushed shale is packed in layers separated by perforated aluminum discs (see Figure 4). The retort is heated at a controlled rate starting from 25 °C and reaching 500 °C in 40 minutes (not a linear rate, though: a standard heating curve is followed), and then held at 500 °C for 20 minutes. The oil that is generated by

Table 6. Elemental composition of western and eastern shales

Component	Average amount of component, Weight % of organic matter	
	Mahogany Zone	New Albany Shale
Carbon	80.5	82.0
Hydrogen	10.3	7.4
Nitrogen	2.4	2.3
Sulfur	1.0	2.0
Oxygen	5.8	6.3
C:H ratio	7.8	11.1

Source: Modified from [16].

Table 7. Approximate carbon:hydrogen ratios in various organic materials

Material	C:H ratio
Conventional petroleum	6.2 - 7.5
Athabasca bitumen	7.5
Green River kerogen	7.8
New Albany organic matter	11.1
Lignitic coal	12.1
Low volatile bituminous coal	19.4
Anthracitic coal	35.1

Source: [16]

Table 8. Chemical composition of the inorganic portion of various grades of shale and of the spent shale products

Chemical Constituent	Very Low-Grade Shale (10.5 gal-ton ⁻¹)	Medium Grade Shale (26.7 gal-ton ⁻¹)	High-Grade Shale (36.3 gal-ton ⁻¹)	Very High-Grade Shale (61.8 gal-ton ⁻¹)
<i>Raw Shale:</i>				
SiO ₂ , percent	40.9	26.1	25.5	26.4
Fe ₂ O ₃	4.3	2.6	2.9	3.1
Al ₂ O ₃	9.4	6.5	6.3	7.0
CaO	11.0	17.5	14.2	8.3
MgO	5.4	5.3	5.6	4.5
SO ₃	0.1	0.6	1.2	1.4
Na	1.8	2.6	2.7	1.9
K ₂ O	3.4	1.0	1.9	1.0
<i>Spent Shale:</i>				
SiO ₂	53.27	41.90	42.36	49.19
Fe ₂ O ₃	5.64	4.10	4.74	5.87
Al ₂ O ₃	12.28	10.53	10.46	13.13
CaO	14.82	28.11	23.54	15.40
MgO	7.00	8.53	9.30	8.35

Source: [16]

Table 9. Mineral content of oil shale versus grade

Fischer Assay, gal·ton⁻¹	Grade			
	10.5	26.7	36.3	57.1
Inorganic minerals, wt. %	92.2	84.0	80.1	67.0
Organic constituents, wt. %	7.8	16.0	19.9	33.0
Oil shale	100.0	100.0	100.0	100.0

Source: [16]

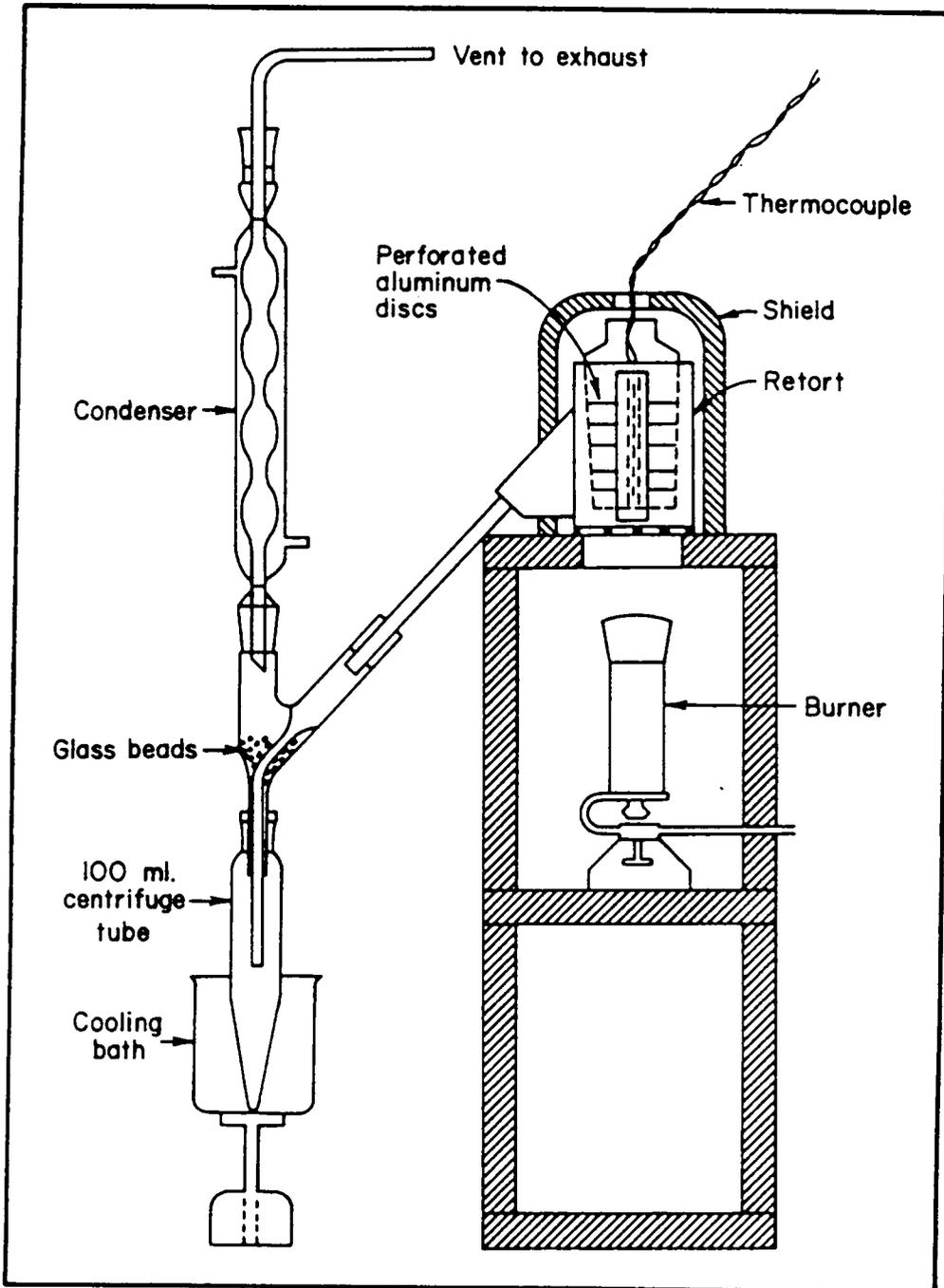


Figure 4. Fischer assay oil shale retorting unit: From [16].

pyrolysis of the kerogen in the shale volatilizes and is collected in the cooling bath. Gases are vented.

The TOSCO modified Fischer assay procedure is an improvement upon the standard Fischer assay in that all the vent gases are also collected. This enables a material balance to be performed. Another modification is that the shale is placed in a thin-walled aluminum can which is then placed inside a steel retort. (The original paper on the TOSCO modified Fischer assay stated that the aluminum can was to be “a 7-ounce Coors aluminum beer can”! [92]) The sample is heated according to a similar temperature profile as for the standard Fischer assay. The TOSCO assay is definitely more useful since it allows a more complete material balance determination.

It should be noted that the Fischer assay is *one* method of retorting shale and not necessarily the most efficient one. Although a lot of pilot and commercial scale retorts have lower recovery rates than the Fischer assay, at least one — the TOSCO II retorting process — has higher yields than the Fischer assay.

Extent of Oil Shale Deposits

The World Bank reported in 1980 that the world oil shale reserves amounted to 3.2×10^{12} barrels, of which 2.2×10^{12} barrels (or 69%) were in the U.S. (Table 10). In the same year, the U.S. Congress' OTA estimated the worldwide reserves to be on the order of 2.0×10^{15} barrels (Table 11). The difference is that the OTA figures include all oil shales, including very lean shales. The OTA figures for Asia probably include the U.S.S.R. (although this is not mentioned), whereas the World Bank figures place U.S.S.R. in Europe.

Different shale deposits vary significantly in composition and oil yields. Table 12 shows these differences. Organic carbon, for example, varies from 7.92% to 81.4% among the samples listed in the table. As noted earlier, the Australian shales are the richest at $200 \text{ gal}\cdot\text{ton}^{-1}$. Although the yield

Table 10. World shale oil reserves according to World Bank estimates

Country	10 ⁹ bbl
<i>Africa</i>	
Madagascar	0.03
Morocco	0.59
South Africa	0.13
Zaire	100.64
Total	101.39
<i>Europe</i>	
Austria	0.01
Belgium	0.69
Bulgaria	0.13
France	0.44
West Germany	2.00
Poland	0.05
Sweden	2.50
U.K.	1.00
U.S.S.R.	112.6
Yugoslavia	0.19
Total	119.61
<i>North America</i>	
Canada	44
U.S.A.	2,166.2
Total	2,210.2
<i>South America</i>	
Argentina	0.38
Brazil	800.84
Chile	0.02
Total	801.24
<i>Asia</i>	
Burma	2.01
China	27.90
Israel	0.02
Jordan	0.04
Thailand	0.82
Turkey	0.02
Total	30.81
<i>Oceania</i>	
Australia	0.25
New Zealand	0.25
Total	0.50
World Total	3,263.75

Source: [163]

Table 11. World shale oil reserves estimated by the U.S. Congress' Office of Technology Assessment

Continent	10¹² bbl
Africa	500
North America	300
South America	250
Asia	700
Australia (& New Zealand)	120
Europe	170
	<hr/>
	2,040
	(2 × 10 ¹⁵ bbl)

Sources: [160, 163]

of the Piceance Creek shales (at 28 gal-ton⁻¹) appears low, it should be remembered that the extent of the deposits is vast.

When compared with other fossil fuels in the world, shale (i.e., the kerogen in the shale) easily ranks as the largest known source (Table 13). However, it is also one of the most widely dispersed deposits — not merely dispersed in the sense that it is found in many locations around the world, but also dispersed within rocks at any one location. This necessitates the processing of large quantities of raw material to get significant yields.

Figure 5 indicates the areas of deposits of oil shale in the U.S. The richest deposits in the U.S. are the Tertiary deposits of the Green River Formation (Figure 6). The Tertiary period belongs to the Cenozoic era, and the Green River deposits are primarily from the Eocene epoch of about 40 to 60 million years ago [49, 101]. The eastern deposits are primarily of the much older Devonian period of the Paleozoic era and are about 400 million years old [101, 202].

The western deposits in the Green River Formation amount to a total of 4.0×10^{12} bbl, with most of the rich deposits (the 25-60 gal-ton⁻¹ deposits) being in the Piceance Creek Basin in Colorado. As can be seen in Table 14, the part of the Green River Formation that is in Utah (the Uinta Basin) has the largest fraction of lean deposits, whereas Wyoming has the smallest fraction overall. The National Petroleum Council (NPC) considered those deposits that were of at least 15 gal-ton⁻¹ richness, and subdivided these into four classes. These classes are probably more representative of the commercial potential of these deposits. These classes and the extents of the deposits are shown in Table 15. The total for Class 1 and 2 deposits is 129×10^9 bbl, which is still significant, although much lower than the total of 1.8×10^{12} bbl, 15 gal-ton⁻¹ minimum.

The eastern deposits have not been as extensively studied as the western ones. Interest in these deposits has only really risen in the late 1970s. One problem with exploiting the western deposits is the shortage of water in the region. The eastern parts of the country do not suffer from such problems. However, the technology for profitably exploiting these leaner deposits has not been

Table 12. Composition and oil yield of some oil shales

Location of Sample	% Organic C	% S	% N	% Ash	Oil Yield (gal·ton⁻¹)
Kiligwa River, Alaska	53.9	1.5	0.30	34.1	139
Piceance Creek, Colorado	12.4	0.63	0.41	65.7	28
Elko, Nevada	8.6	1.1	0.48	81.6	8.4
Dunnet, Scotland	12.3	0.73	0.46	77.8	22
Ione, California	62.9	2.1	0.42	23	52
São Paulo, Brazil	12.8	0.84	0.41	75.0	18
Puertollano, Spain	26.0	1.7	0.55	62.8	47
Shale City, Oregon	25.8	2.2	0.51	48.3	48
Coolaway Mt., Australia	81.4	0.49	0.83	4.4	200
Soldiers Summit, Utah	13.5	0.28	0.39	66.1	17
Ermelo, South Africa	52.2	0.74	0.84	33.6	100
New Glasgow, Canada	7.92	0.70	0.54	84.0	9.4

Source: [230]

Table 13. Fossil fuel deposits of the world

Organic Sediment	Amount present (10¹² tons)
Concentrated	
Petroleum	0.6
Asphalts	0.3
Coals (including lignite, peat)	7.0
Diluted	
Hydrocarbons	60
Bitumen (extractable non-hydrocarbons)	100
Kerogen (non-extractable non-hydrocarbons)	3200

Source: Adapted from [230].

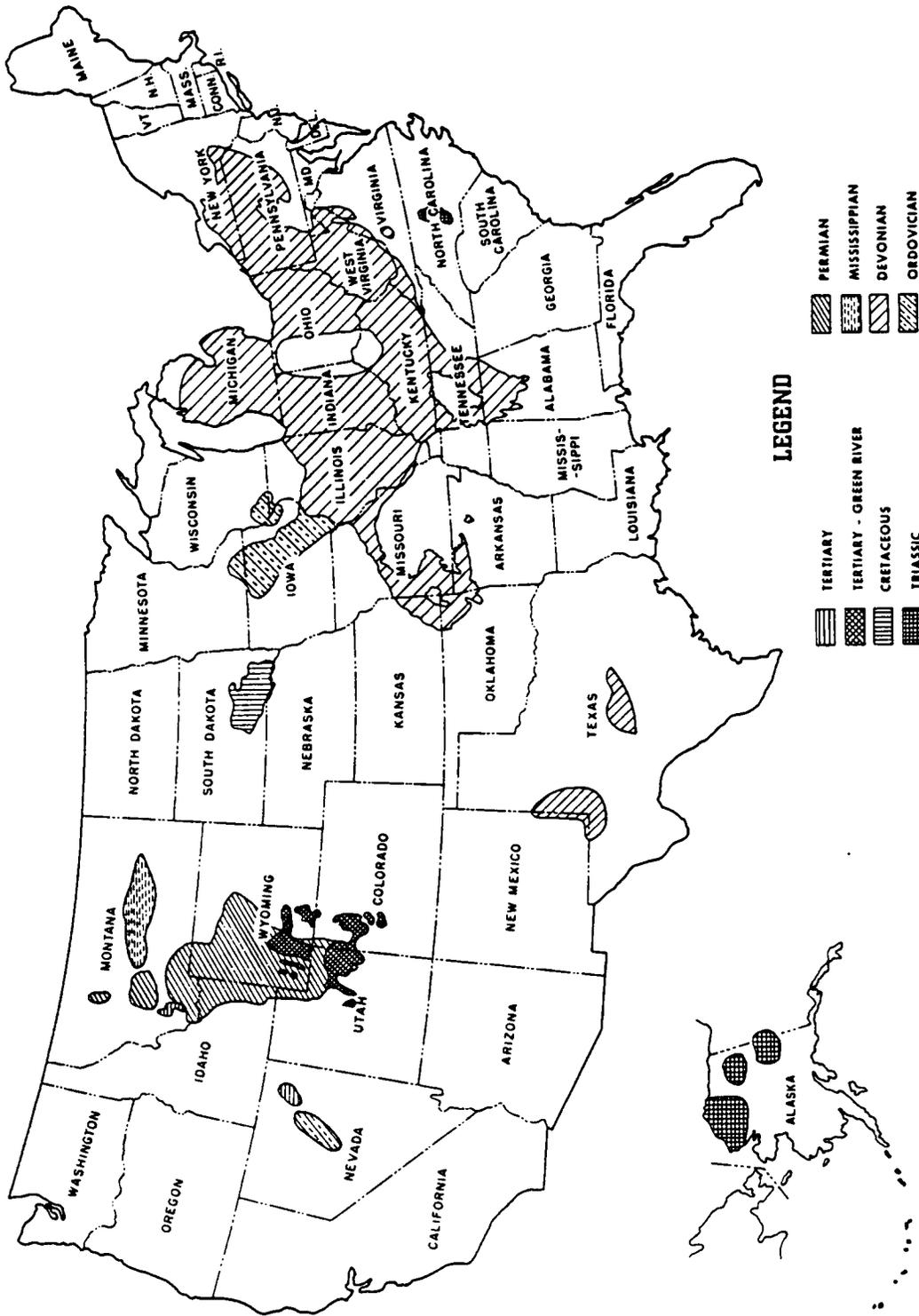


Figure 5. Oil shale deposits of the U.S.A.: From [202].

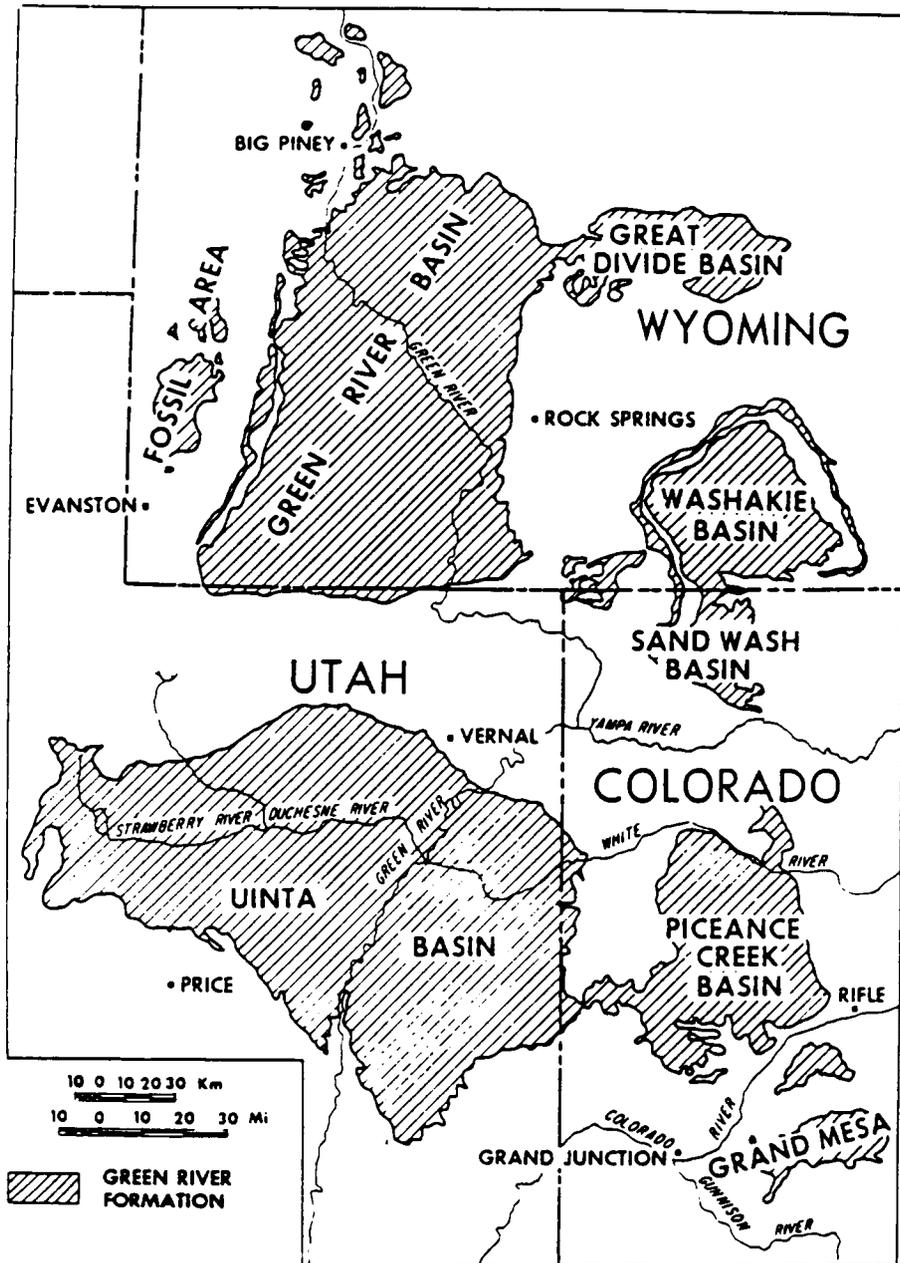


Figure 6. The Green River Formation: From [202].

Table 14. Oil reserves in known deposits in the Green River Formation

Shale Grade, gal·ton⁻¹	10⁹ Barrels of Oil Equivalent		
	Piceance Creek Basin, Colorado	Uinta Basin, Utah	Green River Basin, Wyoming
25-65	450-500	90	30
10-25	800	230	400
5-10	200	1,500	300
Area totals	1,500	1,820	730

Formation total = 4,050 × 10⁹ bbl

Source: [16]

Table 15. Summary of U.S. oil shale resources of the Green River Formation

Location	Resources, 10 ⁹ bbl				Total
	Class 1	Class 2	Class 3	Class 4	
Piceance Creek Basin, Colorado	34	83	167	916	1,200
Uinta Basin, Colorado and Utah	—	12	15	294	321
Wyoming	—	—	4	256	260
Total	34	95	186	1,466	1,781

NPC Classes 1 and 2 — These are the resources satisfying the basic assumption limiting resources to deposits at least 30 feet thick and averaging 30 gallons of oil per ton of shale, by assay. Only the most accessible and better defined deposits are included. Class 1 is a more restrictive cut of these reserves and indicates that portion which would average 35 gallons per ton over a continuous interval of at least 30 feet.

NPC class 3 — Class 3 resources, although matching Classes 1 and 2 in richness, are more poorly defined and not as favorably located. These may be considered potential resources and would be exploitation targets at the exhaustion of Class 1 and 2 resources.

NPC class 4 — These are lower grade, poorly defined deposits ranging down to 15 gallons per ton which, although not of current commercial interest, represent a target in the event that their recovery becomes feasible. These may be considered speculative resources.

Source: [27]

available until recently. One of the most promising of these processes for recovery of oil from shale is the HYTORT® process developed by the IGT, and assigned to HYCRUDE Corporation [73, 177-179]. The process has oil recoveries of up to 250% of the Fischer assay value [115]. IGT estimates of total shale oil recoverable from eastern shales using the HYTORT® process are given in Table 16. The total amount of 423×10^9 bbl is 24% of the amount considered recoverable in the Green River Formation ($1,781 \times 10^9$ bbl). As far as the potential for commercial exploitation of these shales is concerned, the IGT conducted a shale sampling program in 11 eastern states and determined the carbon content of the shales in these states. The results of the study, and for the state of Michigan reported in the study but obtained from other sources, are shown in Table 17. The commercial development prospects of shales from the states of Ohio, Kentucky, Tennessee, Alabama, Indiana and Michigan are considered to be good. The Michigan shale is known as Antrim shale, and was the shale used in the present study.

Methods of Processing Oil Shale

The basic method of producing oil from shale is that known as retorting. Retorting essentially consists of applying heat to the shale to enable the pyrolysis of the kerogen content to oil. The oil is usually driven off as a vapor and then condensed into a liquid and a gas fraction.

Perhaps the most obvious way to extract the oil is to mine the shale, crush it to appropriate size, put it into a suitable vessel called a retort, and then apply heat in some manner. Since this is technologically a simple method to design for and operate this was the first method used. The name for the procedure is surface retorting, or *ex situ* retorting. The main problem with surface retorting is the amount of raw material to be mined and handled, and the amount of waste or spent shale produced. The spent shale usually increases in volume after processing. This is due to the expansion of the organic matter during pyrolysis and can be likened to the popping of popcorn.

Table 16. Estimated resources of shale oil recoverable from eastern Devonian shales by the IGT HYTORT process

State	Recoverable Resource, 10 ⁹ bbl
Kentucky	190
Ohio	140
Tennessee	44
Indiana	40
Michigan	5
Alabama	4
Total	423

Notes: Organic carbon content > 10%
Overburden thickness < 200 ft
Shale thickness > 10 ft

Source: [163]

Table 17. Results of IGT shale sampling program

State	Number of Locations	Number of Samples	Rock Unit	Thickness, ft	IGT Data		Published Data		Commercial Prospects
					Wt. % Carbon		Fischer Assay, gal·ton ⁻¹		
					Average	Maximum	Average	Maximum	
West Virginia	40	63	Millboro	1400	2.3	6.7	—	—	Uncertain
Ohio	17	40	Beaver Dam	50	1.0	1.5	—	—	—
			Cleveland	60 to 100	10.6	12.6	10	15	Good
			Huron	300	7.0	11.9	4	10	—
Kentucky	16	98	Lower Huron	100	10.0	11.9	10	10	—
			Ohio	40 to 100	10.6	17.9	10	23	Good
			Sunbury	30	12.6	19.7	—	—	—
			New Albany	70	12.5	15.8	—	—	—
			Chattanooga	40 to 60	13.0	14.1	—	—	—
Tennessee	17	39	Chattanooga	5 to 50	13.6	19.1	12	42	Good
Alabama	4	11	Chattanooga	5 to 40	10.2	20.6	2	3	Good
Indiana	5	14	New Albany	100 to 300	10.1	15.6	—	—	Good
Illinois and Eastern Missouri	5	33	Clegg Creek	40	14.4	15.6	—	—	—
			New Albany	100 to 300	5.0	9.4	—	—	Uncertain
			Antrim	100 to 650	—	—	0 to 10	17	Good
Michigan	1	8	Chattanooga	10 to 40	8.3	10.3	—	—	Uncertain
Georgia	9	29	Arkansas	75 to 525	2.9	6.4	—	—	Uncertain
Arkansas	3	7	Novaculite	200	6.1	7.0	—	—	—
			Fayetteville	10 to 70	2.9	4.3	—	—	—
			Chattanooga	unknown	7.5	9.3	—	—	—
			Caney Creek	5 to 70	3.1	3.8	11.5	15.3	Uncertain
			Woodford	0 to 70	—	—	1.2	1.9	—
Chattanooga	—	—	—	—	—	—	—	—	
Total	117	342							

Source: [115]

In order to minimize the solid wastes generated from the point of view of surface handling, *in situ* retorting process development was started. This consists of rubblizing the shale *in situ* by blasting. Then the shale is burned under controlled conditions and the oil trapped and recovered. However, *in situ* retorting (also called true *in situ* retorting) has not been developed satisfactorily yet.

The modified *in situ* (MIS) retorting process is a combination of the surface and true *in situ* processes. Part of the shale bed is mined and retorted *ex situ*. This creates a cavity in the bed into which the remaining shale is rubblized and then retorted *in situ*.

Over the years, literally hundreds of surface retorts have been developed [160]. However, only a few have proved to be useful from the point of view of commercialization. The *in situ* and MIS technologies are also interesting since they appear to be the direction toward which retorting technology is developing. It would, thus, be useful to review some of the specific retorting techniques that have been developed.

Ex Situ or Surface Retorts

Note: Unless otherwise stated, all information in this section on surface retorts is derived from reference [16].

The N-T-U Retort

This process is of some historical importance. It was originally developed by the N-T-U Company, which operated a 40-ton retort near Santa Maria, California. (The letters N-T-U stand for Nevada-Texas-Utah.) The principal part of the retort is illustrated in Figure 7. It is essentially similar in concept to an *in situ* retort in that the retort is charged with crushed shale which is then ignited and allowed to burn in a controlled manner. In fact, the LETC in Laramie, Wyoming, uses

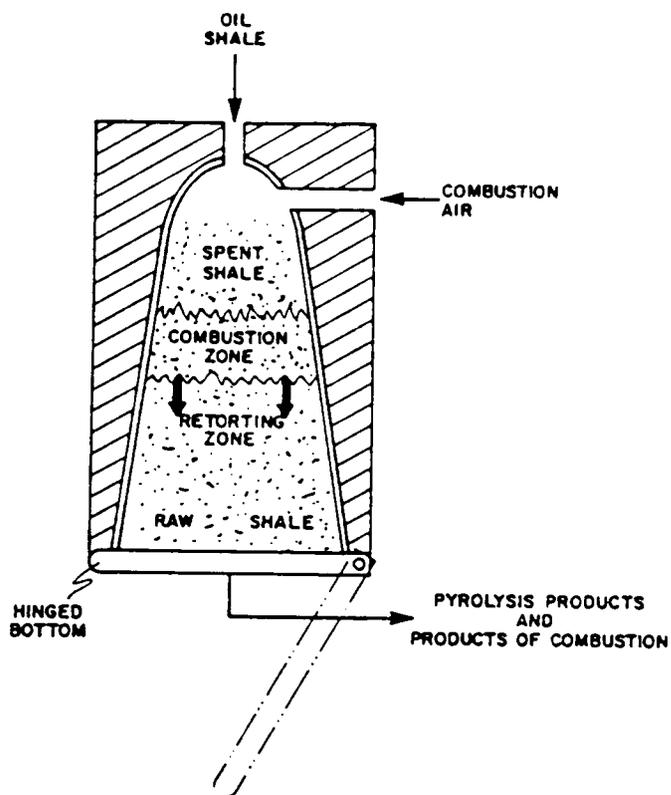


Figure 7. Flow diagram of the N-T-U process: From [16].

its 10-ton and 150-ton N-T-U retorts to conduct experiments on *in situ* retorting. The shale in the combustion zone heats the raw shale in the retorting zone ahead of it and pyrolyzes the kerogen. "Because the retorting zone precedes the combustion zone through the shale bed, the fuel for the combustion is not valuable raw oil shale, but rather the residual carbon left after retorting" [16]. Once combustion is complete, the spent shale is discharged.

The N-T-U process has a recovery efficiency of 60-90%, and was used at Marangaroo, New South Wales, Australia, during 1944-45 to produce almost 2×10^6 gal (47,600 bbl) of oil. The N-T-U process is a vertical retorting process that reaches a maximum bed temperature close to 870 °C.

The Kiviter Retort

This retorting process (Figure 8) has been developed from 1945 onwards to recover oil from the shales in Estonia in the U.S.S.R. It is a vertical kiln retort with continuous operation where raw crushed shale is fed from the top and spent shale is discharged at the bottom. The retort reaches a maximum bed temperature of 900 °C during operation and usually recovers 75-80% of Fischer assay. The kerogen is pyrolyzed in the two semicoking chambers near the top of the retort by the hot gases rising from the two sets of gas burners. The spent shale is directly discharged into a quenching unit. The feed shale must be between one and five inches in size, and there must be no fines present. This retorting technique is currently being used commercially in the U.S.S.R., with the largest designed unit being able to process 1,100 ton-d⁻¹.

The Petrosix Process

The Petrosix retort (Figure 9) was developed by the national Brazilian oil company Petrobrás. It was specially developed for use with the shales of the Irati formation in Brazil, but since these shales are similar to the Devonian shales of the eastern U.S. the technology is being tested with eastern

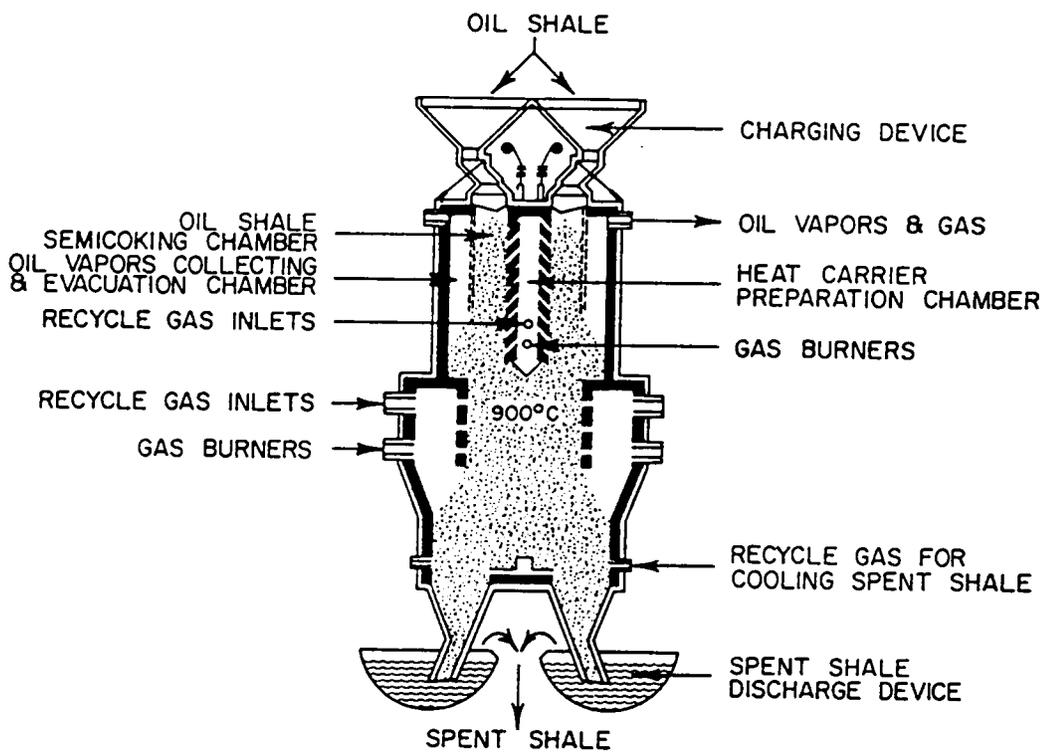


Figure 8. Diagram of Kiviter retorting process: From [16].

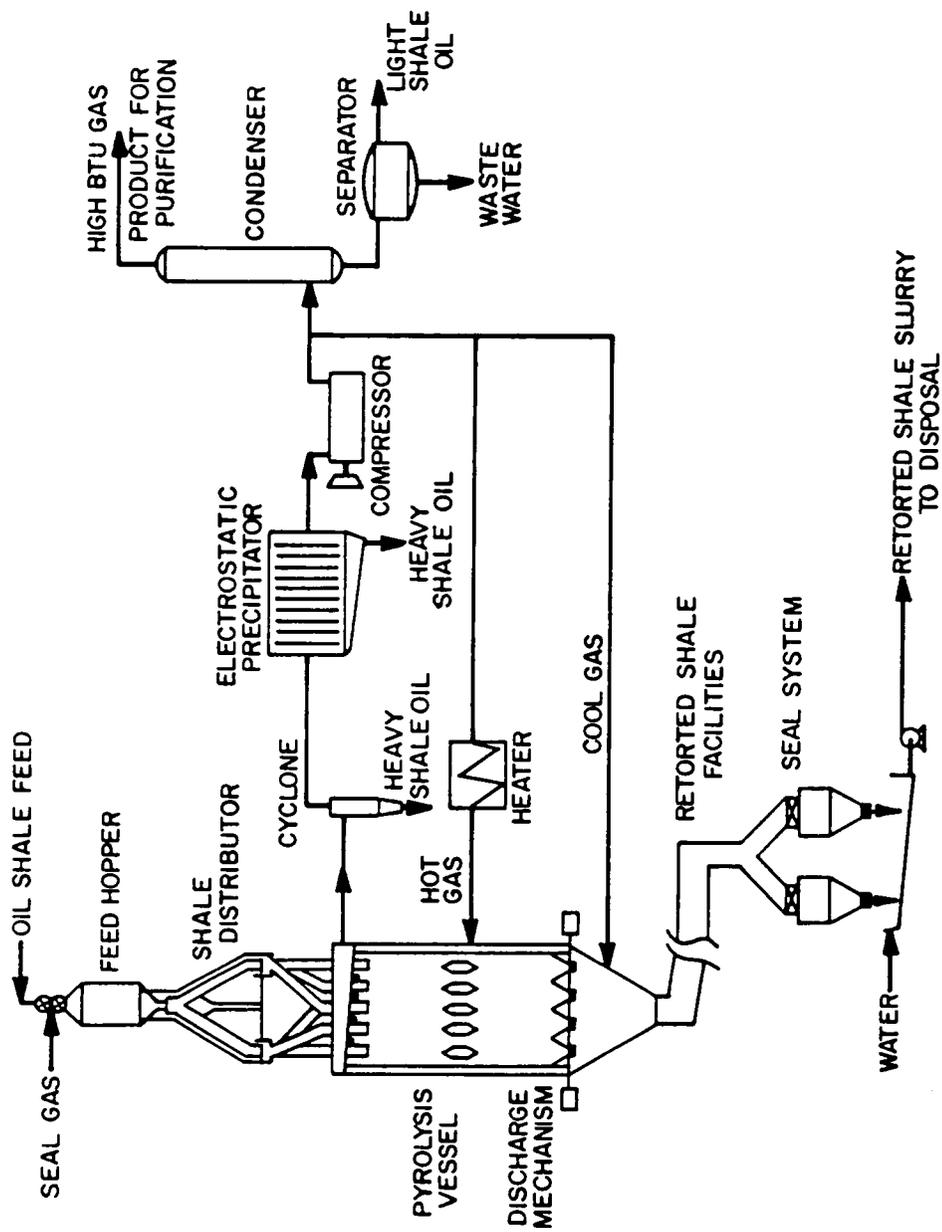


Figure 9. Flow diagram of Petrosix retorting process From [16].

shales [2, 116, 170]. The name Petrosix is derived from Petrobrás-S.I.X., which stands for Petroleo Brasileiro—Superintendencia da Industrializacao do Xisto (Brazilian Petroleum Company—Superintendency for Industrialization of Shale). The demonstration retort unit started operation in mid-1972 but has been operating as a commercial plant since 1980 [116].

The Petrosix process is a continuous vertical retort with raw, crushed shale feed from the top of the kiln. Oil yields are ~115% of Fischer assay. Much of the operating data is proprietary, but the Petrosix is a lower temperature process than other similar vertical retort processes (this is deduced from the fact that the spent shale from this process is darker in color than that from other processes, thus indicating more residual carbon) [116].

The Paraho Process

The Paraho process was developed between 1972-75 and a test retort was first used at the Anvil Points facility. The retorting system developed by the Paraho Development Corporation (a consortium of 17 companies) is illustrated in Figure 10. The process is a vertical kiln process where the shale is fed continuously from the top. The pyrolyzed shale is burned in a combustion zone at the bottom of the retort, and the hot gases from this pass through two partial combustion zones before they reach the zone of pyrolysis. Heavy and light oils and gases are recovered by the process, to a 93% Fischer assay yield.

The IGT HYTORT Process

The IGT HYTORT® process is shown in Figure 11. The process was developed as a pyrolysis process but as a hydrogasification process. In hydrogasification the organic matter is converted to methane, propane and other hydrocarbons under high pressure and temperature and in a hydrogen atmosphere. The process has been modified by IGT to produce both oil and gas, although the oils

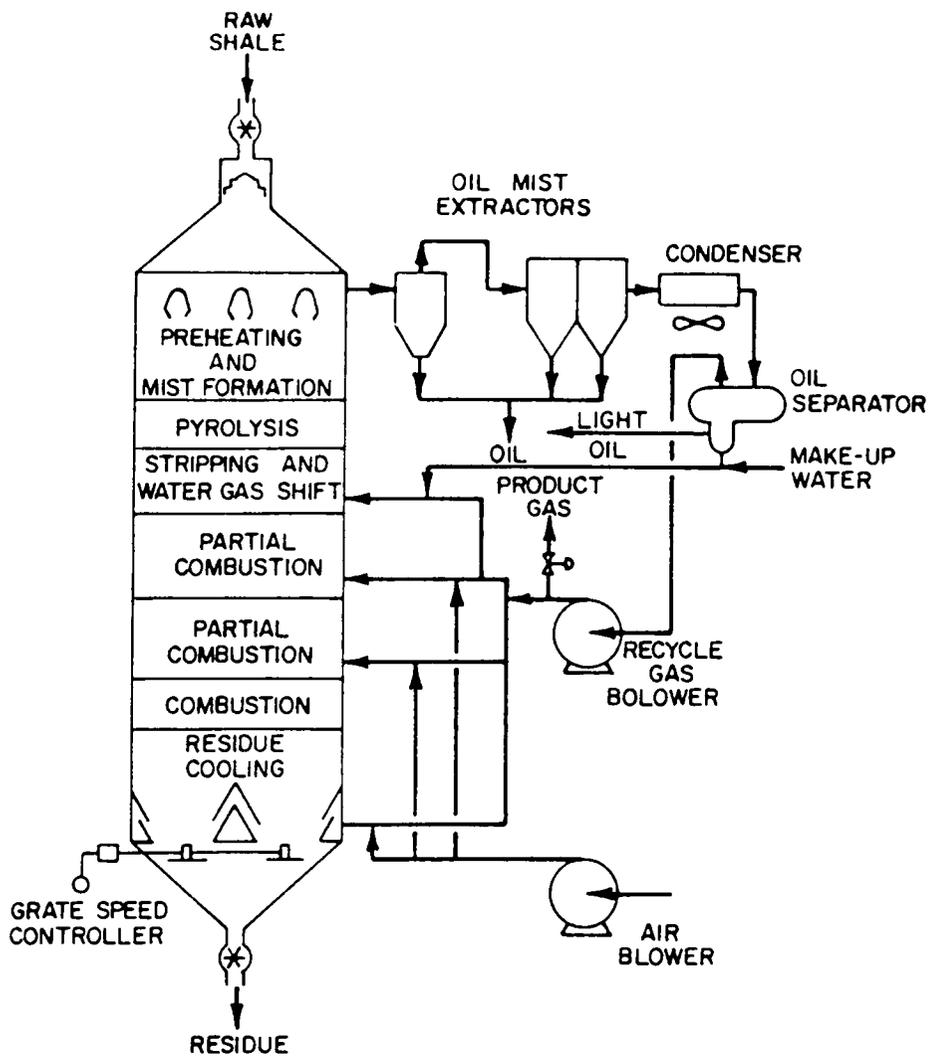


Figure 10. Diagram of Paraho retorting process: From [16].

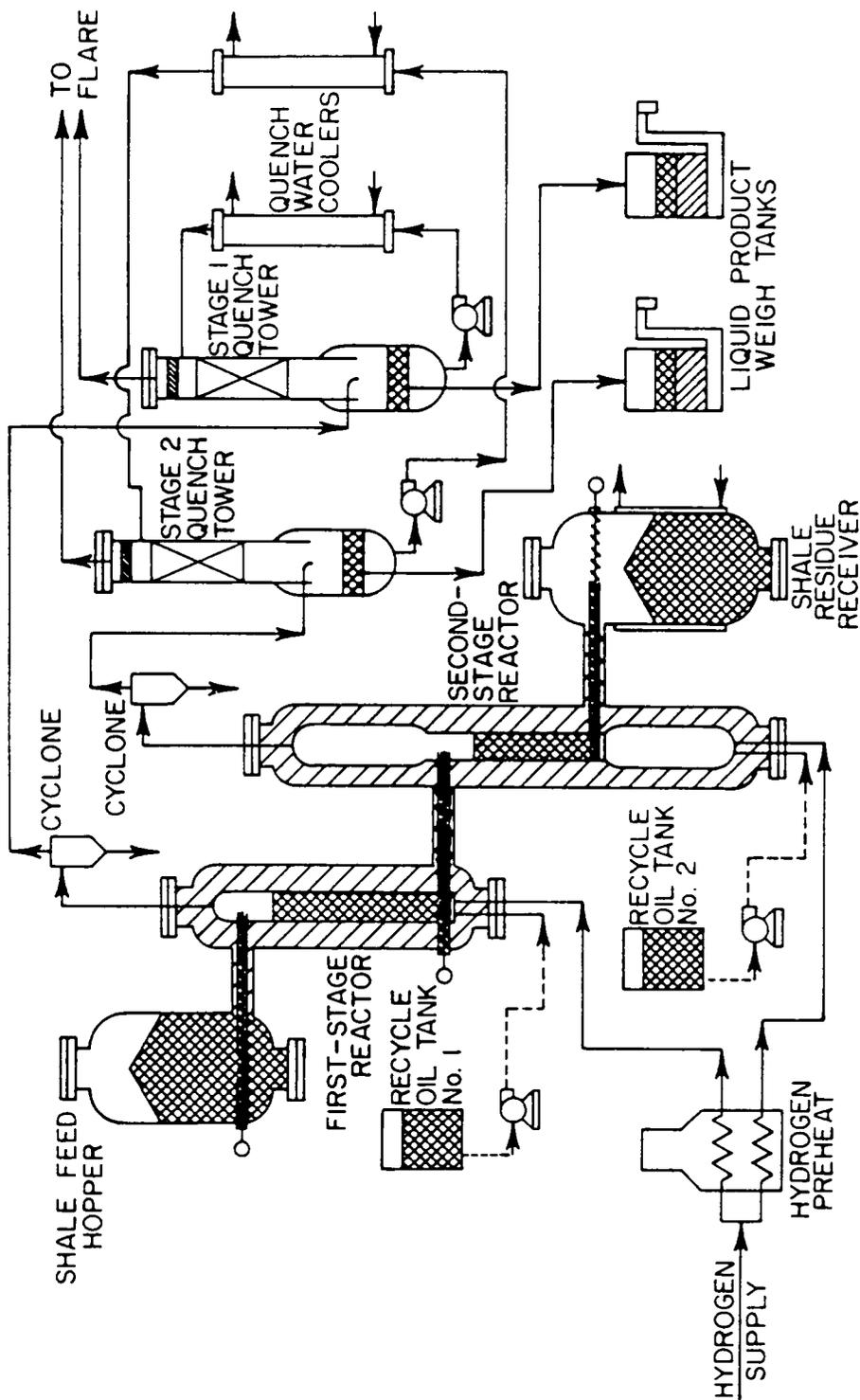


Figure 11. Diagram of 1GT shale gasification process From [16].

produced are light oils. As mentioned earlier, the HYTORT® process can produce up to 250% of Fischer assay [115]. The reactor pressure is about 500 pounds per square inch gage (psig), and the maximum temperature achieved in the reaction zone is usually around 800 °C. The HYTORT® process seems to be most promising for application to the retorting of eastern shales.

The Lurgi-Ruhrigas Retort

Developed by Lurgi and Ruhrigas AG in Germany, the Lurgi-Ruhrigas process is illustrated in Figure 12. Spent shale solids or sand grains are heated and then mixed with raw shale that has been crushed to less than ¼-inch size. When this mixture is passed through a sealed screw conveyor, pyrolysis occurs. The temperature in the lift pipe where the sand or spent shale is heated is kept to 400 °C, whereas the temperature in the separation bin, before these solids contact the raw shale, is 650 °C. The ratio of heat-carrying solids to raw shale is kept to 6-8:1. The overall thermal efficiency of the process is quite high and most of the residual carbon in the spent shale is used. Oil yield is usually 95-110% of Fischer assay. The process produces heavy oil, middle oil, naphtha and gas.

The TOSCO II Retort

The TOSCO II process shown in Figure 13 has gained in popularity over the years since it was introduced during the 1960s. Like the Lurgi-Ruhrigas process, it uses a horizontal, rather than a vertical, retort. Crushed raw shale that has been preheated to 260 °C (500 °F) is mixed with ceramic balls heated to 650 °C (1200 °F) and passed through a rotating pyrolysis drum. The balls to shale ratio is kept to 2:1 and this raises the temperature of the shale to 480 °C (900 °F). The balls are then separated from the spent shale, reheated and recycled. The process is also called the “hot balls” process, and it usually produces oil at > 100% Fischer assay.

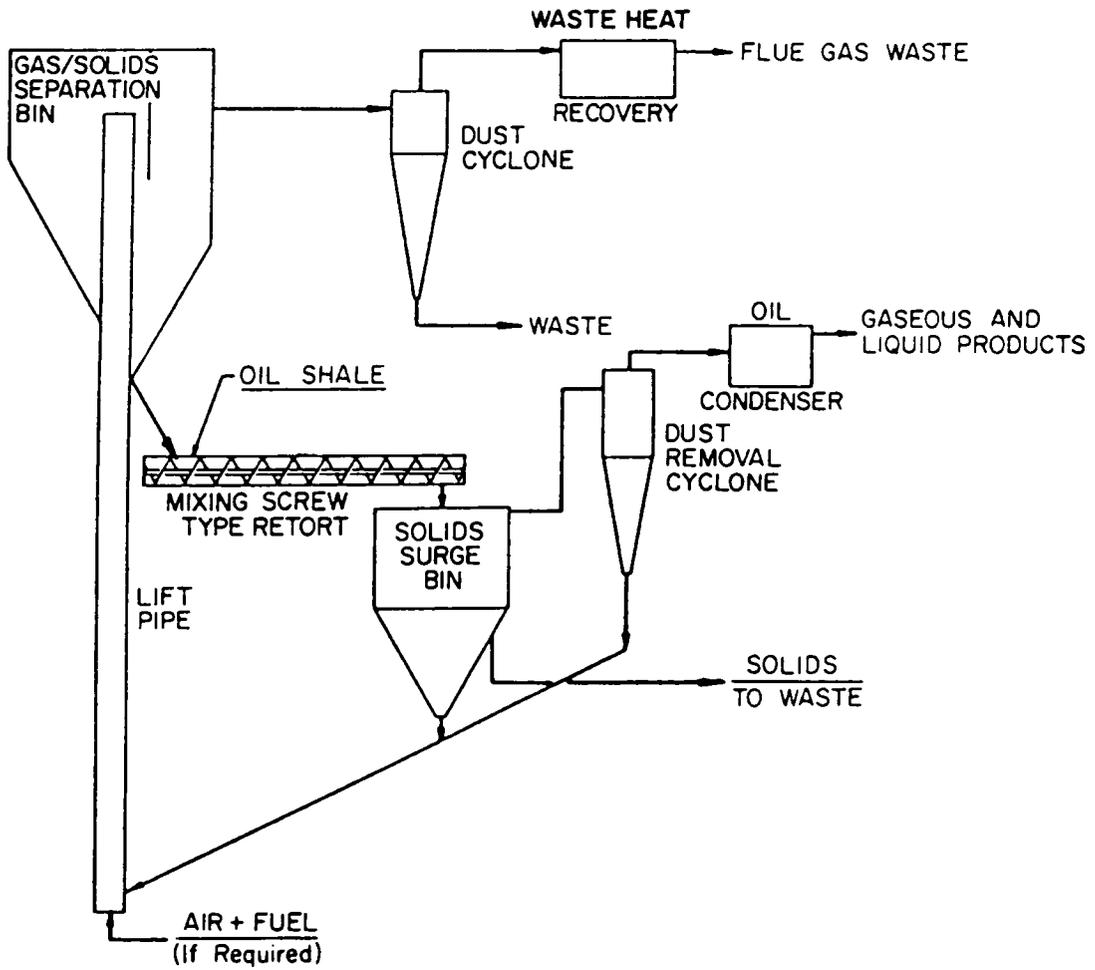


Figure 12. Lurgi-Ruhrgas retorting process: From [16].

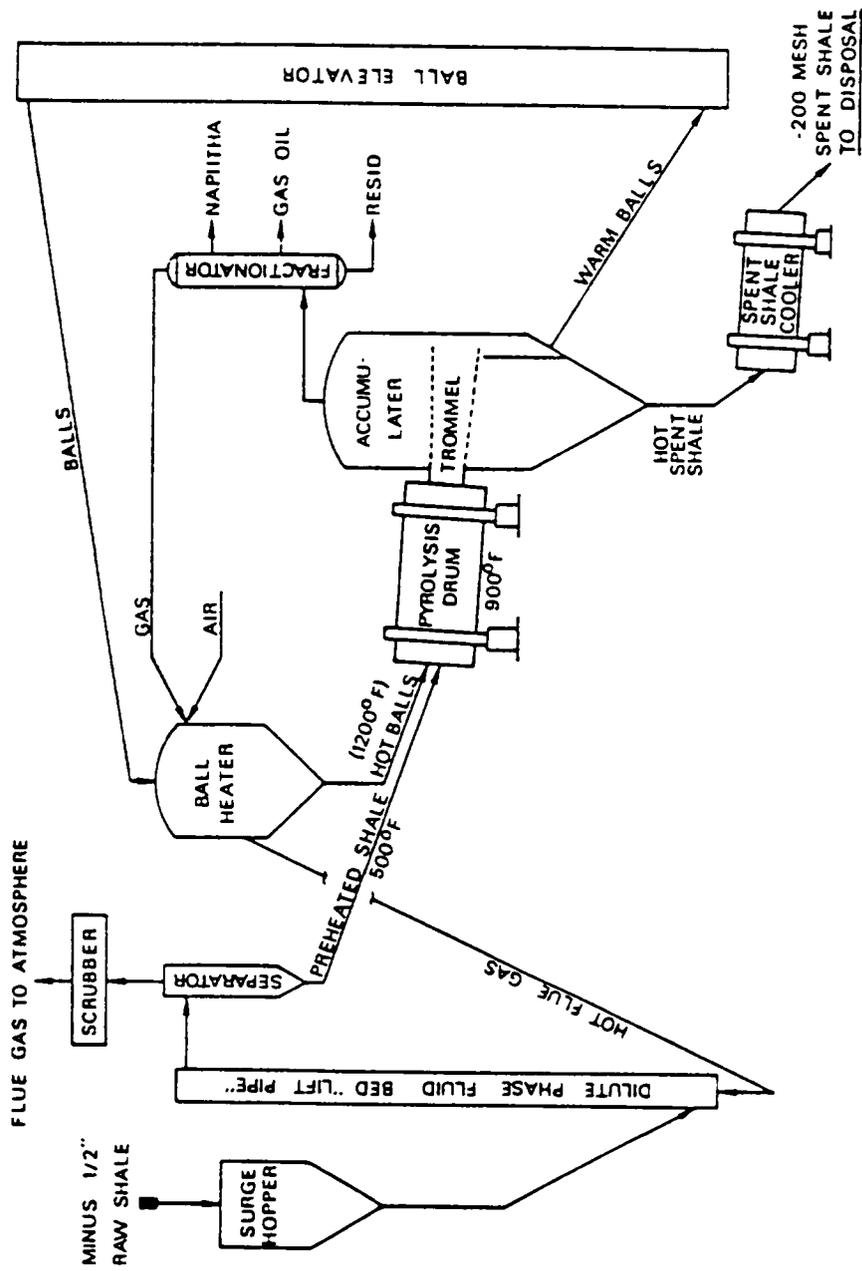


Figure 13. TOSCO II retorting process From [16].

The Galoter Retort

Finally, among the *ex situ* retorts is the Galoter retorting process developed since 1945 in Estonia (U.S.S.R.). The process was developed simultaneously with the Kiviter process and is shown in Figure 14. The Galoter process can only work with crushed shale upto an inch in diameter, whereas the Kiviter process can only handle sizes larger than one inch. Therefore, both processes are normally used simultaneously at any retorting facility. As in the other two horizontal-retort processes — Lurgi-Ruhrigas and TOSCO II — the Galoter process uses a heat-carrier to heat the raw shale and cause pyrolysis at 500 °C. The heat-carrier used is spent shale. The process recovers oil upto 85-90% of Fischer assay and generally produces a better quality, sulfur-free gas than that produced by the Kiviter process.

In Situ Retorting Techniques

The LETC Retort

There are very few true *in situ* retorting techniques. Perhaps the only one that has gained any importance is that developed at the LETC in Laramie, Wyoming, using the 10-ton and 150-ton N-T-U retorts to simulate *in situ* retorting. These experiments were started in the early 1960s and some field experiments were also performed at Rock Springs, Wyoming. The process is illustrated in Figure 15. [65]

First, injection and production wells are bored. Then the shale is fractured by hydraulic fracturing followed by slurry-type explosive charges. To start-up the retort, hot gases are injected into the injection well until the shale reaches a temperature sufficient to maintain combustion, at which time air is introduced to start combustion. As the combustion front progresses, oil, gas and water are

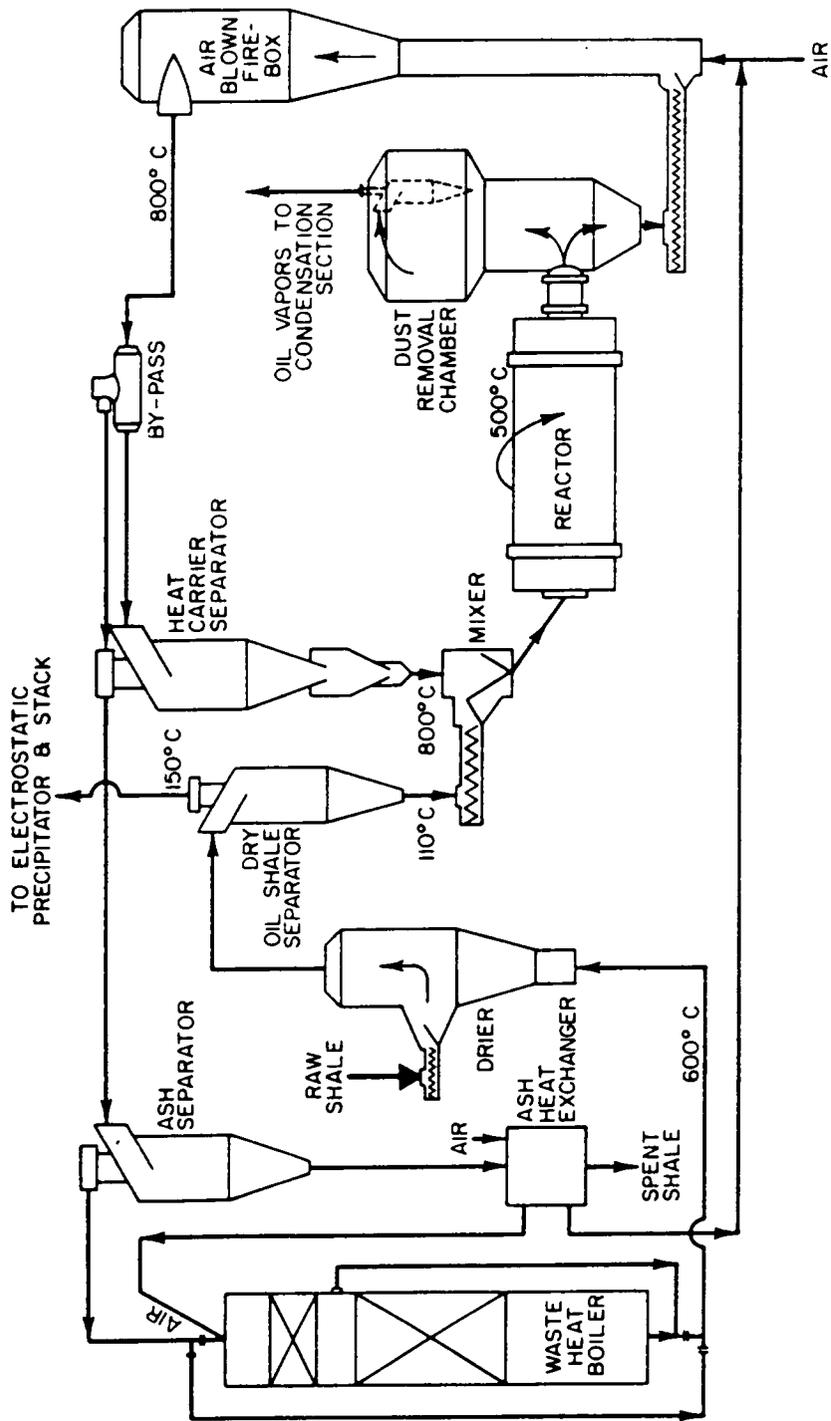


Figure 14. Diagram of the Galoter retorting process From [16].

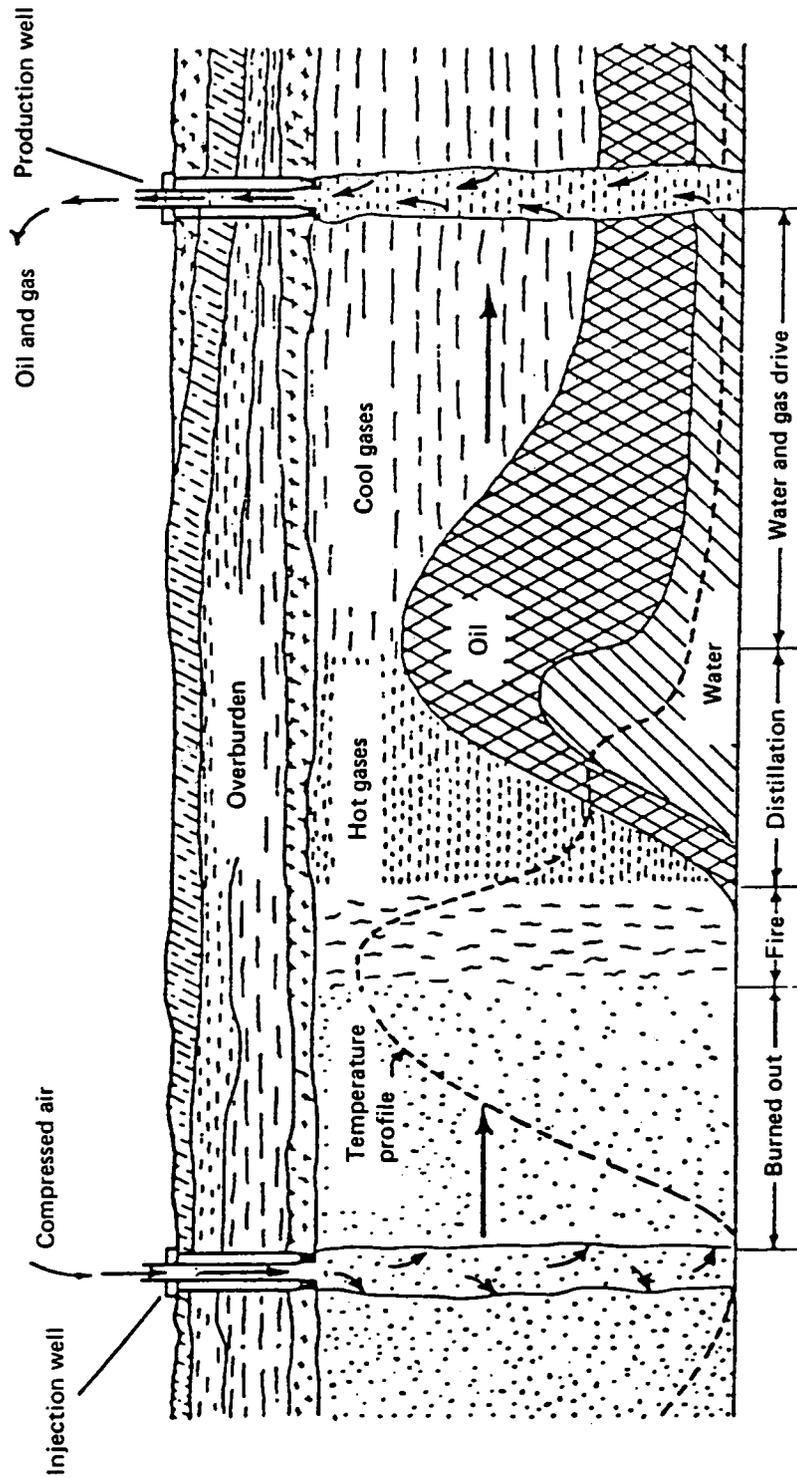


Figure 15. LETC *in situ* retorting process From [65].

collected at the production well. [65] In a test conducted at Rock Springs at a retort located 137 feet deep, the maximum temperature reached in the retort was 1260 °C [133], which is above the ~1200 °C at which spent shale fuses and further combustion stops [203].

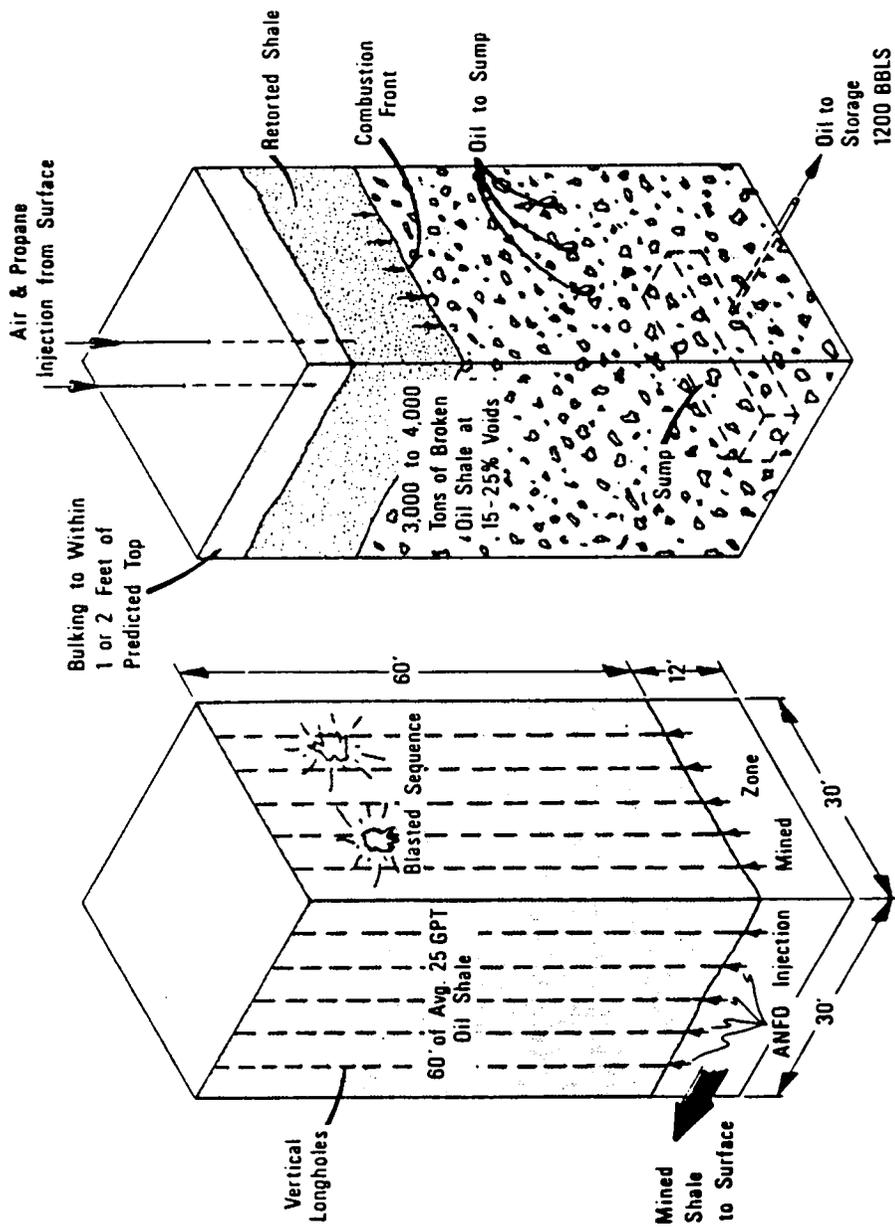
Modified *In Situ* Retorting Techniques

The Occidental Retort

MIS retorting techniques hold better promise than the true *in situ* techniques. The best-known MIS technique is the Occidental MIS process developed by the Occidental Petroleum Corporation. The process is called Oxy, which is derived from 'Occidental'.

The Oxy program began in 1972 with the testing of various retorting sites. Initially, a 57,000 bbl-d⁻¹ commercial facility was planned to be operational at Colorado lease tract C-b in 1983, but in 1980 this was postponed until 1987. [65] There was apparently another delay because this author has been unable to unearth any recent information about the commercialization of the Oxy process.

The process itself consists of mining up to 20% of the raw shale from under the retort to create a sump, then fracturing of the shale above it to create voids (see Figure 16) [16]. Air and steam are then blown down through the retort and the shale is ignited. Retorting proceeds downwards as the combustion front moves and oil is collected at the bottom and pumped out. Gas is collected separately (see Figure 17) [65]. As shown in Figure 16, the retorting of 3,000-4,000 tons of shale produces 1200 bbl of oil. This indicates a shale richness of 12.5-17 gal·ton⁻¹ — not very rich, which is why the Oxy process is felt to be more economical for leaner shales.



RETORTING

MINING & BLASTING

Figure 16. Occidental's modified *in situ* recovery process From [16].

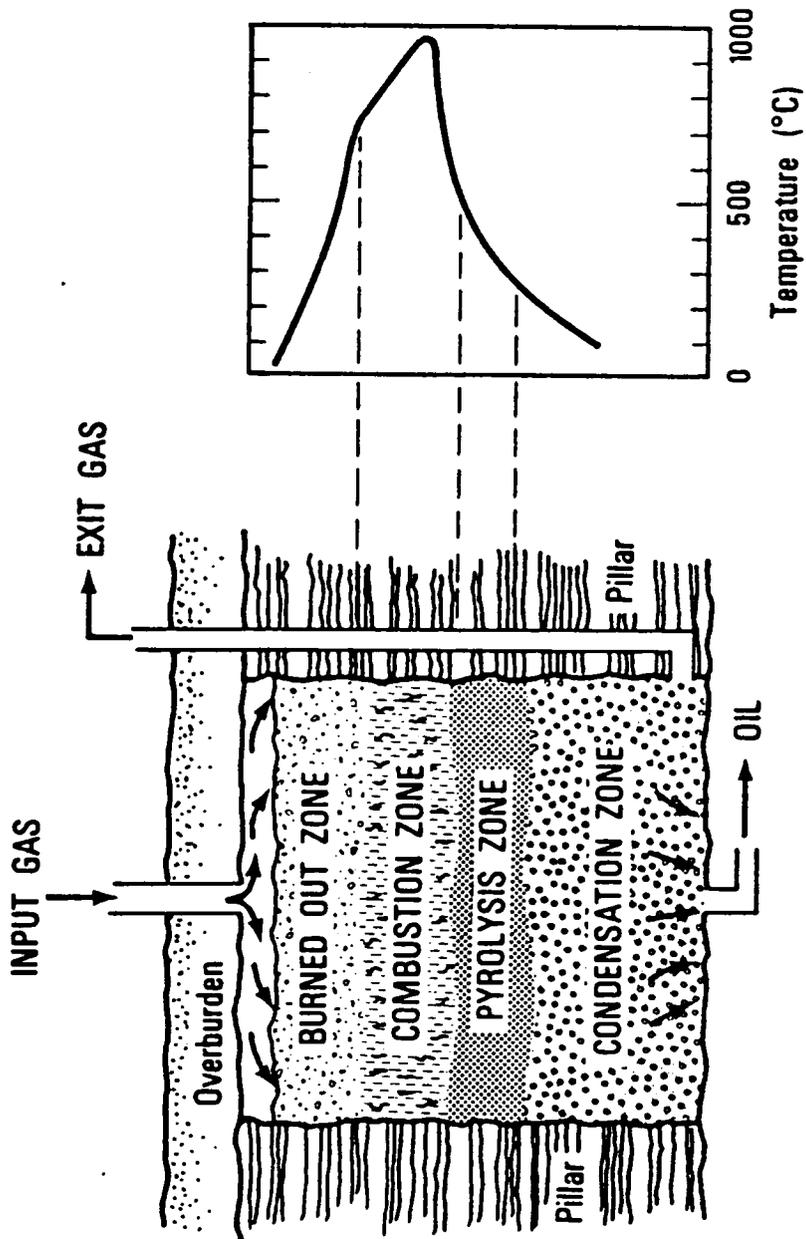


Figure 17. Schematic of the Occidental modified *in situ* retorting process From [76].

Amounts and Characteristics of Products and Wastes Produced from Oil Shale

Elemental Composition of Raw Shale

Different raw shales have different elemental compositions. The amounts of the major elements present — for example, C, H, O, N, Na, Ca, Si and S — varies from shale to shale and depends upon the richness of the shale. Table 18 lists the elemental analysis of an “average” Antrim shale from Michigan. This “average” shale is a combination of Antrim shales studied by the Dow Chemical Company in the mid-1970s.

Nearly 50% (by weight) of the raw shale consists of oxygen and another 25% is silicon. The remaining 25% consists of 36 elements, of which 12 occur in appreciable amounts (the “major element” category in the table). The Antrim shales have a sulfur content of about 3%, most of it in the form of pyrites (FeS_2). However, it should be emphasized that these numbers are averages and the actual composition, especially of the major elements, can vary considerably. For example, the same study of Antrim shales shows a carbon concentration range of 1-16% (by weight) for one core sample between the depths of 1200 to 1440 ft. In one section of the core the carbon concentration was about 6% at 1420 ft, 16% at 1430 ft and 6% at 1440 ft — a variation of 10% in just 20 feet [156]. This indicates the nature of the deposits — they occur in seams just like coal. And this is not unexpected, since oil shale was formed in a similar fashion to coal from organic sediments.

The elemental analysis given in Table 18 is by no means complete. A multi-laboratory study conducted by the Colorado School of Mines, the University of Colorado, Colorado State University, Battelle Pacific Northwest Laboratory, the Lawrence Berkeley Laboratory, and the Lawrence

Livermore Laboratory, reported 52 elements found in Antrim shale [80]. Most of these elements appear both in the spent shale [80] and in retort waters [71].

Retorting Characteristics, Products and Energy Balance for a Western and an Eastern Shale

In 1977, a report published by the Laramie Energy Research Center (now Western Research Institute, called LETC in this document) under ERDA (now DOE) contained preliminary results from the retorting of Michigan Antrim shale at the LETC's 10-ton retort. The results of that retorting experiment (designated in the report as Run S-42) were compared in the report with a previous retorting experiment performed on Colorado shales. It is very interesting to follow the results of that study and note the differences in the products, etc., between the two shales. All the material in this sub-section of this document is reproduced from the report [139].

Both shales studied were crushed and the retort charged and then ignited. The size distributions of the crushed shales are shown in Figure 18. The Antrim shale was crushed to smaller size fractions than the Colorado shale. A larger proportion of fines leads to greater bed compaction, and, if there is too large an amount of fines, can lead to a slowdown in the burning rate as well as reduce the rate of gas flow through the bed.

Table 19 lists the summary data from the retorting for both the production runs — S-20 and S-42. The Antrim production run was longer than the Colorado shale production run by more than a day. The charge amounts for both runs were about the same and the air flow rates were also approximately equal — the Antrim shale just retorted slower at an advance rate of $0.98 \text{ in}\cdot\text{hr}^{-1}$ as opposed to $1.24 \text{ in}\cdot\text{hr}^{-1}$ for the Colorado shale. This is surprising since the maximum bed temperature achieved for the Antrim run ($1460 \text{ }^\circ\text{F}$, $790 \text{ }^\circ\text{C}$) was 40% higher than that for the Colorado shale

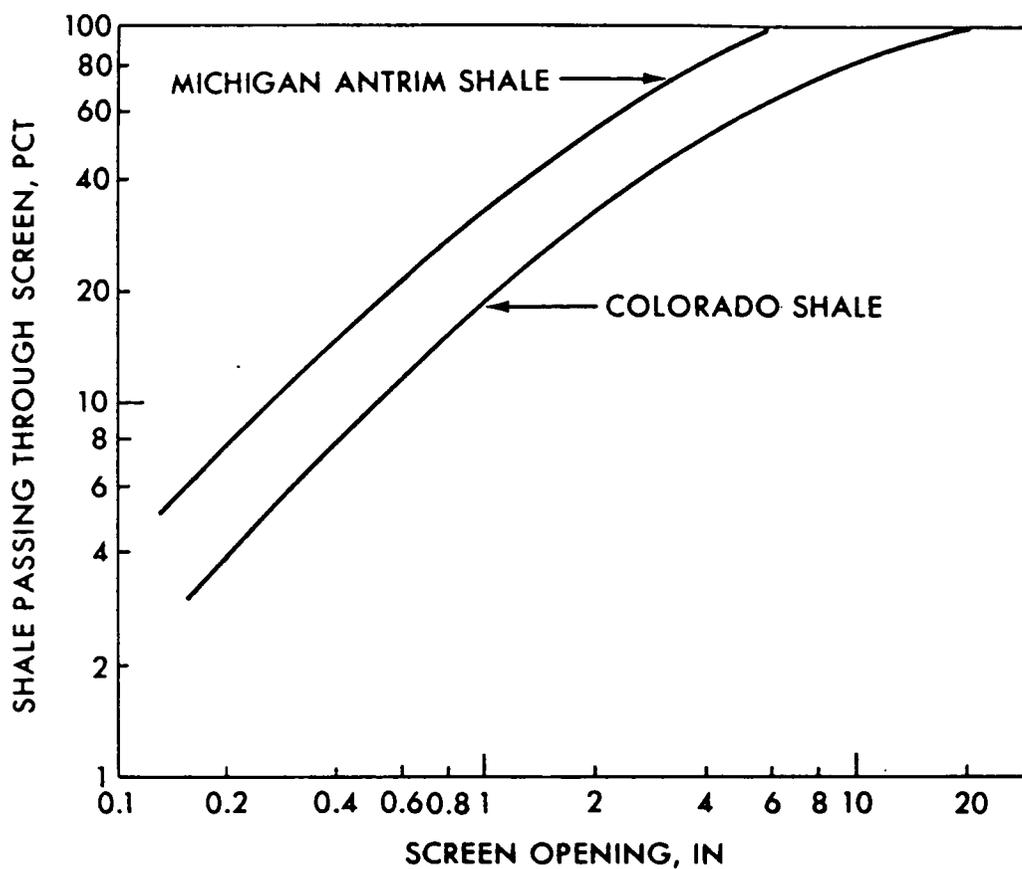


Figure 18. Size distribution of retorted Michigan Antrim and Colorado shales: From [139].

Table 19. Summary data comparing the retorting of Colorado oil shale to Michigan Antrim shale

	Colorado shale	Michigan Antrim shale
Run number	S-20	S-42
Run length, days.....	4.32	5.54
Operating conditions:		
Shale charge, tons.....	7.57	7.38
Spent shale discharged, tons	5.76	6.57
Air rate (dry), scfh	1,140	1,201
Air rate (dry), scf-ton ⁻¹	16,890	26,725
Recycle gas rate (dry), scfh	680	724
Recycle gas rate (dry), scf-ton ⁻¹	8,290	10,938
Stack gas rate (dry), scfh	1,250	1,219
Stack gas rate (dry), scf-ton ⁻¹	18,520	27,122
Gas produced in retort, scfh.....	110	18
Gas produced in retort, scf-ton ⁻¹	1,630	397
Oxygen content of retorting gas, %.....	13.9	13.3
Superficial gas velocity through retort, scfm-ft ⁻²	1.95	2.05
Max. ΔP across retort, inches H ₂ O.....	0.1	2.4
Max. bed temperature, °F.....	1,040	1,460
Max. bed temperature, °C.....	560*	790*
Avg. retorting advance rate, in-hr ⁻¹	1.24	0.98
Shale feed properties:		
Oil content, gal-ton ⁻¹	22.5	9.7
Oil content, wt. %	8.6	3.8
Water content, gal-ton ⁻¹	5.3	7.9
Water content, wt. %	2.2	3.3
Fischer assay gas + loss, wt. %.....	2.4	2.3
Ash, wt. %	86.8	90.6
Hydrogen, total wt. %.....	1.7	1.3
Mineral carbon, wt. %.....	4.9	0.4
Organic carbon, wt. %.....	10.4	8.3
Carbon dioxide, wt. %.....	17.8	1.2
Mineral carbonate, wt. %	24.4	1.7
Total carbon, wt. %.....	15.3	8.6
Nitrogen, wt. %	0.3	0.3
Sulfur, wt. %	0.5	3.5
Gross heating value, Btu-lb ⁻¹	1,870	1,678
Density, lb-ft ⁻³	140.3	154.7
Density, g-cm ⁻³	2.25*	2.48*
Liquid recovery:		
Oil water emulsion, lb.....	2,004	1,460
Water in oil, lb	1,295	1,184
Oil recovered, lb	709	276
Oil recovered, gal.....	93.4	35.5
Oil recovery, gal-ton ⁻¹	12.3*	4.8*
Oil recovery, vol. % of Fischer assay.....	54.7	49.5

Table 19. Continued

	Colorado shale	Michigan Antrim shale
Oil properties:		
Naphtha, vol. %	6.8	3.5
Light distillate, vol. %	24.9	41.1
Heavy distillate, vol. %	43.6	38.6
Residuum, vol. %	23.9	16.3
Specific gravity, 60°/60 °F	0.911	0.934
Gravity, ° API	23.8	20.0
Pour point, °F	50	5
Viscosity, SUS @ 100 °F	75	64
Hydrogen, wt. %	12.5	11.1
Nitrogen, wt. %	1.6	0.7
Sulfur, wt. %	1.0	2.1
Carbon, wt. %	84.7	83.6
Ash, wt. %	0	0
Heating value, Btu·lb ⁻¹	18,422	18,343
Stack gas analysis (average):		
Ar, vol. %	0.9	0.8
H ₂ , vol. %	0.05†	1.2
O ₂ , vol. %	1.9	0.6
N ₂ , vol. %	72.3	78.3
CH ₄ , vol. %	0.4	0.6
CO, vol. %	0.5	2.2
C ₂ H ₆ , vol. %	0.2	0.2
CO ₂ , vol. %	23.6	15.4
H ₂ S, vol. %	‡	0.4
COS, vol. %	‡	0.1
Higher hydrocarbons, vol. %	0.1	0.2
Heating value, Btu·ft ⁻³	11.0§	25.3
Specific gravity, Air = 1	1.10	1.05
Spent shale properties:		
Oil content, gal·ton ⁻¹	0.1¶	0
Water content, wt. %	0.4	0.3
Hydrogen, wt. %	0.3	0.1
Mineral carbon, wt. %	3.9	0.2
Organic carbon, wt. %	2.0	2.8
Carbon dioxide, wt. %	14.4	0.7
Mineral carbonate, wt. %	19.7	0.9
Total carbon, wt. %	5.9	2.9
Ash, wt. %	99.1	99.2
Nitrogen, wt. %	0.1	0.2
Sulfur, wt. %	0.4	1.8
Gross heating value, Btu·lb ⁻¹	50	461

* Calculated from original table by present author.

† Value is low. Newer GC equipment consistently indicates values of 4 to 6 vol. %.

‡ Lower than 0.01 vol. %. Not indicated by mass spectrometry.

§ Value is low, probably due to H₂ error. Normally, values of 25 to 30 Btu·ft⁻³ are calculated.

¶ Spent shale samples for S-20 were lost. All spent shale values for the Colorado shale are from a similar run having similar properties.

Source: [139]

(1040 °F, 560 °C). However, it could be that the overall smaller size fractions of the Antrim shale may have led to a greater bed compaction, thus retarding combustion.

The temperature difference probably arises because of the differences in conversions of organic matter to oil for the shales. Two-thirds of the organic matter of Green River shales is usually converted to oil, while only one-third of the organic matter of Antrim shale is so converted [139]. Therefore, a greater amount of carbon as coke is left behind on the Antrim shale, leading to a greater amount available for burning.

As can be expected for the more finely crushed shale, the pressure drop across the retort is much greater for the Antrim shale (2.4 inches H₂O) as compared to the Colorado shale (0.1 inches H₂O). The shales differed by 12.8 gal·ton⁻¹ in richness of oil content, the Antrim being the leaner shale at 9.7 gal·ton⁻¹ and the Colorado being the richer shale at 22.5 gal·ton⁻¹. The water content of the Antrim shale was about 50% greater than that of the Colorado shale, and this may also have contributed to retarding combustion. The final ash content of the two shales was similar, with the Antrim being higher to compensate for the difference in oil content. There was a big difference in the mineral carbon, carbon dioxide and mineral carbonate contents — the Colorado shales being generally higher by an order of magnitude (in wt. %). However, Antrim shale contained a very high amount of sulfur (3.5%) compared to Colorado shale (0.5%).

The efficiencies of both retort production runs were about the same at 50% Fischer assay. However, the Antrim shale produced a lower proportion of naphtha (by about 50%) and a greater proportion of light oil (by about 65%) than did the Colorado shale, although the heavy oil fractions were about equal for both shales. The greater proportion of light oils explains why the pour point of the Antrim shale oil (5 °F, -15 °C) is much lower than that of the Colorado shale oil (50 °F, 10 °C). The heating value of the produced oil is essentially identical for both shales.

The spent shales generated from both runs had major differences in the non-organic carbon contents, which was to be expected considering the differences in the raw shales. The gross heating

values of the spent shales also were as expected with the Antrim having a much higher value, indicating a greater amount of combustible residual organic carbon.

Table 20 lists the observed stack gas composition with respect to certain gases. A lot of the data were not determined and are not available for comparison. However, the great differences in the THC/CH_4 concentrations between the two shales may be due to “the decision to sustain a high oxidizer temperature by using large volumes of fuel gas” for the Antrim shale run. “Excess fuel would account for the THC/CH_4 increase.” [139]

Tables 21 and 22 provide information on the composition of the retort waters. The Colorado shale with its higher nahcolite content has a much higher sodium content than the Antrim shale. What is surprising is the great difference in the ammonium ion content of the waters, since the nitrogen content of both the feed shales was the same (see Table 19). Other major differences are in the carbonate and bicarbonate contents of the two shales, the sulfate and chloride contents, the total dissolved solids (TDS) content, the conductance values and the COD values. The pH of both waters was slightly alkaline.

The arsenic content of the Colorado shale is high enough to result in the waters being considered hazardous. Lead levels are higher than the EPA maximum contaminant level (MCL) of 0.05 ppm. It is also interesting to note the high levels of tin, nickel and iron in the Colorado retort water, and those of zinc, copper, phosphorus and sulfur in the Antrim retort water.

Table 23 gives the material balance of both runs, and indicates a good closure in both material balances.

Finally, Table 24 provides the energy balance for both runs. The high amounts of unaccountable energy loss have not been successfully explained [139].

Table 20. Process line and stack effluent analyses for Antrim and Colorado shales

Effluent	Run R-16 Colorado shale				Run S-42 Antrim shale				
	Before stack		After stack		Before stack		After stack		
	Avg. low, ppm*	Avg. high, ppm*	Avg. low, ppm*	Avg. high, ppm*	Avg. low, ppm*	Avg. high, ppm*	Avg. low, ppm*	Avg. high, ppm*	
H ₂ S†	2.89	168	NA‡	NA	NA	NA	NA	NA	NA
H ₂ S†	13.40	163	NA	NA	NA	NA	NA	NA	NA
SO _x	NA	NA	0.02	0.03	NA	NA	NA	1.70	58
Total sulfur	NA	NA	0.67	3.72	1.85	260	0.32	30	
THC/CH ₄	NA	NA	146	4,690	4,600	13,200	4,930	94,300	
NO _x	NA	NA	1.62	66.57	0.4	9.0	0.74	22	
NO	NA	NA	0.91	71.41	5	7	0.25	18	
NO ₂	NA	NA	0.40	33.89	NA	NA	0.48	5.44	

* Concentrations in ppm are volume/volume

† Two different analyzers used for these analyses

‡ NA — Not analyzed

Source: [139]

Table 21. Retort water analysis comparison for Michigan shales and Colorado shales

	Run S-29 Colorado shale water	Run S-42 Antrim shale water
Calcium, ppm	0.6	5.5
Magnesium, ppm	3.2	4.4
Sodium, ppm	210	8.8
Potassium, ppm	8	6.3
Ammonium, ppm	18,200	1,300
Nitrate, ppm	33	nr
Carbonate, ppm	5,800	0.0
Bicarbonate, ppm	38,000	3,500
Total CO ₃ , ppm	24,000	1,700
Hardness (CaCO ₃), ppm	15	32
Sulfate, ppm	1,600	180
Chloride, ppm	5,000	310
Fluoride, ppm	31	7.6
Total dissolved solids, ppm	13,700	390
Boron, ppm	5.2	2.0
Conductance, $\mu\text{mhos}\cdot\text{m}\ell$	49,600	6,150
pH	8.7	7.9
COD	28,000	16,000

nr — Not reported.

Source: [139]

Table 22. Trace element composition for Antrim shale retort water and Colorado shale retort water

Element	Run S-29 Colorado shale water, ppm	Run S-42 Antrim shale water, ppm
Aluminum	0.110	0.075
Antimony	0.009	0.026
Arsenic	5.900	0.011
Barium	0.012	0.012
Bismuth	< 0.001	0.001
Bromine	0.019	0.052
Cesium	0.002	< 0.001
Chromium	0.011	0.020
Cobalt	0.074	0.051
Copper	0.008	1.900
Gallium	< 0.001	0.002
Germanium	0.001	0.006
Iodine	0.005	0.200
Iron	77	1.100
Lanthanum	0.010	< 0.001
Lead	0.120	0.120
Manganese	0.042	0.280
Mercury	0.100	0.0002
Molybdenum	0.056	0.049
Neodymium	0.002	< 0.001
Nickel	1.100	0.005
Niobium	0.001	0.003
Phosphorus	0.580	39
Praseodymium	0.003	< 0.001
Rubidium	0.036	0.013
Selenium	0.010	< 0.001
Silicon	1.700	2.600
Strontium	0.007	0.020
Sulfur	14	69
Tantalum	< 0.001	0.003
Tin	8.900	0.005
Titanium	0.640	0.013
Tungsten	0.003	< 0.001
Uranium	0.023	< 0.001
Vanadium	0.037	0.011
Zinc	0.260	6.900
Zirconium	0.079	0.003

Source: [139]

Table 23. Material balances for Colorado and Antrim shale production runs

	Run S-20 Colorado shale		Run S-42 Antrim shale	
	Pounds	Percent	Pounds	Percent
<i>Material in:</i>				
Oil shale	15,140	60.5	14,770	49.2
Natural gas	90	0.4	100	0.3
Air (dry)	9,760	39.0	15,060	50.2
Water in air	30	0.1	70	0.3
<i>Total in</i>	<i>25,020</i>	<i>100.0</i>	<i>30,000</i>	<i>100.0</i>
<i>Material out:</i>				
Spent shale	11,520	45.2	13,140	42.6
Shale oil (dry)	710	2.8	276	0.9
Water in oil	1,300	5.1	1,184	3.8
Stack gas (dry)	11,770	46.2	16,000	52.0
Water in stack gas	170	0.7	210	0.7
<i>Total out</i>	<i>25,470</i>	<i>100.0</i>	<i>30,810</i>	<i>100.0</i>
Material recovery, %	101.8		102.7	

Source: [139]

Table 24. Energy balances for production runs of Colorado and Antrim shales

	Run S-20 Colorado shale	Run S-42 Antrim shale
All values are in Btu-ton ⁻¹ of raw shale.		
Energy entering retort:		
Enthalpy of raw shale	-26,000	-16,000
Enthalpy of air	-6,530	-21,660
Enthalpy of recycle gas	-6,360†	-8,640
Heating value of raw shale	3,746,000	3,356,000
Heating value of recycle gas	97,460	306,340
Heating value of ignition gas	296,940	336,000
<i>Total energy entering</i>	<i>4,101,510</i>	<i>3,952,040</i>
Energy leaving retort:		
Enthalpy of spent shale	350,010	400,610
Enthalpy of offgas	47,010	54,820
Heat of vaporization of uncondensed water	191,700	187,450
Enthalpy of oil	3,260	1,140
Enthalpy of condensed water	0	0
Heating value of spent shale	307,500‡	820,810
Heating value of oil	1,725,100‡	685,020
Heating value of offgas	272,750	962,870
Energy into cooling ring	31,250	8,230
Energy loss to atmosphere	613,870	266,010
Carbonate decomposition	132,470	15,640
<i>Total energy leaving</i>	<i>3,674,920</i>	<i>3,402,600</i>
Total unaccountable energy loss	426,590	549,440
Unaccountable energy loss, %	9.6	13.9

Note: All heating values are gross.
 Reference temperature is 77 °F.
 Standard cubic feet taken at 60 °F.

† — This value is given incorrectly as positive in the original reference
 ‡ — Value taken from other data; S-20 sample was not available for analysis.

Source: [139]

Composition of Shale Oil

The composition of a Paraho shale oil is given in Table 25. This is an oil derived from a Colorado shale.

The empirical formula from this is $C_{264}H_{35}N_6O_5S_2$; and $C_{211}H_{28}N_5O_4$ if sulfur is neglected. When the polar fraction of the oil is considered, the empirical formula of the shale oil is $C_{17}H_{21}N_1O_2$ and that of crude oil (petroleum) is $C_{44}H_{58}N_1O_4$ [189]. The non-polar fraction of shale oil contains a larger proportion of carbon (by weight) as compared to hydrogen, nitrogen and oxygen. Also, shale oil has a larger proportion of lighter fractions than does crude oil. This is shown in Figure 19, where the distillation curves of shale oils derived from various retorting procedures are compared to Kuwaiti crude oil.

The quantitative distribution of specific organic families present in the polar fractions of Utah shale oils is shown in Table 26 for two different retorting processes — Union 'B' and Paraho DH (direct heated) — and for three different distillation ranges. It should be noted that quinolines are present in medium to large amounts, naphthols are present in trace to medium amounts, and phenols are present in small to large quantities. The research reported in this document studied two phenols, one naphthol and one quinoline.

Characteristics of Spent Oil Shale

Retorting subjects oil shale to high temperatures, and this leads to a change in the chemical composition of the shales. Besides the pyrolysis of kerogen at 400 °C, the decomposition and dehydration of minerals starts at a temperature of 500 °C [165]. The sodium carbonate minerals dawsonite, nahcolite, shortite and trona decompose to form sodium carbonate, CO_2 and H_2O at a temperature of 500 °C [169]. Calcite decomposes at slightly higher temperatures, and dolomite

Table 25. Composition of Paraho shale oil

Characteristic	Value
Carbon, wt. %	84.5
Hydrogen, wt. %	11.2
Oxygen, wt. %	1.6
Nitrogen, wt. %	1.96
Sulfur, wt. %	0.64
Nickel, ppm	3.5
Vanadium, ppm	0.2
Iron, ppm	100
Pour point, °C	72

Source: Abstracted from [65].

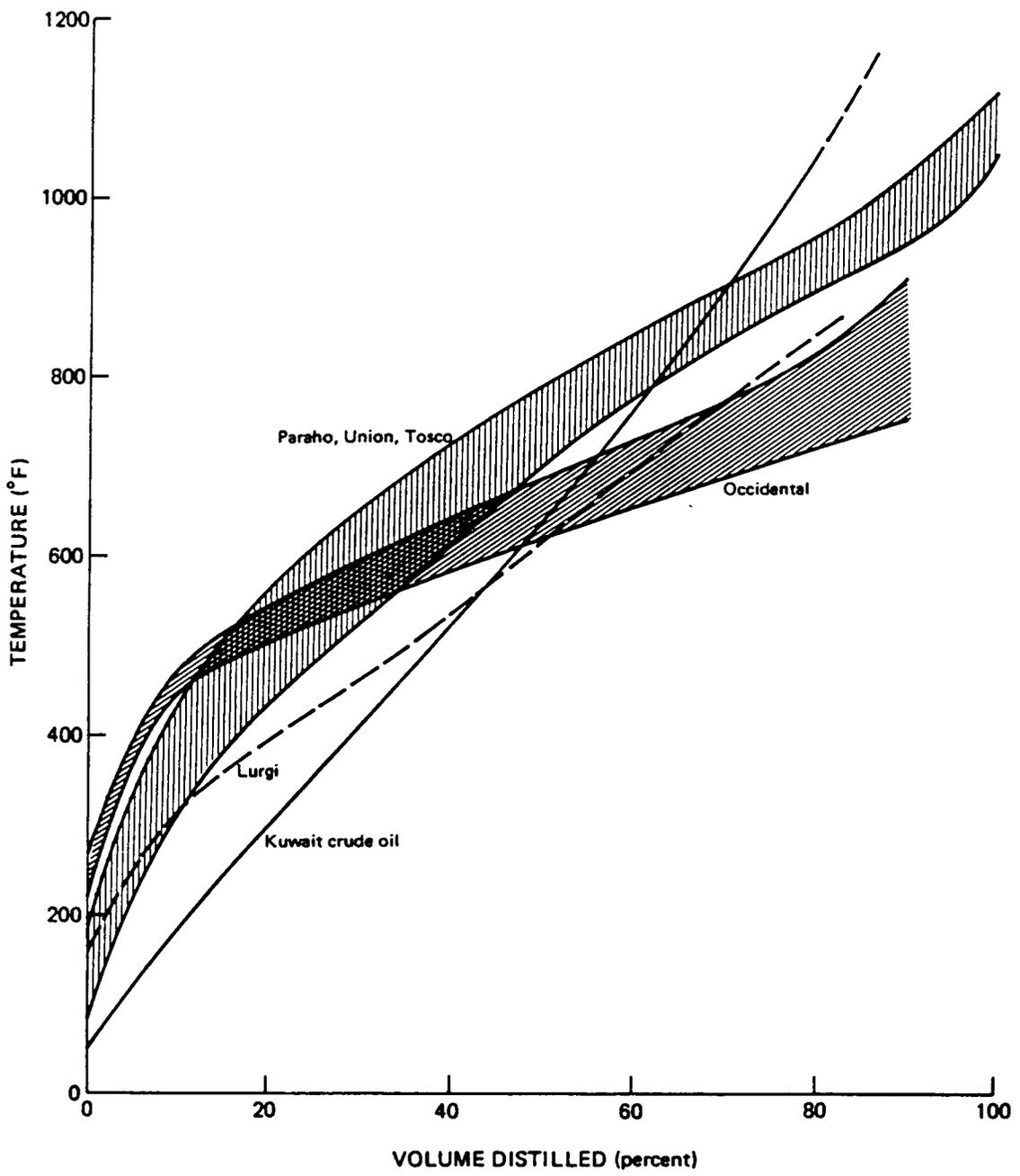


Figure 19. Distillation curves of shale oils: From [65].

Table 26. Qualitative MS characterization of the polar fractions of Utah shale oils

		UNION "B"			PARAHO DH		
		425- 500°F	500- 650°F	650- 850°F	425- 500°F	500- 650°F	650- 850°F
QUINOLINES	CYCLOALKYLINDOLES	M	M	M	M	L	M
NAPHTHOLS	INDENOLS	T	M	M	T	M	S
INDOLES	INDENO-PYRIDINES	M	L	M	M	L	S
CHROMANS		S	M	S	S	S	S
CYCLOALKYLPYRIDINES		M	M	M	M	M	M
INDANOLS		M	M	M	S	M	M
PYRIDINES	ANILINES	M	M	M	M	S	M
PHENOLS		L	S	M	L	S	S
ACRIDINES	BENZOQUINOLINES	M	S	M	S	S	M
DIHYDROXYPHENOLS CATECHOL RESORCINAL QUINOL	FURANS PYROLES	S	S	S	S	S	S
ALKYLCARBAZOLES	ACRIDANS	S	S	L	S	S	L
ACENAPHTHYLENOLS	BENZINDANONES	S	S	M	T	T	M
PHENYL-PYRIDINES		S	M	M	T	M	M
ACENAPHTHENOLS		T	S	S	T	S	S

L-LARGE, M-MEDIUM, S-SMALL, T-TRACE

Source: [134]

decomposes at 650-750 °C to form periclase, calcite and CO₂; the calcites react with quartz at 800 °C to form calcium silicates or with feldspars to form calcium aluminum silicates, whereas the periclase also forms silicates at higher temperatures [169]. In subsurface (*in situ*) retorts the temperature reached is usually much higher. When the temperature reaches around 1200 °C the spent shale fuses and this stops combustion and further generation of heat [203]. The relative abundances of various minerals at different temperatures are shown in Figure 20. The chemical formulas for some of the minerals associated with oil shale and the processing of oil shale are given in Table 27.

Table 28 indicates the distribution of some inorganic species present in Green River raw and spent shales. The relative abundance of the species does not change appreciably upon retorting, although, as the totals indicate, the total fraction of the constituents is higher in the spent shale — as expected.

Table 29 displays the elemental composition of TOSCO raw and spent shales (i.e., shales retorted by the TOSCO process). The relatively high concentrations of F and Ba are worth noting, as are the high concentrations of As and Pb from the environmental standpoint.

One factor that would play a part in studying the sorptive behavior of spent shale would be the surface area of the shale. Table 30 lists the areas of some spent shales and a granular activated carbon (the one used in this study). These areas were determined by the BET-N₂ adsorption method. For the most part, the surface areas of the shales were independent of the particle size, indicating that very little of the surface area was due to any internal pores. There are probably very few pores in spent shale fines (which are what the reported data are for), although the larger size fractions of shale may have some. This author has been unable to find the results of any surface area determinations performed on larger size fractions. The TOSCO II spent shale is the only shale that shows some correlation between surface area and particle size. Another trend that is apparent is that the surface areas of the shales depend on the temperature at which they were retorted. This relationship is shown in Figure 21.

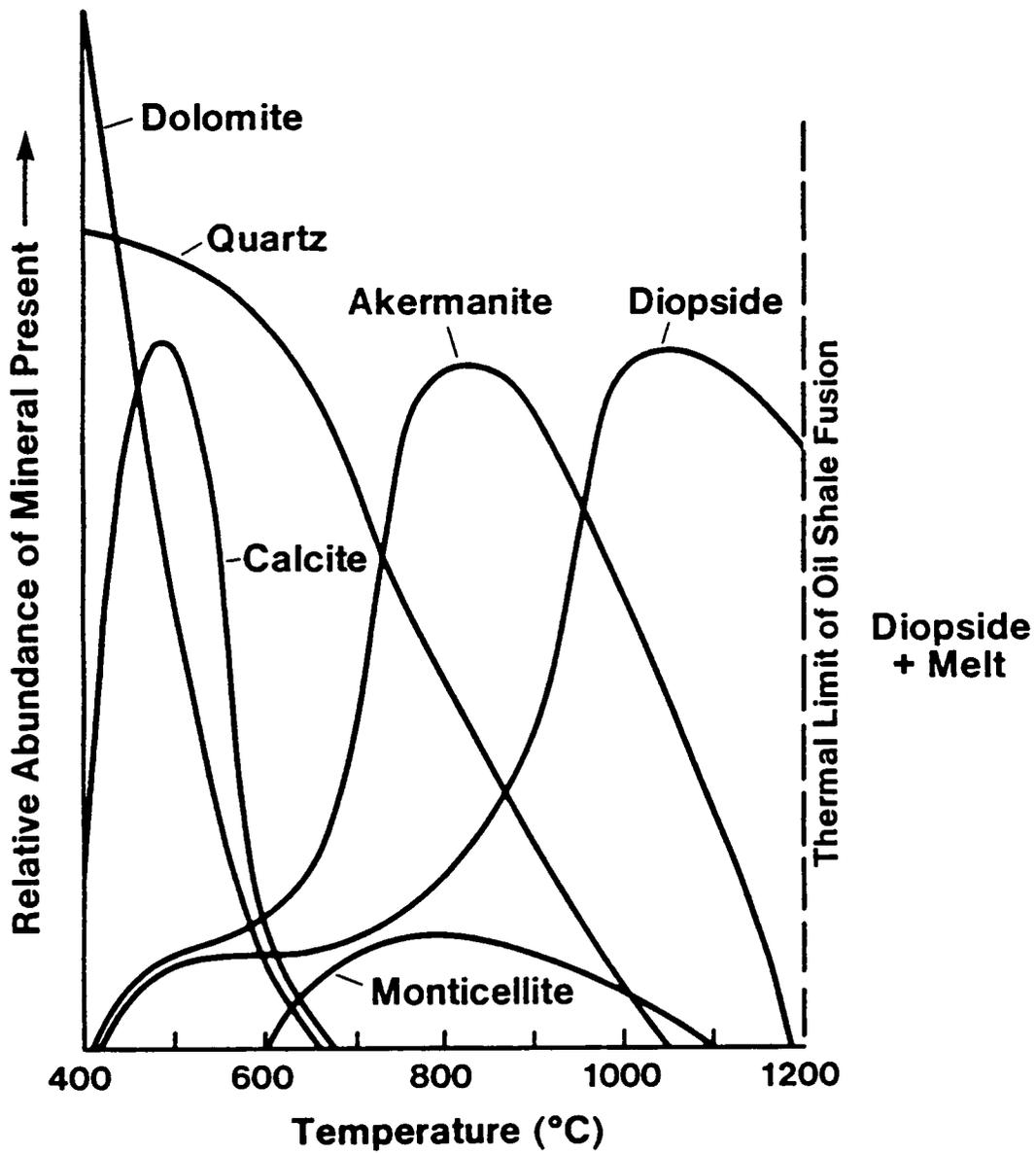


Figure 20. Relative mineral abundance versus temperature of oil shale: From [141].

Table 27. Chemical formulæ for minerals associated with oil shales and their processing

Akermanite - Gehlenite	$\text{Ca}_2(\text{Si}_2\text{O}_7) - \text{Ca}_2\text{Al}(\text{Si},\text{Al})_2\text{O}_7$
Analcime	$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$
Calcite	CaCO_3
Diopside (Augite)	$(\text{Ca},\text{Na},\text{K},\text{Mg},\text{Fe},\text{Ti},\text{Al})_2(\text{Si},\text{Al})_2\text{O}_6$
Dolomite	$\text{Ca}(\text{Mg},\text{Fe})(\text{CO}_2)_2$
Hematite	Fe_2O_3
Illite	$\text{KAl}_2(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$
K-Feldspar	KAlSi_3O_8
Monticellite - Merwinite - Forsterite	$\text{CaMg}(\text{SiO}_4) - \text{Ca}_3\text{Mg}(\text{SiO}_4)_2 - \text{Mg}_2(\text{SiO}_4)$
Na-Feldspar	$\text{NaAlSi}_3\text{O}_8$
Nahcolite	NaHCO_3
Periclase	$(\text{Mg},\text{Fe})\text{O}$
Pyrite	FeS_2
Quartz	SiO_2
Trona	$\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$
Wollastonite	$\text{Ca}(\text{SiO}_3)$

Sources: [16, 141]

Table 28. Green River raw and spent shale inorganic constituents

Inorganic Compound	Raw Shale, wt. %	Spent Shale, wt. %
CaCO ₃	27.7	33.5
MgCO ₃	13.8	16.7
Fe ₂ O ₃	2.60	3.14
Al ₂ O ₃	4.14	5.0
SiO ₂	30.1	36.4
Na ₂ O	1.21	1.46
K ₂ O	0.89	0.66
Total	80.44	96.86

Source: [228]

Table 29. Best values for the element concentrations in TOSCO raw and spent shales

Element	Concentration Unit	Raw Shale OS-1	Spent Shale SS-2
Al	%	3.4	4.2
As	ppm	70	82
B	ppm	110	146
Ba	ppm	1310	1580
Ca	%	9.8	11.3
Cd	ppm	1.05	0.98
Ce	ppm	35	44
Cr	ppm	36	42
Cs	ppm	4.4	6.0
Cu	ppm	48	62
Dy	ppm	2.1	2.5
Eu	ppm	0.52	0.64
F	ppm	1020	1490
Fe	%	1.89	2.45
Hf	ppm	1.44	1.85
Hg	ppm	0.15	0.045
K	%	1.25	1.5
La	ppm	18.7	22
Mg	%	2.6	3.9
Mn	ppm	271	334
Mo	ppm	28	36
Na	%	1.43	1.74
Nb	ppm	4.5	6.0
Nd	ppm	16	18
Ni	ppm	29	34
Pb	ppm	30	41
Rb	ppm	71	94
Sb	ppm	3.0	3.7
Sc	ppm	4.9	6.0
Se	ppm	4.1	4.9
Si	%	13.0	16.0
Sn	ppm	2.7	3.3
Sr	ppm	640	780
Tb	ppm	0.31	0.38
Th	ppm	5.2	6.2
Ti	%	0.14	0.19
V	ppm	5.4	6.6
Y	ppm	8.1	12
Yb	ppm	1.0	1.26
Zn	ppm	72	105
Zr	ppm	55	68

Source: [225]

Table 30. Specific surface area of spent shales and a granular activated carbon determined by BET-N₂ adsorption

Sample	Average Maximum Centerline Temperature (°C)	Particle Size Range (μm)	Specific Surface Area (m ² ·g ⁻¹)	Specific Surface Area for Sphere† (m ² ·g ⁻¹)
Surface retorted shales				
Paraho	590	< 63	3.50	> 0.038
		63-250	3.37	0.010-0.038
Lurgi‡	530/700	< 63	4.76	> 0.038
		63-250	4.77	0.010-0.038
TOSCO II	480	< 63	6.63	> 0.038
		63-250	9.20	0.010-0.038
		> 250	10.15	< 0.010
Simulated <i>In situ</i>				
L-1	900-1200	< 250	2.10	> 0.010
S-14	1010	63-250	2.40	0.010-0.038
S-55	650	< 300	4.20	> 0.008
Granular Activated Carbon				
Filtrosorb 300	—	800-1000	950-1050	0.0024-0.003

† — Estimated for a sphere with a diameter equivalent to the particle size range and a density of 2.5 g·cm⁻³ from $S_w = \frac{6}{(\text{density} \times \text{diameter})}$.

‡ — The shale was retorted at 530 °C and burned 700 °C.

Sources: Compiled from [26, 82, 83].

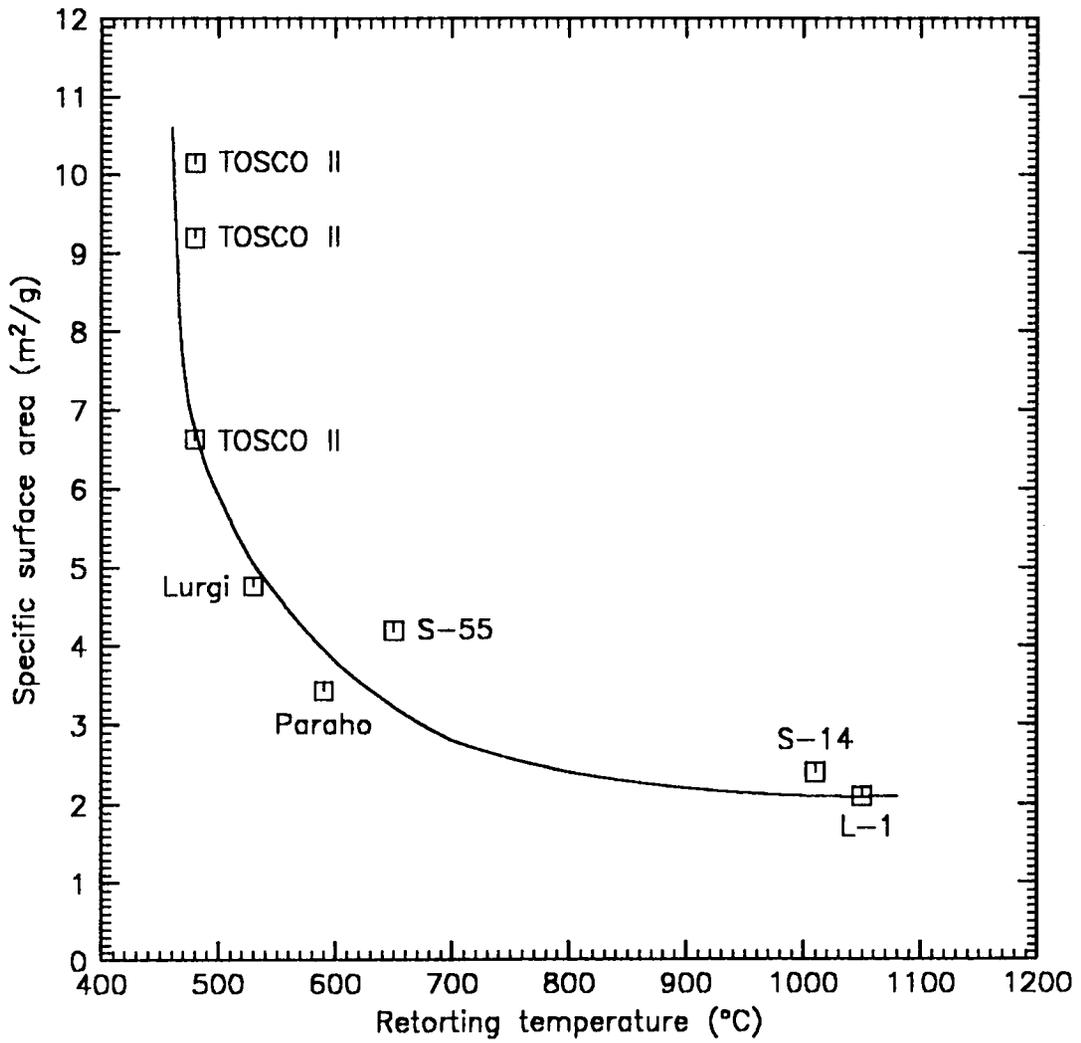


Figure 21. Relationship between specific surface area and retorting temperature: After [83], derived from data in Table 30.

Characteristics of Retort Water

Retort waters derived from shale processing typically have high alkalinity, high chemical oxygen demand (COD) and a wide variety of inorganic constituents. Some of these are listed in Table 31. The values reported were derived from 18 retort waters. The values for total Kjeldahl nitrogen (TKN) and solids are also very high. Interesting to note is the range of carbonate concentrations — the lowest value is zero.

A comparison of retort waters derived from Green River shale and Antrim shale is shown in Table 32. Some notable differences in the retort waters are in the concentrations for arsenic, the inorganic carbon, nickel, potassium and sodium. The concentration of the latter two elements shown that the Green River shales have a higher amount of soluble sodium compounds and the Antrim shale has a higher amount of soluble potassium compounds.

Work done at Argonne National Laboratory on the process water from an Oxy *in situ* retort (designated Oxy-6) separated the liquid and particulate phases of the retort waters and then characterized the organic constituents by the neutral, acid and base fractions. These results are shown in Tables 33-38. The study determined that the concentration of organic constituents in the liquid phase was 10 to 400 times greater than that in the particulate phase [174]. There were some high background interferences in the neutral fraction, and this hampered the identification of compounds in this fraction [174]. Some other points to be noted are that most peaks in the neutral and acid fractions were identified and that the liquid phase in both these fractions had a simpler matrix of compounds. The base fraction contained more compounds overall, more unidentified compounds and the particle phase had fewer compounds than the liquid phase. Primary compounds in the neutral fractions were furans, thiazoles and cyclohexanes. The acid fractions principally contained carboxylic acids, cresols and phenols. Pyridines and quinoline were the principal constituents of the base fractions.

Table 31. Chemical composition of various oil shale process waters

Parameter	Range		Average ¹
	Low	High	
Alkalinity, total, mg·ℓ ⁻¹ CaCO ₃	18,200	110,900	
Aluminum	0.041	16.6	
Arsenic	0.46	10	1.8
Barium	0.002	0.47	0.07
Beryllium	< 0.001	< 0.001	
Bicarbonate, mg·ℓ ⁻¹ HCO ₃	4,200	73,640	
Biochemical oxygen demand, 5-day	350 ²	5,500 ²	
Bromine	< 0.001	1.94	0.082
Cadmium	< 0.001	0.005	
Calcium	0.0	94	7.6
Carbon, inorganic	1,960	19,200	7,500
Carbon, organic	2,200	19,000	4,700
Carbonate, mg·CO ₃ ⁻ ·ℓ ⁻¹	0.0	15,210 ²	
Chemical oxygen demand	8,500 ²	43,000 ²	18,500 ²
Chlorine	0.007 ²	1910 ²	
Chromium	0.009	0.08	0.015
Cobalt	0.002	0.65	0.12
Conductivity, μmho·cm ⁻¹	15,100	193,000	31,000
Copper	0.003	160	0.019
Fluoride	0.1 ³	270 ³	
Hardness	20	1,500	88
Iodine	< 0.001	1.3	
Iron	0.091	77	7.6
Lead	0.002	0.83	
Lithium	< 0.001	7.1	0.70
Magnesium	3.2	350	22
Manganese	0.001	0.39	0.099
Mercury	< 0.001	0.39 ²	
Molybdenum	0.033	1.2	
Nickel	0.014	2.6	
Nitrogen, ammonia, mg-NH ₃ -N·ℓ ⁻¹	1,700	13,200	7,000
Nitrogen, ammonium, mg-NH ₄ -N·ℓ ⁻¹	930	24,450	10,000
Nitrogen, nitrate, mg-NO ₃ -N·ℓ ⁻¹	1.4	8.7	
Nitrogen, nitrite, mg-NO ₂ -N·ℓ ⁻¹	< 1.0		
Nitrogen, organic	73.3 ⁴	1,510 ⁴	
Nitrogen, Kjeldahl	6,600	19,500	
Oil and grease	3,800	3,800	
pH	8.1	9.4	8.7
Phenols	2.2 ²	169 ²	
Phosphorus	0.23 ²	19.0 ²	1.25 ²
Potassium	8	120	37
Selenium	< 0.001	1.7	
Silica, mg-SiO ₂ ·ℓ ⁻¹	4 ³	128 ³	17

Table 31. Continued

Parameter	Range		Average ¹
	Low	High	
Silver.....	< 0.001	0.23	
Sodium.....	.45 ³	1,600 ³	320
Solids, dissolved.....	1,750 ²	24,500 ²	6,800 ²
Solids, total.....	6.350 ²	121,000 ²	
Solids, volatile.....	2,070	119,300	
Sulfur, sulfate, mg-SO ₄ ⁻ · ℓ ⁻¹42	2,200	1,400
Sulfur, sulfide, mg-S ⁻ · ℓ ⁻¹	0.0	156 ²	
Sulfur, total.....	14	2,320	
Uranium.....	0.018	93	
Vanadium.....	0.004	> 190	0.27
Volatile acids.....	.807	1,481	
Zinc.....	0.020	15.1	0.28

¹ An average is reported only if more than 15 waters were available. Most values are based on 18 waters.

² Significant chemical interferences suspected.

³ Significant discrepancies noted in reported values determined with alternate analytical methods. Values shown are for spark source mass spectrometry.

⁴ Based on two values only.

Source: [81]

Table 32. Comparison of elemental abundances in retort waters from Green River and Antrim shales

Unfiltered retort water. All values in mg·ℓ ⁻¹ , unless otherwise noted.			
Element	Green River Shale		Antrim Shale
	Average	Range	
Aluminium.....	—	12.5 to 16.4	—
Antimony.....	0.20	0.0033 to 1.10	0.92
Arsenic.....	4.5	0.284 to 15.3	1.83
Barium.....	0.30	0.097 to 0.57	—
Bromine.....	0.19	0.038 to 0.53	0.37
Cadmium.....	0.01	0.00069 to 0.054	0.0065
Calcium.....	16	6 to 26	14
Carbon, %			
Organic.....	0.35	0.20 to 0.56	0.17
Inorganic.....	0.86	0.33 to 1.76	0.22
Cerium.....	0.01	0.0037 to 0.027	0.014
Cesium.....	0.032	0.0056 to 0.066	0.081
Chlorine.....	365	11 to 1175	387
Chromium.....	0.45	0.028 to 1.40	0.09
Cobalt.....	0.32	0.031 to 0.643	0.027
Copper.....	—	< 0.09 to 139	0.35
Europium.....	—	< 0.00008 to 0.0002	< 0.0002
Gallium.....	0.05	< 0.06 to 0.013	0.06
Germanium.....	—	< 0.06 to 0.13	0.05
Hafnium.....	0.0028	0.0014 to 0.0049	0.0048
Iodine.....	0.16	0.13 to 0.25	0.15
Iron.....	7.7	1.21 to 27.2	2.7
Lanthanum.....	0.03	0.00025 to 0.12	0.008
Lead.....	—	< 0.24 to 1.15	< 0.24
Magnesium.....	—	< 3.1 to < 39	29
Manganese.....	0.23	0.0022 to 0.39	< 0.02
Mercury.....	0.08	< 0.0005 to 0.196	0.080
Molybdenum.....	0.47	0.010 to 1.39	2.84
Nickel.....	2.45	0.24 to 10.7	1.0
Nitrogen, %.....	1.69	1.00 to 2.97	1.13
Potassium.....	23	< 4 to 54	163
Rubidium.....	0.36	0.019 to 0.80	1.21
Samarium.....	—	0.00006 to 0.0017	—
Selenium.....	0.64	0.228 to 1.42	0.44
Sodium.....	621	3.06 to 1780	193
Strontium.....	0.4	0.10 to 0.91	0.37
Sulfur, %.....	0.17	0.05 to 0.85	1.15
Tantalum.....	—	0.0056 to 0.051	—
Thorium.....	0.0038	0.0008 to 0.0094	0.17
Titanium.....	—	< 0.57 to 2.7	0.69
Tungsten.....	0.06	0.0057 to 0.13	—
Uranium.....	0.062	0.0011 to 0.195	0.73
Vanadium.....	—	0.023 to 0.19	< 0.06
Ytterbium.....	0.0014	0.00094 to 0.0021	—
Yttrium.....	—	< 0.15 to 0.8	< 0.15
Zinc.....	1.8	0.09 to 13.3	0.92

Source: Modified from [75].

Table 33. Compounds in the neutral fraction of the particulate extract of Oxy-6 retort water

1 $\mu\ell$ splitless

Retention Time, min.	Tentative Identification	Area Counts	Concentration, $\mu\text{g}\ell^{-1}$
15.71	C ₂ -furan	168	0.7
19.59	C ₂ -furan	1,249	5.2
20.98	methyl thiazole	2,688	20.0
21.49	methyl thiazole	464	3.5
25.35	<i>n</i> -decane	1,518	6.3
26.01	C ₃ -furan	787	3.2
26.84	C ₂ -thiazole	677	5.0
28.87	C ₂ -thiazole	2,355	17.5
29.17	C ₂ -thiazole	746	5.6
29.34	C ₂ -thiazole	742	5.5
30.00	C ₃ -thiazole	1,128	8.4
30.90	C ₃ -thiazole	1,213	9.0
31.61	C ₃ -thiazole	3,598	26.3
32.41	C ₃ -thiazole	2,012	13.0
32.96	<i>n</i> -hendecane	4,222	17.4
40.39	<i>n</i> -dodecane	8,260	34.0
42.02	C ₂ -cyclohexane	1,557	20.0
43.07	C ₂ -cyclohexane	6,564	29.4
45.22	trimethyl-cyclohexane	6,504	28.7
45.64	C ₂ -cyclohexane	8,600	38.5
46.68	C ₁₄ -alkane	10,790	47.2
47.45	<i>n</i> -tridecane	8,480	34.9
52.71	C ₁₅ -alkane	7,464	31.2
54.12	<i>n</i> -tetradecane	11,170	46.0
58.23	C ₁₆ -alkane	12,200	51.0
60.41	<i>n</i> -pentadecane	12,630	52.0
66.38	<i>n</i> -hexadecane	13,510	55.6
69.35	C ₁₈ -alkane	13,940	58.3
72.03	<i>n</i> -heptadecane	14,780	60.8
72.59	pristane	19,080	78.5
73.34	unidentified	3,182	—
73.66	unidentified	3,104	—
74.24	unidentified	2,849	—
77.37	<i>n</i> -octadecane	8,588	35.9
78.07	phytane	8,648	36.1
82.46	<i>n</i> -nonadecane	7,594	31.7
87.34	<i>n</i> -eicosane	4,235	17.7
91.97	<i>n</i> -heneicosane	2,642	11.0
96.43	<i>n</i> -docosane	1,802	7.5
100.68	<i>n</i> -tricosane	1,353	5.7
103.57	unidentified	1,967	—
104.79	<i>n</i> -tetracosane	890	3.7
108.73	<i>n</i> -pentacosane	1,091	4.6
112.50	<i>n</i> -hexacosane	646	2.7
116.15	<i>n</i> -heptacosane	685	2.9
119.68	<i>n</i> -octacosane	541	2.3
123.06	<i>n</i> -nonacosane	580	2.4
126.36	<i>n</i> -triacontane	377	1.6
129.54	<i>n</i> -hentriacontane	307	1.3
132.64	<i>n</i> -dotriacontane	99	0.4
136.09	<i>n</i> -tritriacontane	114	0.5
140.12	<i>n</i> -tetratriacontane	50	0.2

Source: [174]

Table 34. Compounds in the neutral fraction of the liquid extract of Oxy-6 retort water

1 $\mu\ell$ splitless, 1:50 dilution

Retention Time, min.	Tentative Identification	Area Counts†	Concentration, $\mu\text{g}\cdot\ell^{-1}$
15.32	C ₂ -furan	498	103
19.02	C ₂ -furan	3,032	627
20.26	methyl thiazole	4,583	1,705
20.85	methyl thiazole	908	338
21.44	unidentified	841	—
23.21	unidentified	743	—
24.79	<i>n</i> -decane	4,896	1,023
25.24	unidentified	910	—
26.14	C ₂ -thiazole	1,698	632
28.11	C ₂ -thiazole	4,840	1,800
28.46	C ₂ -thiazole	2,298	855
28.78	C ₂ -thiazole	2,200	818
29.91	C ₃ -thiazole	4,016	1,494
30.22	C ₃ -thiazole	5,741	2,136
31.03	C ₃ -thiazole	4,093	1,523

† Area counts for 1:50 diluted sample.

Source: [174]

Table 35. Compounds in the acid fraction of the particulate extract of Oxy-6 retort water

3 $\mu\ell$ splitless

Retention Time, min.	Tentative Identification	Area Counts	Concentration, $\mu\text{g}\cdot\ell^{-1}$
6.93	acetic acid	4,486	11.1
8.40	unidentified	687	—
9.09	unidentified	354	—
9.94	unidentified	526	—
11.15	propionic acid	9,910	24.6
15.25	isobutyric acid	46,360	115.0
15.82	hydroxybutyric acid lactone	717	1.8
16.92	<i>n</i> -butyric acid	20,690	51.3
18.54	unidentified	703	—
18.94	hydroxyvaleric acid lactone	2,520	6.2
19.90	C ₅ -carboxylic acid	14,540	36.1
20.84	C ₅ -carboxylic acid	34,160	84.7
21.25	C ₅ -carboxylic acid	18,450	46.0
21.78	C ₅ -carboxylic acid	29,810	73.9
24.41	<i>n</i> -valeric acid	75,510	187.3
24.73	unidentified	2,982	—†
25.16	unidentified	3,579	—†
25.47	unidentified	3,962	—†
26.33	C ₆ -carboxylic acid	9,939	24.6
27.52	C ₆ -carboxylic acid	34,590	85.8
28.09	C ₆ -carboxylic acid	15,350	38.1
28.93	phenol	40,760	101.1
30.54	<i>n</i> -caproic acid	50,550	125.4
30.60	unidentified	1,859	—
30.82	unidentified	3,053	—
31.03	unidentified	4,473	—
32.34	unidentified	10,700	—
32.53	cresol	14,090	34.9
33.37	C ₇ -carboxylic acid	17,370	43.1
33.87	unidentified	8,034	—
34.38	unidentified	6,934	—
34.78	cresol	26,300	65.2
36.65	<i>n</i> -heptoic acid	41,140	102.0
37.26	unidentified	5,189	—
38.01	C ₂ -phenol	6,896	17.1
38.42	C ₂ -phenol	9,512	7.9
38.84	C ₂ -phenol	7,348	18.2
39.62	C ₂ -phenol	10,040	24.9
40.17	C ₂ -phenol	6,000	14.9
40.52	C ₂ -phenol	29,200	72.4
41.43	C ₂ -phenol	3,197	7.9
42.70	<i>n</i> -caprylic acid	18,230	45.2
43.95	unidentified	6,686	—
45.42	unidentified	26,110	—
46.32	C ₃ -phenol	10,840	—
48.61	<i>n</i> -pelargonic acid	9,310	23.1

† Values of 7.4, 8.9 and 9.8, respectively, were given in the original reference.

Source: [174]

Table 36. Compounds in the acid fraction of the liquid extract of Oxy-6 retort water

1 $\mu\ell$ splitless, 1:10 dilution

Retention Time, min.	Tentative Identification	Area Counts†	Concentration, $\mu\text{g}\cdot\ell^{-1}$
10.56	propionic acid	44,150	3,280
14.54	isobutyric acid	65,320	4,860
16.55	<i>n</i> -butyric acid	60,610	4,510
16.65	unidentified	1,616	—‡
18.85	C ₅ -carboxylic acid	20,440	1,520
19.55	C ₅ -carboxylic acid	24,810	1,850
20.67	C ₅ -carboxylic acid	48,360	1,600
23.39	<i>n</i> -valeric acid	82,610	6,150
25.71	C ₆ -carboxylic acid	16,940	1,260
26.01	phenol	39,030	2,900
26.80	C ₆ -carboxylic acid	15,710	1,170
29.95	<i>n</i> -caproic acid	98,880	7,360
30.32	cresol	10,490	780
32.26	cresol	7,410	550
32.34	cresol	15,170	1,130
33.16	unidentified	4,245	—‡
36.61	<i>n</i> -heptoic acid	105,400	7,840
38.61	C ₂ -phenol	15,510	1,150
42.78	<i>n</i> -caprylic acid	89,060	6,630
43.28	C ₂ -phenol	10,900	810
43.61	C ₂ -phenol	13,740	1,020
48.21	<i>n</i> -pelargonic acid	35,870	2,670
53.30	<i>n</i> -capric acid	4,916	370

† Area counts based on 1:10 diluted sample.

‡ These were given as 120 and 320, respectively, in the original reference.

Source: [174]

Table 37. Compounds in the base fraction of the particulate extract of Oxy-6 retort water

1 $\mu\ell$ splitless, 1:10 dilution

Retention Time, min.	Tentative Identification	Area Counts†	Concentration, $\mu\text{g}\cdot\ell^{-1}$
8.89	pyridine	986	2.5
12.12	2-methyl pyridine	210	0.5
12.48	methyl pyrazole	752	1.9
14.22	3-methyl pyridine	63	0.2
14.51	4-methyl pyridine	875	2.3
15.45	C ₂ -pyrrole	407	1.0
16.31	C ₂ -pyridine	139	0.4
17.11	C ₂ -pyrazole	824	2.0
19.15	2,4-dimethyl pyridine	1,636	4.2
19.62	C ₂ -pyrrole	205	0.5
20.04	C ₂ -pyridine	450	1.2
20.86	C ₂ -pyrazole	618	1.5
23.36	2,4,6-trimethyl pyridine	7,704	19.9
23.96	C ₂ -pyridine	6,087	15.7
24.40	unidentified	583	—
25.03	C ₂ -pyridine	1,012	2.6
25.99	C ₃ -pyridine	2,538	6.6
27.98	unidentified	1,090	—
28.52	C ₃ -pyridine	4,500	11.6
29.15	C ₃ -pyridine	2,427	6.3
29.99	aniline	6,049	10.9
30.31	C ₃ -pyridine	4,437	11.5
30.76	unidentified	2,820	—
31.18	C ₄ -pyridine	3,213	8.3
32.11	unidentified	3,768	—
32.73	methyl aniline	8,556	15.4
34.69	unidentified	12,470	—
35.03	C ₄ -pyridine	10,450	27.0
35.53	unidentified	7,198	—
40.79	unidentified	8,606	—
41.10	quinoline	8,862	16.6
41.39	unidentified	4,047	—
42.24	unidentified	10,010	—
42.56	isoquinoline	7,310	13.7
44.52	unidentified	8,614	—
45.79	unidentified	8,710	—
45.99	unidentified	1,902	—
46.08	unidentified	5,044	—
46.31	C ₁ -quinoline	12,140	22.8
47.58	C ₁ -quinoline	4,903	9.2
48.27	C ₁ -quinoline	5,434	10.2
49.10	C ₁ -quinoline	6,379	12.0
49.46	C ₁ -quinoline	5,215	9.8
50.57	unidentified	8,500	—
51.28	unidentified	6,005	—
52.78	C ₂ -quinoline	8,778	16.5
53.62	unidentified	3,986	—
53.88	C ₂ -quinoline	8,932	16.8
54.41	unidentified	4,936	—
55.13	C ₂ -quinoline	17,010	32.0
55.62	C ₂ -quinoline	7,690	14.4
55.93	unidentified	6,065	—

Source: [174]

Table 38. Compounds in the base fraction of the liquid extract of Oxy-6 retort water

1 $\mu\ell$ injection

Retention Time, min.	Tentative Identification	Area Counts ¹	Concentration, $\mu\text{g}\cdot\ell^{-1}$
7.99	pyridine	1,986 ²	153.9
11.49	2-methyl pyridine	1,995 ²	154.6
11.92	methyl pyrazole	622 ²	46.3
13.75	3-methyl pyridine	815 ²	63.2
14.02	4-methyl pyridine	5,301 ²	410.8
15.01	C ₂ -pyrrole	1,634 ²	121.6
15.90	C ₂ -pyridine	1,192 ²	92.4
16.74	C ₂ -pyrazole	6,388 ²	475.3
18.86	2,4-dimethyl pyridine	11,160 ²	864.9
19.33	C ₂ -pyrrole	2,597 ²	193.2
19.76	C ₂ -pyridine	4,000 ²	310.0
20.62	C ₂ -pyrazole	7,394 ²	550.1
23.26	2,4,6-trimethyl pyridine	18,805 ³	1457.4
23.80	C ₂ -pyridine	21,800 ³	1689.5
24.86	C ₃ -pyridine	5,023 ²	389.3
25.90	C ₃ -pyridine	6,335 ³	491.0
28.40	C ₃ -pyridine	18440 ²	1429.1
29.08	C ₃ -pyridine	20,760 ²	1608.9
29.94	aniline	18,620 ³	1003.9
30.27	unidentified	8,705 ³	—
30.44	C ₃ -pyridine	5465 ³	423.3
31.15	C ₄ -pyridine	9,110 ³	706.0
32.72	methyl aniline	16,015 ³	863.4
35.05	C ₄ -pyridine	25,485 ³	1975.1
41.14	quinoline	33,190 ³	1870.7
42.61	isoquinoline	18,090 ³	1019.6
44.26	unidentified	14,310 ³	—
44.57	unidentified	14,795 ³	—
45.81	C ₁ -quinoline	31,815 ³	1793.2
46.11	C ₅ -pyridine	11,640 ³	902.1
46.34	C ₁ -quinoline	26,200 ³	1476.1
47.64	C ₁ -quinoline	11,090 ³	625.1
48.13	C ₁ -quinoline	11,580 ³	652.7
48.32	unidentified	12,605 ³	—
48.99	C ₁ -quinoline	10,010 ³	564.2
49.15	C ₁ -quinoline	8,350 ³	470.6
49.49	unidentified	10,975 ³	—
50.29	C ₁ -quinoline	9,580 ³	540.0
50.62	C ₁ -quinoline	11,040 ³	622.3
52.81	C ₂ -quinoline	20,920 ³	1179.1
53.93	C ₂ -quinoline	18,995 ³	1070.6
55.13	C ₂ -quinoline	18,115 ³	1021.0
55.64	C ₂ -quinoline	10,115 ³	570.1
55.98	C ₂ -quinoline	8,200 ³	462.2

Table 38. Continued

Retention Time, min.	Tentative Identification	Area Counts ¹	Concentration, $\mu\text{g}\cdot\ell^{-1}$
62.94	unidentified	10,188 ⁴	—
63.65	unidentified	5,630 ⁴	—
64.04	unidentified	8,869 ⁴	—
64.69	unidentified	14,710 ⁴	—
65.92	unidentified	8,964 ⁴	—
66.79	unidentified	5,639 ⁴	—
67.39	unidentified	10,803 ⁴	—
68.78	unidentified	16,617 ⁴	—
69.47	unidentified	14,847 ⁴	—
70.09	unidentified	11,881 ⁴	—
70.48	unidentified	7,640 ⁴	—
70.82	unidentified	6,059 ⁴	—
71.27	unidentified	4,678 ⁴	—
71.85	unidentified	7,256 ⁴	—
72.05	unidentified	6,302 ⁴	—
72.36	unidentified	16,199 ⁴	—
73.82	unidentified	4,311 ⁴	—
74.27	unidentified	6,099 ⁴	—
75.52	unidentified	8,119 ⁴	—
75.83	unidentified	19,171 ⁴	—
76.54	unidentified	2,668 ⁴	—
78.43	unidentified	3,802 ⁴	—
79.01	unidentified	6,397 ⁴	—
79.55	unidentified	3,363 ⁴	—

¹ For 1:10 diluted sample

² From 1:10 diluted sample, splitless injection

³ From 1:50 diluted sample, splitless injection

⁴ From 1:19 split, split injection

Source: [174]

Further analysis of the same Oxy-6 retort water done by the USGS for the identification of organic compounds succeeded in identifying 50% of the total dissolved organic carbon content [128]. The results of that study for a condensate water and a retort water are shown in Table 39. Aliphatic monocarboxylic acids represented 42% of the total dissolved organic carbon (DOC) content (i.e., about 85% of the identified DOC) of the retort water, but only 0.36% of the total DOC of the condensate water. The condensate water consisted primarily of phenols and aromatic amines. These differences in the two waters indicates that separate treatment of the waters may be easier in some cases. Normally, though, the combined process stream would be the one being treated.

Air Pollutants

The Green River resources of oil shale lie close to the Class I (pristine) areas of the Dinosaur National Monument and the Flat Tops Wilderness Areas. The prevention of significant deterioration (PSD) regulations for pristine areas would perhaps be the biggest stumbling block to the development of the oil shale industry from the aspect of air pollution. The PSD regulations for Class I areas are very stringent and a great degree of control will be required to meet the standards [8, 30].

The two main emissions (besides fugitive dust generated from mining and crushing operations [74]) are of sulfur compounds (primarily H₂S) and polyaromatic hydrocarbons, including benzo(*e*)pyrene and benzo(*a*)pyrene [88]. Tables 40 and 41 provide some information on these constituents. Table 20 also contains information on air pollutants. Over 75 organic compounds have been identified in aerosol emissions, and it is estimated that a 50,000 bbl·d⁻¹ *in situ* retort would generate upto 8 kg·d⁻¹ (17.6 lb·d⁻¹) of mercury [30]. Seventy-six percent of all mercury in shale can be released in the gases [77]. Other constituents would also be a problem, specially for an *in situ* retort where there is very little control over air emissions.

Table 39. Retort water organic analyses

Compound	DOC classification	Condensate water (DOC = 790 mg-ℓ ⁻¹)		Retort water (DOC = 3000 mg-ℓ ⁻¹)	
		conc., mg-ℓ ⁻¹	DOC, mg-ℓ ⁻¹	conc., mg-ℓ ⁻¹	DOC, mg-ℓ ⁻¹
aliphatic monocarboxylic acids					
formic acid	HPI-A	1.0	2.87	ND	1263.8
acetic acid	HPI-A	3.4	0.26	1188	475
propanoic acid	HPI-A	1.2	1.36	364	177
2-methylpropanoic acid	HPI-A	0.5	0.58	119	64.9
butanoic acid	HPI-A	0.4	0.27	117	63.8
pentanoic acid	HPI-A	0.3	0.22	110	64.7
2- and 3-methylbutanoic acid	HPO-A	NA	0.18	151	88.8
hexanoic acid	HPO-A	NA	NA	109	67.9
heptanoic acid	HPO-A	NA	NA	149	96.6
octanoic acid	HPO-A	NA	NA	131	87.6
nonanoic acid	HPO-A	NA	NA	81	55.5
decanoic acid	HPO-A	NA	NA	31	22.0
aliphatic dicarboxylic acids					
ethanedioic acid	HPI-A	NA	NA	41.6	1.4
propanedioic acid	HPI-A	NA	NA	4.9	1.3
butanedioic acid	HPI-A	NA	NA	8.1	2.8
pentanedioic acid	HPI-A	NA	NA	2.0	0.8
hexanedioic acid	HPI-A	NA	NA	21.2	10.0
heptanedioic acid	HPI-A	NA	NA	4.7	2.3
octanedioic acid	HPI-A	NA	NA	7.2	3.8
nonanedioic acid	HPO-A	NA	12.8	11.5	6.2
decanedioic acid	HPO-A	NA	7.4	11.7	7.0
aromatic carboxylic acids					
benzoic acid	HPO-A	ND	NA	25.4	16.6
thiocyanate	HPI-A	8.1	1.68	78.6	16.1
			0.2		0.5

Table 39. Continued

Compound	DOC classification	Condensate water (DOC = 790 mg-ℓ ⁻¹)		Retort water (DOC = 3000 mg-ℓ ⁻¹)	
		conc., mg-ℓ ⁻¹	DOC, mg-ℓ ⁻¹	conc., mg-ℓ ⁻¹	DOC, %
phenols			17.8		2.2
phenol	HPO-A	54.3	140.2	64.5	
2-hydroxytoluene	HPO-A	41.8	41.8	20.0	
3- and 4-hydroxytoluene	HPO-A	23.2	18.1	7.1	5.5
1,2-dimethyl-4-hydroxybenzene	HPO-A	42.6	33.1	9.6	7.4
remaining dimethylhydroxybenzene isomers	HPO-A	5.6	4.4	4.6	3.6
	HPO-A	54.5	42.8	36.1	28.3
aromatic amines			19.3		0.3
aniline	HPO-B	21.3	152.1	9.74	
2-aminotoluene	HPO-B	3.4	16.5	1.6	1.24
3- and 4-aminotoluene	HPO-B	5.2	2.7	0.2	0.16
pyridine	HPI-B	14.7	11.2	NA	NA
2-methylpyridine	HPO-B	9.2	7.1	2.3	1.75
3-methylpyridine	HPO-B	6.5	5.0	NA	NA
4-methylpyridine	HPO-B	6.3	4.9	NA	NA
2,6-dimethylpyridine	HPO-B	9.5	7.5	1.8	1.41
remaining dimethylpyridine isomers	HPO-B	37.6	29.5	NA	NA
2,4,6-trimethylpyridine	HPO-B	70.1	55.5	4.0	3.17
quinoline	HPO-B	5.8	4.8	1.9	1.59
isoquinoline	HPO-B	2.4	2.0	0.5	0.42
2-methylquinoline	HPO-B	1.6	1.3	NA	NA
aliphatic amines ^a					
methylamine	HPI-B	1.8		1.8	
ethylamine	HPI-B	3.0		2.4	
hydroxypyridines					
2-hydroxypyridine	HPI-B	ND		31.5	1.1
3-hydroxypyridine	HPI-B	ND		8.6	
4-hydroxypyridine	HPI-B	ND		13.6	5.6
2-hydroxy-6-methylpyridine	HPI-B	ND		4.0	2.5
	HPI-B	ND		25.6	16.9

Table 39. Continued

Compound	DOC classification	Condensate water (DOC = 790 mg·ℓ ⁻¹)		Retort water (DOC = 3000 mg·ℓ ⁻¹)	
		conc., mg·ℓ ⁻¹	DOC, mg·ℓ ⁻¹	conc., mg·ℓ ⁻¹	DOC, %
pyridinecarboxylic acids					
2-pyridinecarboxylic acid	HPI-B	NA		0.70	tr ^a
3-pyridinecarboxylic acid	HPI-B	NA		0.18	
4-pyridinecarboxylic acid	HPI-B	NA		0.29	
		NA		0.23	
aliphatic amides			0.3	38.5	1.2
formamide	HPI-N	2.0	2.46	ND	
acetamide	HPI-N	4.0	0.53	52.7	21.4
propionamide	HPI-N	0.6	1.63	23.2	11.4
butyramide	HPI-N	ND	0.30	2.0	1.1
urea	HPI-N	NA		22.8	4.6
nitriles					
acetonitrile	HPI-N	38.9	34.3	4.3	0.1
propionitrile	HPI-N	8.5	22.8	5.8	
isobutyronitrile	HPO-N	2.3	5.6	ND	
butyronitrile	HPO-N	2.5	1.6	ND	
valeronitrile	HPO-N	0.6	1.7	ND	
benzonitrile	HPO-N	2.7	0.4	ND	
			2.2	ND	
aliphatic alcohols					
methanol	HPI-N	3.4	27.26	3.5	1.5
ethanol	HPI-N	3.4	1.28	ND	tr
propanol	HPI-N	0.2	1.46	ND	
isopropyl alcohol	HPI-N	26.6	0.12	ND	
sec-butyl alcohol	HPI-N	13.0	16.0	2.5	1.50
			8.4	ND	
aliphatic ketones					
acetone	HPI-N	19.5	20.7	2.6	0.1
2-butanone	HPO-N	10.2	12.1	3.9	2.42
2-pentanone	HPO-N	0.9	7.9		
			0.7		

Table 39. Continued

Compound	DOC classification	Condensate water (DOC = 790 mg-ℓ ⁻¹)		Retort water (DOC = 3000 mg-ℓ ⁻¹)	
		conc., mg-ℓ ⁻¹	DOC, mg-ℓ ⁻¹	conc., mg-ℓ ⁻¹	DOC, mg-ℓ ⁻¹
aliphatic aldehydes acetaldehyde	HPI-N	ND		2.4	1.31 1.31
lactones γ-butyrolactone	HPO-N	9.6	12.1	13.7	16.7
γ-valerolactone	HPO-N	11.3	5.4	15.2	7.6
			6.8		9.1
pyrrole	HPO-N	4.9	3.56	ND	
Identified DOC			397.3	50.3	1508.4
					50.3

DOC = dissolved organic carbon

NA = not analyzed

ND = not detected

HPI-A = hydrophilic acid

HPO-A = hydrophobic acid

HPI-B = hydrophilic base

HPO-B = hydrophobic base

HPI-N = hydrophilic neutral

HPO-N = hydrophobic neutral

^a Tentative data not included in carbon balance^b Trace

Source: [128]

Table 40. Hydrogen sulfide emissions from *in situ* and surface oil shale retorts

Retort	Type	Sulfur emissions (as H ₂ S)			
		kg·d ⁻¹	lb·d ⁻¹	kg·bbl ⁻¹	lb·bbl ⁻¹
Occidental retort 6	<i>in situ</i>	936	2064	5.5	12.1
Rio Blanco retort 1	<i>in situ</i>	3,414	7,528	15.9	35.1
Geokinetics retort 25	<i>in situ</i>	377	831	3.8	8.4
Paraho semiworks	<i>ex situ</i>	159	351	1.0	2.2
Union B proposed	<i>ex situ</i>	14,180	31,267	1.4	3.1
TOSCO II	<i>ex situ</i>	175,000	385,875	3.2	7.1

Source: Modified from [30].

Table 41. Polyaromatic hydrocarbon (PAH) components and concentrations from Rio Blanco retort 1

PAH Component	Concentration ($\mu\text{g}\cdot\text{m}^{-3}$)	
	In Raw Gas ^a	After Scrubbing and Incineration
Naphthalene	1.82×10^{-2}	1.22×10^{-2}
Acenaphthylene		1.22×10^{-2}
Acenaphthene	1.66×10^0	3.68×10^{-2}
Fluorine		
9,10-Dihydroanthracene	1.64×10^{-1}	6.12×10^{-2}
Phenanthrene	8.21×10^{-3}	1.02×10^{-1}
Anthracene	2.74×10^{-2}	2.86×10^{-2}
2-Methylanthracene	2.52×10^{-1}	1.76×10^{-1}
9-Methylanthracene	2.34×10^0	1.91×10^0
Fluoranthene	3.13×10^{-1}	3.23×10^{-1}
Pyrene	5.03×10^{-1}	5.73×10^{-1}
Benzo(<i>e</i>)anthracene	1.19×10^{-1}	9.42×10^{-2}
Chrysene	4.60×10^{-1}	4.00×10^{-1}
Benzo(<i>k</i>)fluoranthene	4.81×10^{-1}	1.67×10^{-1}
Benzo(<i>b</i>)fluoranthene	1.10×10^{-1}	1.64×10^{-2}
Benzo(<i>e</i>)pyrene	2.15×10^0	3.75×10^{-1}
Benzo(<i>a</i>)pyrene ^b	8.53×10^{-2}	1.31×10^{-1}
Indeno(1,2,3- <i>cd</i>)pyrene	4.57×10^{-2}	
Dibenzo(<i>a,h</i>)anthracene		
Benzo(<i>g,h,i</i>)perylene		
Total weight of PAH fraction	13.2	4.7

^a Stack conditions: 600 mm Hg, 71 °C.

^b A large and broad peak obscured the peak for benzo(*a*)pyrene.

Source: [30] (adapted from [88]).

Leachates from Spent Shale

Quite a few researchers have studied the character and composition of leachates from spent shale — from *ex situ*, MIS and *in situ* retorted shales. A comprehensive analysis of the work in this area is beyond the scope of this document. For the most part, the compounds identified in spent shale (see the earlier section on this) are those that would be leached from spent shale. The most extensive and recent review of the work on the leaching of oil shale that this author has found is the one by Fox, performed for the DOE [76]. That document consists of 250 pages and covers leaching from raw shale, *ex situ* spent shale and *in situ* (including MIS) spent shale, and also has a section detailing needed research in the area. Dr. Fox maintains an up-to-date library of oil shale research and can be contacted for information on practically any aspect of the oil shale field [79].

It would be useful to review the factors that may affect the leaching of various constituents from oil shale. Briefly, the most important factors are:

1. **Final disposal of the spent shale** — This factor is most important since the final disposal method chosen will affect what amount of leaching occurs. For example, if the shale is disposed in lined pits or in valley fills it is most important to ensure a tight seal so that contaminants do not escape into the groundwater environment. Also, if the pit top is kept open during the time that disposal to a pit is being carried out — usually a period of months or years — then surface runoff is of concern. Ensuring a perfectly sealed lining in a landfill is not possible, specially if the material is to be isolated for a long period of time. It, therefore, becomes important to determine how much will leach and what the harmful effects of the leachate will be.

If the shale is from an *ex situ* operation and is disposed of in a landfill, then such other factors as the height of the groundwater table, the annual rainfall and the possibilities of revegetation to slow down erosion must be considered. If, however, the shale is from an *in situ* process, or will be disposed in an underground mine as has been suggested [62], then such factors as the

impermeability of the overburden, and the occurrence of channeling must also be considered. The influx of water into production reservoirs from overlying, undercompacted, overpressured shale beds has also been studied [61].

2. **Annual rainfall and other weather conditions** — The annual rainfall in an area must be considered. The West does not normally get as much precipitation as the East does. However, the West does get a significant amount of snowfall, and a slow snow melt is another factor to be considered. Erosion of top cover by winds and rainfall intensity are two other concerns. Weathering of a 50-year old shale pile was studied, and it was found that there had been “no detectable migration of elements from the waste pile into underlying slope wash” [211].
3. **Vegetation and wildlife** — The natural vegetation in the area, and its capability of growing upon spent shale are also of some importance. Vegetation may uptake leached contaminants and the wildlife in the area may consume the vegetation. Most frequently, though, the problem of revegetation is given more importance than is that of uptake by plants.
4. **Groundwater and aquifer movement** — The groundwater table is an obvious concern. If it seasonally or otherwise intrudes into, say, an *in situ* rubble area, then contaminants will enter the aquifer. The rate of aquifer movement is also important from the point of view of dispersion of the pollutants — a slow-moving aquifer will retain the contamination for a long time, whereas a fast-moving aquifer will spread the contamination rapidly. The concentration of the contaminant in a slow-moving aquifer is likely to be higher than that found in a fast-moving one.
5. **Mobility of the constituents** — “The mobility of elements can be affected by several factors, including decomposition or reactions of the original mineral hosts, the ability of newly formed spent shale minerals to accommodate major, minor, and trace elements in their crystalline structures, and the oxidizing or reducing nature of the atmosphere” [169]. A similar argument can be made for organic contaminants. Most frequently, leachate tests are performed in the

laboratory under controlled conditions, and the data derived from these must be interpreted with care. “For practicality, it is necessary to condense several years of leaching under field conditions into a short period of time in the laboratory by using a high liquid-to-solid ratio. However, this temporal contraction precludes reproduction of the kinetics of pollutant release in a landfill, and necessitates neglect of those factors which are time-dependent in the field, such as microbial activity, temperature variations and possible interactions among wastes” [43]. Solubility of the contaminants is another consideration.

Health Problems Associated with the Oil Shale Industry

Most data on the effects of oil shale and its products on human health exist from observations made on workers and users connected with the oil shale industries of Scotland and Estonia (U.S.S.R.). The Scottish industry reported skin diseases as the most common health effects. Among these were “several dermatoses and epithelioma (paraffin worker’s cancer)” principally due to a lack of good hygiene and good practices. Lubricating oils used in the textile industry to lubricate spindles (called mules) resulted in hundreds of deaths caused by cancer of the scrotum or vulva (called mule spinner’s cancer). However, a significant proportion of these cases were related to a lack of proper hygiene. [30] The Scottish pneumoconioses were sometimes called “shalosis”.

In the Estonian oil shale districts, the incidence of stomach and lung cancer is higher in the general population of these district as compared to the general population of other Estonian districts. Other health problems noted were an increase of skin cancer among female workers, chronic bronchitis, pneumoconiosis, emphysema, and diseases affecting the mucous membranes of the nasopharynx — rhinitis for example. [30]

The only human health study done in the U.S. was an observational study performed between 1952 and 1954 upon workers at the Anvil Points Demonstration Plant near Rifle, Colorado. The study

reported the presence of skin lesions on a number of workers, although the sample was considered too small (a total of 266 men) to allow a firm conclusion to be reached [42].

A level of upto $1 \mu\text{g}\cdot\text{kg}^{-1}$ of benzo(a)pyrene was found in the muscular tissues of various fish found in bodies of water in Estonia [215]. The results of some acute toxicity studies reported by the American Petroleum Institute and Gulf Oil Corporation are given in Table 42.

Environmental Concerns Related to the Oil Shale Industry

An environmental impact statement issued by the U.S. Department of the Interior in 1975 on the proposed 47,000 bbl·d⁻¹ operations of the Colony Development Corporation in Colorado summarized the following environmental impacts [25]:

1. Decrease in ambient air quality.
2. Decrease in water quality.
3. Annual consumption of 9,000 acre-feet of water.
4. Topographic alterations on 1,217 acres.
5. Disturbance of 2,196 acres of soil.
6. Disturbance of 2,196 acres of vegetation.
7. Removal of 1,889 acres of soil and vegetation from production.
8. Mining of 440 million tons of oil shale over a 20-year period.
9. Damage and destruction to wildlife habitat.
10. Reduction of æsthetic quality.
11. Increased population of 4,100 in Mesa and Garfield counties.
12. Possible disturbance and destruction of unknown archaeological and paleontological values.
13. Changes in employment levels.

Table 42. Acute toxicity studies of oil shale products and wastes on animals

Test	Sample	Number	Results
Oral LD ₅₀ (Rat)	Crude Shale Oils	4	8-10 g·kg ⁻¹
Dermal LD ₅₀ (Rabbit)	Crude Shale Oils	4	5-20 ml·kg ⁻¹ *
Eye Irritation (Rabbit)	Crude Shale Oils	4	Minimal/reversible
	Oil Shales (Ore)	3	Negative
	Retorted Shales	4	Irritating/Reversible
Dermal Irritation (Rabbit)	Crude Shale Oils	4	0.5 g/72 hr. Abraded/unabraded
Sensitization (Guinea Pig)	Crude Shale Oils	4	
	Oil Shales (Ore)	3	Negative
	Retorted Shales	4	

* Not firmly established

Source: [219]

14. Impacts on infrastructure facilities.

An ERDA Environmental Development Plan of 1977 lists the following physical disturbances and pollution [213]:

1. Aquifer local interruptions, land disconfiguration due to strip-mining, roof collapse, and re-torted (spent) shale waste piles due to surface and MIS retorting, along with subsidence or uplift due to *in situ* retorting.
2. Runoff and leachate (mainly salts) from raw shale piles.
3. Dust from mining, fracturing, crushing and grinding operations.
4. Runoff and leachate (metals, organics and salts) from the spent shale piles.
5. Contaminated retort water (metals, organics and salts) in settling ponds.
6. Fugitive emissions and off-gases vented to the air from retorting.

The two most obvious solid and liquid wastes are the spent shale and the retort water. However, some of the other wastes generated by oil shale operations are [195]:

1. Mine waters,
2. Raw shale dust,
3. Coke,
4. Spent catalysts,
5. Diatomaceous earth,
6. Deactivated carbon,
7. Lime and alum flocculants, and,
8. Other miscellaneous proprietary solids.

Note that some of the wastes listed above arise out of possible treatment schemes for feed and retort waters, as well as from retort heating operations. They do not include those pollutants that may arise from oil purification and distillation operations.

The compounds present in spent shale and retort waters have been discussed earlier. It is obvious that the matrix of compounds — both inorganic and organic — is quite large and complex. Moreover, whereas quite a good degree of the elemental composition of the inorganic constituents is known, a lot of the specific organic compounds are unknown. Perhaps it is not necessary to analyze an oil shale waste exactly as far as particular organic compounds are concerned (from the point of view of treatment), and information upon the families of compounds present can prove to be quite useful.

Amount of Waste to be Treated

The amounts of wastes generated by oil shale processing are very large, and vary according to the richness of the shale and the retorting method used. Thus, a moderately rich shale would produce spent shale on the order of about 70 lb·gal⁻¹ of oil produced [82]. Wastewater production rates for *in situ* processes can vary tremendously — from 0.40 to 22 gallons of water per gallon of oil produced [72]. *Ex situ* processes normally use less water. It was estimated that “for a 500,000 barrel per day plant, which represents about 6% of the 1977 US crude oil production, about 2 to 460 million gallons of water and about one million tons of spent shale may be generated per day” [82]. It should be emphasized that these figures represent *daily* generation rates. The results of more recent estimates for 50,000 bbl·d⁻¹ plants, providing a more detailed breakdown, are given in Table 43. These amounts of wastewaters are significant particularly when it is realized that such waters contain a wide variety of inorganic and organic agents, some in low enough quantities to be environmentally significant but not economically feasible to treat. As mentioned earlier in this document, there is disagreement between industry researchers and other researchers about the economic feasibility of treating retort waters, with the industry position being one that it is possible to do so and other researchers strongly disagreeing [162].

Table 43. Summary of estimates for major water requirements at 50,000 bbl-d⁻¹ oil shale plants

All values in million gallons per day (MGD)		
	Surface	MIS
Water needs:		
Spent shale, moistening	0.864 - 1.944	0.533
Spent shale, revegetation	0.374 - 0.965	0.360
Dust control, at mine	0.547	0.202
Dust control, other	0.173 - 0.403	0.166
Cooling water make-up*	2.304	3.168
Boiler feed water*	0.216 - 2.304	7.200†
Total	4.478 - 8.467	11.628
Wastewater produced:		
Gas condensate	0.576	3.168
Retort water‡	—	1.296
Blowdowns*	1.440 - 2.592	5.544
Total	2.016 - 3.168	10.008
* Excluding upgrading requirements.		
† 3.168 MGD consumed in retort.		
‡ Terminology varies; what is normally called retort water is actually process water and includes all three types of wastewaters listed here.		

Source: Modified from [109].

Potential Uses for Oil Shale Wastes

During the course of a study at Lawrence Berkeley Laboratory reported in 1979, “a normally non-adsorbing dye, pontacyl pink, was passed through a packed bed of spent shale to study the flow of water through the column; the experiment failed because the dye was removed by the column” [82]. Another study determined that spent shale may be used in treatment of retort waters “to reduce the organic and inorganic carbon, conductivity, color and odor and to elevate the pH” [83]. Based on these studies and some additional work it was thought that spent shale could be used either on a large scale (i.e., abandoned *in situ* retorts) or in packed columns to treat retort waters [84, 86]. Such research is proceeding in Australia also [17]. Table 44 contains the results of studies for DOC removal from retort water on various spent shales. Other studies have dealt with the removal of SO₂ and H₂S by packed beds of spent shale [36, 105, 110, 166].

It is thought that the residual carbon on spent shale is responsible for the adsorptive properties. But, “in general, the shales are poor organic adsorbents on an equivalent weight basis compared to activated carbon. However, when removals are normalized to carbon content of the shale, shale adsorptive capacity is within a factor of two of activated carbon, substantiating the proposal that residual carbon is largely responsible for retorted shale’s adsorptive capacity.” [78] Figure 22 demonstrates this.

In Scotland, as mentioned earlier, spent shale was used for making bricks and paving roads [39]. But, besides being used for such purposes, there have been few, if any, proposed commercial uses for the solid spent materials. The use of spent shale for the removal of contaminants from retort water seems like a logical thought — most of the contaminants were present in the shale in their original form to begin with (others were generated by the breakdown of compounds during retorting), and so the shale may retain some natural affinity for them.

Table 44. Specific adsorption and percent reduction in dissolved organic carbon in retort water in contact with spent shale

		120 hr of contact with spent shale in batch experiments using 50 g shale per 50 ml water									
Retort Water	DOC in Untreated Water (mg-ℓ ⁻¹)	Ex situ spent shales					In situ spent shales				
		Units	Paraho	Lurgi	TOSCO II		L-1	S-14	S-55	Activated Carbon*	
Omega-9	915±50	a	0.44±0.10	0.09±0.12	0.42±0.00		0.18±0.07	0.10±0.11	0.11±0.9		
		b	49%	NS	45%		18%	NS	12%		
150-ton	3300±140	a	0.82±0.13	0.12±0.16	1.6±0.2		0.12±0.17	0.09±0.11	0.23±0.11	50.0±0.2	
		b	24%	NS	48%		NS	NS	7%	75%	
L-2 High Temperature	1675±80	a	0.89±0.12	0.30±0.12	1.1±0.1		0.22±0.9	0.00±0.10	0.29±0.12		
		b	51%	17%	66%		13%	NS	18%		
L-2 Low Temperature	1300±75	a	0.57±0.12	0.27±0.12	0.95±0.10		0.16±0.09	0.10±0.19	0.07±0.09		
		b	45%	21%	27%		73%	NS	NS		

* 5 g activated carbon in 50 ml retort water

a Specific adsorption in mg DOC/g shale

b Percent reduction in DOC

NS Not significant

Source: [82]

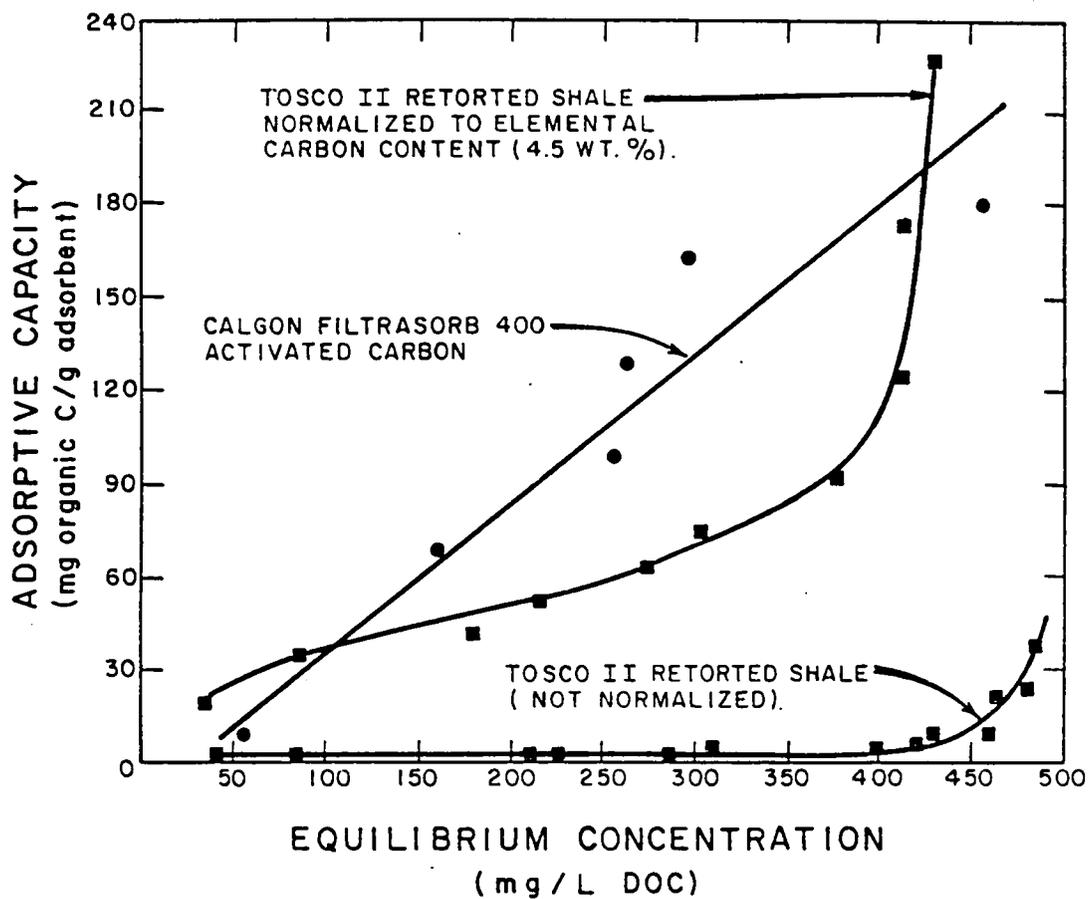


Figure 22. Adsorption of LETC 150-ton retort water on Calgon Filtrasorb 400 activated carbon and TOSCO II retorted shale: Adapted by [79] from [127].

Retort waters, on the other hand, has had no uses in the past, except for proposed use as a moistening agent for the compaction of spent shale [207]. This would in effect be co-disposal of the spent shale and the retort waters and has been proposed [114, 201]. It has also gained the interest of the U.S. Environmental Protection Agency [15]. Much research work needs to be done in order to gain the acceptance of co-disposal under RCRA guidelines; currently it is not allowed.

Treatment of Oil Shale Wastes

In some ways, the proposed treatments for oil shale wastes are linked to the use of these wastes. The use of spent shale for scrubbing of gases and for treatment of retort waters and the use of retort waters for moistening of spent shale were mentioned in the previous sub-section, as was the codisposal alternative.

The land disposal and underground injection of retort waters has been studied and found to have some problems — principally the leaching of toxic inorganic substances and salts from the land and the difficulty and expense involved in monitoring groundwater contamination [148]. Biotreatment of retort waters has generally been found to be unacceptable without fair-to-extensive physicochemical modification prior to biotreatment [54, 107, 117, 147]. Steam stripping has been proposed for stripping retort waters that contain high levels of ammonia and carbon dioxide [54, 103, 110, 149].

Various other methods to treat retort waters have been tried with different degrees of success. Among these are electrolytic treatment [224], ion exchange [102], and chemical oxidation, UV irradiation and ozonation [51].

Reclamation and Revegetation of Spent Oil Shale

Quite a few studies on reclamation and revegetation of spent shale have been reported. At the Petrobrás plant in Brazil spent shale has been land disposed with a 2.5 m cover of soil on top. A good deal of success was achieved when Canadian Pine, *Mimosa Scrabela (Bracatinga)* and Eucalyptus trees were grown at the site [116]. Stands of fescue grass have been grown on retorted Kentucky shale [13, 181].

Covering of shale with soil is recommended because there are several problems associated with growing plants directly on the shale. One of these is the high salt content of spent shale. “Even if a stand of vegetation could be established initially, the long-term maintenance of such a stand is questionable” [176]. Compaction does not make the shales impermeable to water percolation. Shales (specially fines) can cement. Spent shales also contain molybdenum and boron and these can be taken up by plants and animals, causing serious hazards. [176] The leaching of salinity from shale, however, may cause biostimulation of algae in lakes near shale sites [33].

In a study on the uptake of B, Mo, As, Se and F from two spent shales by western wheatgrass and fourwing saltbush, it was found that the amounts of B and Mo (in combination with Cu) taken up would make the plants unacceptable as forage for ruminants. However, the uptake of As, Se and F were found to be below limits considered safe for plant and animal toxicity. [122]

The TOSCO Corporation has studied over 100 species of plants and found that at least 25 show good potential for revegetation at study plots in Colorado on TOSCO II spent shale [150]. Researchers at Colorado State University have presented a nice summary paper on various revegetation research studies [175].

Chapter III

Literature Review — Sorption

History

The history of the study and use of sorption phenomena parallels the history of the use of carbon materials like bone chars, blood chars, wood charcoal, decolorizing carbon and activated carbon. The reason for this is that the various sorptive forms of carbon were the most prominently used materials in different applications. Also, the formal study of sorption did not begin until the latter part of the 18th century, and consequently the discovery of the sorptive properties of other materials had to, for the most part, wait upon this.

An Egyptian papyrus dated to 1550 B.C. mentions the use of charcoal in medicine. Wood chars were used in Hippocrates' time for the treatment of certain ailments.[106] So, sorption phenomena have been used for a long while, although they were not recognized as such.

The first formal experiments of absorption of gases on charcoal were conducted by Scheele and Fontana in 1777 [98]. The decolorizing of solutions by charcoal was mentioned by Lowitz in 1785 [106, 124], followed by the removal of odors from gangrenous ulcers by char mentioned by Kehl in 1793 [106]. A few years after Lowitz' discovery, cane sugar purification by wood char was first tried and in 1808 this same material was tried out for the purification of beet sugar [106]. Then, in 1811, Figuers discovered that bone char had a greater decolorizing power and the sugar manufacturers rapidly started using bone char instead, first as pulverized bone char that was used once and discarded, and then (because supplies were limited) as regenerated granular bone char [56]. Granular bone char is still used for refining cane sugar [106].

A carbon with 20 to 50 times the decolorizing power of bone char was developed by Bussy in 1822 by the heating of blood and potash, and for many years this became the predominant char used in laboratory studies. In 1865, Hunter produced coconut char and Stenhouse heated a mixture of flour, tar and magnesium carbonate to produce a decolorizing char. Paper mill wastes were heated with phosphates by Winsor and Swindells to produce yet another char. The first carbon to purify water was made by Lipscombe in 1862, and Stenhouse described the use of carbon in gas masks in 1854. Most of these experimenters obtained British patents for their products. [106]

De Saussure in 1814 first proposed that the surface area of a solid determined its efficiency of absorption. In 1843, Mitscherlich proposed that the pores play an important role. He estimated that the pores in charcoal had an average diameter of $1/2400$ in., and that carbon dioxide condensed in the pores into layers 0.005 mm thick and that these layers resembled the liquid form of carbon dioxide. Kayser coined the term "adsorption" in 1881, and McBain suggested the term "sorption" to include both absorption and adsorption, as well as capillary condensation. [98]

The commercial production of activated carbon was difficult because of the corrosive nature of the various activating methods, and the first methods of commercial production were patented by Ostrejko in 1900 and 1901. Expectations for a blossoming market in activated carbon were belied. At least until the advent of World War I and 1915, when on April 22 at Ypres the Germans released

chlorine from cylinders in the first known incidence of chemical warfare. Although the agonized Allied soldiers fled, the Germans could not push home their advantage because they had no protection against the chlorine, either. In the months that followed, feverish research and development went on in an effort to perfect a gas mask. Since powdered activated carbon (PAC) was not suitable for gas masks good GACs were developed. [106]

Since the end of the First World War, the uses for activated carbon have resulted in a veritable explosion of activity. Applications quickly spread from the purifications of gases and liquids to the sorption of penicillin onto activated carbon and subsequent elution to yield a concentrated penicillin solution, developed during World War II. Today, activated carbon is used in various applications, from home water purification units, to the purification of gases in space vehicles, and in white-sidewall tires. The activated carbon is incorporated in the dark rubber to prevent its color molecules from migrating to the white rubber and discolorizing it. [106]

The study of activated carbon has necessitated the study of surface phenomena, one of which is sorption. Consequently, the study of sorption has blossomed from the study of surface phenomena as applied to activated carbon to many, many other substances.

J. Willard Gibbs established the thermodynamics of adsorption at the gas|liquid interface in 1878, and Traube established a relationship between surface activity and chain length in 1891 [159]. Freundlich developed an equation for the sorption of gases onto solid surfaces in 1909 and Irving Langmuir developed one in 1918 for the adsorption of gases on glass, mica and platinum [126]. Bohart and Adams described the adsorptive behavior of chlorine on beds of charcoal in 1920 [20]. Glueckauf, in a series of 10 papers written between 1946 and 1955 on the theory of chromatography, made important contributions to the mathematics of sorption and desorption [34, 93-97]. Douglas Everett made important contributions to the theory of the thermodynamics of adsorption between the years of 1950 and 1964 [66-69].

Adsorption remains one of the most intensely researched areas in the field of chemistry.

Some Terms Related to Sorption

Some of the terms related to sorption, as used in this document, are defined in Appendix A. Specifically, these terms are: absorption, adsorption, sorption, adsorbent, adsorbate, physisorption and chemisorption.

Quite frequently, the distinction between absorption and adsorption is blurred, and it is safer to use the term sorption as a general term, even if only adsorption is involved. One case where it becomes difficult to differentiate between absorption and adsorption is at a liquid|liquid interface. Molecules of one may be attached to the other at the surface. But, there may also be a region or band where the molecules of both liquids are intimately mixed. In such a case, it becomes difficult to determine whether to classify the interaction as a surface phenomenon (hence adsorption) or a bulk phenomenon (hence absorption), and the thickness of such a layer becomes important in determining the proper term. It is felt that the work described in this document has no situation such as the one described above and since it did not involve a gas|solid interface, it is further felt that absorption will not be a factor. Therefore, the terms sorption and adsorption will be used interchangeably to refer to adsorption.

Interfaces

There are four possible systems in which adsorption can be present: vapor|liquid, vapor|solid, liquid|liquid and liquid|solid.

Due to the almost omnipresence of adsorption in nature, and the great practical applicability, a vast amount of literature is available. This discussion, however, will be restricted mainly to the

liquid|solid interface and the adsorption of small molecules from solution, although references to other systems will be made.

Types of Sorption

Sorption is normally categorized into two types:

1. Physisorption, due to van der Waals forces, and
2. Chemisorption, due to chemical interactions,

of which physisorption is by far the most prevalent type.

“In physical adsorption, it is conventional to assume that the surface of the adsorbent is unperturbed, that its only function is to supply a potential field for the adsorbate, and that the adsorbate may be regarded as a separate thermodynamic phase. In chemisorption, these are not fruitful assumptions. The surface and the adsorbate should be viewed together as a new chemical entity.” [32]

Table 45 lists the differences between physisorption and chemisorption. For example, chemically adsorbed species may be sorbed in the dissociated (ionized) form rather than in the native state, whereas in physisorption the compound is usually undissociated since sorption is due to van der Waals forces. In addition to the factors listed in Table 45, physisorption can be due to, or affected by various factors, some of which are: the lyophobic or lyophilic nature of the solute (sorbate), the attraction of the sorbate to the sorbent, the rate limiting step, the surface area of the sorbent, etc. These same factors can also affect chemisorption. Moreover, there is not always a single type of sorption present in any given system. For instance, physisorption may occur on a chemisorbed layer [123].

Table 45. Differences between physisorption and chemisorption

Physisorption	Chemisorption
Low heat of adsorption (< 2 or 3 times latent heat of evaporation)	High heat of adsorption (> 2 or 3 times latent heat of evaporation)
Non-specific	Highly specific
Monolayer or multilayer	Monolayer only
No dissociation of adsorbed species	May involve dissociation
Only significant at relatively low temperatures	Possible over a wide range of temperatures
Rapid, non-activated, reversible	Activated, may be slow and irreversible
No electron transfer, although polarization of sorbate may occur	Electron transfer leading to bond formation between sorbate and surface

Source: [191]

Since all of the factors that affect sorption may have complex relationships, it is of use to consider these in sorption studies.

Factors That Influence Sorption

It is difficult to rank the factors that influence sorption by order of importance since the factors that are important will vary from one system to the next. However, this section discusses the factors in an order of decreasing importance felt to be representative of most systems.

The Rate-Limiting Step

A conceptual depiction of a carbon bead is shown in Figure 23. As the sorbate follows the diffusion path shown, it must diffuse [158]:

1. Across a stationary solvent film surrounding each adsorbent granule,
2. Through the macropores,
3. Through the micropores, and,
4. Adsorb at an appropriate site.

If a sorbent bead does not have a microgranular structure as shown in the figure (for example, oil shale), then steps 2 and 3 above become a single step, since then each bead can be thought of as one of the adsorption sites labeled on the figure and will have its own film around it. The slowest step of those given above will be the rate-limiting step for the entire process.

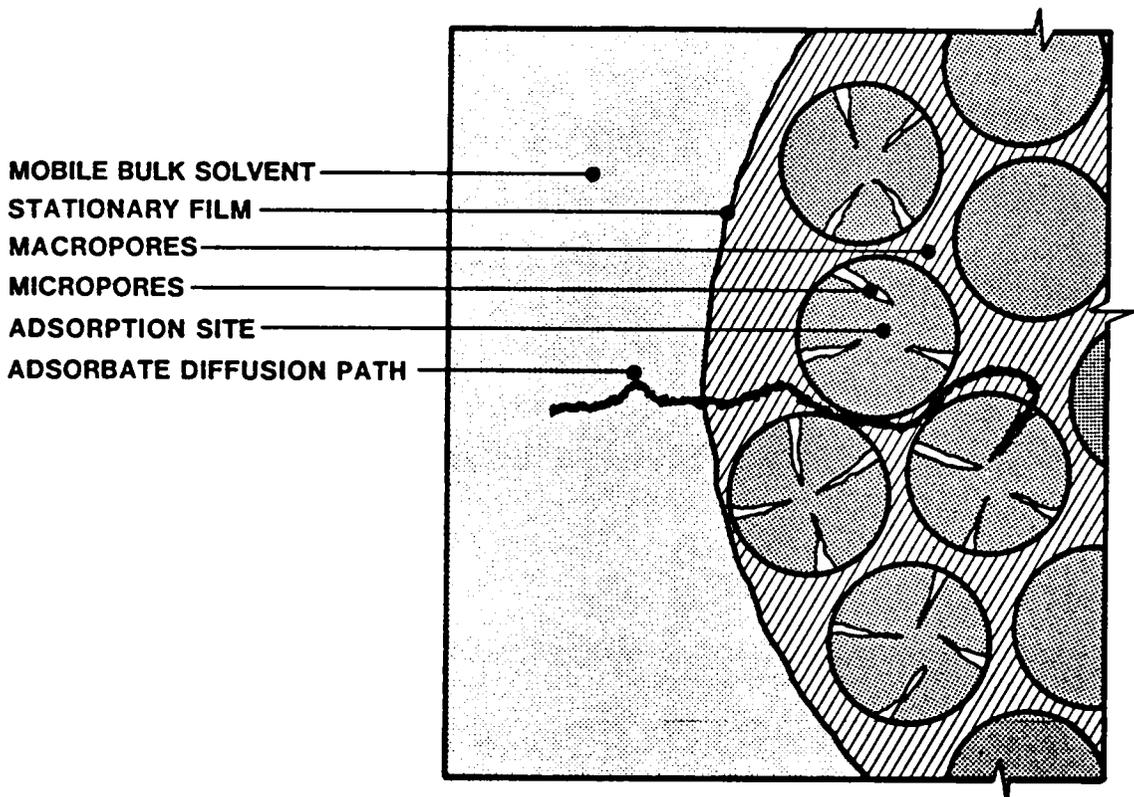


Figure 23. The dynamic adsorption process: Showing a partial cross-section of a polymer carbon adsorbent bead (not drawn to scale) including a portion of the surrounding solvent. From [158].

The Rate of Diffusion Through the External Film Surface

This depends on the film resistance [221] and may also depend on the diffusion or convection rate within the bulk phase [171], and is usually represented by the film diffusion coefficient. Mandelbaum and Bohm [138] discuss mass transfer occurring in packed beds at low Reynolds numbers. In this situation, both free and forced convection are of importance. Wilke and Chang [227] proposed a popularly utilized correlation of diffusion coefficients in dilute solutions. Recently, other investigators have correlated the surface diffusivity with the self diffusivity [231] and have outlined a method of predicting diffusivities in multicomponent liquid systems [12]. The film diffusion resistance (and the bulk diffusivity also in some cases) has been extensively studied, analyzed and subjected to theoretical developments. In fact, even a cursory perusal of the literature will leave one with the impression that either film diffusion or pore diffusion is thought to be the rate-limiting step. In some cases, the effect of both diffusion resistances is considered. Some studies that incorporated film diffusion (and, in a few instances, bulk diffusion) are those by Liapis and Rippin [131] for binary sorption in activated carbon columns, Liles and Geankoplis [132] for axial diffusion of liquids in packed beds, Harriott [104] for mass transfer to particles suspended in agitated tanks and a pipeline, Akrotanakul *et al.* [3, 4] for sorption processes in soil influenced by pore water velocity, Famularo *et al.* [70] for the prediction of the performance of carbon columns based on pure-solute data, Keinath and Weber [120] for the design of fluid-bed adsorbers, and Balzli *et al.* [11] for multicomponent sorption in activated carbon columns. There are also model developments of a theoretical nature that utilize film diffusion [3, 47, 130, 140, 154, 173, 200].

The Rate of Diffusion Through the Pores

This depends on the resistance to intraparticle diffusion, i.e. pore diffusion [171, 221]. There are almost as many proponents for a pore diffusion control mechanism as there are for a film diffusion control mechanism. Some studies that have considered pore diffusion on a purely theoretical basis

are those by Liapis and Rippin [130], Raghavan and Ruthven [173], Crittenden *et al.* [47], Masamune and Smith [140], Glueckauf [97], Grzywna and Petropoulos [99, 100], Edeskuty and Amundson [63], Sorensen and Stewart [205], Rosen [184], Cooper and Liberman [41], and Weber and Chakravorti [220]. Other studies have considered pore diffusion in carbon column performance prediction from pure-solute data [70], in the model-based design of fluid-bed adsorbers [120], in multicomponent sorption in activated carbon columns [11], in finite- and infinite-bath systems [59, 60], and for the prediction of breakthrough curves of the Freundlich type for multicomponent sorption on fixed-beds [196-198].

Some of the work that has been mentioned for film and pore diffusion utilized both types in the analysis of results [11, 70, 120] or model development [47, 130, 140, 173]. Weber [221] makes the observation that pore diffusion being the rate-limiting step is possible perhaps only in highly agitated batch systems in liquid-solid reactors, and perhaps not even then.

Balzli *et al.* [11, 130, 131] developed the General Pore Diffusion Model (GPDM) for the prediction of column performance under multicomponent sorption conditions. The equation describing equilibrium conditions for solute i among n solutes is a hybrid of the multicomponent Langmuir and Freundlich isotherms:

$$C_{si}^* = \frac{a_{i0} C_{pi}^{b_{i0}}}{\left[c_i + \sum_{j=1}^n a_{ij} C_{pj}^{b_{ij}} \right]} \quad (1)$$

$$= f_i(C_{p1}, C_{p2}, \dots, C_{pn})$$

where C_{si}^* is the equilibrium value of the concentration of solute i in the solid phase ($\text{kg}\cdot\text{m}^{-3}$), C_{pi} is the concentration of solute i in pore fluid phase ($\text{kg}\cdot\text{m}^{-3}$), a_{i0} , a_{ij} , b_{i0} , b_{ij} and c_i are constants, and f_i is the equilibrium function. "The Langmuir and Freundlich and other well known isotherms can be deduced as special cases" of equation (1) [11]. Some of these cases are derived in [87].

The GPDM model can be simplified for the case of sorption from dilute solutions flowing through a fixed bed of uniformly-sized, homogeneous, spherical particles. If axial diffusion is considered, and under the assumptions that pore diffusion controls and that a “local equilibrium exists between solid and fluid phases at each point in the pore” [11], sorption in the particle for solute i is given by:

$$\varepsilon_p \frac{\partial C_{pi}}{\partial t} + \sum_{j=1}^n \left(\frac{\partial f_j}{\partial C_{pj}} \right) \left(\frac{\partial C_{pi}}{\partial t} \right) = \varepsilon_p \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{pii} \frac{\partial C_{pi}}{\partial r} \right) \quad (2)$$

where ε_p is the void fraction in particle, t if the time from start of sorption, r is the radial distance in particle (m), and D_{pii} is the effective self-diffusivity of solute i in pore fluid ($\text{m}^2 \cdot \text{s}^{-1}$). The initial and boundary conditions for equation (2) are

$$C_{pi}(r, x, t) = C_{pi}(r, x) \quad \text{at } t \leq 0 \text{ for } 0 \leq r \leq r_0, 0 \leq x \leq L \quad (3)$$

$$\varepsilon_p D_{pii} \frac{\partial C_{pi}}{\partial r} \Big|_{r=r_0} = K_{fi} [C_{di}(t, x) - C_{pi}(r_0, x, t)] \quad \text{for } 0 \leq x \leq L, t > 0 \quad (4)$$

$$\frac{\partial C_{pi}}{\partial r} \Big|_{r=0} = 0 \quad \text{for } 0 \leq x \leq L, t > 0 \quad (5)$$

where r_0 is the radius of particle (m), L is the length of column (m), K_{fi} is the film mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$), C_{di} is the concentration of solute i in fluid phase ($\text{kg} \cdot \text{m}^{-3}$), and x is the axial distance in the column. For “a batch experiment in which adsorbent particles are in contact with a fixed quantity of liquid of which the composition at any time is uniform”, equation (2) is unchanged and “the variable x no longer appears” in equations (3) to (5) [11].

Adsorption of Solute on the Surface

This normally refers to the net adsorption of the solute on the internal pore surface once the molecule has reached the active site and is thought to be a rapid, and hence, not a rate-limiting step [123, 158, 221].

Other Rate-Limiting Factors

In addition to the three possible rate-limiting steps mentioned above, the rate of sorption may also be limited by (a) the rate of transfer of heat liberated by the sorption process, and (b) the surface migration rate [171]. The influence of any particular rate-limiting step may also change with changes in other factors (e.g. size of particles, temperature, concentration of solute), and there may be a shifting of responsibility for being the rate-limiting step from, say, pore diffusion to film diffusion. Besides the kinetics, one is also interested in the extent of sorption possible (i.e. at equilibrium), and the other factors that influence both kinetics and equilibrium will now be considered.

The Sorbate

Solubility

The first characteristic of the sorbate that one needs to consider is its solubility. The two major rules connected with this aspect are Lundelius' rule and Traube's rule. Lundelius' rule states that a "a polar (nonpolar) adsorbent will preferentially adsorb the more polar (nonpolar) component of a nonpolar (polar) solution" [1], since, because of polarity, the more polar (nonpolar) component will have a lower solubility in a nonpolar (polar) solvent than the less polar (nonpolar) component. Traube's rule, which is an extension of Lundelius' rule, states that "adsorption from aqueous sol-

ution increases as an homologous series is ascended” [221]. A homologous series is “a series of compounds in which each member differs from the next member by a constant amount” [153], and the ascension of a series refers to the addition of this constant amount to form more complex molecules. It is emphasized that these rules are generally applicable to dilute solutions, but that they may be applicable to concentrated solutions in some cases [123]. The behavior that these rules postulate has been demonstrated [217, 222] and documented [123].

Size of Sorbate Molecules

In general, the rate of sorption decreases with increasing molecular size of the sorbate [221, 222]. This applies to molecules in the same class or series, and, indeed, small molecules of one class may be sorbed less rapidly than large ones of another class [221]. The assumptions implicit in these statements are that the same specific area is available to all the molecules in the series, and that pore diffusion is the rate-limiting process. Although the rate of sorption may decrease with increasing molecular size, the extent of sorption may remain constant. The formation of micelles by some solutes in solution introduces another factor to be considered [164] — whether the micelles are sorbed, or whether the micelles are so weak that they break up near the sorbent surface, thus allowing the single molecule to be sorbed.

The solubility of sorbate molecules generally decreases with increasing size and this may contribute to an increase in sorptive capacity [5]. Also, “the larger the molecule, the higher its affinity to the ... surface” [5].

Degree of Ionization

The degree of ionization of the sorbate can also play a major role in both the rate and extent of sorption. Weber [221] states that for structurally simple species, “adsorption is at a minimum for

the charged species and at a maximum for the neutral species". Ionization effects become less important as the sorbate becomes more complex. Amphoteric compounds, by the above rule, sorb best at the isoelectric point, i.e. at the pH where both the basic and acidic ends are ionized resulting in a net zero charge on the compound [221]. The measurement of Zeta potential or the pH of zero charge are two of the methods by which the effects of ionization can be quantified [1].

Orientation of the Molecule on the Surface

This arises out of the interaction between the sorbate and the sorbent surface. Kipling has the following succinct and admirably clear passage:

Thus long-chain alcohols and fatty acids may be adsorbed by polar solids with the chain perpendicular to the surface. The limiting number of moles adsorbed per gram of solid is then independent of chain-length, but the limiting volume of the adsorbate increases with chain-length. On the less polar solids, these solutes may be adsorbed with the chain parallel to the surface. When a complete monolayer is formed, the area covered is the same for all members of the series (but the number of moles adsorbed per gram varies), and the limiting volume of adsorbate remains approximately constant. [123]

Geometry of the Molecule

The importance of steric effects (coupled with the size of the molecule) has been emphasized [1, 123, 171]. Optical and *cis-trans* isomers, although being very close in the extent of sorption, may have a sufficient difference to enable separation in chromatography [123]. Moreover, the geometry of the molecule can be of paramount importance in the utilization of molecular sieves for separation [1, 171]. A more branched molecule will be hindered from diffusing into micropores. On the other hand, a larger molecule would normally possess a lower solubility, thus enhancing sorption.

Other Properties

The dipole moment of sorbate as it relates to sorption has been studied [164]. Some studies have also been done on the relationship between an index of sorption (which has been defined as a function of the equilibrium constant of the phase exchange reaction) and the Hammett σ -constant [52, 53, 182], but the meaning of the relationship is not clear [164]. The Hammett σ -constant refers to the deviations between adsorption rates of substituted and non-substituted compounds, and is thus a factor that accounts for various substituted groups [125]. This index of sorption, K_1 , for a phase exchange reaction with an equilibrium constant of K , is given by $K_1 = (x_1^l)_s(K - 1)$, where $(x_1^l)_s$ is the saturation mole fraction of the solute in the liquid phase [52].

The Sorbent

Surface Area

This is the most important property from the point of view of adsorption equilibrium, since the surface area of the sorbent determines how much sorbate can be sorbed. A distinction must be made between the actual surface area and the area available for sorption [221]. At one extreme the area available for sorption may consist of the entire external and internal (pore) surface area, while at the other extreme it may be restricted only to a few sites that are specific to a particular sorbate. One of the most popular techniques for the determination of the maximum available surface area is what is termed as the BET method, usually with nitrogen as the adsorbate [171]. However, this may not give a true representation of the actual surface area available for sorption, and, where considerations such as molecular size are important, it is suggested that molecules of varying sizes be used as “measuring” molecules [123]. These measurements make use of the BET theory, but sorption is usually performed from solution to more accurately reflect the actual conditions at the

liquid|solid interface and to allow for the use of larger molecules which may not be available in gaseous form.

In general, on a mass basis, for a non-porous sorbent or a porous sorbent when film diffusion controls, the rate and extent of sorption are inversely proportional to the particle diameter [221]. For a highly porous sorbent, the extent of sorption is independent of particle diameter [221], and, when pore diffusion controls, the rate is a function of the particle diameter raised to a power greater than unity [46]. The particle diameter is of importance since it not only decides the ultimate surface area (smaller size particles obtained from larger ones may lead to an opening up of small, sealed pores, thereby increasing area [221]), but also determines the speed at which the sorbate can penetrate to the insides of the pores.

Maximum Surface Area of Activated Carbon

“The specific surface area of a monolayer of carbon (with a graphite structure) including the area on both sides of the plane is $2620 \text{ m}^2\cdot\text{g}^{-1}$. Exposure of both sides of every carbon atom is an impossibility for a solid with any physical integrity. True surface areas for carbons must be significantly less than this value.” [158]

Surface of the Sorbent

The importance of surface area has been discussed earlier. Various other properties of the surface are also of importance. These include the presence of specific surface groups, the degree of heterogeneity of the surface, the lyophilic or lyophobic nature of the surface, and whether the surface is charged or not. The presence of specific surface groups may be related to the history of the sorbent in some cases. For example, titanium dioxide may be derived from either the sulfate or the

chloride process [164]. These surface groups may either hinder, promote, or have no effect on sorption.

The presence or absence of certain specific groups may lead to a charge on the surface, or a lyophilic or lyophobic behavior. In this author's experience with the sorption of organic compounds from aqueous solution on to oil shale, it was noticed that although most shales were more or less neutral with respect to water, one shale from a particular process was quite visibly hydrophobic. This nature would certainly hamper sorption from aqueous solutions. Indeed, many oil shale surfaces are considered hydrophobic [78], but the presence of various organic compounds on their surface may act as wetting agents. The surface charge is also quite commonly measured in the oil shale industry [22, 137]. The presence of charge on activated carbon is also well known [164, 221]. However, the surface groups present on carbon that contribute to this charge have not been adequately characterized [40]. These surface groups include carboxyl, hydroxyl and carbonyl groups [40].

Most surfaces available for sorption are quite heterogeneous in character [123, 164, 171, 221], and if, as in the case of oil shale, a heterogeneous sorbent is used, the character of the surface becomes important from the point of both sorption and desorption [169].

Characteristics of the Pores

These include pore size, the uniformity of the pores, and the tortuosity of the pores. Pore size may vary from micropores (usually between 10-1000Å) to macropores (usually > 1000Å) [221]. Considerations as to whether the pores can best be characterized as capillaries, channels and interstices, or molecular sieves, are important [232]. Another factor of importance is the uniformity of the pore, i.e. whether the pore is of constant, varying, decreasing, or increasing cross-sectional area as it penetrates into the sorbent particle. For example, a pore of varying cross-sectional area may prevent a large solute molecule from penetrating beyond a constriction in the pore, thus making unavailable a portion of the inner surface area. The tortuosity (the degree of twisting) of the pores

is important, particularly in the diffusion of larger molecules. (Tortuosity is also used to refer to the path that a liquid has to take in flowing through a packed bed [192] — this is a macroscopic-scale tortuosity and is not the microscopic-scale tortuosity, or internal tortuosity, meant here.)

Shape of the Particle

The shape of the particle is not of much practical concern from the point of view of sorption, but is important with respect to packing of the bed, and in mathematical modelling [47, 59, 60, 63, 70, 104, 120, 130, 131, 140, 173, 184, 221, 222]. Practically all models use a spherical shape of particle.

The Solvent

The solvent may influence sorption by “(a) interacting with the solute in solution, hence contributing to solubility and departures from ideality, (b) its interaction with the adsorbent, which will depend on the chemical structure of both, and (c) its interaction with the solute in the adsorbed layer” [164]. In most cases, the monolayer consists of molecules of sorbate and molecules of solvent [123]. This factor has been overlooked most often, specially in carbon sorption. Not only can the solvent take away from the surface area available to the sorbate, but it can also serve to hydrate and expand the sorbent [1].

Sorbate-Sorbent Interactions

Sorbate-sorbent interactions are illustrated in Figure 24. Situation A indicates the attraction and/or repulsion of the sorbate (solute) to the sorbent. Situation B indicates the lyophobic or lyophilic nature of the sorbate — if lyophilic, it will tend to stay in solution, and vice versa. Situation C in-

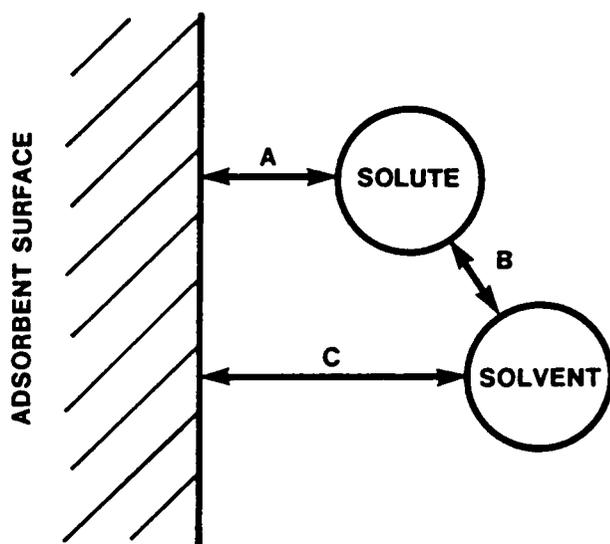


Figure 24. Solute/solvent competition for adsorbent sites: A, adsorption potential for solute; B, interaction potential between solute and solvent (solubility); C, adsorption potential for solvent. From [158].

icates whether the solvent itself has any attraction to the sorbent surface — if this interaction is quite positive, than the solvent itself will compete with the sorbate for surface sites.

The Presence of More than One Solute

As expected, the factors mentioned above are compounded when more than one solute is present. Each solute may have a synergistic or an antagonistic effect on the sorption of the other solutes, or may sometimes have no effect. Usually, the effect is an antagonistic one since the solutes have to share the same surface area [123]. A situation can be envisioned, however, where one solute may not be a good sorbent when present alone in solution, but may attach itself to another solute upon the second solute's addition to the solution and may thus be sorbed when the second solute is sorbed. This would not be true sorption since the solute is not attached to the sorbent, but in terms of the removal of the solute from the mixture, this would appear as sorption. This author has not been able to find a clear case of this kind in the literature. A solute bonding with water that is sorbed to the surface of the sorbent is a possible example of such behavior.

An independent behavior would be the result of each solute having sites of sorption that are specific to itself and none of the other solutes in that particular solution. This is not so common an occurrence, but has been reported for the case of adsorption of stearic acid by titania from petroleum ether not being affected by the presence of other, short-chain, solutes [123].

The various interactions that are possible in the multicomponent system are too complex to be detailed here, but attempts have been made by researchers to model these systems [11, 12, 48, 130, 131, 154, 155, 172, 196-198, 205]. These have met with varying degrees of success since they are either able to predict behavior with any degree of accuracy only in some systems or are purely mathematical developments.

The Effect of pH

The sorption of ions is affected by pH since the H^+ and OH^- ions are sorbed quite strongly [221]. Amphoteric compounds sorb best at their isoelectric point. The degree of ionization is also influenced by pH. Since activated carbon usually has a net negative surface charge, a decrease in pH can result in an increase in the amount of organic matter sorbed, the decrease in pH causes a neutralization of the surface charge [221].

The Effect of Temperature

Sorption reactions are generally exothermic and a decrease in the temperature results in an increase in the amount sorbed for vapors [221]. However, although this property is important in vapor-solid sorption, the heat of sorption is usually quite low when sorption is from the aqueous phase. This is due to the fact that water generally has to be desorbed, a process that is endothermic [221]. In liquid-solid multicomponent systems selectivity decreases with higher temperatures [123].

“The form in which the molecule may adsorb in the pores (i.e., as a solid vs. liquid)” may influence kinetics [89]. Modelling of multicomponent sorptive behavior may be successful if all components were sorbed at a temperature well below their melting points [199]. But, if some solutes are above their melting points while some are below it, then deviations from expected behavior predicted from single-solute equilibrium data may result in the failure of modelling efforts [89].

The Effect of Pressure

Pressure is of little or no importance in liquid-solid systems. Kipling [123], however, cites a case where the pressure was increased from 1 to 2000 atm and resulted in a slight increase in the sorption of acetic acid from an aqueous solution on to charcoal.

Types of Isotherms

Equilibrium sorption isotherms obtained from batch experiments have been classified into four basic shapes (see Figure 25). Class S is named for the S-shaped curve characteristic of the class, where the initial portion of the isotherm is convex to the abscissa. The initial portions of the isotherms are indicated by curve 1 in each class. "The L (Langmuir) class is the most common and is characterized by an initial region which is concave to the concentration axis. The L.2 isotherm reaches a plateau, further adsorption above this value gives the L.3 isotherm, and if that reaches a second plateau it is designated L.4. The fifth L type shows a maximum and reflects a special set of circumstances — they are found with solutes that associate in solution (tensides and certain dyes) and contain highly surface-active impurities (a maximum is not thermodynamically possible in a pure system). A similar set of isotherms are associated with the other classes, although not all have been observed. ... The H (high affinity) class results from extremely strong adsorption at very low concentrations giving an apparent intercept on the ordinate; the C (constant partition) class has an initial linear portion which indicates constant partition of the solute between solution and adsorbent, and occurs with microporous adsorbents." [164]

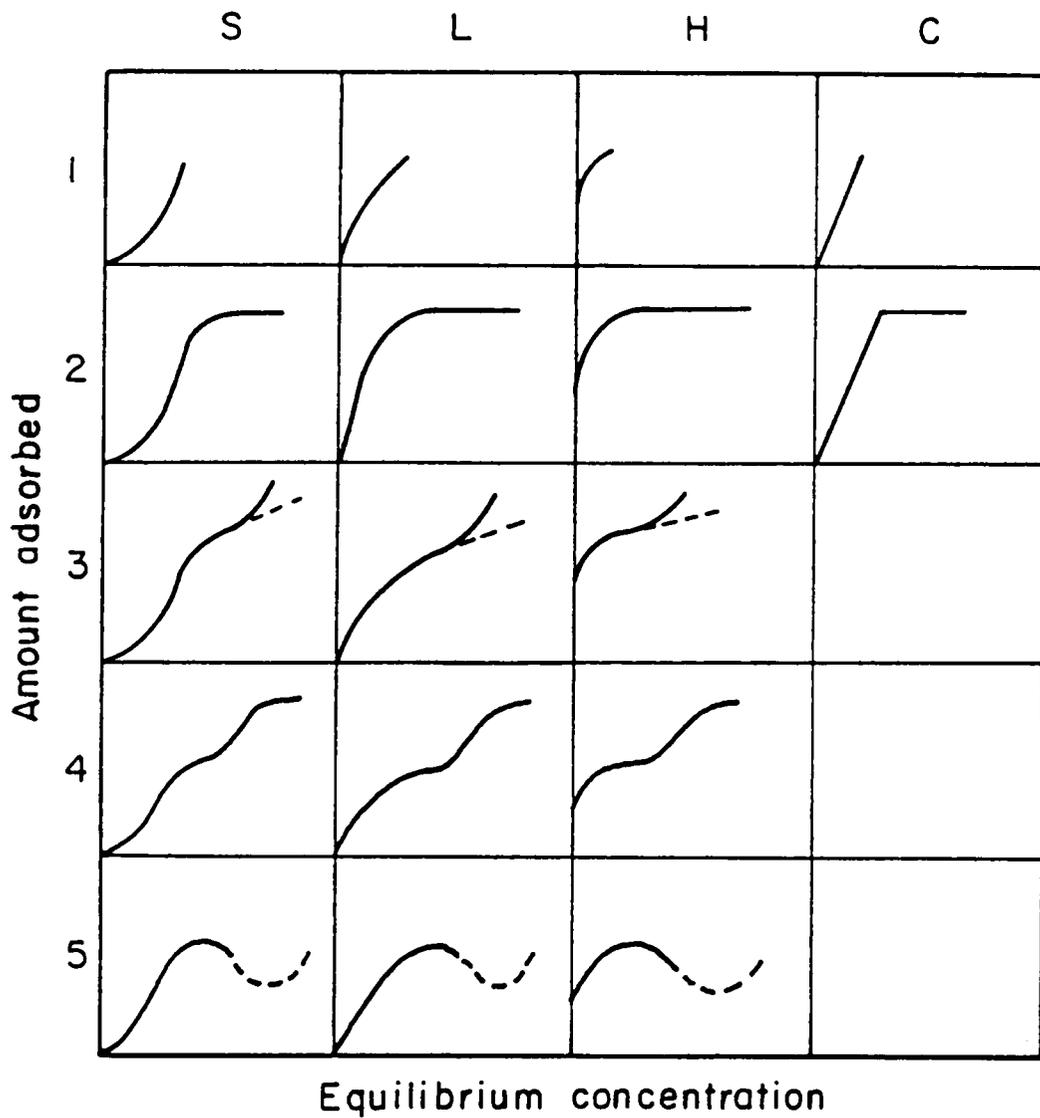


Figure 25. Classification of isotherm shapes: From [164].

These shapes are representative of single-component adsorption isotherms. In multicomponent systems the isotherm of any one component may change (from its single-component one) in various ways, each of which has different implications upon the nature of the interactions involved:

1. The slope of the isotherm in the multicomponent situation may be lesser than that of the single-component system. This is the most frequently observed case, and indicates the effects of competition.
2. The slope of the isotherm may increase in the multicomponent system. This is not a frequently observed phenomenon and would indicate a synergistic effect upon the sorption of one solute caused by the presence of the other solutes. The effect could be due to either (a) decreased solubility of the solute caused by the presence of the other solutes, or (b) the facilitation of the sorption of the solute due to what may be thought of as a “catalytic” effect brought about by the other solutes. The “catalytic” effect could be similar to the action of a wetting agent whereby sorption is facilitated, or could be a situation where the solute in question sorbs onto (or otherwise reacts with — physically or chemically) another solute and is subsequently sorbed onto the sorbent along with the other solute.
3. The slope of the isotherm may remain unchanged. This indicates that the presence of the other solutes does not effect the sorptive capacity for the solute in question, and could be due to either (a) the solute being so strongly sorbed with respect to the other solutes that their presence does not affect its behavior, or (b) the presence of sorption sites on the sorbent that have an exclusive affinity for the solute, or (c) a combination of the two effects.
4. The shape of the isotherm may change. For instance, an H class isotherm may shift to an L type one, indicating decreased affinity.

Much effort has been devoted to the mathematical modelling of isotherms.

Equilibrium Models of Adsorption

There are essentially two types of models that have been developed:

1. Kinetic models — that is, models that quantitate the dynamics of adsorption. These models utilize rates of transfer, shape of the adsorbent particle, the activity of surface groups, etc., to define a time-based picture of adsorption.
2. Equilibrium models — that is, models that quantitate the final, or equilibrium, state in a given adsorption system. These models generally utilize thermodynamic principles to arrive at a definition of the equilibrium that an adsorption system achieves.

Frequently, parameters derived from equilibrium studies are used in kinetic models to predict the dynamic behavior of adsorption systems.

The Langmuir, Freundlich and BET Models

These were among the earliest models developed to describe adsorption isotherms, but are still current. The Langmuir model was reported in 1918, and was developed for the adsorption of gases on plane surfaces. One of its assumptions is that adsorption takes place as a monolayer of adsorbate on the adsorbent [126]. When applied to liquid|solid systems the model may result in a good fit of the data but does not describe the actual processes and situations [164]. The equation for the model is:

$$q = \frac{abC}{(1 + bC)} \quad (6)$$

where C is the equilibrium concentration of the solute in the solvent ($\text{mole}\cdot\ell^{-1}$), a is a constant that is the amount of solute sorbed per unit weight of sorbent in forming a complete monolayer ($\text{mole}\cdot\text{g}^{-1}$), b is a constant related to the energy of sorption ($\ell\cdot\text{mole}^{-1}$), and q is the amount of solute adsorbed per unit weight of sorbent at concentration C ($\text{mole}\cdot\text{g}^{-1}$). The Langmuir constants a and b can be evaluated either by performing a non-linear regression fit to the equation from isotherm data or by performing a linear regression fit to one of the following two linearized forms of the equation:

$$\frac{1}{q} = \frac{1}{a} + \left(\frac{1}{ab}\right)\left(\frac{1}{C}\right) \quad (7)$$

or

$$\frac{C}{q} = \frac{C}{a} + \frac{1}{ab} \quad (8)$$

Essentially an empirical relationship, the Freundlich equation was derived for the sorption of gases on solid surfaces in 1909 and is given as:

$$q = kC^n \quad (9)$$

where n is a constant that varies between 0 and 1, and k is another constant with units of $\text{mole}\cdot\text{g}^{-1}\cdot(\ell\cdot\text{mole}^{-1})^n$. Over moderate ranges of equilibrium concentration, C , the Freundlich and Langmuir equations agree quite well. However, at very low concentrations, the Freundlich equation does not reduce to a linear form, as does the Langmuir equation, and it does not agree well at very high concentrations with the Langmuir equation [221]. The Freundlich expression is also frequently written as $q = kC^{1/n}$, where $n > 1$. It should be kept in mind which version is being meant. This document will use the version given as equation (9). The Freundlich constants can be determined either by a non-linear fit or a fit to the following linearized form of the expression:

$$\log q = \log k + n \log C. \quad (10)$$

If the saturation concentration of the solute, C_s (in mole·ℓ⁻¹), is known, then the Brunauer, Emmett, Teller (BET) equation (developed for the adsorption of gases in multimolecular layers and reported in 1938 [24]) may be used:

$$q = \frac{aBC}{(C_s - C)[1 + (B - 1)(C/C_s)]} \quad (11)$$

where B is a constant related to the energy of interaction with the surface [221], and the other terms are as defined earlier. The linearized form of the equation is:

$$\frac{C}{(C_s - C)q} = \frac{1}{aB} + \left(\frac{B - 1}{aB} \right) \left(\frac{C}{C_s} \right). \quad (12)$$

The Langmuir and Freundlich equations are used most frequently because the saturation concentration, C_s , is often not known.

Multicomponent Models

There are few useful multicomponent equilibrium models. A large proportion of the multicomponent models are kinetic models. Success with modeling multicomponent behavior can also be situation-specific. There is no one model that can reasonably predict the behavior of various multicomponent isotherm experiments as can the Langmuir and Freundlich models for single-component systems. Quite frequently, existing models are modified by the addition of parameters to improve the prediction. This is more a curve-fitting technique than modelling based on mechanistic considerations, although it can lead to a model that can be used for predictions in similar situations or when the chemicals involved are similar to the ones for which the model was initially calibrated. Some of the multicomponent models will be briefly introduced.

Multicomponent Langmuir Isotherm

In a mixture containing N solutes, the expression for the i th solute is given as [221]:

$$q_i = \frac{a_i b_i C_i}{1 + \sum_{j=1}^N b_j C_j} \quad (13)$$

where the a_i and b_i constants are determined from the individual isotherms of the components in single-component systems.

Multicomponent Freundlich Type Isotherm

A multicomponent Freundlich type isotherm was developed by Sheindorf, Rebhun and Sheintuch [196-198]. The equation for the isotherm is:

$$q_i = k_i C_i \left(\sum_{j=1}^N \psi_{ij} C_j \right)^{n_i - 1} \quad (14)$$

where the ψ s are determined from plots of bicomponent systems comprising combinations of the solutes. Mono- and bicomponent experiments have to be performed in order to obtain the coefficients for this isotherm. The need to perform the additional bicomponent isotherm experiments is probably the reason why this model has not gained much popularity. To obtain the ψ s from the bicomponent data, plots of $\frac{C_i}{C_j}$ against $\frac{\beta_i}{C_j}$ ($i \neq j$) are made. These should yield a straight line with slope = 1, and intercept of $-\psi_{ij}$. In order for ψ_{ij} to be positive, the intercept must be negative [196-198]. The β s are defined as:

$$\beta_i = \left(\frac{k_i C_i}{q_i} \right)^{1/(1-n_i)} \quad (15)$$

The Simplified Ideal Adsorbed Solution Theory

A model based on the Ideal Adsorbed Solution (IAS) theory was discussed by DiGiano *et al.* [57, 58]. Called the simplified Ideal Adsorbed Solution (SIAS) model, it is based on the assumption that the single-solute equilibrium isotherm of each solute is of the Freundlich type. The SIAS theory agrees exactly with the IAS theory when “sorption of the solutes can be described by either identical Freundlich equations or by Freundlich equations with equal n values” [58]. That is, either both k and n in $q = kC^n$ are identical, or at least the n values are equal. However, the concepts of the IAS theory can be applied via the SIAS model to systems where the values of n are not equal [58]. The model is:

$$q_i = k'^{(n'-1)/n'} (k_i C_i^{n_i})^{1/n'} \left[\sum_{j=1}^N \left(\frac{k_j}{k'} C_j^{n_j} \right)^{1/n'} \right]^{(n'-1)} \quad (16)$$

where

$$k' = \left(\prod_{i=1}^N k_i \right)^{1/N} \quad (17)$$

and

$$n' = \frac{\left(\sum_{i=1}^N n_i \right)}{N} \quad (18)$$

If there is only one sorbate, the SIAS model reduces to the familiar Freundlich equation.

Chapter IV

Results of Related Previous Studies at Virginia Polytechnic Institute and State University and Their Relationship to the Present Study

Three previous studies at Virginia Polytechnic Institute and State University have dealt with oil shale research. In order to put the current study in perspective, and to summarize the findings of the previous research, this chapter will first reproduce verbatim the objectives and conclusions of these studies.

Study by Cowher

This study was work done for a Master's thesis [44]. The objectives and conclusions are given below.

Objectives

1. Determine the background levels of soluble, leachable inorganic substances, such as arsenic, calcium, cadmium, fluoride, iron, potassium, carbonate, and bicarbonate present in spent and raw shale, and the time required for an equilibrium state to be reached between the shale and distilled water;
2. Assess the ability of various shales to act as an adsorbent for various inorganic ions;
3. Compare batch and column experimental procedures for the assessment of adsorption capacity and extent of elution.

Conclusions

1. Retort temperatures and porosity values of the various shales had a significant effect on the quantity of inorganic constituents leached from the spent shales. Most of these constituents were flushed from the columns during elution trials in the first two to eight pore volumes of effluent.
2. Shales retorted at lower temperatures, which also had higher porosity values, exhibited greater sorption capacity for As, Cd and F. As, Cd, and Fe were removed to below detection limits for most of the sorption trials. High pH values of the eluents were most likely responsible for the removal of Cd and Fe through precipitation.
3. Although there was almost complete adsorption and/or precipitation of many of the ions considered in the batch sorption trials, these experiments did give an indication of how the agents would behave in the presence of shale. The continuous-flow column experiments pro-

vided for a more accurate analysis of the sorption/desorption capacity and elution properties of the shales.

Boardman, et alii

This was a two-year project with the DOE. A two-volume report was produced at the end of this study [18, 19]. The study covered all the work done by Cowher and that done by Lu (see next section), and also had additional work.

Objectives

1. Evaluate the sorption/desorption behavior of several cations and anions and three organic agents in the presence of four types of oil shale;
2. Contrast the ability of a western soil to sorb the various solutes of interest with the sorption capacities of the shales;
3. Relate and contrast the results of batch sorption tests to data obtained through continuous-flow, column trials; and,
4. Determine if a novel spectrophotometric method might be used to quantitatively analyze mixtures of organic agents in the shale leachates.

Conclusions

1. Retort temperature and porosity values appeared to be correlated with the distribution and quantity of inorganic agents that eluted from the shales.
2. Most of the inorganic agents considered in this study eluted from columns of shale in the first two to eight pore volumes of effluent.
3. Shales retorted at lower temperatures appeared to have a greater capacity to remove arsenic, cadmium, and fluoride than the other shales considered. Arsenic, cadmium, and iron were generally removed to below detection limit in the sorption trials. Removals of cadmium and iron were effected primarily by precipitation.
4. 2-Hydroxynaphthalene was generally sorbed to a greater extent by the shales than 1,2,3,4-Tetrahydroquinoline, which was in turn generally sorbed more completely than 2,3,5-Trimethylphenol.
5. Overall, it appeared that Antrim shale had the greatest capacity to sorb the organics considered, whereas Run 16 exhibited the lowest capacity. Intermediate to the performance of these two shales were the sorption capacities of Anvil Points and Oxy 6 shales which often behaved similarly.
6. Competition for adsorptive sites on the shales was clearly evident in many of the trials conducted with inorganic and organic agents. In many cases there were distinct differences in the ways solutes behaved when administered alone, as opposed to being part of a mixture.
7. The western soil appeared to have some affinity for arsenic, cadmium, iron, and fluoride, whereas calcium, potassium, ammonium, and sulfate sorbed poorly and/or eluted from the soil.

8. A truly just comparison of the soil and shales would have to include details about batch vs. continuous-flow trials, the behavior of individual solutes, and single- vs. multi-sorbate systems, as were developed in the results and discussion of this report. However, an overall impression derived from this study about the two types of materials was that the soil generally effected removals of the organic compounds of interest which were as high as, if not better than, those removals accomplished by the shales. Whereas, in many cases, the shales exhibited a greater capacity than the soil to remove the inorganic agents considered. The performance of the shales was, of course, a function of the availability of sorption sites and the alkaline nature of the shales.
9. The batch trial generally provided data that related well to the column test results. However, there were instances when an agent adsorbed or eluted differently in the two systems. For many of the solutes studied the composition of the test solution (i.e., single- and multi-sorbate) assumed greater significance than the physical configuration of the test.
10. The spectrophotometric procedures investigated for the analysis of solute mixtures showed some promise for aqueous systems; however, if the mixture is very complex, an analysis of the results becomes a rather monumental, linear programming task. Accuracy of the technique is a function of the level and location of interferences on a scale of wavelengths, the number of solutes in a mixture, the intensity of light absorption by the compounds, how well the absorption of light spectra by one agent can be resolved from that of another, etc. It is, of course, imperative that accurate extinction coefficients for the agents of interest be obtained and one should be aware that absorption spectra can shift in response to changes in aqueous conditions; e.g., shifts in spectra due to pH changes were noted in this study. The spectrophotometric method was ultimately abandoned in this project because the interferences caused by materials present in the shale leachates were excessive. The method still might be used to analyze for compounds that absorb light well outside the range in wavelengths where light absorption by shale leachate materials is significant. In any event, a set of programs was developed in this

project to analyze spectrophotometric data and was submitted to the Department of Energy under separate cover.

Study by Lu

This was a study done for a Master's thesis [135].

Objectives

The primary objective of this project was to evaluate the sorptive behavior of three organic compounds in the presence of four shales (Antrim, Anvil Points, Oxy 6, and Run 16) and a western soil. An attempt was made to evaluate competitive sorption effects of chemical species on shales and soil. The study was undertaken with single- and multi-component solutions and a series of batch and continuous-flow column experiments. Similar work was also conducted to assess the adsorptive capacity of the western soil with several inorganic anions and cations.

Conclusions

1. All of the five sorbents studied demonstrated a substantial sorption capability for 2-Hydroxynaphthalene and 1,2,3,4-Tetrahydroquinoline, yet poor sorption capacity for 2,3,5-Trimethylphenol.

2. Considering the overall sorption capacity, Antrim shale was a better sorbent for the organic compounds than the other three shales. Sorption capacity of the Run 16 shale appeared to be relatively poor.
3. The sorption behavior of each organic compound was adversely affected by the presence of the other organics. Competition effects among the organic compounds increased with increases in the number of solutes. The less effectively adsorbed the compound was the more adversely it was affected by competition.
4. The overall sorptive capacities of the oil shales and the soil increased with the number of organic compounds in the solution. The increase in adsorption capacity of the oil shales with increases in number of solutes in solution emphasized the importance of this factor on the performance of spent shales in the co-disposal option where spent shales are used for the removal of complex mixtures of organic constituents in retort waters.
5. The western soil appeared to be a good sorbent for arsenic, cadmium, and iron, and possessed some affinity for fluoride. Potassium, calcium, ammonium, and sulfate were sorbed poorly and eluted well from soil.
6. Sorption of inorganic agents in multicomponent solutions by the soil was influenced not only by competition for sorption sites by solutes, but also by intramolecular interactions between the solutes. The inorganic solute interaction can be very significant in effecting multisorbate sorption of cations by the soil.

Summary Statement on Previous Studies as Related to the Current Study

The ability of three spent shales, one raw shale and one soil to adsorb specific inorganic and organic agents was characterized in the previous studies. Those studies determined that spent shale was a promising sorbent for the organic materials tested. Antrim spent shale was determined to be the best sorbent (from among the spent shales). The shales had the best sorptive capacity for 2-Hydroxynaphthalene, followed by 1,2,3,4-Tetrahydroquinoline, and then 2,3,5-Trimethylphenol.

However, all the batch experiments that were conducted were kinetic experiments and in some cases the compound was sorbed completely. These factors reduce the usefulness of the information gathered. In addition, all the column studies were multicomponent experiments. It should be noted that the primary motivating objective in those studies was to evaluate whether or not the shales could be used as sorbents. Once that was shown, it became necessary to systematically evaluate a spent shale.

Development of the Current Study

In order to retain some continuity with the previous studies, the same organic compounds were used. However, the three compounds consisted of a phenol (2,3,5-Trimethylphenol), a naphthol (2-Hydroxynaphthalene, a homolog of phenol) and a quinoline (1,2,3,4-Tetrahydroquinoline, unrelated to phenol). It was felt that the addition of Phenol would enhance the work. The group of three phenolics would then consist of the native compound, a compound with three methyl substituent groups and a homolog. In this manner, it was hoped that the effects of the addition of substituents and ascending a homologous series could be studied. Furthermore, the fourth

compound was unrelated to the three phenolics and it was hoped that it would provide a good contrast in behavior since the base group was different.

Antrim spent shale, being the best sorbent both in terms of amount sorbed and consistency of behavior, was chosen as the sorbent. It may be argued that selecting a shale with consistent sorptive behavior would prevent the observation of problems that could arise if a shale that behaved inconsistently were used instead. However, it was felt that at this stage it was more important to characterize the behavior and explain it. The latter would become more difficult with an inconsistent shale. Spent shale is a complex sorbent even if it exhibits consistent sorptive behavior.

Another factor considered was that it would be useful to index the sorptive behavior of the spent shale to the performance of a conventional sorbent. Toward this end a granular activated carbon was chosen as a second sorbent.

Batch isotherm experiments are used traditionally to obtain an idea of the extent of sorption possible on a sorbent. It was felt that single-component batch sorption experiments on both the shale and the carbon would not only provide basic information on the sorptive behavior of the sorbents but would also allow a comparison of their sorptive characteristics to be made. The behavior of shale could in this manner be related to the behavior of the granular activated carbon.

In order to determine how the sorptive behavior of the shale changed when the sorbates were present in multicomponent systems, and whether there were any competitive effects, multicomponent batch isotherm experiments were performed. Another reason for performing these experiments was to determine if the multicomponent behavior could be predicted by a mathematical model with data obtained from the single-component experiments.

It is envisioned that spent shales would eventually be used as a pretreatment for retort waters and/or codisposed with retort waters. Retort water has an extremely complex matrix of compounds. It would be impossible to test the sorptive behavior of all the compounds present in retort water in

any reasonable amount of time. Therefore, if a mathematical relationship could be found to describe multicomponent behavior, it would help in better assessing the behavior of retort water on spent shale.

If spent shales are to be used as a pretreatment step for retort waters, it is important to see how they would behave in flow-through column experiments, since in a pretreatment system the shales would probably be used in packed towers. Single-solute column experiments were conducted in the present study toward this objective. Perhaps column behavior could be predicted from the batch experiments. If this were the case, then the time spent on column experiments could be avoided in future studies.

Chapter V

Materials and Methods

Two sorbents (a spent shale and a granular activated carbon), four organic compounds, and batch and column experiments were used in the study.

Antrim Shale

The shale that was used was obtained from LETC at Laramie, Wyoming. It was an eastern shale from Michigan that had been retorted at LETC and was called Antrim shale. The size fraction used was 8-30 mesh, i.e., that fraction which passed through a no. 8 mesh and was retained on a no. 30 mesh. The retorting conditions for the shale were [139]:

Obtained from	Huron-Allentown Cement Division, National Gypsum Co., Alpena, MI
Retorted at	Laramie Energy Technology Center, Laramie, WY
Type of retort	10 ton simulated <i>in situ</i> (Run S-42)
Retort gas	Air and recycle
Maximum bed temperature	793 °C
Length of run	5.54 days

Complete information about the retorting conditions, and other information, is given in Table 19 through Table 24. The shale was dried for at least 96 hours in a 105 °C oven before use.

Filtrisorb 300 Activated Carbon

The activated carbon used was a GAC obtained from Calgon Carbon Corporation (Pittsburgh, PA) and was called Filtrisorb 300 (F-300). More than 80% of the activated carbon was in the 8-30 mesh range, with a maximum of 15% larger than no. 8 and a maximum of 4% smaller than no. 30 [26]. The carbon was dried for at least 96 hours in a 105 °C oven before being used.

Other properties of the carbon were as follows [26]:

Total surface area by BET-N ₂ method:	950-1050 m ² ·g ⁻¹
Maximum moisture content	2.0%
Bulk density	28 lb·ft ⁻³
Particle density wetted in water	1.3-1.4 g·cm ⁻³
Pore volume	0.85 cm ³ ·g ⁻¹
Effective size	0.8-1.0 mm
Minimum Iodine number	900
Minimum abrasion number	75

Chemicals Used

The chemicals used were:

2-Hydroxynaphthalene (designated as HN) — also called 2-Naphthol and β -Naphthol; C₁₀H₇OH; m.w. = 144.17; obtained from Aldrich Chemical (Milwaukee, WI) at a purity level of 99%.

Phenol — also called carboic acid, benzenol and hydroxybenzene; C_6H_5OH ; m.w. = 94.11; obtained as a liquid from Fisher Scientific (Fairlawn, NJ) at a purity level of 90.7% (10.05% water).

2,3,5-Trimethylphenol (designated as TP) — also called *iso*-pseudocumenol; $(CH_3)_3C_6H_2OH$; m.w. = 136.19; obtained from Aldrich Chemical at a purity level of ~99%.

1,2,3,4-Tetrahydroquinoline (designated as THQ) — $C_9H_{11}N$; m.w. = 133.19; specific gravity = 1.061; obtained from Aldrich Chemical as a liquid at a purity level of 97%.

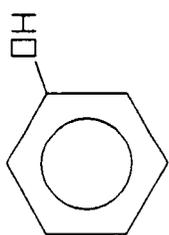
The structures of the chemicals are given in Figure 26.

Tests on Shale

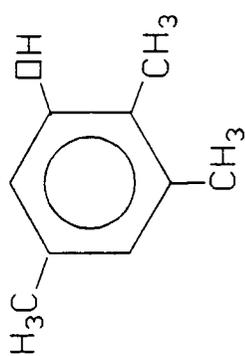
The bulk density, solid density and porosity of the shale were determined. A Proctor mold with a volume of 944 cm³ (1/30 ft³) was used to determine the maximum and minimum densities of the shale [50]. The shale was placed in the mold and leveled. The weight of the shale divided by the volume of the mold provided the minimum bulk density. In a similar manner, the maximum density was determined. However, for this the mold with the shale in it was vibrated to allow the shale to settle, and more shale added and the mold vibrated again, the procedure being repeated until no further settling of the shale occurred.

The specific gravity determination procedure was used to determine the solid density of the shale [50]. A pycnometer was used for the purpose.

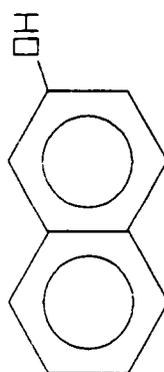
Minimum and maximum porosities were subsequently calculated using the following relationship:



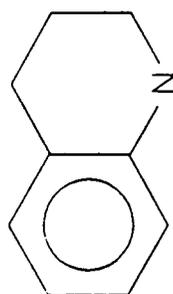
Phenol



2,3,5-Trimethylphenol



2-Hydroxynaphthalene



1,2,3,4-Tetrahydroquinoline

Figure 26. Structure of the organic compounds used in this study

$$\text{Porosity} = 1 - \left(\frac{\text{Bulk density}}{\text{Solid density}} \right).$$

Surface Characterization

Surface area determinations were attempted upon the shale at the Agronomy Department at Virginia Polytechnic Institute and State University. The BET-N₂ apparatus was used for the purpose.

Scanning electron microscopy was performed for the author upon both the sorbents. The instrument used was a Cambridge 120 model scanning electron microscope (SEM). The samples were glued to aluminum stubs with a conductive silver paint and then sputtered with gold in an argon atmosphere at reduced pressure for 60 seconds. They were then examined in the secondary electron mode (i.e., the electrons that were emitted from the samples were collected) at an acceleration voltage of 30 kilovolts.

Batch Experiments

Batch isotherm experiments were performed using both the shale and the GAC as sorbents. The four compounds were used singly for both the shale and the GAC, whereas they were also used in all combinations of two and four upon the shale. Eight 250 milliliter (mℓ), glass, Erlenmeyer flasks containing the sorbent and the sorbate in solution were placed in a reciprocating shaker bath (Fisher Scientific; Model 129), with a reciprocating rate set to approximately 2 strokes·s⁻¹ and the bath set

to 25 ± 3 °C. The flasks were covered with Parafilm® (American Can Company, Greenwich, CT), and allowed to shake continuously for 96 hours (considered sufficient to reach equilibrium based on results of a previous, related study [19]), at which time the liquid contents were filtered through a 0.45 micrometer (μm) membrane filter (Gelman Science, Ann Arbor, MI; GN-6 Metricel) and analyzed. The pH was also recorded. All solutions were in distilled, deionized water, and the experiments were performed in triplicate.

For the shale experiments, 3 g of shale were placed in the flasks with 100 mL of the solution — a liquid:solid (L:S) ratio of 33:1. Each of the sorbates (whether in the single- or multi-sorbate experiment) was present in the solution at concentrations of 0 (control), 10, 25, 35, 50, 65, 80 and 100 milligrams per liter ($\text{mg}\cdot\ell^{-1}$). A total of 46 batch isotherm replicates were performed upon the Antrim shale and the GAC. Of the batch isotherms on the shale, 12 were single-solute experiments (3 replicates for each of 4 compounds), 18 were bisorbate (3 replicates for 6 combinations of bisorbate mixtures), one tri-component (consisting of the three phenolic compounds — Phenol, 2-Hydroxynaphthalene and 2,3,5-Trimethylphenol), and 3 tetra-solute (3 replicates of the 4 compounds in a multicomponent solution). For two of the four-component isotherm experiments the range of concentrations was extended to: 0 (control), 2, 4, 8, 10, 25, 35, 50, 65, 80, 100, 125, 150, 180, 210 and 250 $\text{mg}\cdot\ell^{-1}$.

For the carbon experiments, 0.1 g of GAC was placed in the flasks with 100 mL of solution — an L:S ratio of 1000:1. Only single-solute experiments were performed with the GAC. For all the experiments with Phenol (since it was not absorbed to a very large extent), and for one experiment each of the other three compounds, the solution concentrations used were: 0 (control), 25, 50, 75, 100, 130, 160 and 200 $\text{mg}\cdot\ell^{-1}$. All the remaining experiments on carbon were performed with initial solution concentrations of 0 (control), 50, 100, 175, 250, 375, 400 and 500 $\text{mg}\cdot\ell^{-1}$. The concentration range was increased because the carbon was efficient in sorbing IIN, THQ and TP, and because it was difficult to measure less than 0.1 g of GAC with any accuracy. A total of 12 isotherm experiments (3 replicates for each of 4 compounds) were performed on the GAC.

Preliminary experiments were conducted using solutions of the highest concentrations of the sorbates placed in flasks with no sorbent. Over a 96-hour period, there was no detectable change in concentrations, indicating that losses due to volatilization and sorption on to the glass surfaces were either not present or small enough to not be detected. Consequently, such controls were not performed with the batch equilibrium isotherm experiments.

Column Experiments

The column experiments were performed on shale only as single-solute experiments with each of the four compounds. The continuous-flow column experimental configuration was as shown in Figure 27. A feed solution of the compound (in distilled, deionized water) at a concentration of $50 \text{ mg}\cdot\ell^{-1}$ was pumped at a flow rate of approximately $1 \text{ mL}\cdot\text{min}^{-1}$. All experiments were performed in triplicate. Formal control experiments with simple distilled, deionized water as the feed solution were not performed because preliminary experiments had indicated (as had the batch experiment controls) that the compounds of interest did not elute from the shale. Twelve column experiments (3 replicates of single-solute feeds) were performed upon the shale.

The feed was initially placed in a water bath (Lauda; Model K-2/RD) kept at $25 \pm 3 \text{ }^\circ\text{C}$. However, the water bath failed after the initial experiment, necessitating leaving the feed at ambient temperature, which ranged from $25\text{-}30 \text{ }^\circ\text{C}$. Due to the low flow rate (with an approximate residence time in the column of 45 minutes) and the column being temperature-controlled, it was felt that this change would not affect the results. The diurnal temperature variation was not too far away from the water bath-controlled one. The feed solution was analyzed at the end of each experiment to determine if there were any biodegradation. The carboy containing the feed solution was wrapped in a double layer of thick brown paper to exclude most incident light.

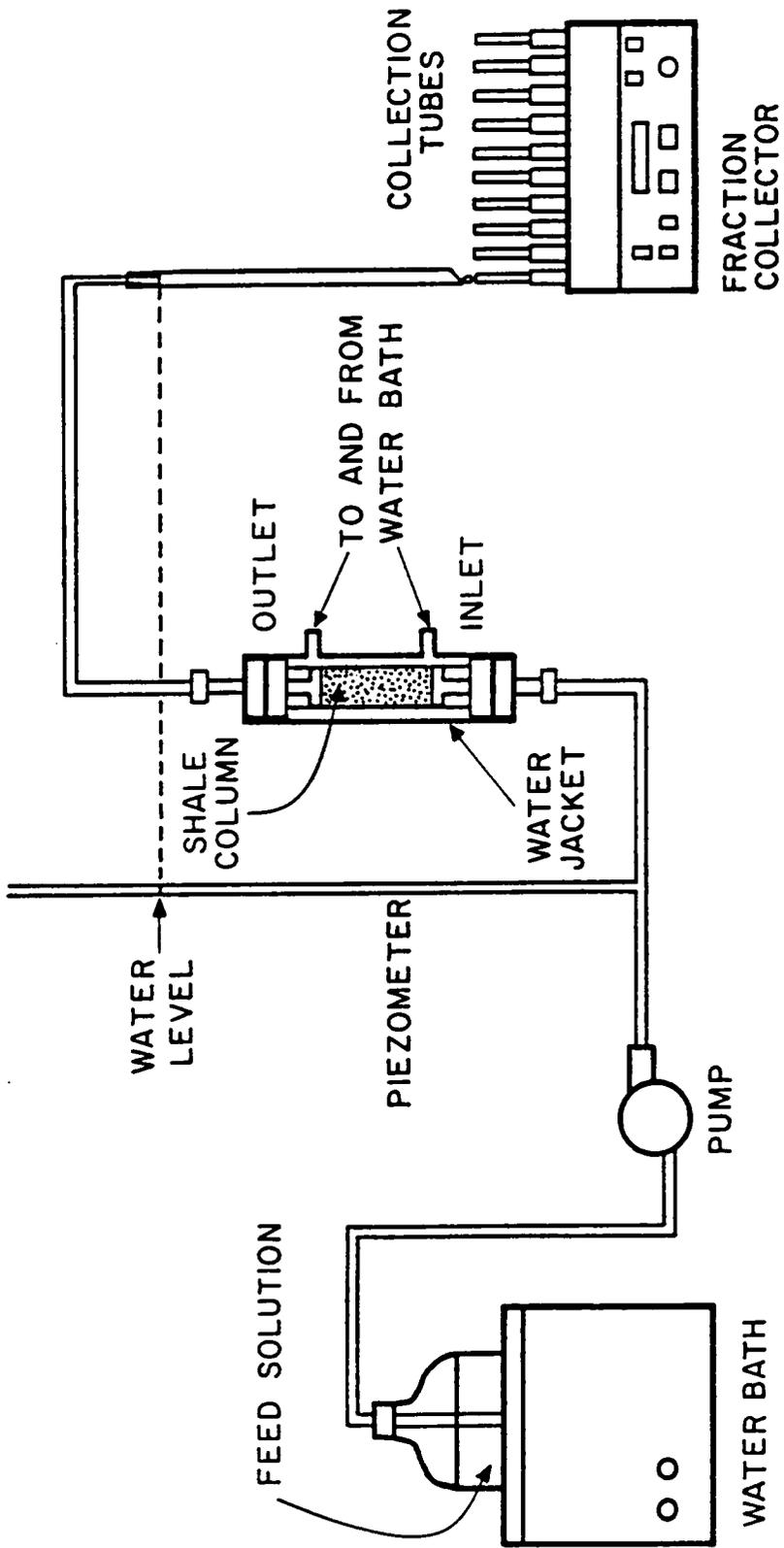


Figure 27. Continuous-flow column experiment configuration

The glass columns used were chromatography columns (I.K.B; no. 2137) of 26 mm inside diameter and total length of 35 cm. The columns were water-jacketed and held at a temperature of 25 ± 3 °C by a circulating water bath (Lauda; K-2/R). Adjustable plungers that fitted into the columns had a removable polyester/polypropylene disc, with pores to distribute the flow, on the ends. A glass carboy contained the feed solution and the solution was pumped by a lab pump (FMI; Model RP-G50) through the column. Effluent from the column was collected by a fraction collector (ISCO; Model 328 or Retriever III) that held glass test tubes that could be screw-capped. The fraction collector was set to allow a 15-minute fraction (equal to approximately 15 mL of flow) to be collected. All connective tubing was made of Teflon®.

The column held 100 g of shale that was poured in. The column was then tapped until the shale settled no further (final volume was usually between 75 – 90 cm³). Each experiment was allowed to continue until about 200 pore volumes of flow had passed through the column for the Phenol and TP experiments, between 250-300 pore volumes for the HN experiments, and between 550-600 pore volumes for THQ. One THQ column was allowed to continue sorbing until 1640 pore volumes had passed through, and then the feed changed to distilled, deionized water and the column allowed to elute until 1750 total pore volumes had passed through. The pore volume figures quoted above represent between 133 hr (for 200 pore volumes) and 1167 hr (for 1750 pore volumes) for a typical pore volume of 40 cm³. All experiments were performed in triplicate.

The pore volume was calculated in the following manner:

1. Volume occupied by the shale.

$$\text{Volume (cm}^3\text{)} = \text{Length of shale column (cm)} \times \text{Cross-sectional area (cm}^2\text{)}$$

2. Bulk density of the shale in the column.

$$\text{Bulk density (g}\cdot\text{cm}^{-3}\text{)} = \frac{\text{Mass of shale (g)}}{\text{Volume (cm}^3\text{)}}$$

3. Porosity of the column.

$$\text{Porosity} = 1 - \left(\frac{\text{Bulk density}}{\text{Solid density}} \right)$$

4. Calculation of the pore volume.

$$\text{Pore volume (cm}^3\text{)} = \text{Porosity} \times \text{Volume (cm}^3\text{)}$$

Appropriate tubes (at pore volume intervals deemed to be necessary to determine the elution profile) of effluent were collected. The samples were filtered through 0.45 μm membrane filters, and analyzed for the compound in the feed. The pH of the sample was also recorded.

Analysis of Samples

Samples were analyzed using a high performance liquid chromatograph (HPLC). The HPLC (Hewlett-Packard; Model 1090M) was fitted with a diode-array detector (DAD) that could continuously monitor all wavelengths from 190 to 600 nanometers (nm), allowing the spectra of the compounds to be gathered also. An ultraviolet (UV) spectrophotometer (Beckman Instruments; Model DU-6) was used to generate the spectrum of each compound in solution and the peaks in the spectra were used for setting the wavelengths to be monitored on the HPLC (upto 8 wavelengths could be monitored simultaneously). The wavelengths monitored on the HPLC were those at 241, 254, 273 and 290 nm, with a bandwidth of 10 nm. These wavelengths were chosen as composites of the best peak wavelengths for the compounds, and different compounds were generally monitored on different wavelengths.

The column used was a reverse-phase C-18, 10 μm column (Fisher Scientific; Resolvex C-18) of 4.6 mm internal diameter and 25 cm length. Based on the compounds and/or combinations of compounds being analyzed for, the isocratic flow rate of the solvents used (Acetonitrile and Water) was varied between 1.0-2.5 $\text{mL}\cdot\text{min}^{-1}$ and the Acetonitrile:Water ratio was varied between 80:20 and 37:63. The column was at a temperature of 27 $^{\circ}\text{C}$. For high sensitivity (i.e., low concentrations) the injection volume was 25 μL , and for lower sensitivity (for higher concentrations) the injection volume was 5 μL .

Approaches to Data Analysis

Upon gathering of the raw data, the first step was to plot equilibrium aqueous phase concentration versus the initial concentration for the compound(s) that were used. A second plot of the change in concentration against the initial concentration was also produced. A plot of the pH variation in the flasks was appended to both these plots. Examples of these plots for 2-Hydroxynaphthalene are given in Figures 28 and 29.

The solid diagonal line on Figure 28 is used as a guide to indicate the change in concentration. This change is the difference between the diagonal line and the data points, and is plotted in Figure 29.

Another consideration is the fact that the isotherms generated in this study were not generated in the usual manner. In most sorption studies, the amount of sorbate (or the concentration) is kept constant, and the amount of sorbent added is varied. In this study, the amount of sorbent was kept constant and the amount of sorbate added (i.e., the concentration) was varied. This was done primarily because the sorbent was available only in limited amounts. Both procedures should theoretically provide the same results, as long as the concentrations are fairly low, and the sorption of

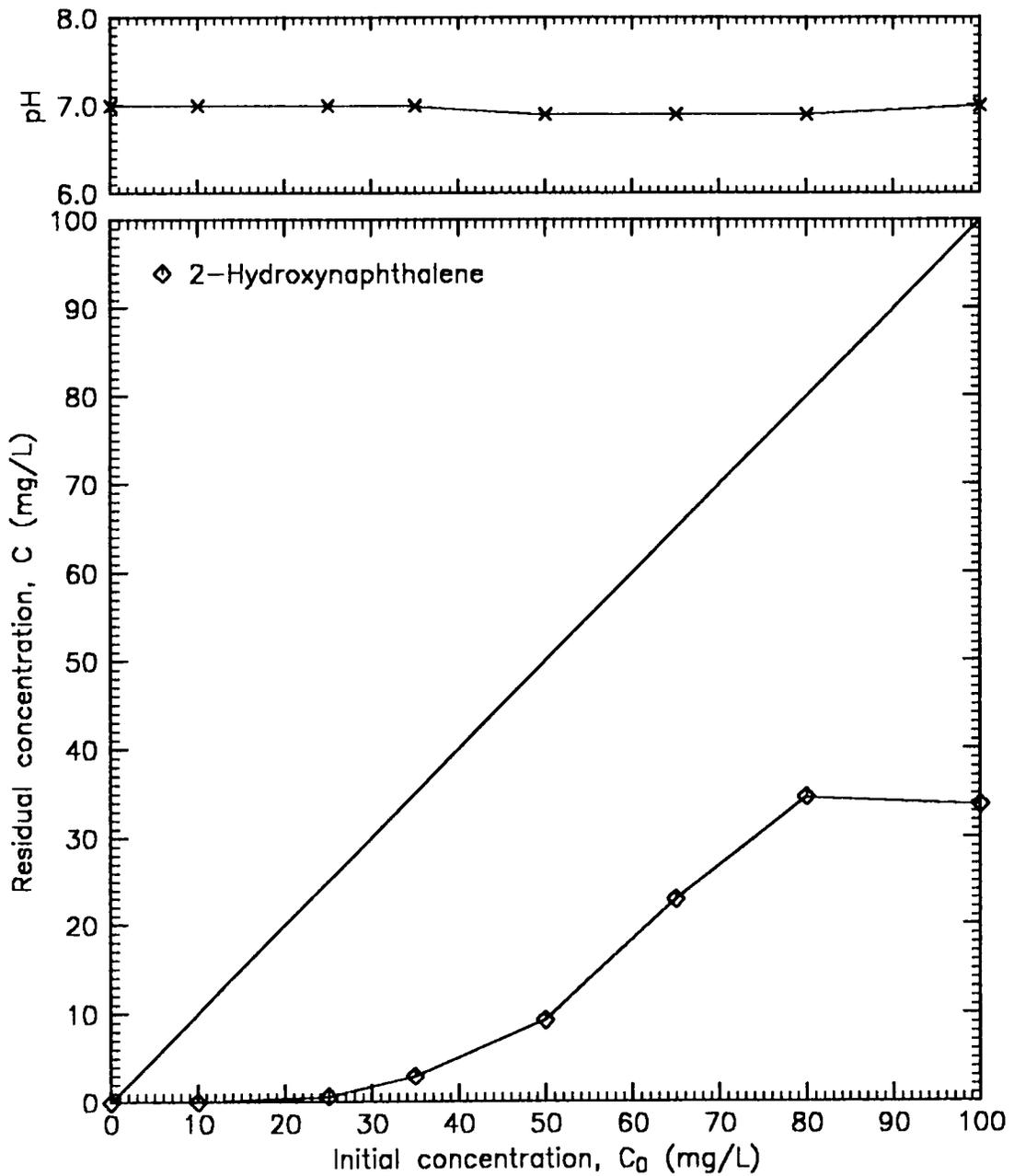


Figure 28. Residual concentration and pH vs. initial concentration for 2-Hydroxynaphthalene: First replicate. The solid diagonal line is used to indicate the amount absorbed — this is equal to the difference between the solid line and the data point.

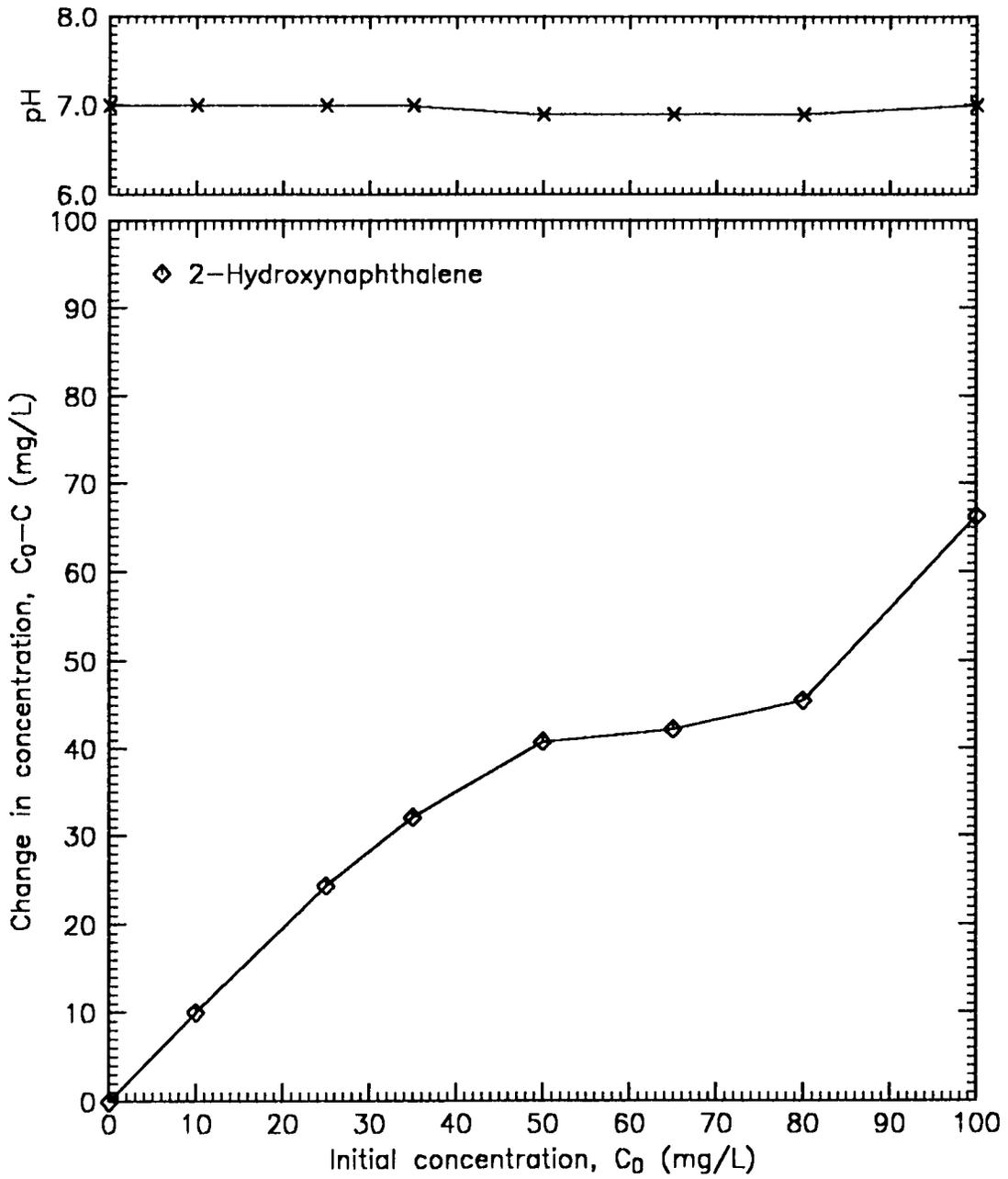


Figure 29. Change in concentration and pH vs. initial concentration for 2-Hydroxynaphthalene: First replicate.

sorbate is not very heavily dependent upon the concentration gradient. The initial concentrations used in this study were fairly low. Although no effort was made to determine whether or not the amount of sorption is dependent upon the concentration gradient, it is felt that in equilibrium studies this is not a major consideration. In the study of the kinetics of sorption, the concentration gradient would be important.

Since the amount of sorbent, M , was kept constant, the change in concentration values obtained from the data are directly related to q ($M = \text{constant}$). This allowed for a quicker evaluation of the sorptive capacity, without any further calculations being necessary.

After these initial plots, further plots were made in order to present the data as isotherms (with sorbate concentration on the shale in $\mu\text{mole}\cdot\text{g}^{-1}$ plotted against the equilibrium concentration in $\text{mmole}\cdot\ell^{-1}$). For this series of plots the results of all replicates were combined, except for those few cases where replicates either were drastically different or the results of the experiment were questionable (due to growth in some flasks as happened in one replicate — a single-solute experiment on shale with Phenol). Representative curves were fitted to the data. In some cases, these curves were segmented.

Following this, the data from the single-component experiments were plotted for both the Langmuir (equation (7)) and Freundlich (equation (10)) curve-fitting procedures, and the coefficients calculated. These initial plots indicated that the Freundlich coefficients provided a better fit to the data. However, it was later felt that due to the mathematical transformations of the data inherent in the linearization, and the fact that there was more than one way in which the Langmuir equation could be linearized, it would be better to perform a non-linear least squares regression fit on the untransformed data and obtain the coefficients in this manner. These were computed by using the NLIN procedure of the SAS® system. The Marquardt method of the NLIN (nonlinear least squares) procedure was used.

Modelling was performed for the multicomponent experiments. The multicomponent isotherm equations given in the chapter titled 'Literature Review – Sorption' were used for this purpose. Furthermore, the SYSNLIN procedure of the SAS/ETS software package was used for performing estimation of the parameters for one of the models (the simplified IAS theory model).

Chapter VI

Results and Discussion

This chapter will detail the results of the experiments and the analyses performed upon the data gathered. All the raw data that were collected are given in Appendix B.

As stated earlier, a total of 46 batch isotherm replicates and 12 column replicates were performed upon the Antrim shale and the granular activated carbon. Of the batch isotherms on the shale, 12 were single-solute experiments (3 replicates for each of 4 compounds), 18 were bisorbate (3 replicates for 6 combinations of bisorbate mixtures), one tri-component (consisting of the three phenolic compounds — Phenol, HIN and TP), and 3 tetra-solute (3 replicates of the 4 compounds in a multicomponent solution). A total of 12 isotherm experiments (3 replicates for each of 4 compounds) were performed on the GAC. Twelve column experiments (3 replicates of single-solute feeds) were performed upon the shale.

These experiments will be presented in the following order:

Batch experiments on shale,

Batch experiments on carbon, and,

Column experiments on shale.

Physical Properties of the Compounds

Table 46 is a compilation of some physical properties of the compounds used in this study. The values for the melting point (M. P.), the boiling point (B. P.) and the specific gravity (Spec. gr.) are provided for information purposes to better characterize the compounds. Some of the values were estimated using various methods (principally that given in [136]) listed in the notes to the table. The description of the method given in [136] is too extensive to be included in this text. Essentially it involves using a known K_{ow} value for a compound and then adding or subtracting values for fractions depending upon whether the fractions have to be added to or removed from the known compound to obtain the desired compound. For example, the K_{ow} for Phenol is known, and to this would be added that for three methyl groups to obtain the K_{ow} for 2,3,5-Trimethylphenol. Corrections would also have to be made for the positions that the methyl groups occupy. The estimated $\log K_{ow}$ (K_{ow} = octanol-water partition coefficient) values for HIN and THQ agree quite closely with the observed values. All the $\log K_{ow}$ values indicate fair to strong partition favorable to octanol over water, since all values (1.46 for Phenol to 3.44 for TP) are greater than 1.0. The estimated value for TP could indicate that the compound is not very soluble in water. This was borne out by observation in the present study, although no efforts were made to determine the solubility of either TP or THQ. How well the $\log K_{ow}$ value correlates with solubility is a moot point since warming of HIN increases its solubility sixteen-fold. However, the $\log K_{ow}$ value is also expected to change with rising temperature.

Table 46. Physical properties of compounds used in this study

Property	Compound			
	HN	Phenol	THQ	TP
Mol. wt.	144.17*	94.11†	133.19*	136.19*
M. P., °C	122†	41†	—‡	92-95*
B. P., °C	295†	182.0†	249*	230-231*
Spec. gr.	1.217@4°C†	1.07†	1.061*	na
Solubility	750 mg·ℓ ⁻¹ @25°C† 12,500 mg·ℓ ⁻¹ warm†	82 g·ℓ ⁻¹ @15°C†	Soluble⊠	na
log K _{ow}	2.84§ 2.88 (est.)⊠	1.46§	2.29◇ 2.13 (est.)◇	3.44 (est.)⊠
pK _a	9.57 @20°C△	9.99△	10.75 (est.)□	10.57 (est.)○

* From [6].

† From [216].

‡ Liquid at room temperature.

⊠ From [218].

§ From [129].

⊠ Estimated using method given in [136].

◇ From [31].

△ From [55].

□ Estimated by addition of difference between Piperidine (11.123) and Pyridine (5.17) to Quinoline (4.80). pK_a values from [55]. Extrapolation suggested by [111].

○ Average of 2,3,4- (10.59), 2,4,5- (10.57), 2,4,6- (10.88) and 3,4,5-Trimethylphenol (10.25). Data from [55].

na Not available.

Physical Properties of the Shale

The physical properties of Antrim shale that were measured are reported below:

Minimum bulk density	1.01 g·cm ⁻³
Maximum bulk density	1.20 g·cm ⁻³
Solid density	2.52 g·cm ⁻³
Minimum porosity	0.52
Maximum porosity	0.60

The minimum and maximum porosities reported were performed by using the Proctor mold and the procedure given in the 'Materials and Methods' chapter. However, it was noted in the column experiments that the minimum porosity of the shale in one of the columns was 0.50, and some others were in the 0.51 range. When compared with the minimum and maximum porosity values reported above (0.52 and 0.60, respectively), this indicates the approximate nature of the porosity determination. Crushed shale has very uneven particle shapes, and the method of packing employed can have a significant effect upon the final porosity of the bed. Therefore, the bulk density and porosity values reported above should be taken to be indicative of the magnitude rather than the absolute ranges.

Such other factors as the amount of fines present in the fraction measured, and the way in which the shale is initially poured into the container make a difference. For example, it was noted while performing the column experiments that inevitably a few larger than average voids would be formed in the shale column while pouring the shale in. No amount of tapping of the column (and these were quite sharp and intense raps — as intense as they could be without breaking the glass columns) would eliminate all these voids. Persons used to handling more uniformly-shaped media or smoother media will find that spent shale has its own peculiarities. However, it should be noted here that the presence of these voids did not seem to significantly alter the column behavior.

Surface Characterization of the Sorbents

Surface area determinations attempted on the shale failed to yield satisfactory results. Apparently the helium that is used in the initial steps to determine the volume of the solid was sorbed irretrievably by the shale. This was described to the author as being akin to the helium forming a solution in the shale. Because of this, the surface area calculations resulted in a negative surface area. The magnitude of the numbers was also meaningless.

Two close-ups at different magnifications of the surface of each sorbent are shown in Figure 30 and Figure 31. The upper photograph is at a magnification of about 240X whereas the lower photograph is at a magnification of about 2000X. The author was aided in the interpretation of the photographs [206].

Two lines of information are printed on the top of each photograph. The top line contains, from left to right, a number indicating the magnification, the acceleration voltage in kilovolts, the working distance in mm, and the serial and photo number. The lower line has a number that indicates the length of the reference bar drawn alongside it in μm .

It should be remembered that these are by no means representative samples, but are in the nature of grab samples. Therefore, no general conclusions can be drawn from the photographs, and they are included here merely to provide some simple information about the surfaces.

The lower-magnification photograph of the shale (Figure 30) displays lighter bands in a darker matrix. These are probably bands of organic matter. This observation would be consistent with the formation of the shale due to sedimentation of organic matter and silt, as also with the presence of varves found in some shales. However, the shale is a spent shale, and this would be residual organic matter. Note the absence of discernible pores on the surface. If this were representative of the bulk of the shale, then most of the surface area of the shale would be external and quite low.

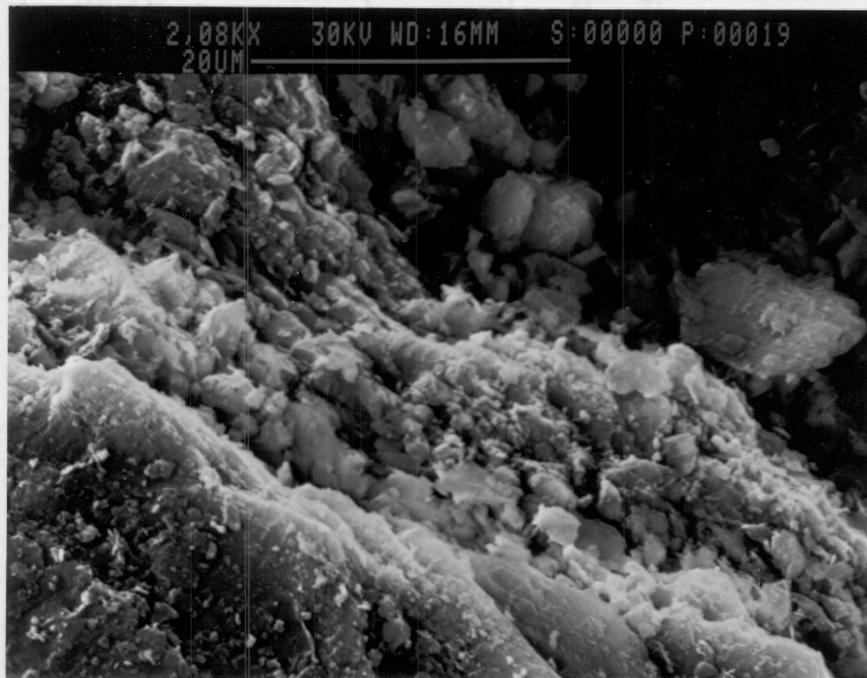
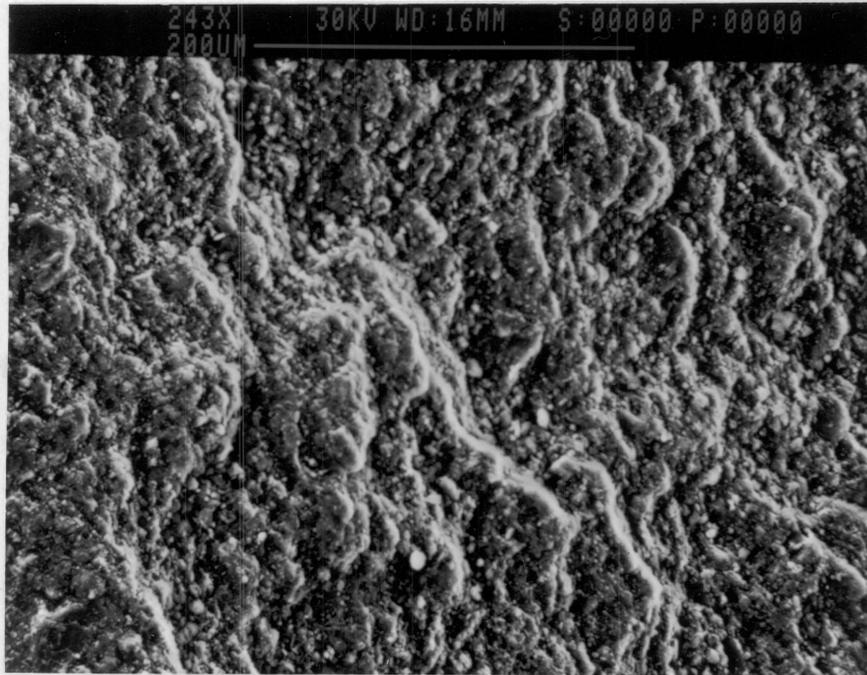


Figure 30. SEM photograph of surface of Antrim spent shale: Upper photo is at a magnification of 243X and lower photo is at 2080X. See the text for a description of other conditions.

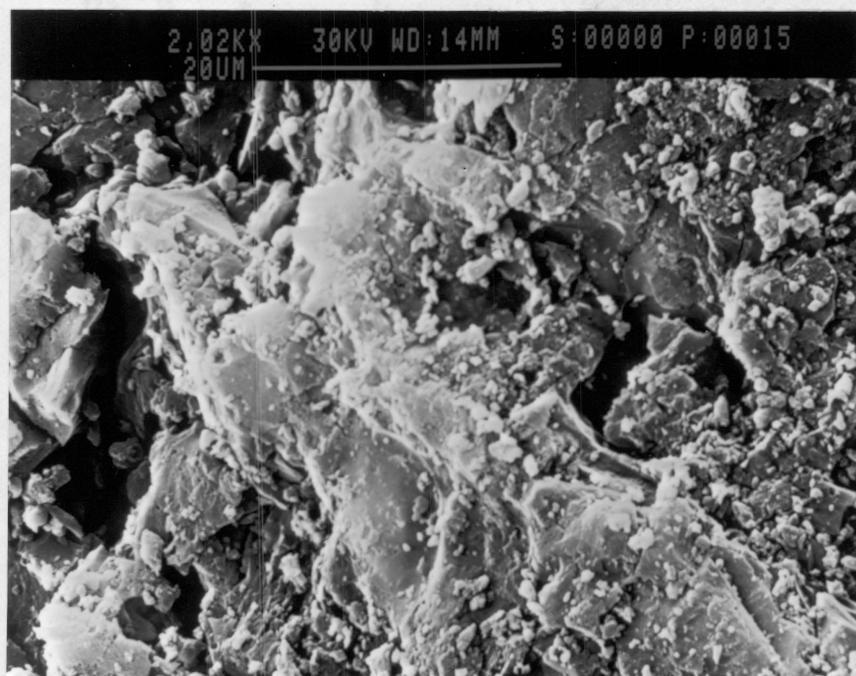
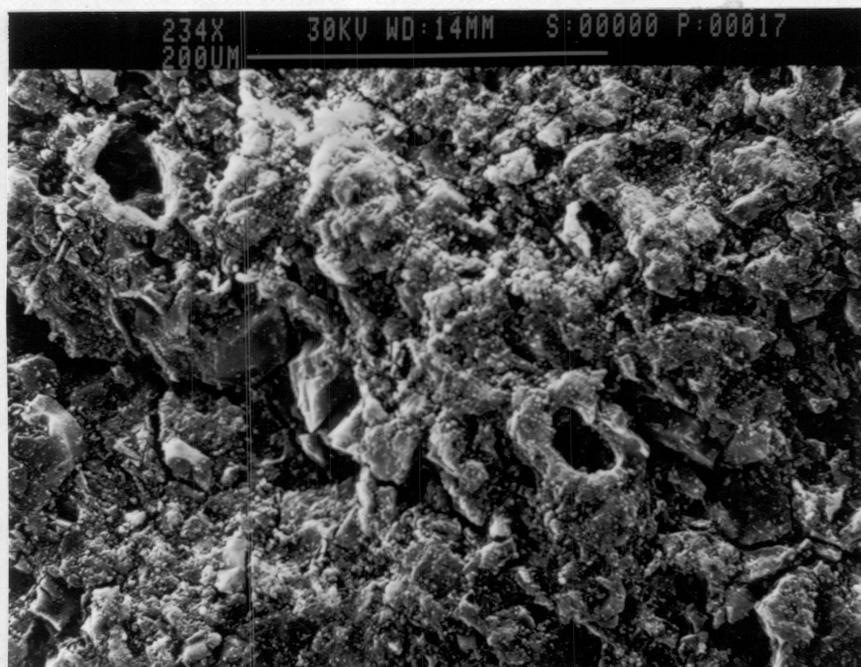


Figure 31. SEM photograph of surface of Filtrasorb 300 GAC: Upper photo is at a magnification of 234X and lower photo is at 2020X. See the text for a description of other conditions.

The photograph taken at a higher magnification (the lower photograph) is a close-up of one of the lighter bands. It is thought that the globular clumps are organic matter, whereas the smoother surfaces are the base inorganic matrix of the shale. This is a spent shale; raw shales would have a surface that would be richer in organic matter with more veins of it discernible.

The lower-magnification photograph of F-300 GAC (Figure 31) displays the different surface character of the carbon. There are more pores to be seen (including two relatively large ones at upper left and middle right), and the surface is more broken, rough and pitted. Cracks and crevasses can be seen, and there is no visible organic matter. The higher-magnification photograph shows what are probably some organic matter granules scattered upon the surface of the carbon, and the presence of micropores. The surface is considerably rougher than that of the shale. Obviously, the carbon, with its more indented and convoluted surface and its pores, would possess a larger surface area.

Batch Experiments on Antrim Shale

A total of 34 batch isotherms were performed using the shale. Various different methods of presenting the data were possible. A short description of the path taken in developing the presentation of the data will, perhaps, prove to be useful.

Variations in pH

The pH of almost all the flasks containing shale in every batch experiment varied principally between 6.0 and 8.0, with most values lying between 6.5-7.5. Essentially, the pH was neutral. This is significantly lower than the pK_a value for the three phenolic compounds. These compounds,

therefore, would not have ionized to an appreciable extent. If the compounds had ionized, dissociation would have removed the H^+ ion, leaving a negatively charged ion (e.g., the phenolate ion in the case of Phenol). The charged species would be more soluble in the water and more likely to stay in solution, specially if the surface of the shale were neutral (which is not the case — the surface of shales is usually polar). Antrim shale is not visibly hydrophobic, although some other spent shales, like Paraho, have been found to be so [44]. For structurally simple species adsorption is low for the charged species [221]; however, ionization effects become less important as the sorbate becomes more complex. It is difficult to say where the transition from a simple to a more complex species occurs, and, as far as sorption interaction effects are concerned, it may vary from one situation to another. From among the compounds used in this study, Phenol can safely be said to be a simple compound in this context. The surface of shale is usually polar, and water is a polar solvent. This makes it difficult to apply Lundelius' rule with respect to sorbability and solubility.

1,2,3,4-Tetrahydroquinoline has the highest pK_a value and would be least dissociated in the neutral pH range. This should enhance its sorption based on solubility principles.

Isotherm Plots

Plots of the sorbate concentration on shale ($\mu\text{mole}\cdot\text{g}^{-1}$) against the equilibrium concentration (in $\text{mmole}\cdot\ell^{-1}$) are plots of q (or X/M) versus C , where X is the amount of sorbate on shale (in μmoles) and M is the mass of shale (in grams).

Single-Solute Data

The plots generated from the single-solute data are given in Figures 32-36. The data for Phenol (Figure 33) is a compilation of two replicates. The third replicate had growth in some flasks, and

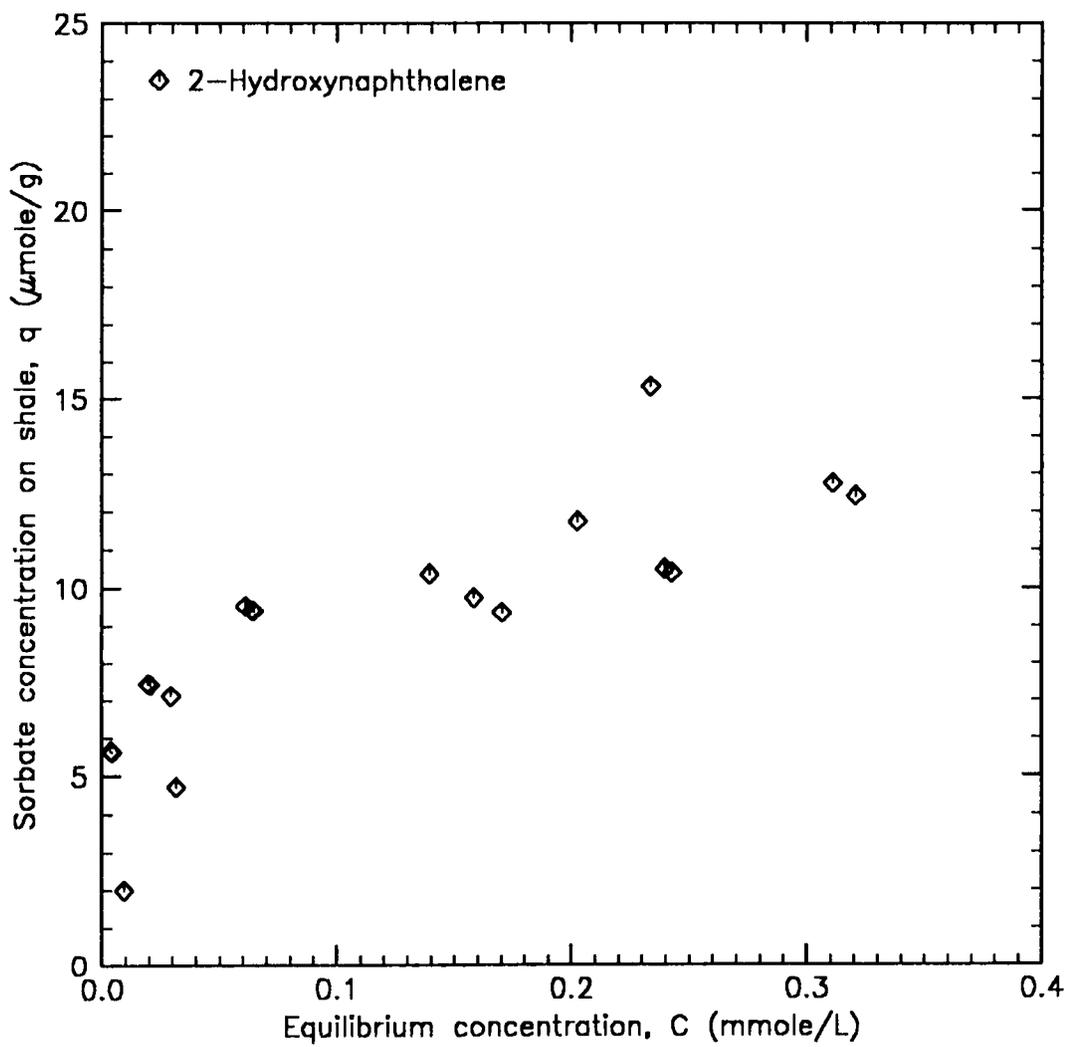


Figure 32. Single-solute isotherm for 2-Hydroxynaphthalene

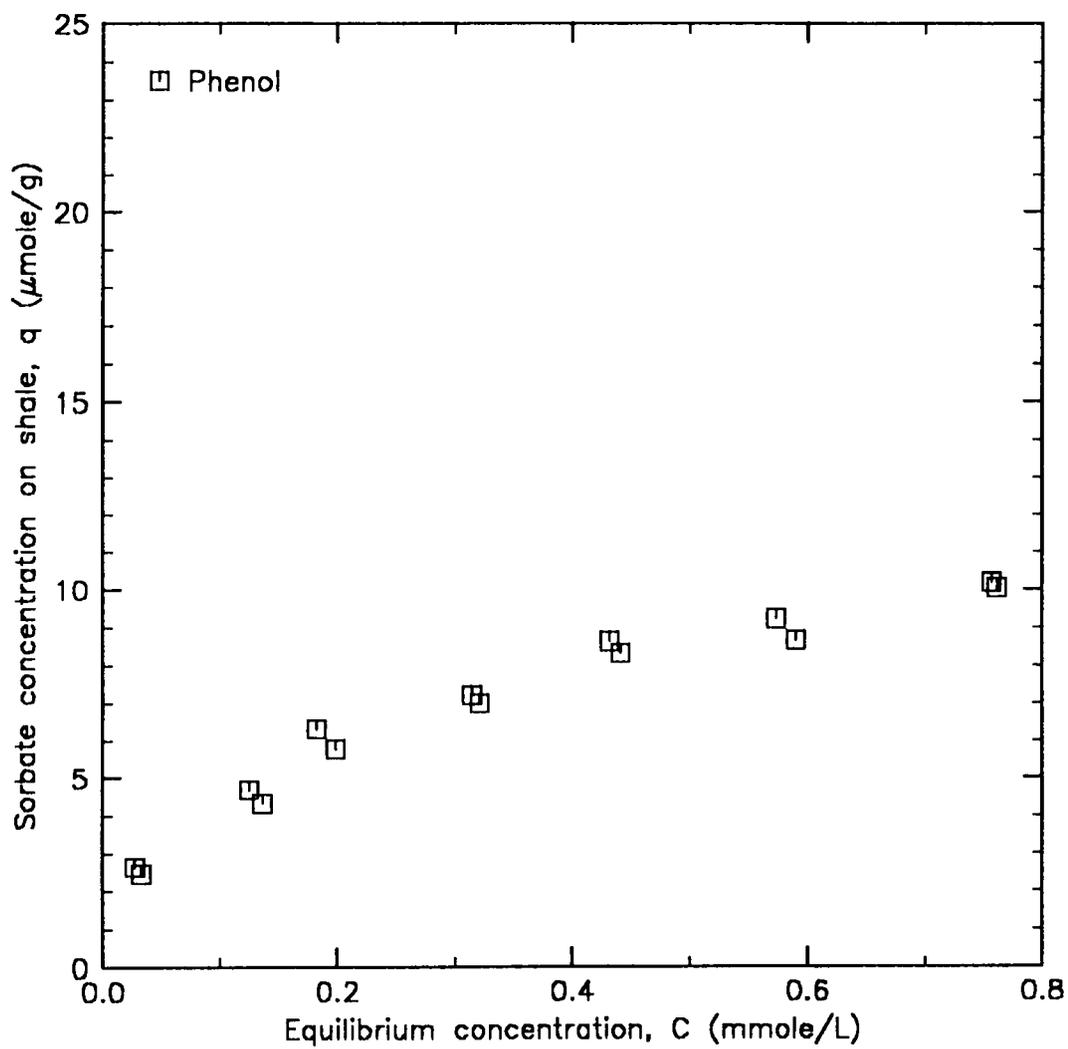


Figure 33. Single-solute isotherm for Phenol

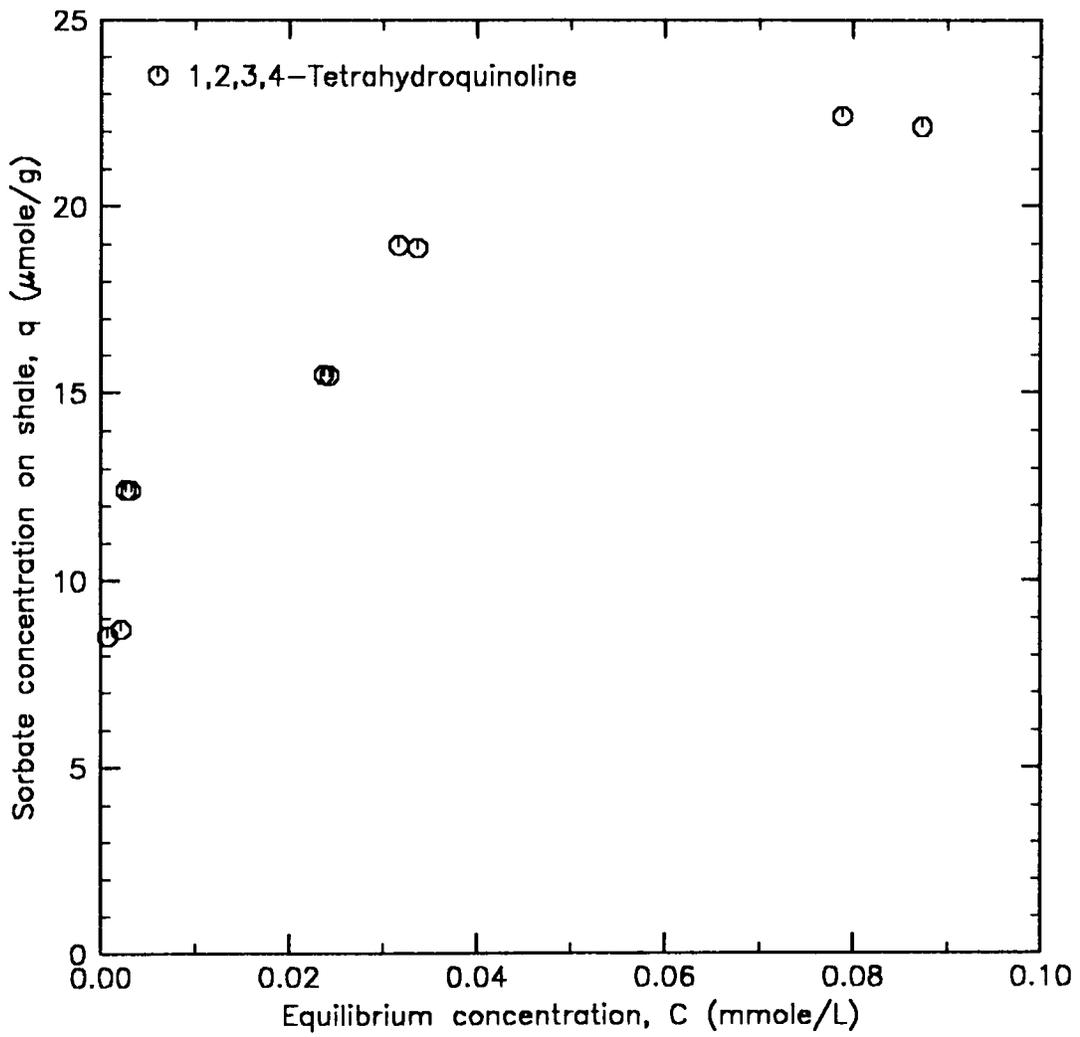


Figure 34. Single-solute isotherm for 1,2,3,4-Tetrahydroquinoline — results of two replicates

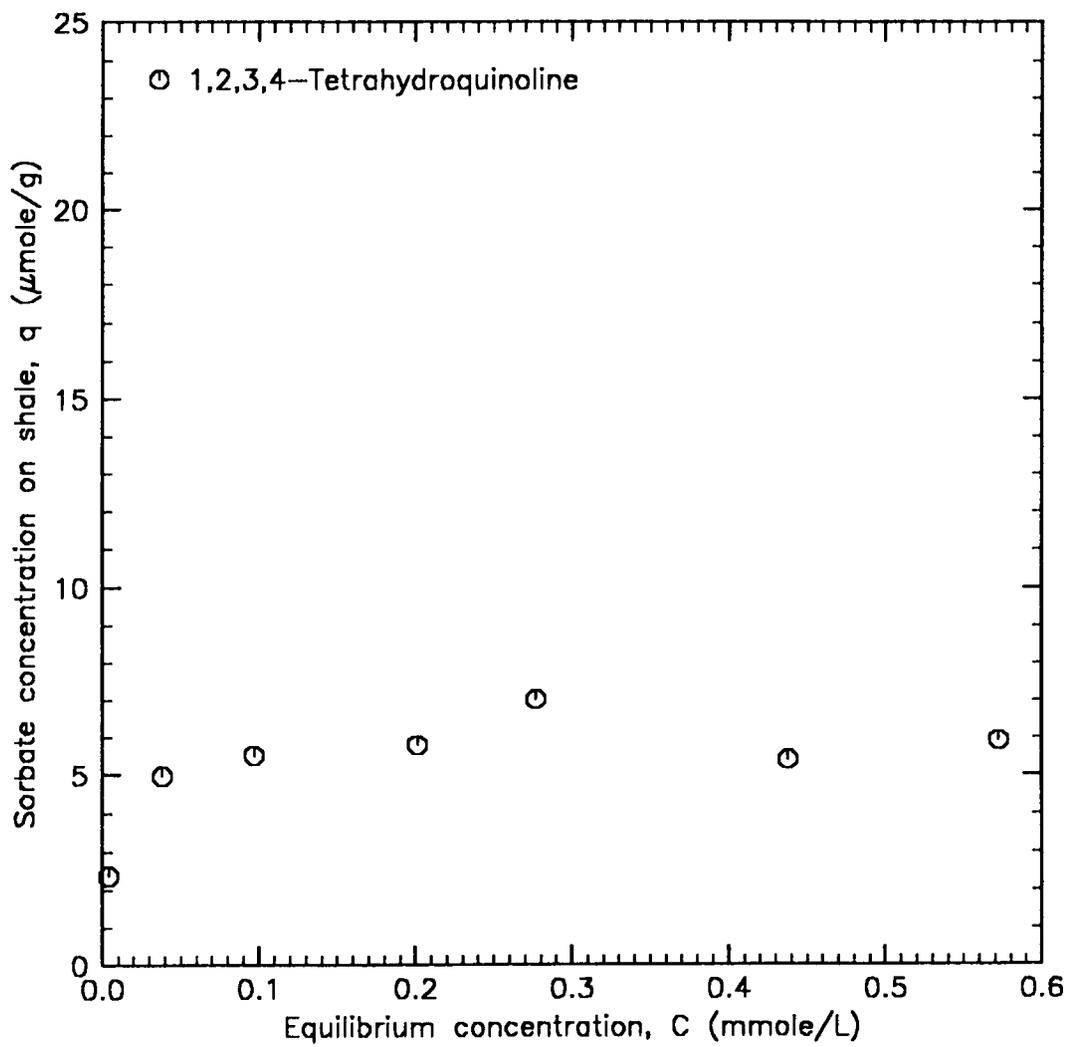


Figure 35. Single-solute isotherm for 1,2,3,4-Tetrahydroquinoline — first replicate

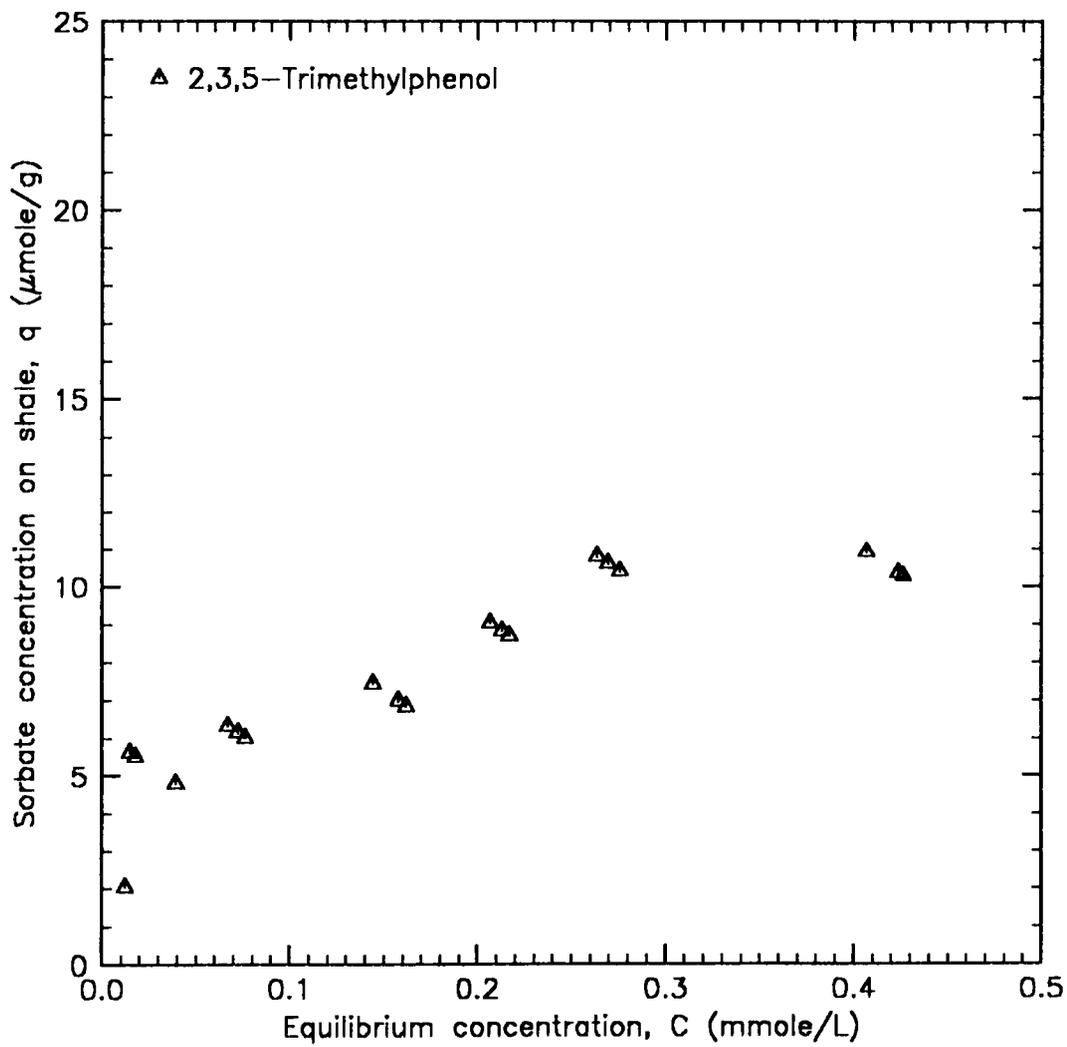


Figure 36. Single-solute isotherm for 2,3,5-Trimethylphenol

the equilibrium concentrations were low. For this reason it was thought best to not use the data from that replicate.

The plot for 1,2,3,4-Tetrahydroquinoline (Figure 34) is also a compilation of the data from two replicates. One replicate (the first one — shown in Figure 35) had final concentrations that were drastically different from the other two replicates. It is difficult to explain why the first replicate gave such different results from the other two replicates. The pH values of the three replicates were in the same general range, and not close to the pK_a value for 1,2,3,4-Tetrahydroquinoline, so the differences could not be due to the ionized form vs. the un-ionized form being in solution. The first replicate (Figure 35) results show that the shale surface was saturated with THQ at a relatively low sorbate concentration (q) of about $5 \mu\text{mole}\cdot\text{g}^{-1}$, whereas the other two replicates show the shale being capable of taking up nearly $23 \mu\text{mole}\cdot\text{g}^{-1}$. The duplicated results of the two replicates that agreed are perhaps more believable, not merely because they agree but because THQ has a nitrogen atom in one of its rings, and it is felt that this would result in the compound having a greater propinquity for interacting with the surface of the shale. Unfortunately the groups present on the surface of the shale are not known, but from the compositional analysis of the spent shale (see Table 19) it can be seen that a significant amount of organic matter (organic carbon = 2.8 wt. %) is present. Therefore, there is reason to believe that there would be chemical groups present on the surface that would be capable of reacting with the compound in solution. However, this does not explain why the THQ in the first replicate did not behave in a similar fashion. Another reason, perhaps, that gives a greater credibility to the data of the two replicates that agree is that THQ has the highest pK_a value of the four compounds, and therefore should be the compound with the lowest solubility at neutral pH values. TP has a pK_a value that is comparable to THQ, but the difference in sorption ability (as opposed merely to solubility) could be due to the nitrogen atom in THQ. On the other hand, THQ has been reported to be 'soluble' (Table 46), although the source did not provide a value for solubility. In view of the fact that there was a discrepancy, and that for the reasons given above the data from the two replicates that agreed were more justi-

fiable, it was thought better to leave out the replicate that did not agree with the other two from further analysis.

As is standard for the plotting of isotherm data, only those data points that resulted in non-zero equilibrium concentrations were plotted. Normally, one replicate should have provided seven data points (eight flasks minus the control). However, in some cases, sorption was either complete, or — more likely — the final concentration was too low to measure on the HPLC. This is the reason that fewer data points than might be expected to appear on certain figures.

The range of the vertical axis of all four plots has been kept the same to facilitate the comparison of the data. As far as possible, the horizontal axes of the plots were kept to the same scale. However, 1,2,3,4-Tetrahydroquinoline was sorbed to such a great extent — i.e., so little was left in solution — that the horizontal scale for Figure 34 is an order of magnitude lower than that for the other plots.

Besides the scatter apparent in the HN data, the other data were quite well-behaved. Perhaps three features should be noted. First, the point at which the trend in the data would intersect with the abscissa. The higher this intersection point, the greater the amount sorbed of that component. From these figures the observation can be made that the order for sorption (from lesser to larger amount) would be Phenol < TP < HN < THQ. One other feature is the almost vertical distribution of the data points at low concentrations. This can be noticed in the plots for HN, THQ and TP, but not for Phenol, and is most evident for HN. These points seem to indicate that a segmented data fit, with a straight-line segment to fit the low-concentration data, might be appropriate. This is a characteristic of the isotherms of substances that are favorably adsorbed. This feature will become more apparent in some of the binary sorption isotherms. It is not so conclusively present in these plots and segmented lines are not drawn.

A final feature to note from these plots is the sorbate concentration at which the data points become level. That sorbate concentration would indicate the sorptive capacity of the sorbent. The

shale has similar sorptive capacities for Phenol, HN and TP ($\sim 10\text{-}12 \mu\text{mole}\cdot\text{g}^{-1}$), but twice that amount for THQ ($\sim 22 \mu\text{mole}\cdot\text{g}^{-1}$).

Bisolute Data

There are six combinations of two possible with four compounds. All six combinations were studied. The results of the bisolute experiments with Phenol and HN are shown in Figure 37. Those data points where the equilibrium concentration was non-zero for both components are plotted.

It is apparent that the range of equilibrium concentrations is not the same for both Phenol ($0.05\text{-}0.9 \text{mmole}\cdot\ell^{-1}$) and 2-Hydroxynaphthalene ($0.0\text{-}0.4 \text{mmole}\cdot\ell^{-1}$). This is due to the fact that the compounds sorb differently. In any one flask the initial concentration of the compounds was the same in terms of $\text{mg}\cdot\ell^{-1}$. The molecular weights of three of the four compounds (HN, THQ and TP) were similar, therefore this would lead to approximately the same initial molar concentration in each flask. The final concentrations, though, were different. This makes a plot of the type shown in Figure 37 difficult to interpret at best. One problem is that one has no way of knowing which data point on the HN curve, corresponds to, for example, the rightmost data point on the Phenol curve. In the particular experiments of the current study, since both initial concentrations were the same, the data point pairs are in general ordered from left to right, but this is not true in all cases, and certainly is not easy to discern. There are some points in the middle ranges of the HN curve where it would be impossible to tell the pairing of the data without looking at the original data sheets. This method of presentation is, therefore, erroneous and can lead to wrong conclusions or inferences if one were to look at the data in this fashion without knowing the pairing. Curves of q versus C in the literature are generally drawn for a constant C for one of the two solutes, and the data are either interpolated from experimental results, or the experiments are conducted in such a manner that the C of one of the two solutes is kept constant. As will be seen shortly, this captures a limited portion of the entire concentration domain.

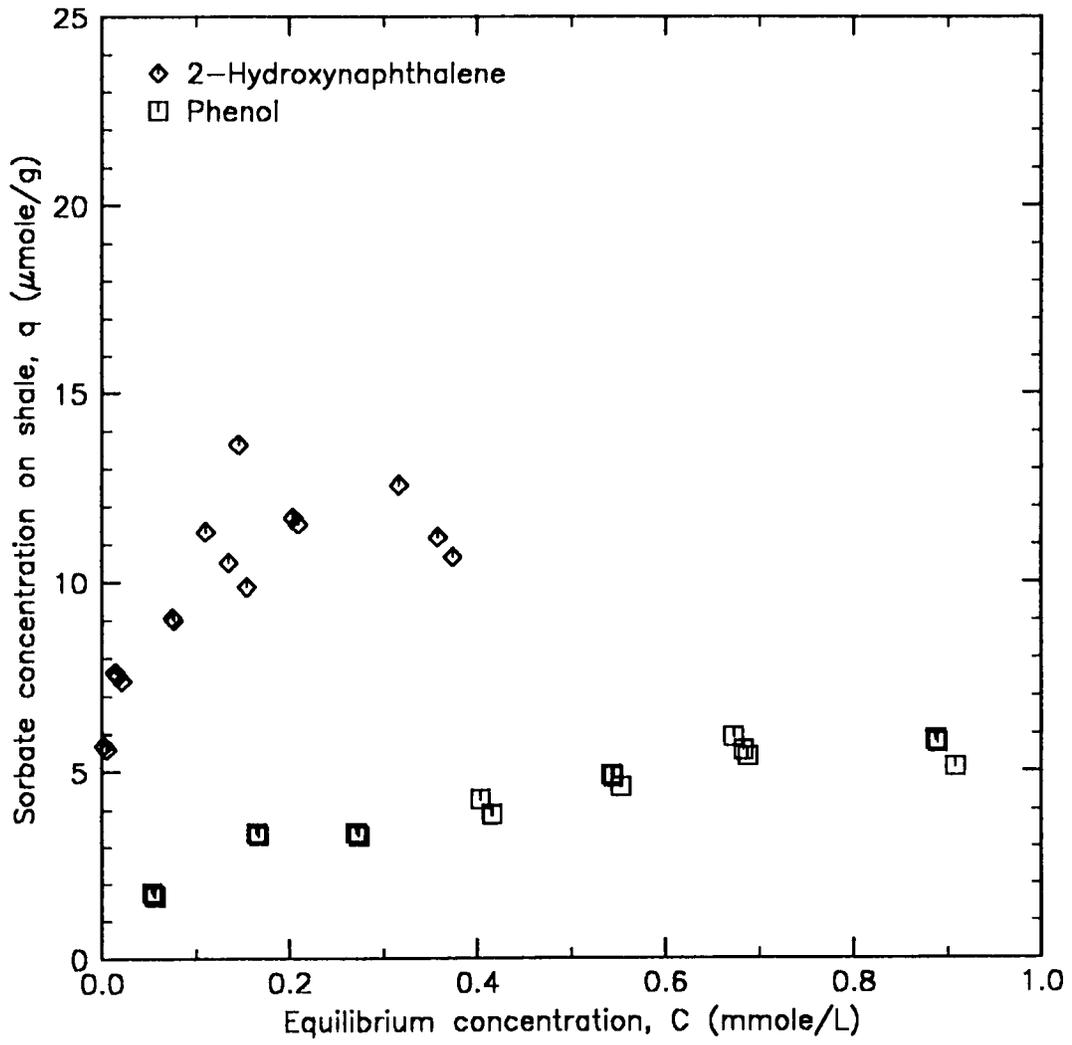


Figure 37. Bisolute isotherms of 2-Hydroxynaphthalene and Phenol

The data from bisolute experiments were, therefore, plotted using a three-dimensional (3D) representation. These results are shown in Figures 38 through 43. The SAS system (SAS Institute, Cary, NC) was used to generate the plots. There are some peculiarities related to the limitations of the 3D plotting procedure. One of these is that it is not possible to control the range of the x- and the y-axis. SAS determines the range based on the actual data. This leads to the odd axis numbering in most cases. This fact must be borne in mind when examining the plots. The fact that not all the axes start at 0.0 should also be noted. The range of the z-axis can be specified, and this has been done for all these plots. The x- and the y-axis represent the concentrations of the solutes, and the z-axis represents the q for each solute. It is important to note in this method of data representation that the q for any one combination of equilibrium concentrations is firmly linked to the position of the combination in the x-y plane. This is necessary in order to see clearly the relationship of the q s and the equilibrium concentrations. The equilibrium concentrations are the independent variables and the sorbate concentration on shale is the dependent variable. When this type of representation is compared to that in Figure 37, it becomes apparent why the method of Figure 37 is wrong. The two-dimensional representation essentially collapses the x- and y-axes of the 3D representation into one axis, and the spread of the data on the x-y plane is lost. If, for example, combinations of equilibrium concentrations were chosen such that the entire x-y area in Figure 38 were covered, then a surface representing q would be developed for each solute. When collapsed to the two-dimensional representation of Figure 37 this surface would result in data points spread over the whole area of the plot.

One drawback of the 3D representation is that it is more difficult to read, specially when the points are toward the front corner of the plots. However, they clearly show the trends of the data. For example, look at Figure 41. The data lie essentially along the front-to-back diagonal. The molecular weights of the two components in this case — HN (144.17) and THQ (133.19) — are quite close to each other, and hence the initial concentrations in $\text{mole}\cdot\ell^{-1}$ would be approximately equal for each flask (since each flask had equal initial concentrations, in $\text{mg}\cdot\ell^{-1}$, of the two solutes). If the sorbability of both the compounds were identical in competition, then all the data would lie

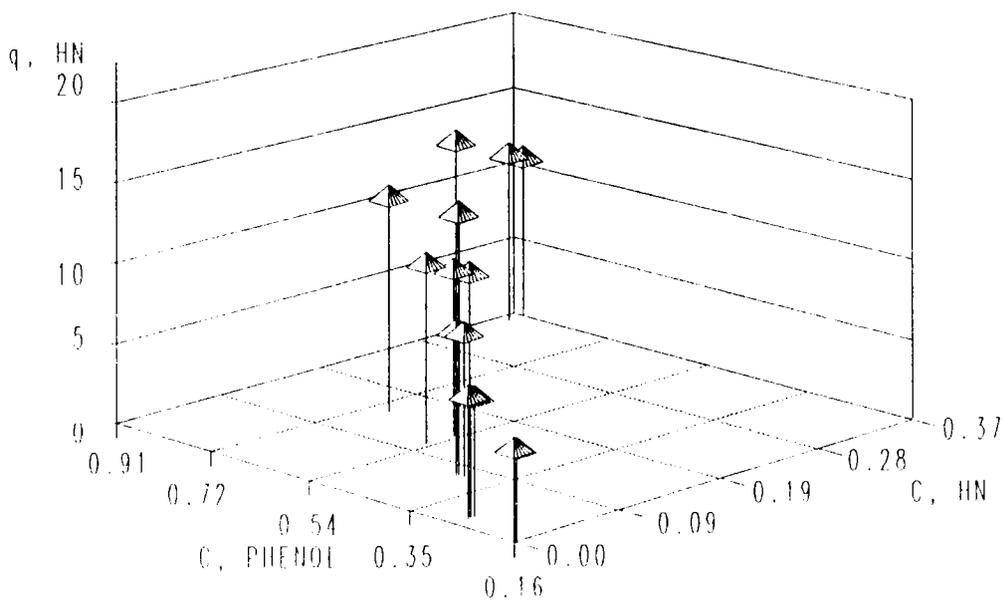
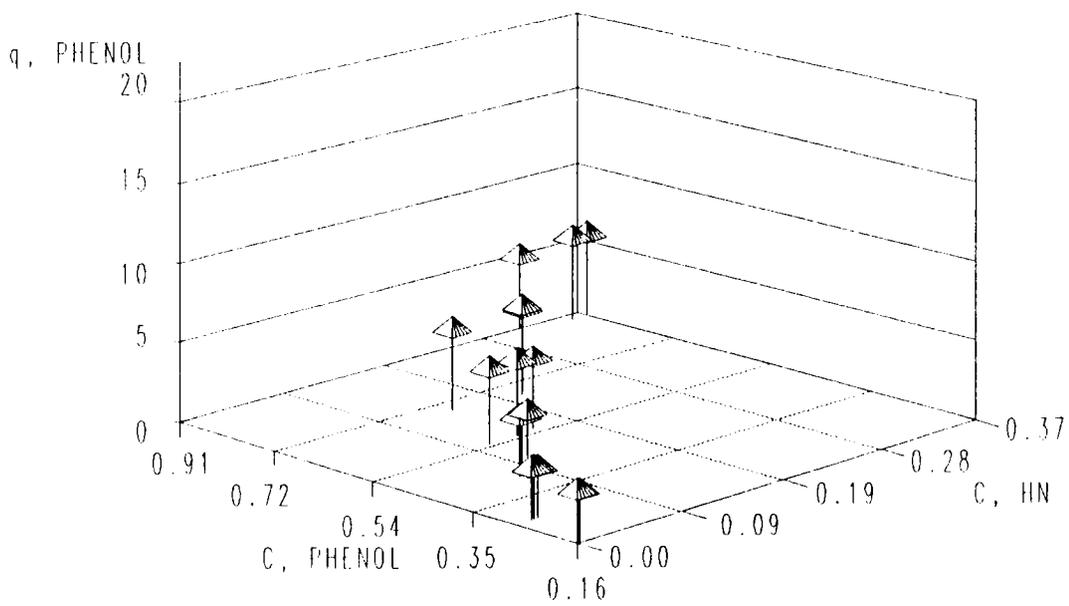


Figure 38. Three-dimensional representation of data from bisolute sorption experiment with Phenol and 2-Hydroxynaphthalene: C in $\text{mmole}\cdot\text{l}^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

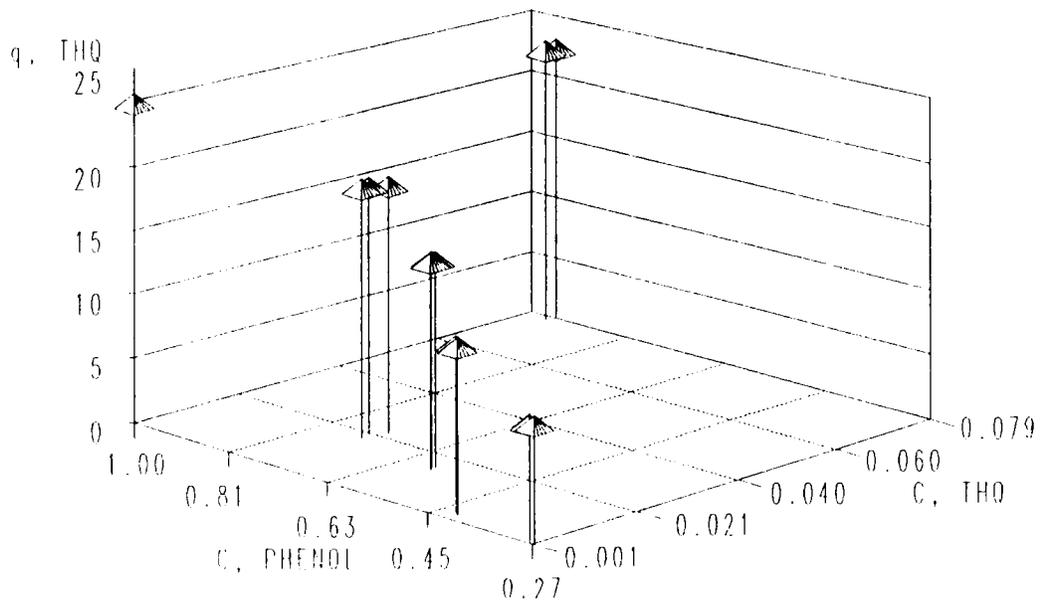
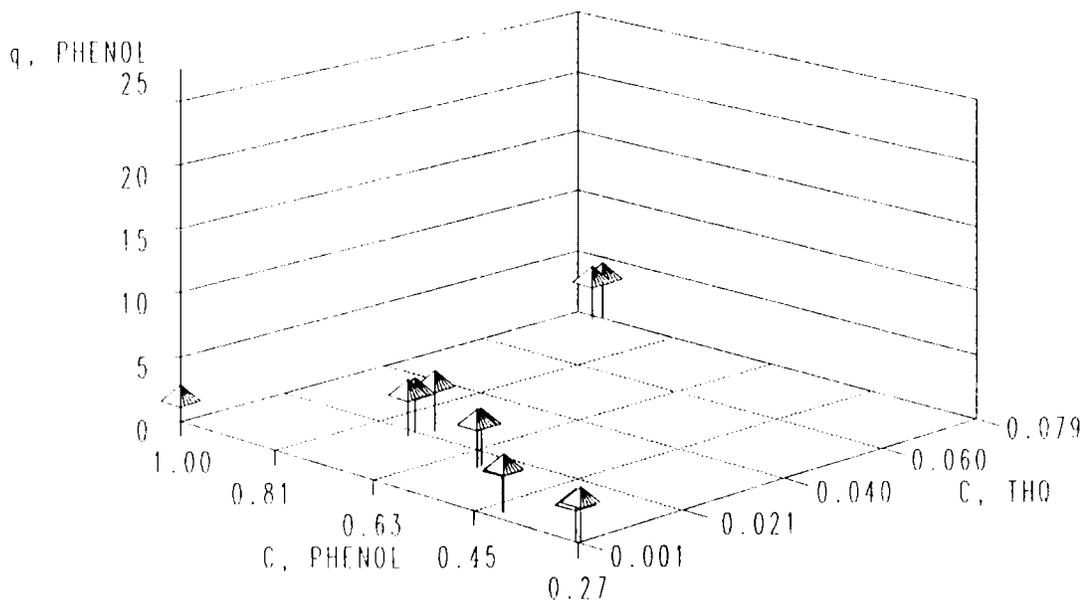


Figure 39. Three-dimensional representation of data from bisolute sorption experiment with Phenol and 1,2,3,4-Tetrahydroquinoline: C in $\text{mmole}\cdot\ell^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

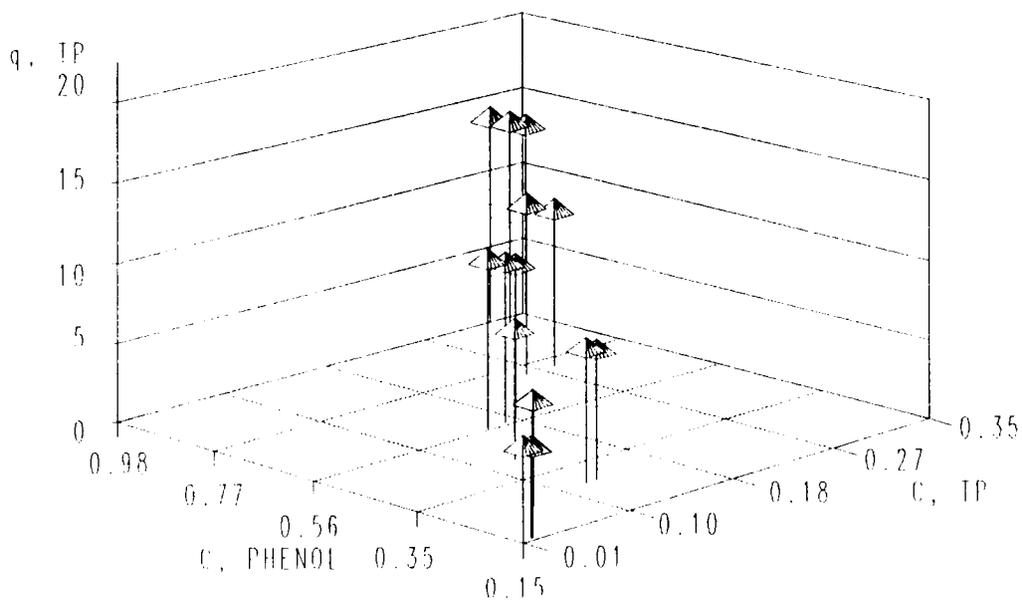
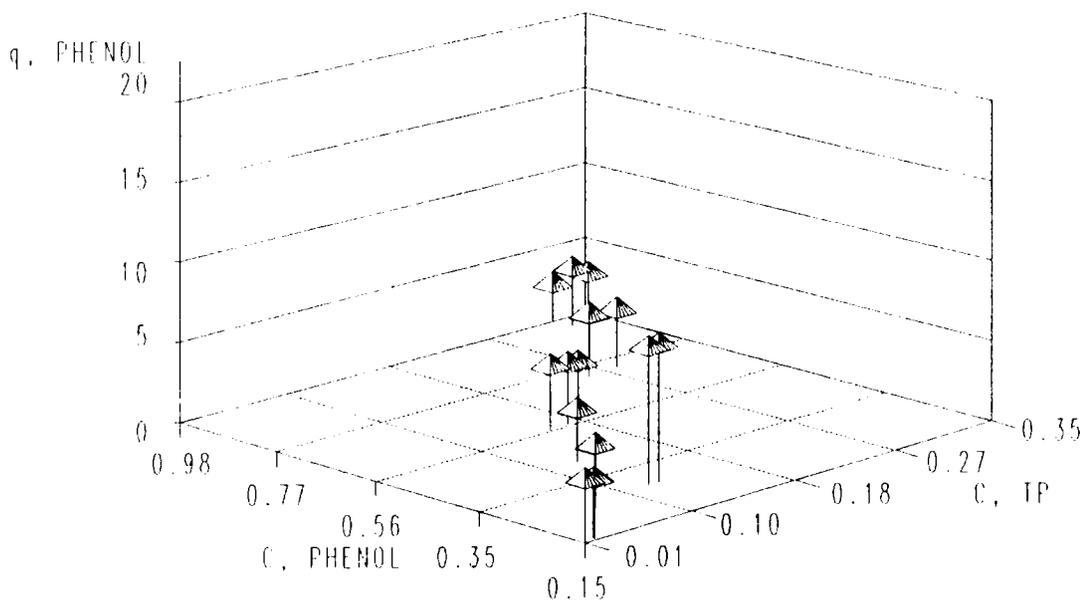


Figure 40. Three-dimensional representation of data from bisolute sorption experiment with Phenol and 2,3,5-Trimethylphenol: C in $\text{mmole}\cdot\ell^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

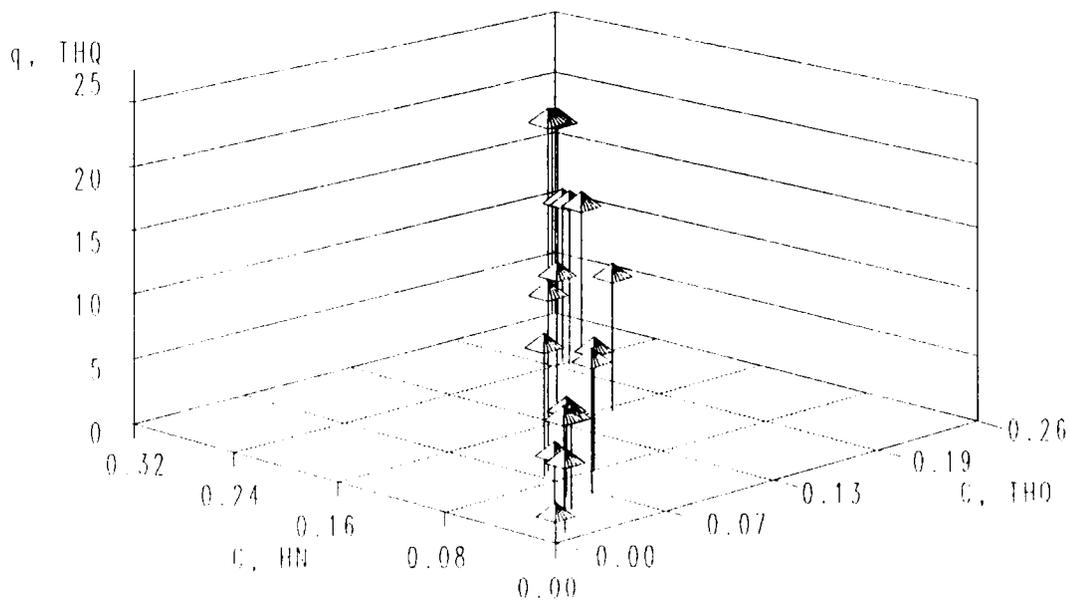
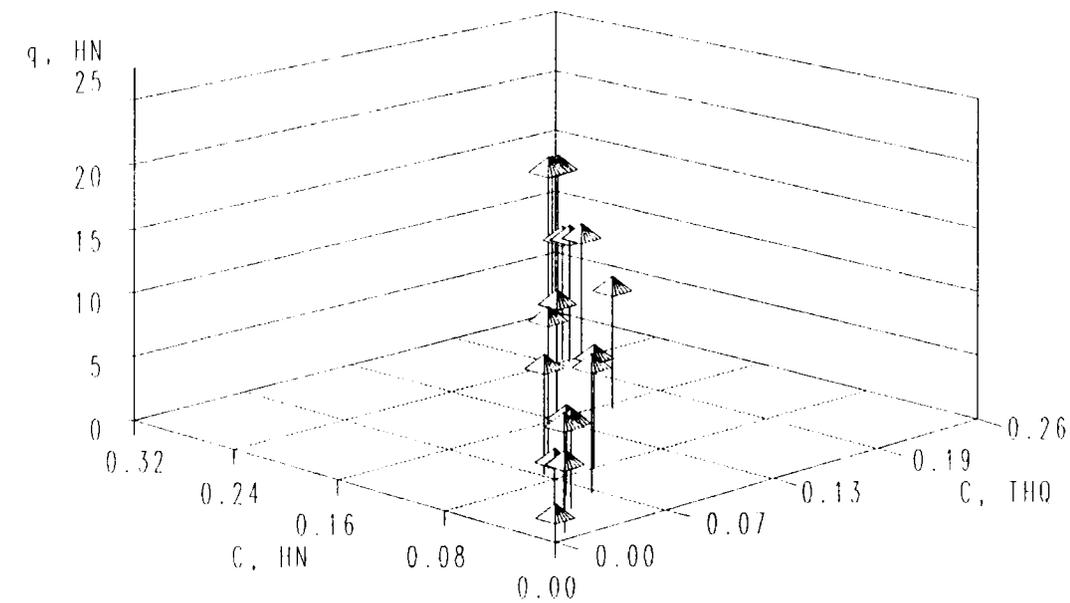


Figure 41. Three-dimensional representation of data from bisolute sorption experiment with 2-Hydroxynaphthalene and 1,2,3,4-Tetrahydroquinoline: C in $\text{mmole}\cdot\ell^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

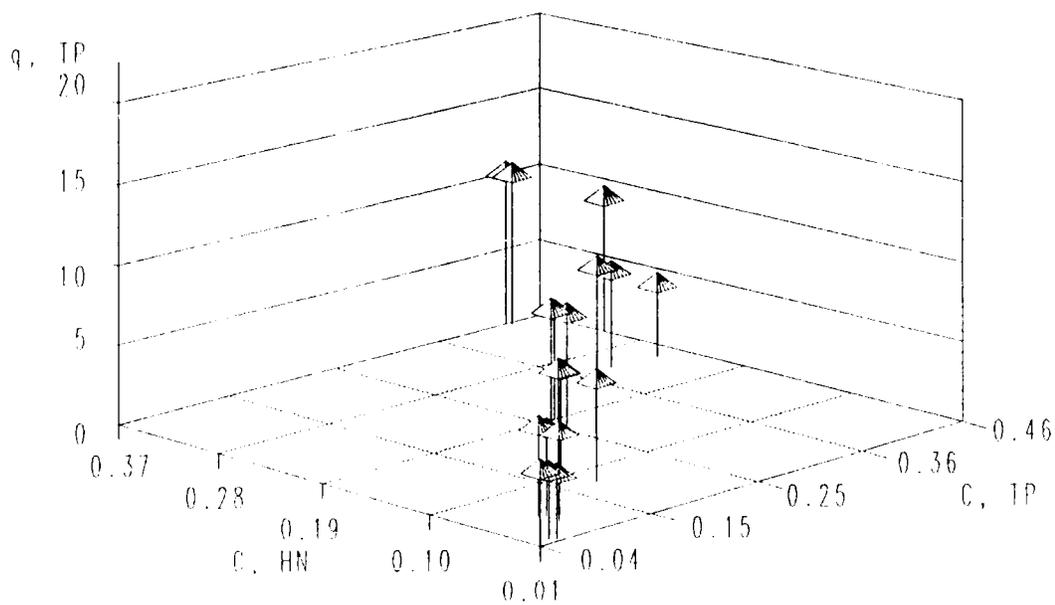
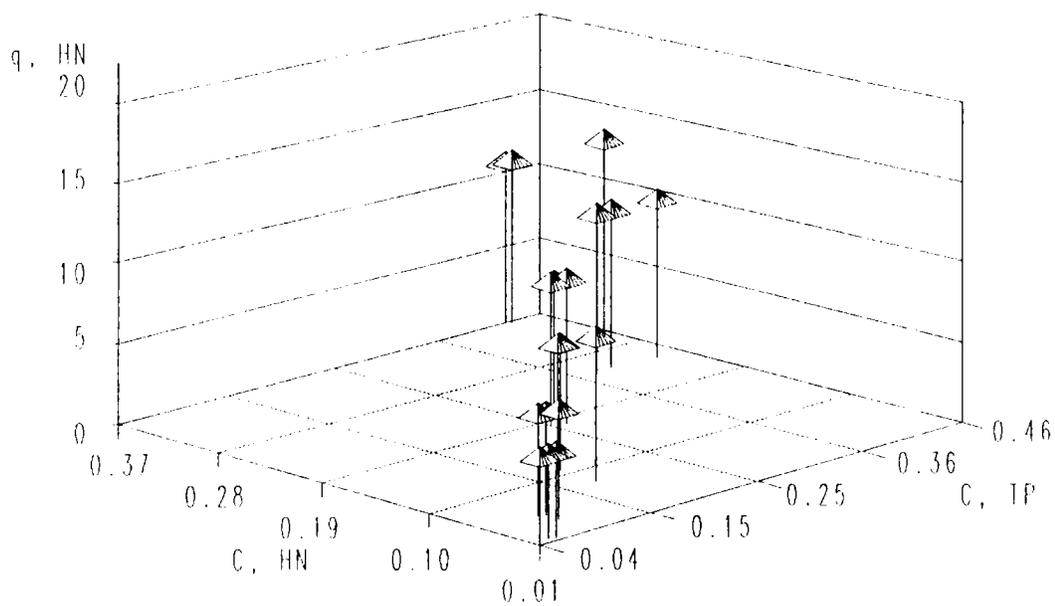


Figure 42. Three-dimensional representation of data from bisolute sorption experiment with 2-Hydroxynaphthalene and 2,3,5-Trimethylphenol: C in $\text{mmole}\cdot\ell^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

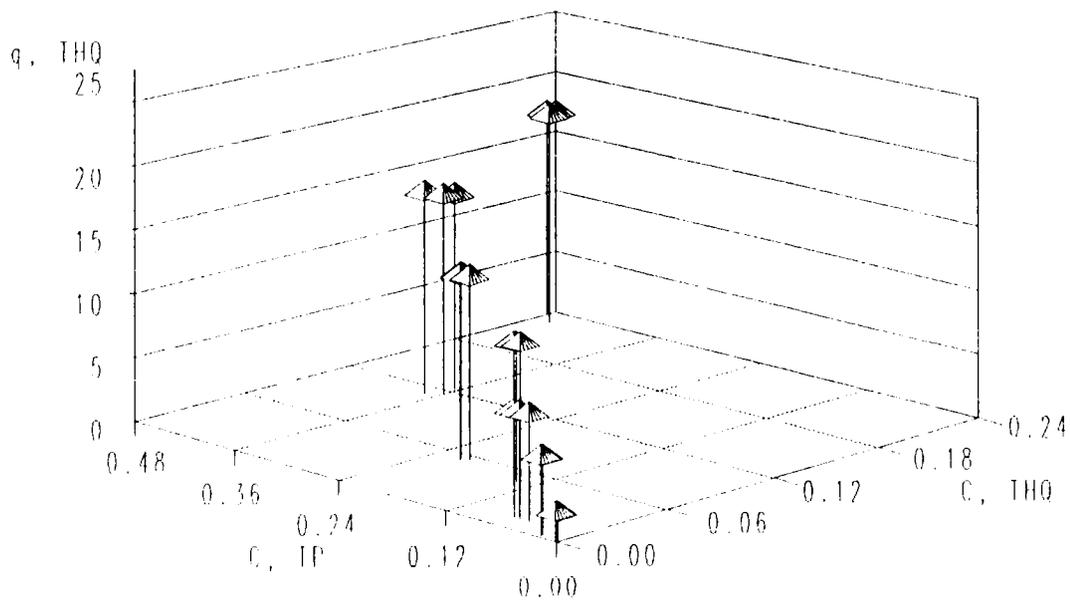
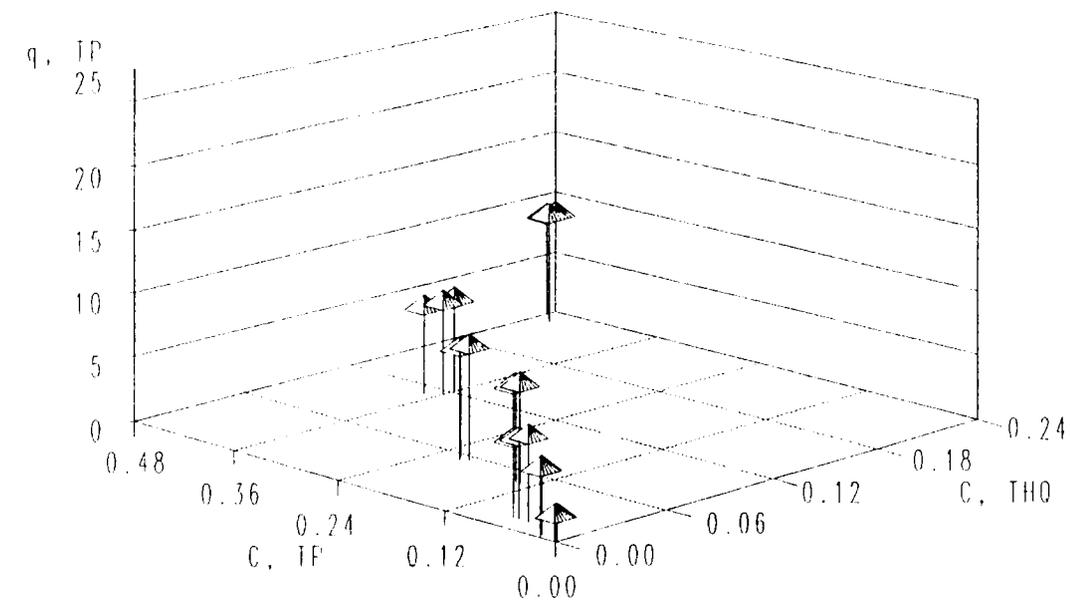


Figure 43. Three-dimensional representation of data from bisolute sorption experiment with 2,3,5-Trimethylphenol and 1,2,3,4-Tetrahydroquinoline: C in $\text{mmole}\cdot\ell^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

exactly along the diagonal. The data in Figure 41 lie approximately along the diagonal, and this would lead to the conclusion that the two compounds have approximately similar sorbabilities when in competition with each other. However, the starting concentrations of THQ were a little higher (because its molecular weight is a little lower), and the concentration axis for THQ in Figure 41 extends to $0.26 \text{ mmole}\cdot\ell^{-1}$, whereas that for HN extends to $0.32 \text{ mmole}\cdot\ell^{-1}$. Therefore, a correction must be made to the above statement about the data lying on the front-to-back diagonal. It should be the 45° diagonal on the x-y plane, and not the front-to-back visual diagonal. This problem with visualizing the diagonal arises due to the lack of control over the range of the axes. This point is brought to the reader's attention because the other 3D plots shown have quite different ranges.

The z-axis range for both plots in each of the 3D figures has been kept the same to facilitate easier comparison. Returning again to Figure 41, imagine the 45° diagonal. Also, remember the fact that the initial molar concentrations of THQ in the flasks were higher than those of HN (because THQ has a lower molecular weight). If the concentration axes in the figure were replaced with axes representing the initial molar concentrations, then the data points would show a concave curve with respect to the concentration axis of THQ. (To indicate what concave and convex mean in this regard, the trend of the data in Figure 38 are convex with respect to the HN axis and concave with respect to the Phenol axis.) Therefore, if the competitive sorbabilities of the two compounds represented in Figure 41 were identical, then one would expect the data to follow the same concavity. However, as can be seen in the figure, the data lie above the 45° diagonal. This indicates that the sorbability of THQ is higher than that of HN, and this is indicated by a comparison of the values of q given in the two stacked plots. The reader may wonder why it was necessary to go into the extensive discussion of concavity and convexity when a comparison of the maximum values of q for the two plots would indicate the same result. In this author's opinion, it is a little easier to visualize the 45° diagonal and the expected concavity or convexity and make a comparison than it is to decide based on the values of q , since the starting molar concentrations were not exactly equal.

In any case, either method could be used for the purpose. The results from the other bisolute experiments can now be looked at and analyzed.

The bisolute experiment with Phenol and 2-Hydroxynaphthalene (Figure 38) shows that HIN is significantly favored over Phenol (q values of between 10-15 for HIN, against $\sim 5 \mu\text{mole}\cdot\text{g}^{-1}$ for Phenol). The results for the bisolute experiment with Phenol and 1,2,3,4-Tetrahydroquinoline (Figure 39) show a similar trend, as does the bisolute experiment with Phenol and 2,3,5-Trimethylphenol (Figure 40). In all three experimental situations where Phenol is present with the other three compounds, then, the other compounds are favored over Phenol. In fact, in the case of the Phenol and THQ bisolute experiment, THQ is very highly favored over Phenol.

There is one data point in the experiment with Phenol and THQ (Figure 39) that is unexpected in the context of the initial concentrations. This is the data point at $C_{\text{THQ}} = 0.001$ and $C_{\text{Phenol}} = 1$. The occurrence of the data point at that particular position is surprising because the initial concentrations of that particular flask were not in any way different from the sequence of the rest of the data points. This behavior is probably due to the heterogeneity of the shale. Heterogeneity could perhaps lead to sites in the particular fraction of shale in the sample being more receptive to the sorption of THQ and less receptive to the sorption of Phenol. As stated earlier in this document, this could be linked to the presence of the nitrogen in THQ reacting more favorably with the surface. Since this was essentially the only data point that behaved in this fashion, it is not possible to form any sort of general inference. On the other hand, the data point may be due to experimental error where the initial concentrations for that flask may not have been made up correctly upon dilution. In view of this, it is sufficient to remark upon the anomaly without appending too much significance to it.

Figure 42 shows that both HIN and TP have approximately equal sorbabilities ($q \approx 5\text{-}10 \mu\text{mole}\cdot\text{g}^{-1}$), although HIN sorbs to a slightly greater extent, and Figure 43 indicates that THQ is favored over TP. An observation should be made here that it would be incorrect to compare the values of q directly, without specifying where they lie on the x - y plane. It might seem that the

maximum values of q could be indicative of the sorbabilities. They are, but they must be coupled with information as to the position they occupy on the x-y plane. Merely taking the maximum value from the whole range would not account for the interactions. This can be seen on Figure 39, where, by the simple procedure of determining the maximum value from the whole range, one would determine that the maximum value of q for Phenol is $\sim 4.5 \mu\text{mole}\cdot\text{g}^{-1}$, whereas that for THQ is $\sim 25 \mu\text{mole}\cdot\text{g}^{-1}$. But, a look at the figure shows that these would be taken, for Phenol, from the data points in the rear corner, and, for THQ, from the data point in the left corner. This, obviously, is incorrect.

Overall, Phenol is the least competitive compound (since it sorbs to much lesser extents than the other three compounds), followed by TP, HN, and THQ, which is the most competitive compound. These results agree with the results from the single-solute experiments — the order of sorbabilities is the same, but understandably the extent is somewhat different for each compound. These changes were a reduction of $\sim 50\%$ for Phenol, and $\sim 0\text{-}23\%$ for THQ, and an increase of $\sim 40\%$ for TP against Phenol and a decrease of $\sim 10\%$ against THQ, and essentially no change for HN. The lack of change may indicate that HN is more strongly sorbed than the other components or that there are some sites on the shale that have an exclusive affinity for HN. Therefore, single-sorbate experiments could be used to predict the order of sorbabilities, but some kind of modelling would have to be done to predict the diminished extent of sorption.

Tri-component Isotherms

Only one tri-component experiment (with no replicates) was performed. This was because it was thought that the tetra-sorbate experiments were more important, and that tri-sorbate experiments would not add any new information, and that this procedure would also reduce the number of trials. This argument could be stated for the tetra-component experiments, too, but since there were four compounds used in the study it was more important to do some experiments with all four compounds present simultaneously.

It is not possible to treat the data from experiments that consisted of more than two solutes in a manner similar to that for the bisolute experiments, since it would require a four- or five-dimensional representation. It was felt that the way to approach this would be to revert to the method of presenting a plot of q versus C with the caution to the reader to be careful in the interpretation. The section that immediately follows the presentation of the tetra-component data explains a method of reducing the data for better interpretation.

The data for the trisolute experiment are shown in Figure 44. Since all the data points for Phenol lie below that for the other two compounds, it can safely be said that Phenol sorbs to a lesser extent than the other two compounds. The maximum q is of the order of $5 \mu\text{mole}\cdot\text{g}^{-1}$, whereas in the single-component experiments it was of the order of $10 \mu\text{mole}\cdot\text{g}^{-1}$. When comparing HIN and TP, it is not so easy to reach a conclusion. It appears that HIN is consistently sorbed better than TP, and this would be expected from the results of the single-component and the bisolute experiments. But, because the ranges of the values of q for the two curves overlap, it is not easy to tell which data points are related (i.e., belong to any one experimental condition). It may well be that there is a crossover. One way to tell if the trends shown are true is to look at the numbers. The raw data of the experiments are given in Appendix B. The columns of numbers whose names begin with 'DEL' are directly related to the values of q . The first column in the data, labelled 'C', is the initial concentration of each of the components in the flask. As can be seen in the table for the three-component experiment, the columns of numbers for HIN and TP (i.e., the columns headed DELHIN and DELTP) show an increasing trend. However, the column for Phenol (headed DELP) does not show a uniformly increasing trend. Nevertheless, if one compares the trends between the uptake of HIN and that of TP, it can be seen that HIN is taken up in larger amounts than TP.

In general, the data from this one tri-component experiment reinforces the conclusions drawn earlier about the relative amounts of the compounds sorbed.

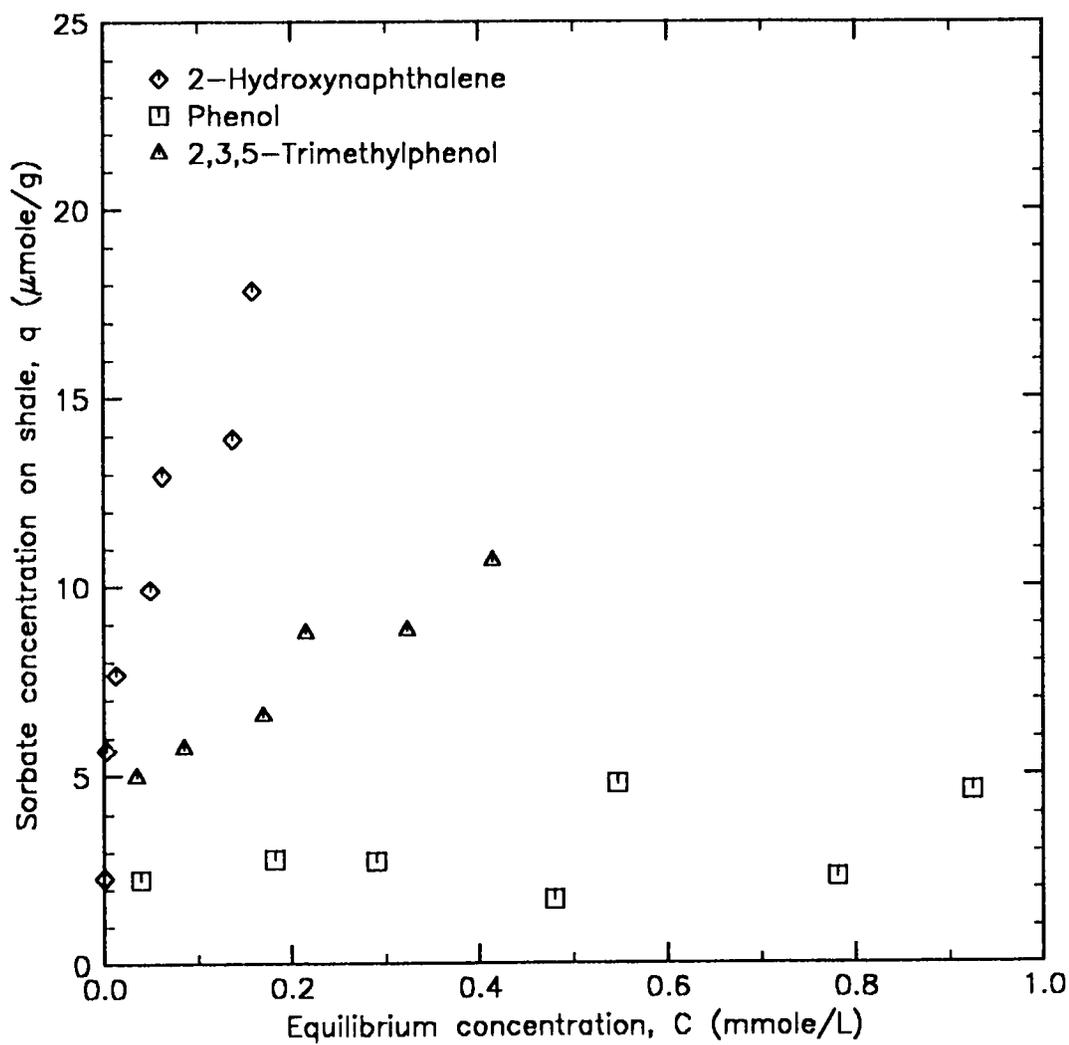


Figure 44. Sorption isotherm data for tri-component mixture of 2-Hydroxynaphthalene, Phenol and 2,3,5-Trimethylphenol

Comparison of the Sorptive Potentials of the Phenolic Compounds

A comparison of the sorptive potentials of the phenolic compounds — HIN, Phenol and TP — is interesting. It has already been seen that HIN sorbs better than TP, and that TP sorbs better than Phenol. The tendency is for the larger molecule to sorb to a greater extent. Perhaps a better way to view this is to say that the structurally more complex molecule is probably less soluble. The solubility of TP is not known, but the solubility of Phenol (as reported in Table 46) is $82 \text{ g}\cdot\ell^{-1}$ at 15°C , and that of HIN at 25°C is $750 \text{ mg}\cdot\ell^{-1}$. The $\log K_{ow}$ values for Phenol, HIN and TP given in the table are 1.46, 2.84 and 3.44, respectively. The value of 3.44 for TP would indicate that TP would be less soluble than HIN. As this author observed while performing the experiments, TP is indeed much less soluble than HIN. However, an actual solubility value was not determined. On the other hand, the steric structures of the three compounds may play a converse role. One would expect that Phenol, being the least-complicated sterically, would sorb more than HIN or TP, since both these ‘cast a larger shadow’, so to speak, and would not be able to diffuse into micropores to the same extent. This would be true provided the sorbent had most of its surface area in internal pores that were fine enough and tortuous enough to cause some hindrance to the diffusion and subsequent sorption of these compounds, and also if the potential for reaction between the molecule of a compound and the surface were the same for all three compounds. It will be seen later (in the section on batch experiments on the GAC) that the pore volume argument did not hold even for the GAC, which has quite a bit more internal pore capacity than the shale. In fact, since shale has such a low surface area, it can be conjectured that its internal surface area due to pores is not high (in comparison with the external surface area) as it is with GAC. On the other hand, the presence of methyl groups on the TP probably increases the interactions between TP and the surface, thereby increasing its potential for sorption.

Another factor is that TP is more branched than Phenol, and should therefore sorb preferentially because the potential for interaction between the branch groups and the surface is greater. HIN, on the other hand, is the next step up on the homologous series from Phenol. Normally, sorption

increases as a homologous series is ascended [123]. Actually, this is due to the increase in complexity and lesser polarization when a series is ascended, provided that the pore factors are not controlling the sorption — i.e., the pores are equally accessible to all the compounds being tested.

Tetra-Component Isotherms

The first replicate of the four-component experiment was performed with the range of initial concentrations being 0-100 mg·ℓ⁻¹. However, in order to more completely describe the isotherms of the four components, the concentration range was increased to 0-250 mg·ℓ⁻¹, with more flasks also added at the lower concentrations. The results from the first two replicates are given in Figures 45 through 48, since the data from these two replicates were essentially duplicated. The results from the third replicate did not agree with those from the first two replicates. These are given in Appendix C.

As for the case of a replicate of the single-solute isotherm of THQ, there is no easy way to explain the difference in agreement between the three replicates. The third replicate cannot be discounted, because the trends shown in the figures appear reasonable. However, judging from the results of the mono-, bi- and trisolute trials, it is felt that the two replicates that agree are more representative of the expected behavior. The largest sorbed amounts for each component are lower than those for the mono-, bi- and trisolute trials. However, recall from the earlier discussion about the presentation of multisolute data, and that there may be areas in the concentration domain of the four species where the third replicate may fit. A different kind of analysis presented in the next section would seem to indicate that this could be the case. Because no figure can be drawn that includes the four concentration axes and the individual q values (these would be five-dimensional plots), it was thought best to separate the replicates into two sets to avoid confusion.

It is difficult to conjecture a reason for this difference in behavior of the third replicate, especially the increased sorptive capacity demonstrated for each of the compounds. Perhaps there was growth

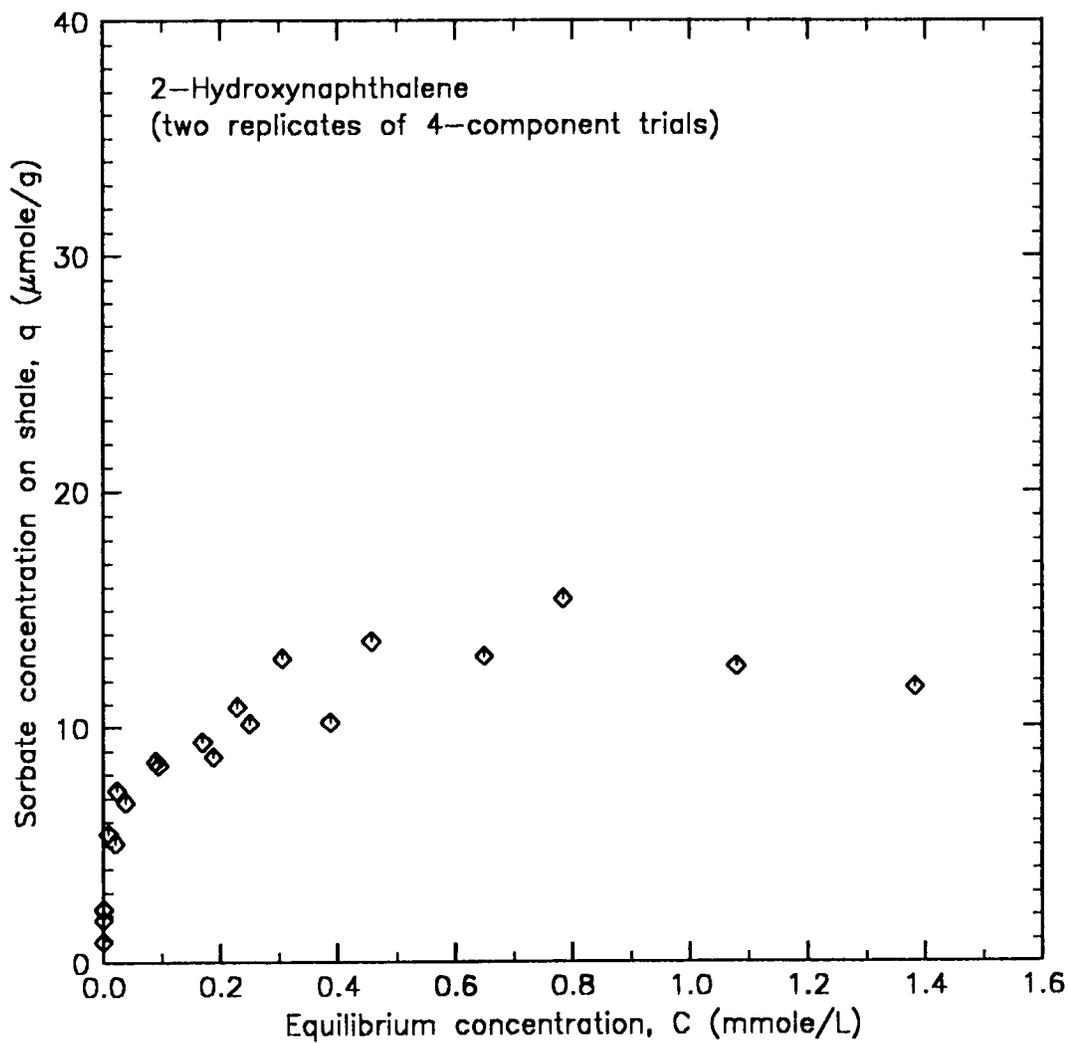


Figure 45. Isotherms of 2-Hydroxynaphthalene from first two replicates of tetra-sorbate trials

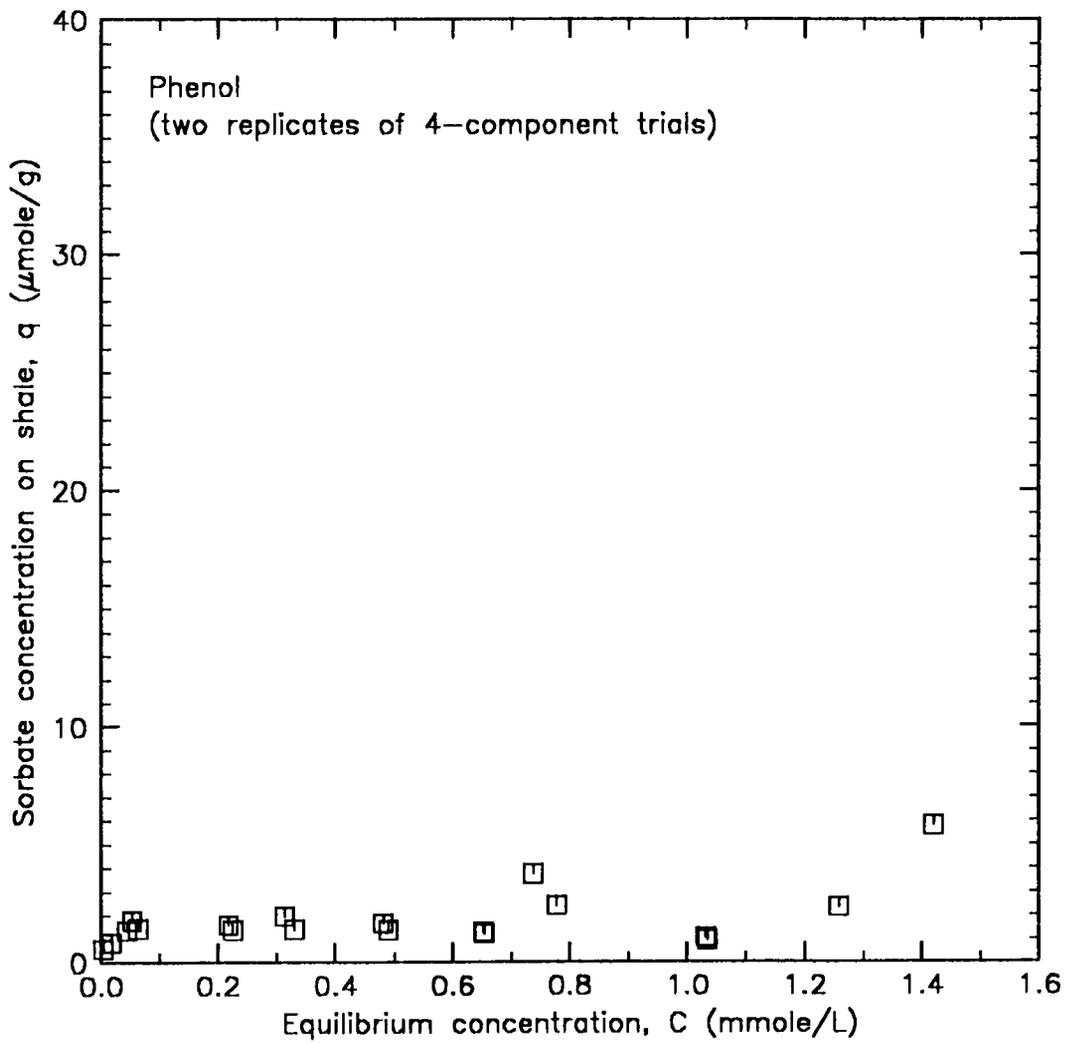


Figure 46. Isotherms of Phenol from first two replicates of tetra-sorbate trials

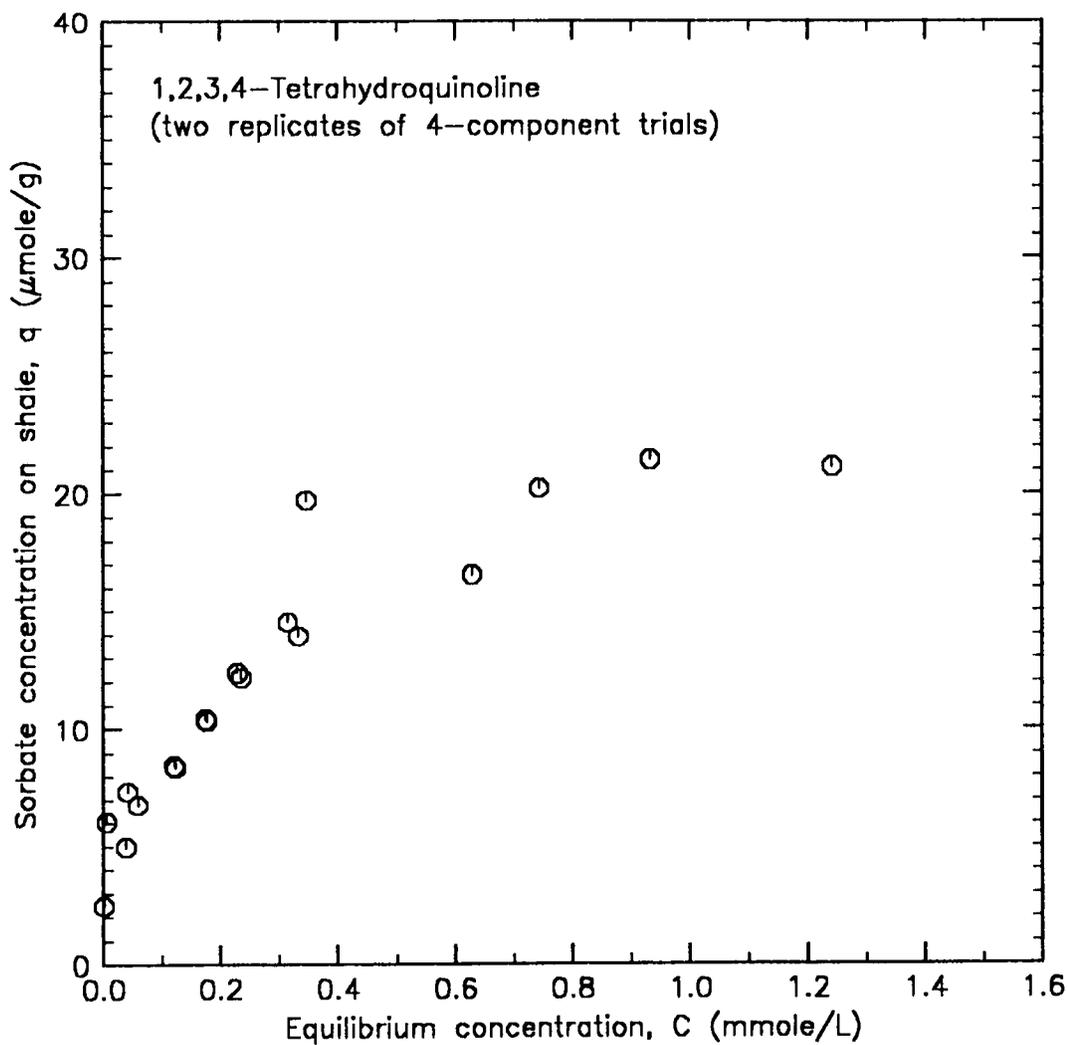


Figure 47. Isotherms of 1,2,3,4-Tetrahydroquinoline from first two replicates of tetra-sorbate trials

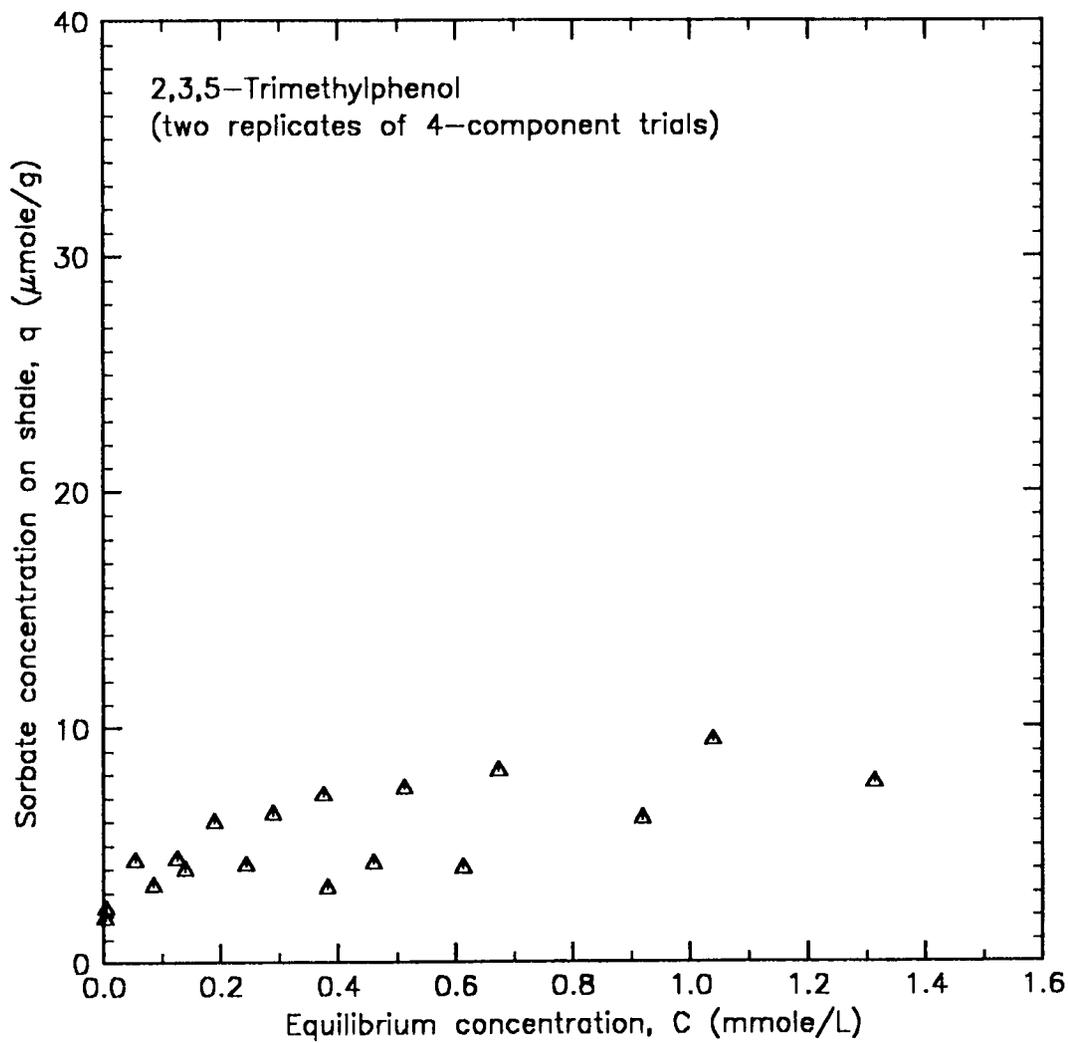


Figure 48. Isotherms of 2,3,5-Trimethylphenol from first two replicates of tetra-sorbate trials

in the flasks, but there was certainly no visual evidence of any. An effect of any growth is that the filterability of the liquid decreases dramatically, even when the growth can barely be discerned. No such loss in filterability was noticed. Yet another factor is that *all* the flasks showed the same trend (although this was less apparent in the flasks with lower initial concentrations, some of which did replicate the results of the second experiment), and therefore if there were any growth it would have had to be present in all flasks. Substantially the conditions for both experiments were identical, and yet there was a difference in the results. With that as a preamble, this author is at a loss to explain the behavior of this set of samples, besides mentioning that the data may fit in the domain of the tetra-component system.

The ranges of the axes for both sets of four plots (Figures 45-48 and those in Appendix C) were kept the same to facilitate comparison. Again, it should be emphasized that the data are not necessarily ordered according to initial concentration. The raw data given in Appendix C show that inconsistent trends are associated chiefly with Phenol. That is, the DELP column does not show a strictly increasing trend with increasing C (the initial concentration column), and this holds true for all three replicates. The other three compounds essentially show an increasing trend.

The Characterization of Multicomponent Sorption by Means of the $\frac{q_i}{q_T}$ Ratio

As a means of characterizing the extent of sorption in multicomponent systems, the following ratio was used:

$$\alpha_i = \frac{q_i}{q_T} \quad (19)$$

where α_i is the defined ratio for the *i*th component, q_i is the concentration of the *i*th sorbate on the sorbent, and q_T is the total of all the q_i s in a particular flask (i.e., at one experimental condition).

The ratios were calculated for all the multisorbate experiments upon shale, and the mean values of the ratios ($\bar{\alpha}_i$) were also calculated. The sum of all ratios will equal 1, by definition. The difference in the numerical value of the ratios will be indicative of the differences in the sorbed amounts of each component. The means and standard deviations of the ratios for all multisorbate experiments are given in Table 47. In the last two tetra-component sets, the values of $\bar{\alpha}_i$ add up to 1.01 due to round-off.

The table contains three sets of computations of the $\bar{\alpha}_i$ values for the tetra-component experiments. The first set was computed by utilizing the data from all three replicates, the second set used the data from the first two replicates (the replicates that were indicated as agreeing in the previous section), and the third set of computations used the data from the third replicate (the replicate that did not agree with the other two). For the discussion that follows, unless otherwise indicated, the tetra-component set that will be referred to should be taken to mean the first set that includes the data points from all three replicates.

As is evident from the $\bar{\alpha}_i$ values for Phenol (which ranged from 0.11 to 0.33), Phenol sorbs to the least extent in all the multicomponent systems. In the bisolute systems, the fraction of Phenol on the surface is the same (0.32 as opposed to 0.33) when Phenol is in competition either with 2-Hydroxynaphthalene or 2,3,5-Trimethylphenol. However, when in competition with 1,2,3,4-Tetrahydroquinoline, the fraction of Phenol on the surface drops to 0.20, a decrease of 62%, indicating that 1,2,3,4-Tetrahydroquinoline provides greater competition than do either HN or TP. If THQ is compared with HN and TP, the fraction of THQ is essentially the same in both cases when the spread of the data, as indicated by the standard deviation, is considered (0.54 ± 0.021 when THQ is competing with HN, and 0.59 ± 0.060 when it is competing with TP). THQ sorbs to a larger amount than either HN or TP. If the 2-Hydroxynaphthalene and 2,3,5-Trimethylphenol system is considered, then HN is seen to sorb to larger amounts ($\bar{\alpha}_i = 0.56 \pm 0.037$) than TP ($\bar{\alpha}_i = 0.44 \pm 0.037$). It should be noted here that the standard deviation of the $\bar{\alpha}_i$ values for both components in a bisolute mixture will mathematically work out to the same value.

Table 47. Means and standard deviations of $\frac{q_i}{q_T}$ ratios for multicomponent experiments

Solute	Number of Points	$\alpha_i = q_i/q_T$	
		Mean	Standard Deviation
Bisolute Experiments			
Phenol	17	0.32	0.026
2-Hydroxynaphthalene		0.68	0.026
Phenol	15	0.20	0.055
1,2,3,4-Tetrahydroquinoline		0.80	0.055
Phenol	18	0.33	0.098
2,3,5-Trimethylphenol		0.67	0.098
2-Hydroxynaphthalene	19	0.46	0.021
1,2,3,4-Tetrahydroquinoline		0.54	0.021
2-Hydroxynaphthalene	18	0.56	0.037
2,3,5-Trimethylphenol		0.44	0.037
2,3,5-Trimethylphenol	21	0.41	0.060
1,2,3,4-Tetrahydroquinoline		0.59	0.060
Trisolute experiment			
Phenol	6	0.15	0.047
2-Hydroxynaphthalene		0.50	0.051
2,3,5-Trimethylphenol		0.35	0.018
Tetrasolute experiments			
<i>All replicates</i>			
2-Hydroxynaphthalene	29	0.32	0.036
Phenol		0.11	0.062
1,2,3,4-Tetrahydroquinoline		0.37	0.059
2,3,5-Trimethylphenol		0.20	0.037
<i>First two replicates</i>			
2-Hydroxynaphthalene	18	0.33	0.033
Phenol		0.08	0.044
1,2,3,4-Tetrahydroquinoline		0.40	0.059
2,3,5-Trimethylphenol		0.20	0.040
<i>Third replicate</i>			
2-Hydroxynaphthalene	11	0.29	0.023
Phenol		0.17	0.046
1,2,3,4-Tetrahydroquinoline		0.33	0.023
2,3,5-Trimethylphenol		0.22	0.027

Therefore, it is seen that shale will sorb the least amount of Phenol in any bisolute mixture, and this fraction is no more than 0.33 ± 0.098 . Whereas THQ is quite highly favored over Phenol (0.80 against 0.20), it is not so highly favored over HN and TP. Finally, HN is favored over TP. In terms of amounts sorbed, then, the order from least favored to most favored is Phenol < TP < HN < THQ. This observation was made in the previous section on bisolute isotherms, but it is easier to see it here when the data are reduced to a fractional index ($\bar{\alpha}_i$), the values of which can be compared more readily than can the values of q since the values of q are spread over different combinations of C for the two components (i.e., on the x-y plane in the 3D plots shown earlier). The order of preference (in terms of sorbed amounts) is maintained in the trisolute and tetrasolute experiments.

A comparison between the three sets of values of $\bar{\alpha}_i$ computed for the tetra-component system shows some difference between the values derived from the first two replicates and those derived from the third replicate. The $\bar{\alpha}_i$ values for HN and TP are essentially the same (when the standard deviations are considered) between the set from the first two replicates and the set from the third replicate. However, the partitioning of amounts between Phenol and THQ is different (though still overlapping a little when the standard deviations are considered) in the two sets. In the last set derived from the third replicate, Phenol seems to be providing much better competition ($\bar{\alpha}_i = 0.17 \pm 0.046$, as opposed to $\bar{\alpha}_i = 0.08 \pm 0.044$). Understandably, then, the spread in the α_i values is greater for Phenol and THQ when the three replicates are combined into the first set reported in the table. However, it is felt that the combined set does represent the data in all three replicates. It was mentioned earlier that the third replicate may be related to the first two, though the equilibrium concentrations do not agree over the whole range, in that it could represent a different location in the complete domain of equilibrium concentrations. The $\bar{\alpha}_i$ values seem to indicate this, although the spread is quite large (specially for the $\bar{\alpha}_i$ value for Phenol in the combined set — 0.11 ± 0.062).

An attempt was also made to see if the tetra-component $\bar{\alpha}_i$ values (those derived from all replicates) could be used to estimate the bi- and tri-component $\bar{\alpha}_i$ values. The results of this estimation are

given in Table 48. The estimation was performed by taking the $\bar{\alpha}_i$ values of the relevant sorbates from the tetra-component system, adding them up, and then determining the values for the bi- or trisolute case. For example, for the bisolute Phenol and HIN case, the $\bar{\alpha}_i$ values of 0.11 and 0.32 were taken from the tetra-solute set (see Table 47). The sum of these was 0.43. Then, estimating the $\bar{\alpha}_i$ for Phenol in the bisolute system: $0.11/0.43 = 0.26$; and for HIN: $0.32/0.43 = 0.74$. The % difference between the estimated values and the original values is determined based on the original value, i.e., for Phenol in the example: $\frac{0.26 - 0.32}{0.32} \times 100 = -18.75$.

The differences between the original and estimated $\bar{\alpha}_i$ values were greatest for Phenol and TP, except for the bisolute system containing those two solutes. The % difference for the other components was generally around 10% or less, and in the case of HIN and THQ the estimated values exactly matched the originally calculated ones. It is not clear how this procedure might be used to estimate the equilibrium concentrations and the final sorbed concentrations from experiments that contain all solutes to experiments that contain combinations of the solutes. However, the estimation procedure can be useful in determining whether the sorptive behavior of the compounds (in terms of amounts sorbed) was consistent when moving from bisolute systems to systems containing more than two solutes. If, for example, a difference of 10-11% or less were taken to be sufficient for consistency, then HIN and THQ could be said to exhibit a consistent sorptive behavior across all systems of two and three components, whereas Phenol and TP exhibit consistency only in the case when they were together in a bisolute system (although TP did have an absolute % difference of less than 10% in the trisolute system). Dropping the criterion for consistency to 5-6% would eliminate most cases, however.

In addition to the above analysis, plots of α_i as a function of C_i (shown in Figures 49 through 54) were also made for the bisolute systems. Least square linear regression lines were drawn through the data contained in these plots.

These plots can be used, perhaps, to indicate whether the sorptive behavior of the study compounds is linked or not. The slope of the lines in Figures 49 and 53, for example, is close to zero, and the

Table 48. $\bar{\alpha}_i$ values estimated for bi- and trisolute systems from the tetrasolute values

Solute	$\bar{\alpha}_i$	$\bar{\alpha}_i$ (est.)*	% difference
Bisolute systems			
Phenol	0.32	0.26	-18.75
2-Hydroxynaphthalene	0.68	0.74	8.82
Phenol	0.20	0.23	15.00
1,2,3,4-Tetrahydroquinoline	0.80	0.77	-3.75
Phenol	0.33	0.35	6.06
2,3,5-Trimethylphenol	0.67	0.65	-2.99
2-Hydroxynaphthalene	0.46	0.46	0.00
1,2,3,4-Tetrahydroquinoline	0.54	0.54	0.00
2-Hydroxynaphthalene	0.56	0.62	10.71
2,3,5-Trimethylphenol	0.44	0.38	-13.64
2,3,5-Trimethylphenol	0.41	0.35	-14.63
1,2,3,4-Tetrahydroquinoline	0.59	0.65	10.17
Trisolute system			
Phenol	0.15	0.17	13.33
2-Hydroxynaphthalene	0.50	0.51	2.00
2,3,5-Trimethylphenol	0.35	0.32	-8.57

* Estimates based on tetra-component values (set of all replicates).

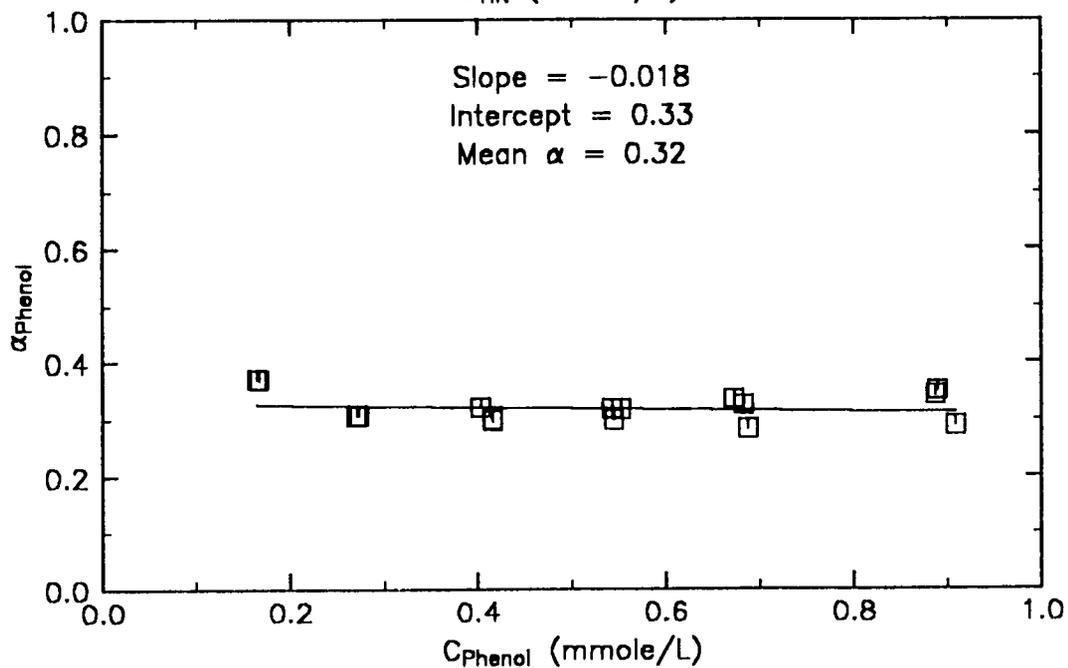
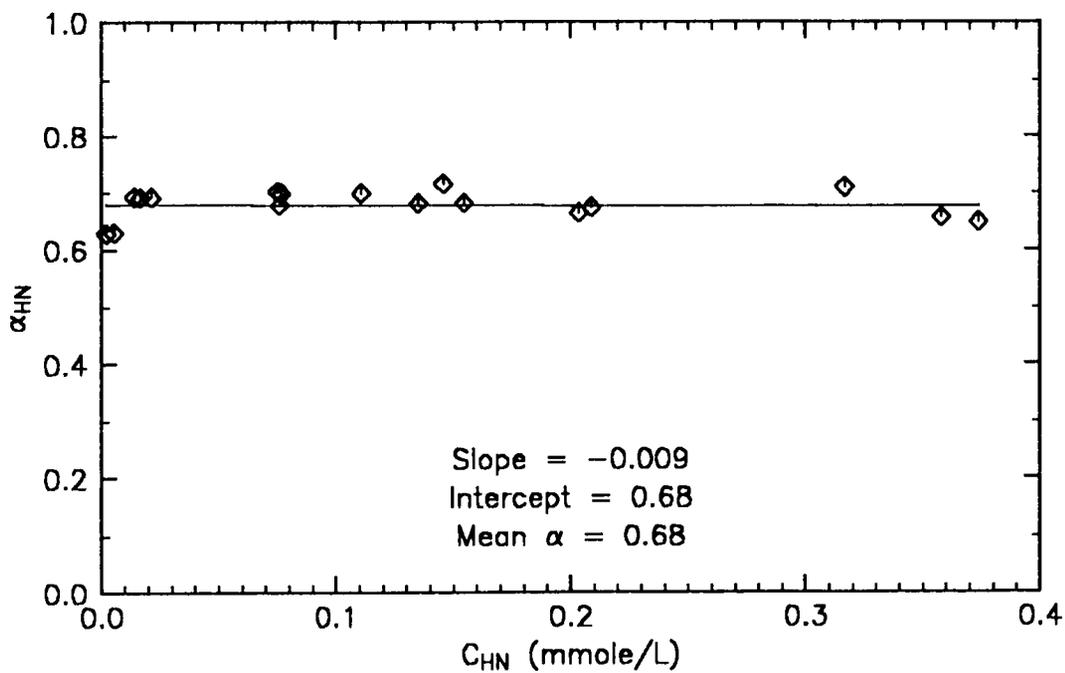


Figure 49. α as a function of equilibrium concentration for bisolute system containing Phenol and 2-Hydroxynaphthalene

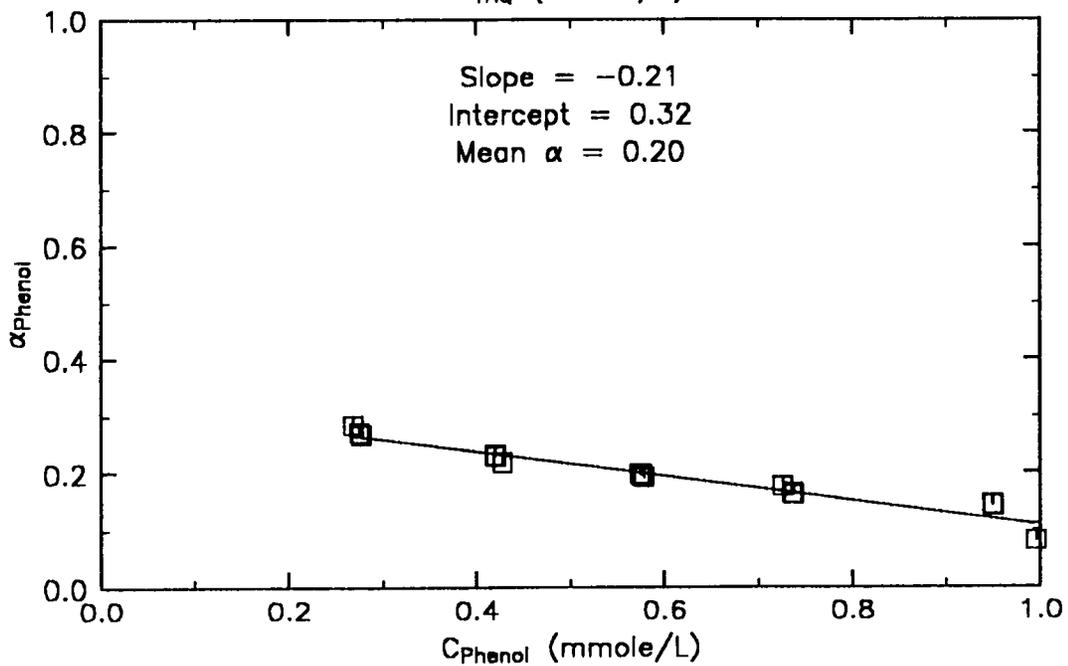
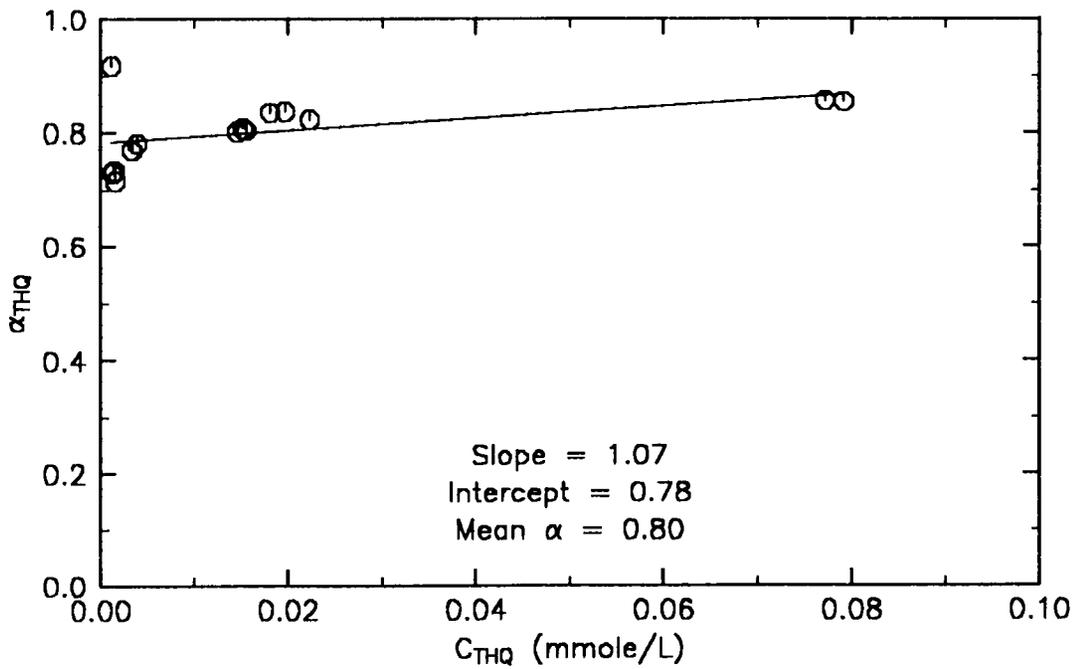


Figure 50. α as a function of equilibrium concentration for bisolute system containing Phenol and 1,2,3,4-Tetrahydroquinoline

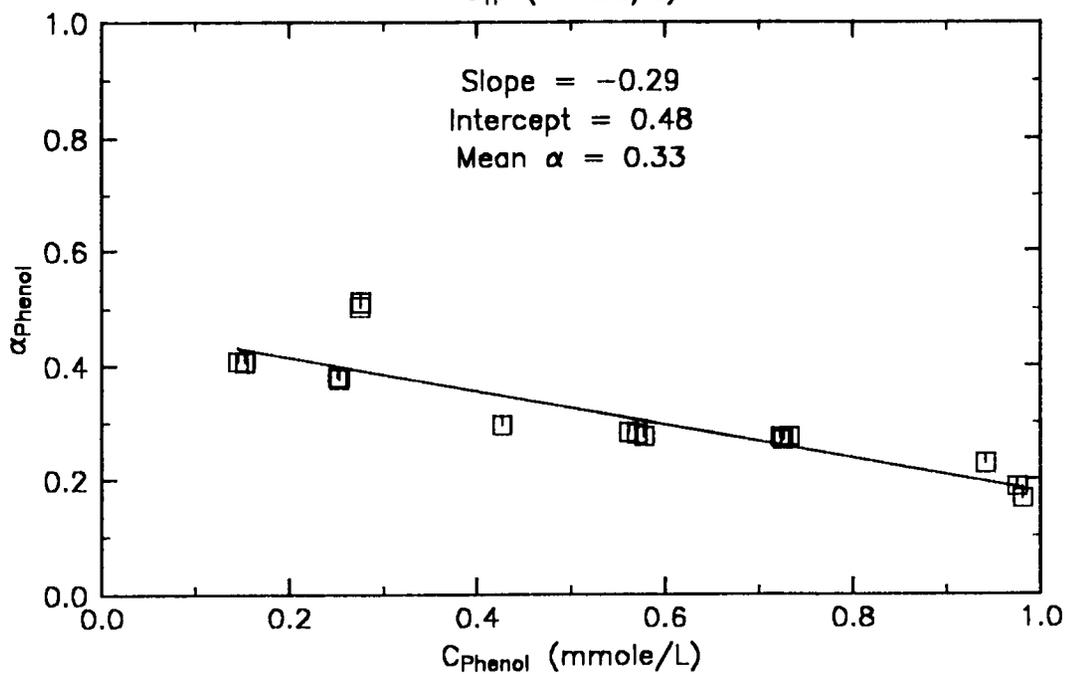
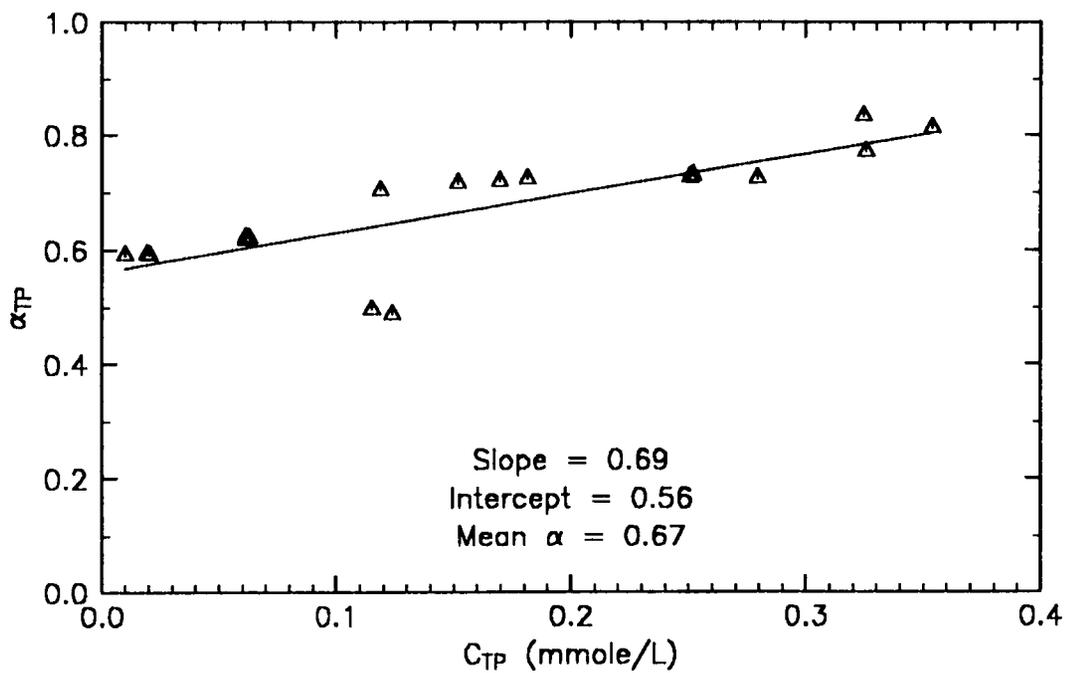


Figure 51. α as a function of equilibrium concentration for bisolute system containing Phenol and 2,3,5-Trimethylphenol

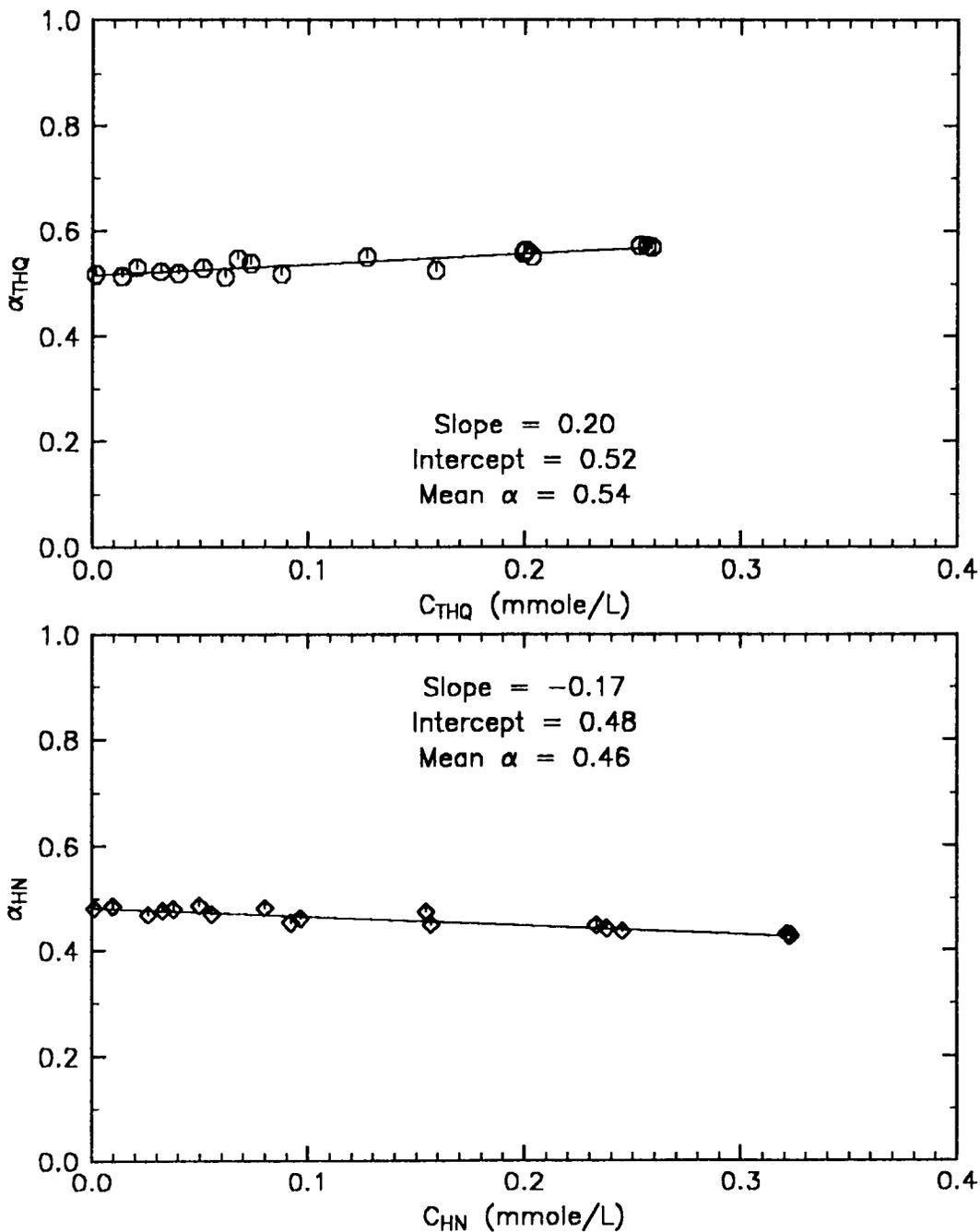


Figure 52. α as a function of equilibrium concentration for bisolute system containing 2-Hydroxynaphthalene and 1,2,3,4-Tetrahydroquinoline

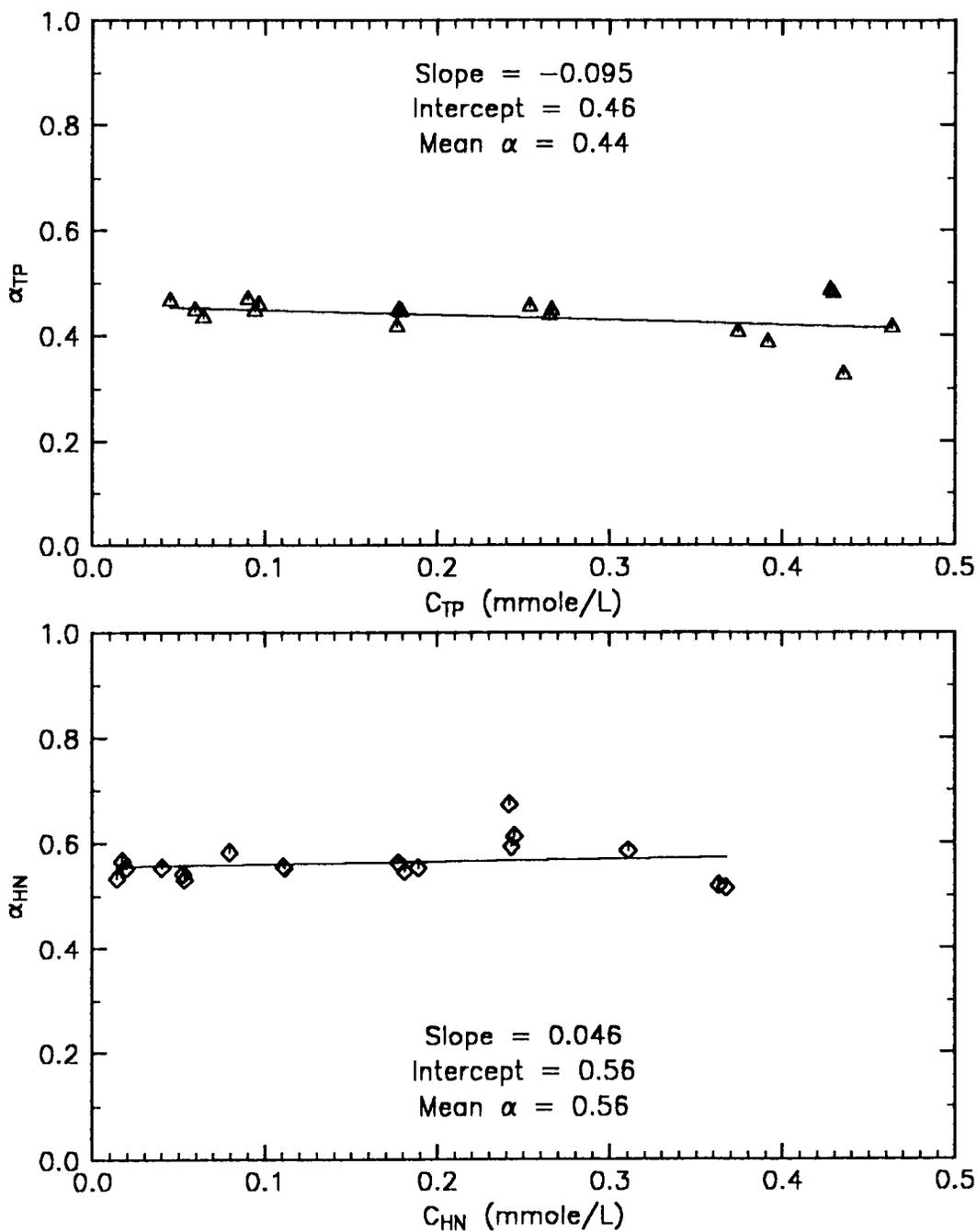


Figure 53. α as a function of equilibrium concentration for bisolute system containing 2-Hydroxynaphthalene and 2,3,5-Trimethylphenol

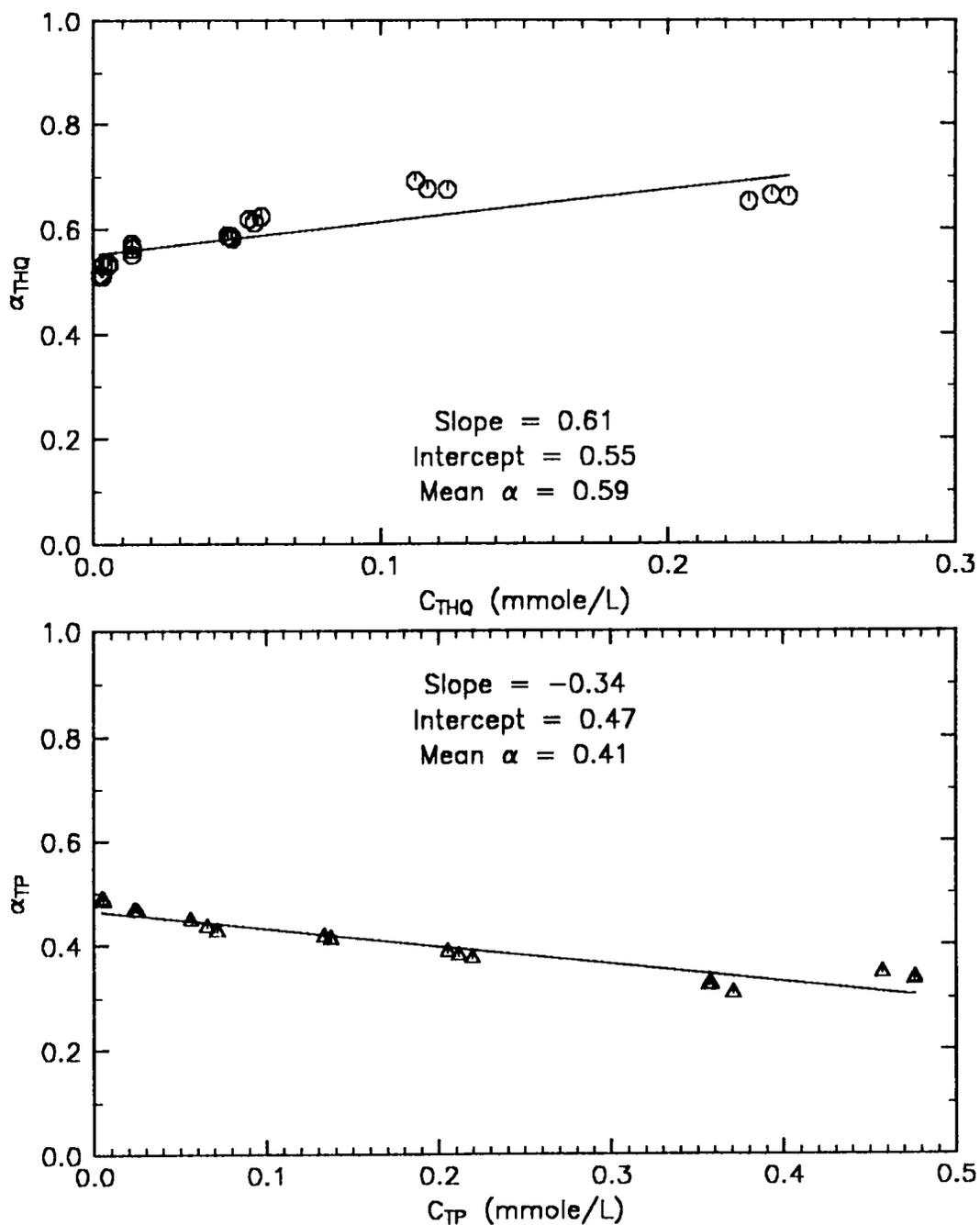


Figure 54. α as a function of equilibrium concentration for bisolute system containing 2,3,5-Trimethylphenol and 1,2,3,4-Tetrahydroquinoline

lines are almost horizontal. This could indicate that the amount sorbed of any one of the components in these cases does not have much bearing on the amount sorbed of the other component (within the range of the study). Figure 52 also has fairly low slopes for the lines in the figure.

The other three cases have at least one line that has a significant slope. Figure 51, for example, has slopes of 0.69 (α_{Phenol} versus C_{Phenol}) and -0.29 (α_{TP} versus C_{TP}). An increase in C_{Phenol} results in a decreased α_{Phenol} , whereas an increase in C_{TP} results in an increase in α_{TP} . This implies that the fraction of TP increases when the equilibrium concentration of the species increases. In other words, increased amounts of TP are taken up at the expense of Phenol. This may be indicative of stronger sorption, although desorption experiments would have to be conducted to confirm that hypothesis. It should be noted that to move from, say, the upper plot to the lower plot, one has to read over to the y-axis on the upper plot at any equilibrium concentration of interest, subtract the value read there from 1.0, then move to the y-axis of the lower plot to the value obtained from subtraction, and finally arrive at the equilibrium concentration of the component on the lower plot by using the line of best fit as a pivot.

The other two cases that have at least one line with a significant slope are those of Figure 50 and Figure 54. In the case of Figure 50 the data on the upper plot are bunched at the low end of the x-axis. The range of the x-axis is also low, and the line has a fairly sharp slope of -1.07 (47°). This indicates that THQ is favored quite highly over Phenol (and the $\bar{\alpha}_i$ values of 0.80 and 0.20, respectively, from Table 47 indicate a 4:1 ratio) in terms of sorbed amounts. In Figure 54, the upper plot would seem to be better fitted with a curve (and, maybe, even the lower plot), and this would seem to indicate that as the equilibrium concentration decreases, the amount of TP sorbed becomes almost equal to THQ, whereas the ratio falls off at a greater than linear rate with increasing equilibrium concentration. In none of the cases did the lines of best fit cross the $\alpha_i = 0.50$ mark.

Summary of Batch Sorption Experiments on Antrim Spent Shale

An analysis of the isotherms indicates that the sorptive capacity for spent shale with respect to Phenol is the least of that of the four compounds studied. The sorptive capacity of 1,2,3,4-Tetrahydroquinoline is the highest, with the order being Phenol < TP < IIN < THIQ. Phenol and 2-Hydroxynaphthalene display a homologous sorptive behavior in that 2-Hydroxynaphthalene is sorbed more than Phenol. This is most likely due to the differences in solubility of the two compounds, i.e., the less soluble species (IIN) will sorb easier (come out of solution easier). The presence of branching in Phenol (i.e., 2,3,5-Trimethylphenol) increases the amount of 2,3,5-Trimethylphenol sorbed, though not to the level of the amount of 2-Hydroxynaphthalene sorbed, indicating in this case that the sorptive potential was affected more by ascending the homologous series than by the presence of branching. Competition depresses the sorbed amounts of all the compounds studied to varying levels, but not enough to cause any change in the sorptive order (with respect to the amounts sorbed).

The presence of a nitrogen atom in 1,2,3,4-Tetrahydroquinoline seems to enhance the amount sorbed. Perhaps the lack of an OH group that would increase solubility by either ionizing at the appropriate pH or participating in hydrogen bonding in the un-ionized form also seems to enhance the sorbed amount. It is debatable whether the presence of the OH group in the other compounds would effect the sorption due to ionization, because the pH of the solutions in all cases was at least 1-1.5 units away from the pK_a of the compounds, and ionization would not have taken place to a large extent. However, hydrogen bonding with the OH group would tend to keep the compound in solution. For similar sized molecules — IIN and THIQ — the sorption of the nitrogen-containing compound (THIQ) was greater than that of the compound containing the hydroxyl group (IIN).

Batch Isotherms Performed on Granular Activated Carbon

Only single-sorbate batch isotherms were performed on the GAC. This resulted in twelve isotherms – three replicates of four experimental conditions. The data obtained from the GAC experiments was treated in the same manner as the data obtained from the shale.

Figures 55 through 58 display the results of the batch isotherm studies performed upon carbon. The first replicates upon the GAC were performed with an initial concentration range of 0-200 $\text{mg}\cdot\ell^{-1}$. However, except for Phenol, the other compounds were almost completely sorbed by the carbon. Therefore, in order to produce more points at higher equilibrium concentrations, the concentration range for HN, THQ and TP was increased to 0-500 $\text{mg}\cdot\ell^{-1}$. The isotherms shown are composites using all three replicates, but the data points from the first replicate all fall very close to the abscissa. The pHs of the GAC trials were less subject to deviation from 7.0, and most stayed very close to 7.0.

One difference that is immediately apparent is the greater sorptive capacity of the GAC. The difference is two orders of magnitude, and the ordinates of the GAC isotherm plots are labelled with units of $\text{mmole}\cdot\text{g}^{-1}$. The other difference that is quite apparent is that HN, THQ and TP are all sorbed to a large extent on the GAC, and, indeed, the sorptive capacity in the range of the experiments is similar for all three compounds and is of the order of 2.5-3.0 $\text{mmole}\cdot\text{g}^{-1}$ (this is not the final sorptive capacity since the curve had not yet become horizontal). There is no clear-cut distinction or ordering as in the case of the shale. The Phenol isotherm also indicates fairly large sorption, but the final extent of sorption is about 1.7 $\text{mmole}\cdot\text{g}^{-1}$ (about 60% of that of the other three compounds).

The segmented isotherms can be fitted with a linear regression (one for each segment) for comparison purposes. The break occurs at about the same point for HN, THQ and TP, and the slopes of the flatter sections are similar (however, note that the abscissæ of the three plots are different).

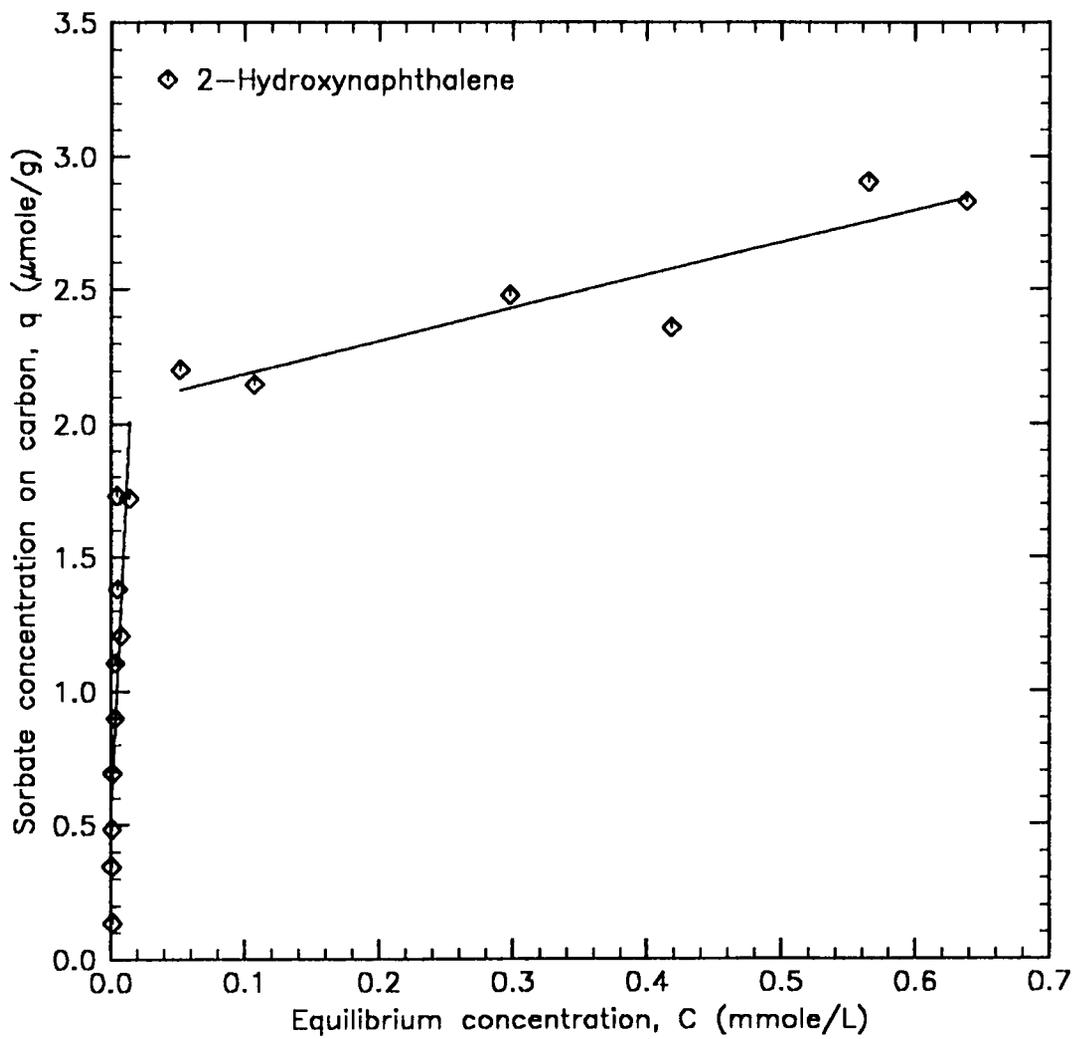


Figure 55. Batch isotherms for 2-Hydroxynaphthalene upon granular activated carbon

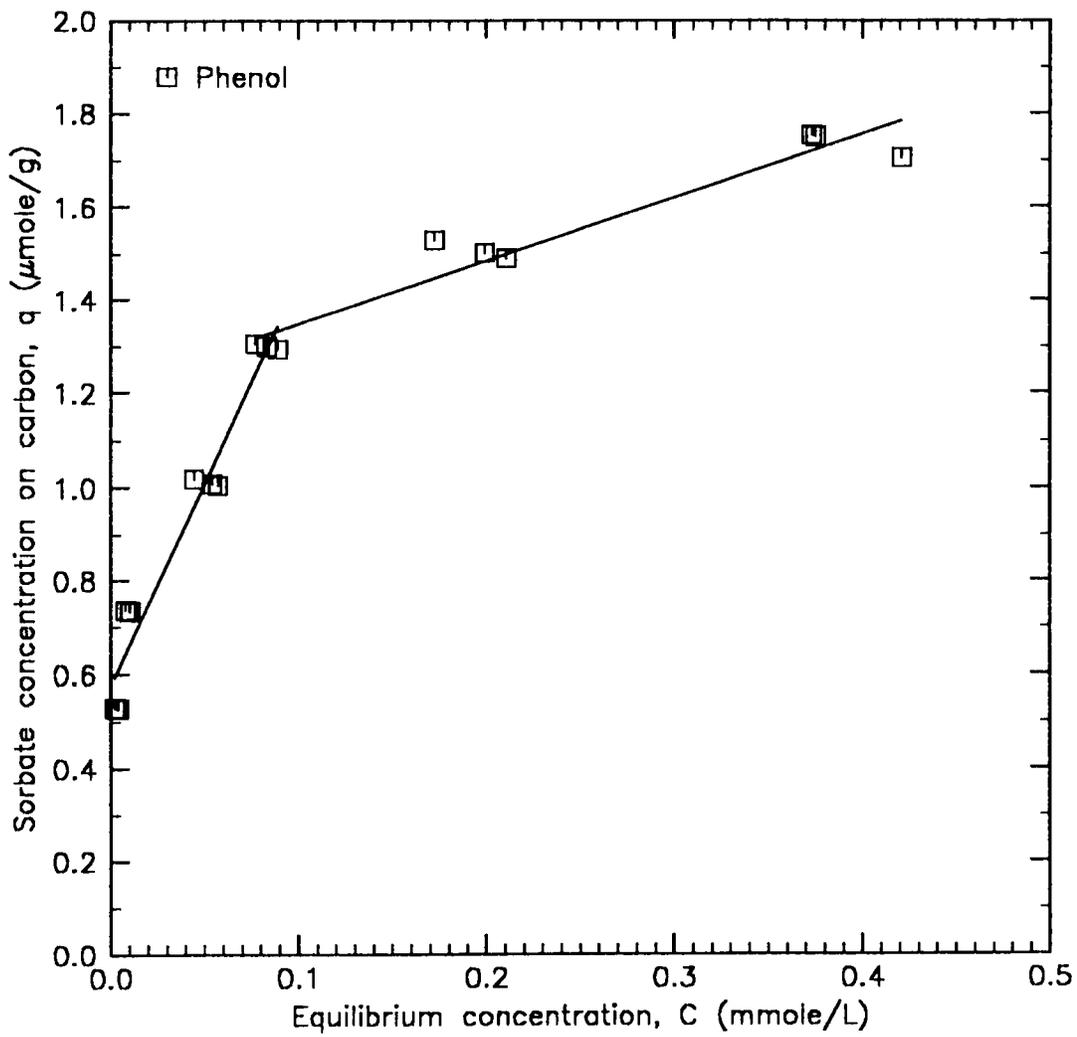


Figure 56. Batch isotherms for Phenol upon granular activated carbon

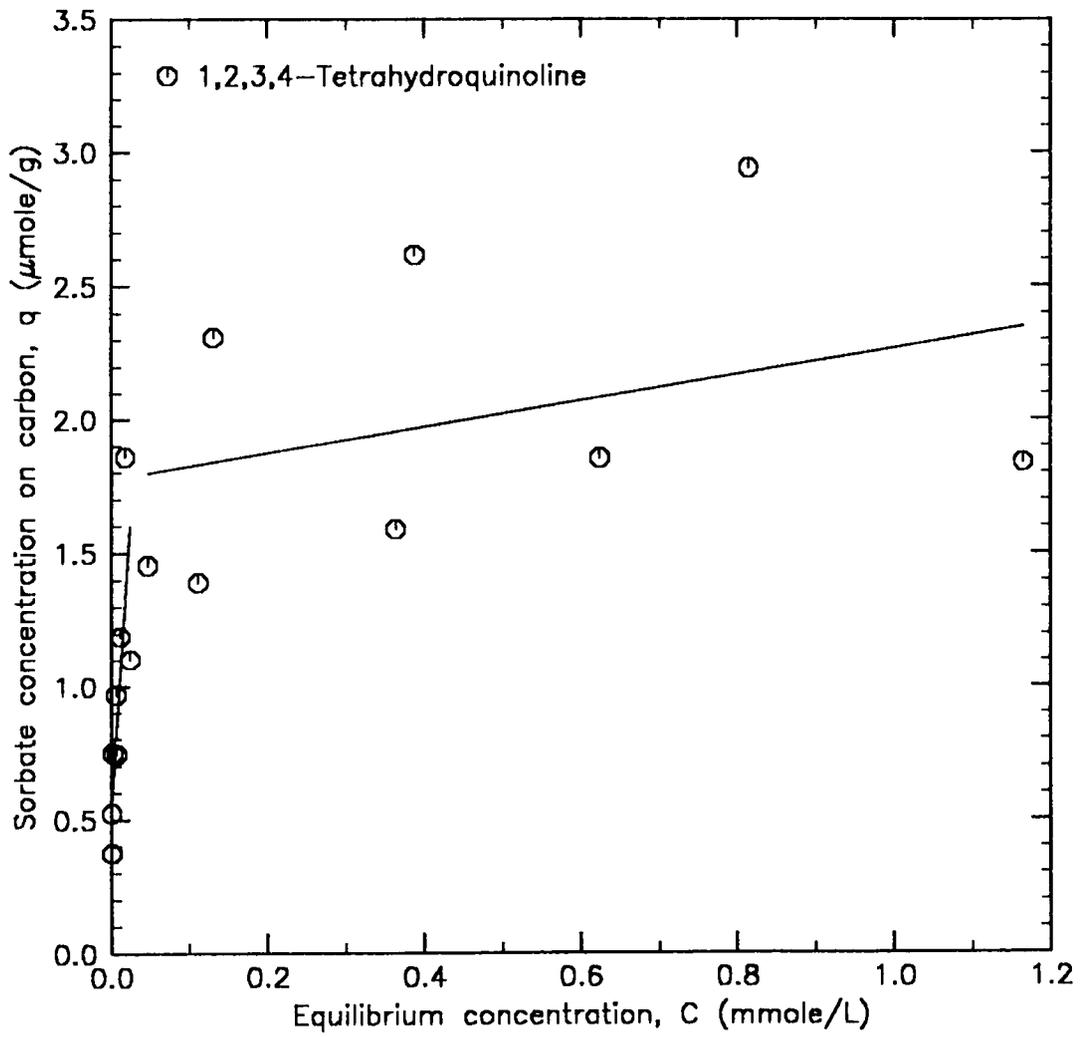


Figure 57. Batch isotherms for 1,2,3,4-Tetrahydroquinoline upon granular activated carbon

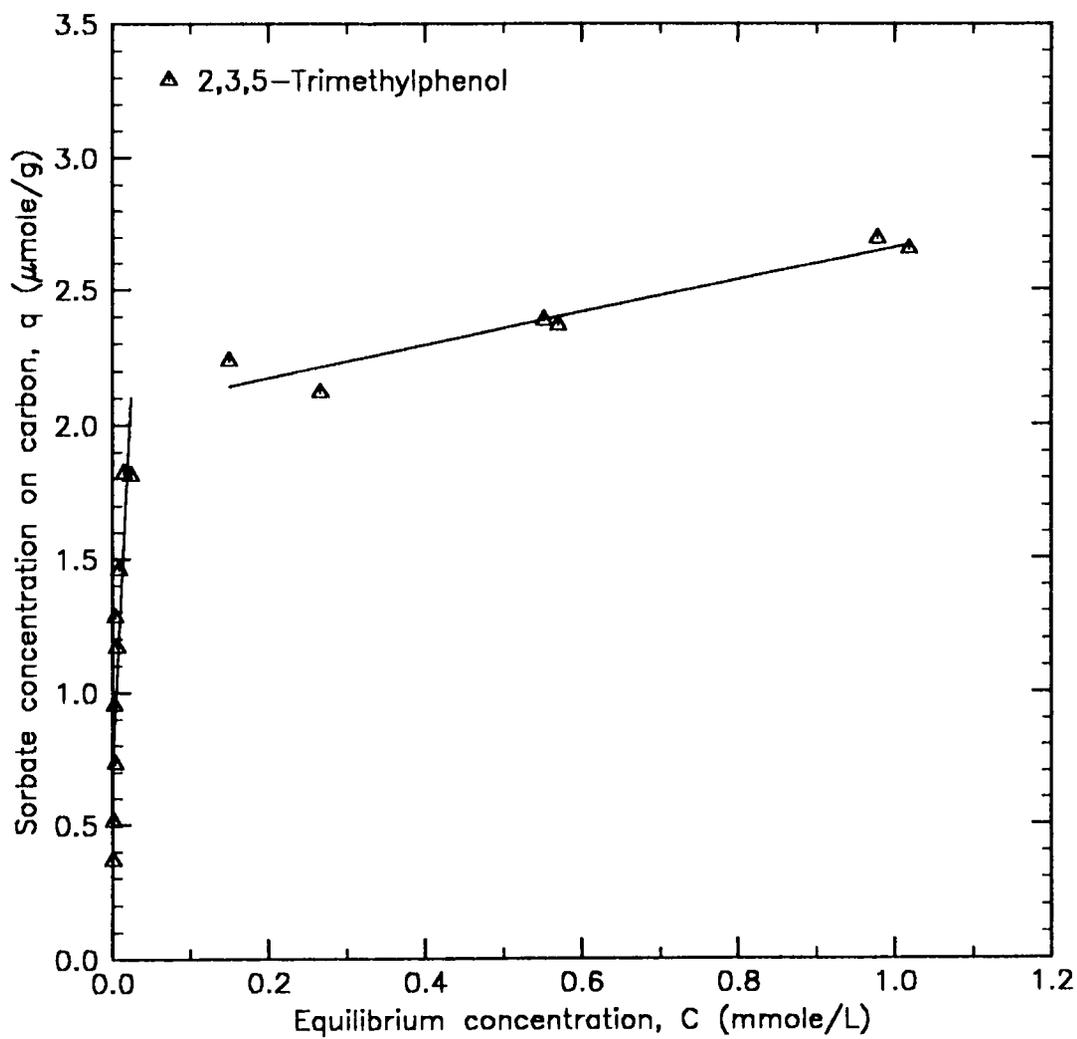


Figure 58. Batch isotherms for 2,3,5-Trimethylphenol upon granular activated carbon

Figure 57 shows two sets of data for THQ at the higher equilibrium concentrations. These are separated at the higher values of C according to the replicates — one above the line and one below (the data points from the third replicate lie close to the ordinate). This difference in the replicates of THQ sorption upon the carbon is not explainable. Perhaps the THQ exhibits some kind of bimodal behavior, wherein under different conditions it sorbs to different amounts. However, this author was unable to discover these conditions, if present. The external variables in the experiments — agitation rate and temperature — were adequately controlled. Again, there was no discernible growth in the flasks. Error in making up the stock solution is a possibility, but the standards made up from the stock solution showed no discrepancy. The lower set of data points were generated from an experiment that was performed about nine months after that which generated the upper set of data points. Perhaps this was the reason for the difference: the carbon may have had a diminished capacity due to aging. However, this would not account for the fact that trials with the other compounds did not show the same diminished capacity. Curiously, a similar difference in replication was obtained with the single-sorbate isotherm experiments with THQ on shale, too.

As for being an index for the shale, the GAC is good in some aspects and not in others. The sorptive capacity of the shale ($10\text{-}22 \mu\text{mole}\cdot\text{g}^{-1}$) is about two orders of magnitude less than that of the carbon ($1.8\text{-}3.0 \text{mmole}\cdot\text{g}^{-1}$). In this connection, it should be noted that whereas the single-component sorption isotherms on the shale had essentially levelled-off at the values given above, those of carbon were still rising, although at a reduced rate. It should also be noted that the surface area of the shale (taken to be approximately $10 \text{m}^2\cdot\text{g}^{-1}$ from Table 30) is about two orders of magnitude lower than that of the carbon ($950\text{-}1050 \text{m}^2\cdot\text{g}^{-1}$ from the same table). It was fortunate that the final pHs of the carbon and the shale isotherms flasks were in the neutral range, mainly between 6.0-7.5. It should be expected that the sorptive capacity relationship between shale and carbon (based upon the surface area differences outlined above) should hold for similar compounds and within the same pH range. Both the sorbents have favored sorption isotherms for all four compounds. However, the more distinct partitioning of sorptive behavior seen with respect to the compounds is not so evident on the carbon as it is on the shale. Considering that the surface areas

are so different, and the fact that sorption is primarily considered to be due to the carbon present on the surface of the sorbent, perhaps a comparison of the type shown in Figure 22 would be desirable. The data to generate that kind of analysis are not available to this researcher.

Calculation of Langmuir and Freundlich Isotherm

Constants

Initially, the Langmuir and Freundlich isotherm constants were calculated by linearization of the data. However, at a later date these were computed using the NLIN procedure of the SAS system wherein a nonlinear least squares fit was performed. The Marquardt method was used, except in the case of the Langmuir fit for THQ on shale (composite of two replicates) which used the DUD procedure. The fits from the procedure, along with the 95% confidence interval were plotted on a plot of q versus C . Examples of these plots can be seen in Figure 59 and Figure 60. The remaining plots are given in Appendix D. Shown in Figure 61 is a Freundlich fit but with the 95% confidence limits drawn with respect to the predictions of the data points, rather than to the model line.

As can be seen from a comparison of Figures 59 and 60, the Langmuir isotherm seems to better fit the data at the bend in the curve, whereas the Freundlich isotherm better fits the data at the higher equilibrium concentrations. However, both fits are quite valid, and one must choose the one to use depending on the range one is working within.

The coefficients for both the Freundlich and Langmuir isotherms are given in Table 49. The main difference to be noted in Table 49 is that the values of the coefficients for the shale are in μ moles whereas those for the GAC are in mmoles.

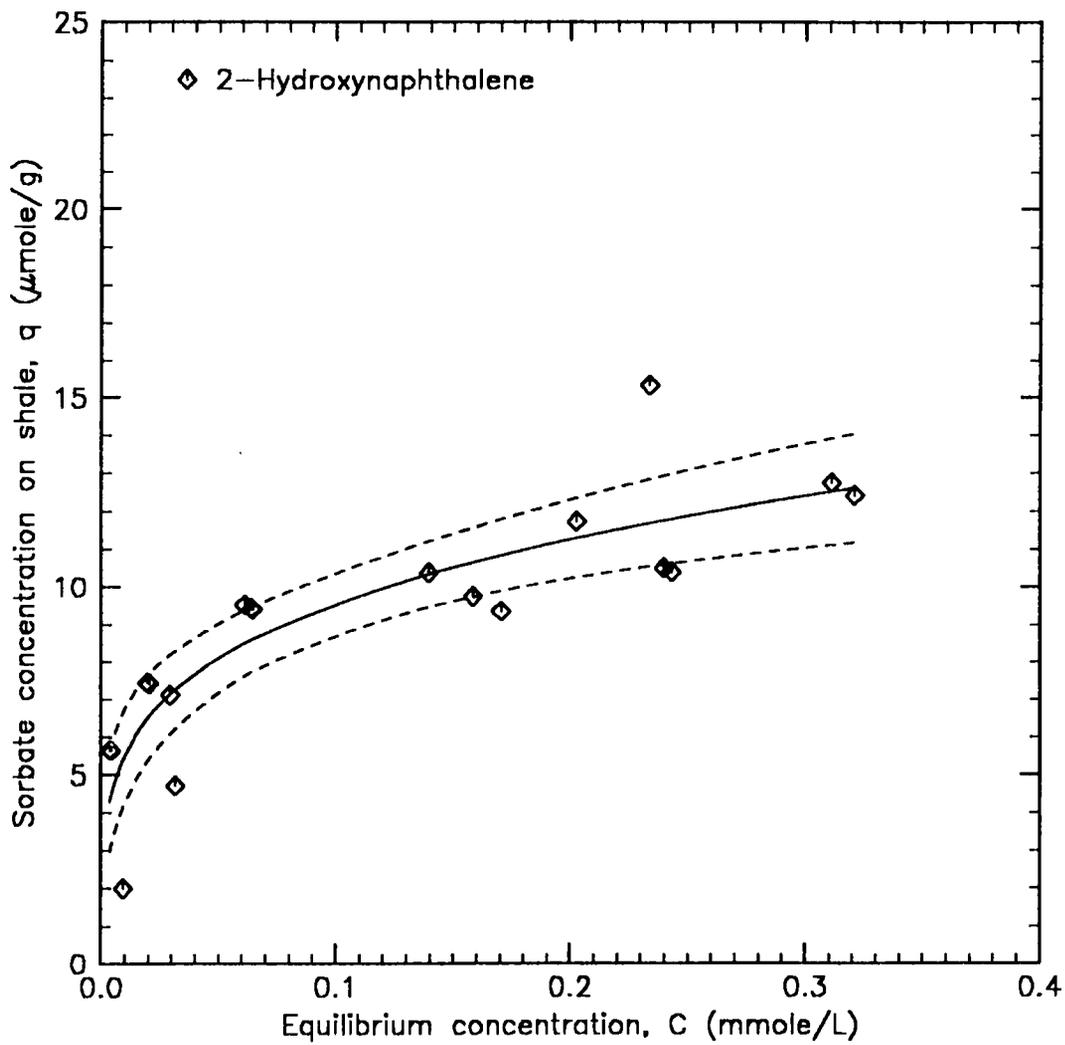


Figure 59. Nonlinear least squares fit to 2-Hydroxynaphthalene data using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

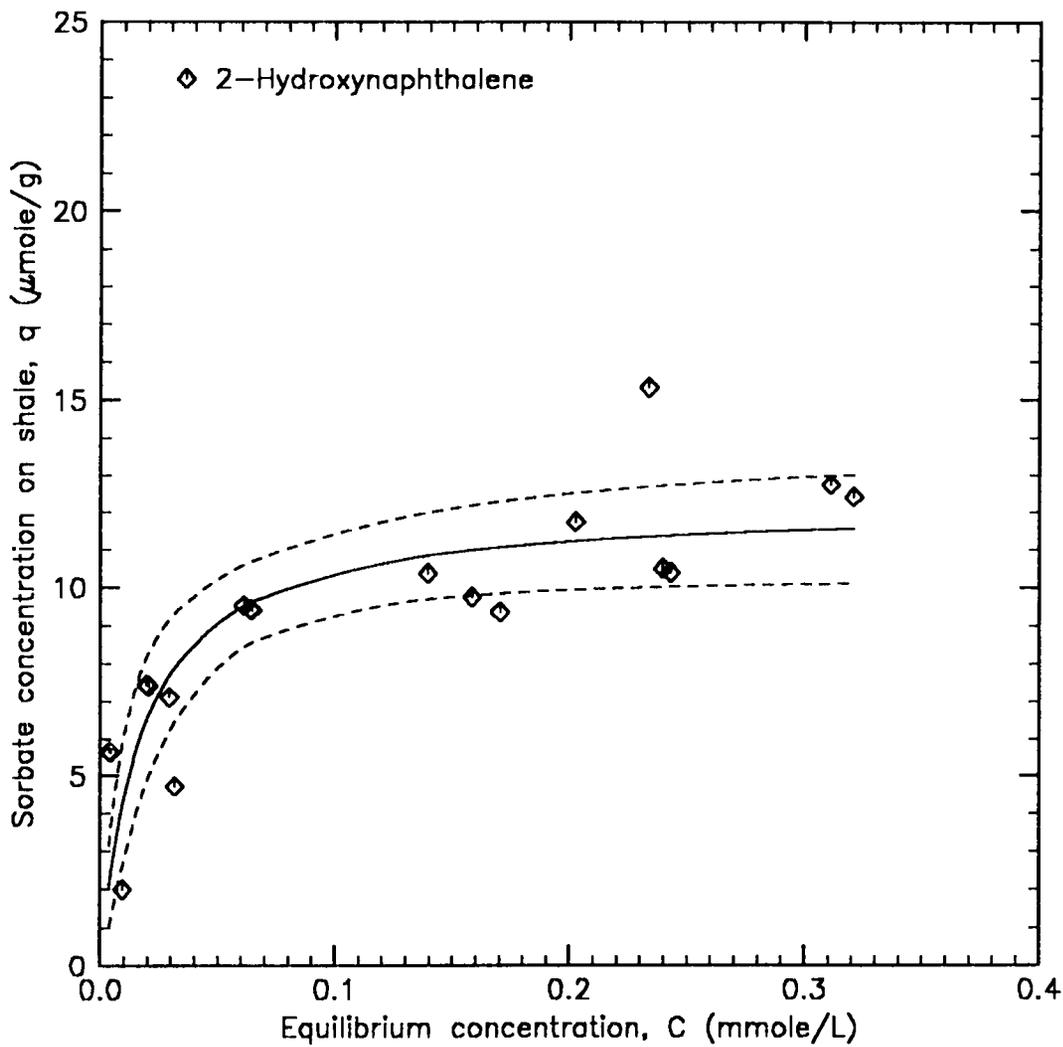


Figure 60. Nonlinear least squares fit to 2-Hydroxynaphthalene data using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

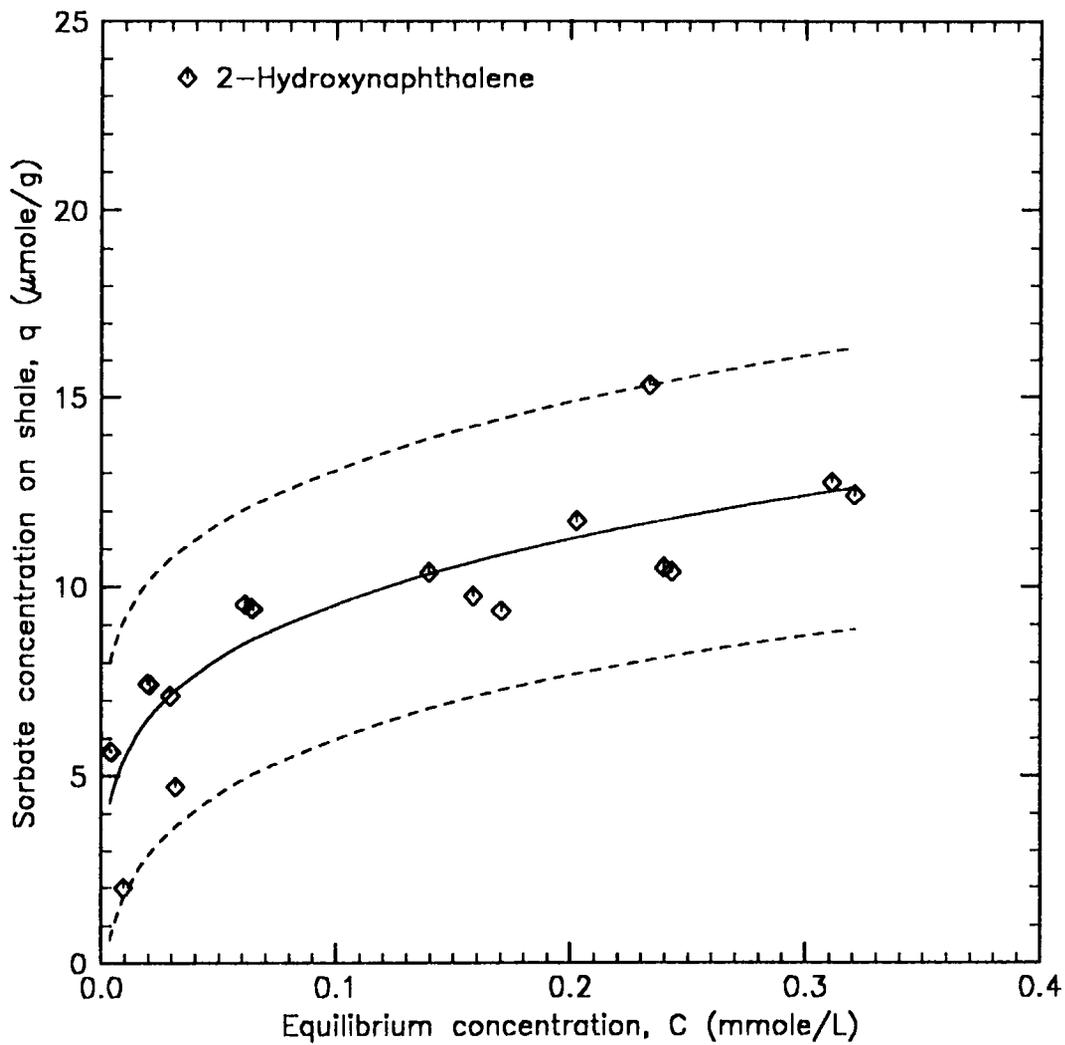


Figure 61. Nonlinear least squares fit to 2-Hydroxynaphthalene data using the Freundlich isotherm, and with 95% confidence limits based on the predicted values: The dashed lines represent the 95% confidence limits.

Table 49. Freundlich and Langmuir constants evaluated from monocomponent batch experiments on Antrim spent shale and Filtrasorb-300 carbon

Antrim Spent Shale				
Compound	Langmuir		Freundlich	
	$a, \mu\text{mole}\cdot\text{g}^{-1}$	$b, \ell\cdot\mu\text{mole}^{-1}$	K^*	n
HN	58.2	12.2	16.5	0.24
P	4.9	12.3	11.5	0.42
THQ (2 reps.)	549.6	19.9	36.1	0.20
(first rep.)	151.1	6.1	7.0	0.14
TP	23.7	10.9	14.1	0.30

Filtrasorb-300 Granular Activated Carbon				
Compound	Langmuir		Freundlich	
	$a, \text{mmole}\cdot\text{g}^{-1}$	$b, \ell\cdot\text{mmole}^{-1}$	K^*	n
HN	212.0	2.55	3.20	0.20
P	84.3	1.57	2.20	0.24
THQ	128.5	2.09	2.42	0.18
TP	186.5	2.43	2.73	0.17

* The units for K are $\mu\text{mole}\cdot\text{g}^{-1}\cdot(\ell\cdot\mu\text{mole}^{-1})^n$ for shale, and $\text{mmole}\cdot\text{g}^{-1}\cdot(\ell\cdot\text{mmole}^{-1})^n$ for carbon

The residual sums of squares (RSS) and the F values of the Langmuir and Freundlich isotherm fits are shown in Table 50. It should be noted that the F values are not true F values since the fit was a nonlinear fit. The F values given in the table were computed by dividing the mean square of the regression by the mean square of the residuals. For the shale, the Freundlich fits (except in the case of the first THQ replicate) had lower RSS values and higher F values. For the GAC, the Phenol data was best fitted with the Freundlich isotherm, whereas those of HIN and TP were best fitted with the Langmuir isotherm. In the case of THQ upon the GAC, both the Langmuir and the Freundlich isotherms had similar RSS and F values, although the Freundlich values were just slightly better. The F values for all the isotherm fits, however, were high, indicating a good fit. For modelling of sorption of the study compounds upon shale, the Freundlich isotherm provides the best fit. This may, in all probability, hold true for other organic compounds. Neither the Langmuir nor the Freundlich isotherms can be used exclusively for the modelling of the sorption of organic compounds upon carbon.

Modelling Efforts

Three models were tried for the modelling of the multicomponent systems. These were the three models given in the chapter titled 'Literature Review – Sorption': the multicomponent Freundlich model of Sheindorf, Rebhun and Sheintuch, the multicomponent Langmuir model, and the simplified IAS model.

The first model that was tried was the Freundlich type multicomponent isotherm described by Sheindorf, Rebhun and Sheintuch [196-198]. Recall that the equation is as given below:

$$q_i = k_i C_i \left(\sum_{j=1}^N \psi_{i,j} C_j \right)^{n_i - 1} \quad (14)$$

Table 50. Residual sums of squares and F values for monocomponent batch experiment data fitted with the Langmuir and Freundlich isotherms

Antrim Spent Shale					
Compound	Number of points	Langmuir*		Freundlich*	
		RSS‡	F	RSS	F
HN	19	64.9	216	45.4	313
P	14	3.7	1,189	1.7	2,537
THQ (2 reps.)	10	49.5	210	13.5	781
(first rep.)	7	1.6	321	3.7	140
TP	19	28.1	373	15.8	670

Filtrisorb-300 Granular Activated Carbon					
Compound	Number of points	Langmuir†		Freundlich†	
		RSS	F	RSS	F
HN	17	0.962	384	1.747	208
P	18	0.523	396	0.066	3,186
THQ	17	2.704	111	2.628	115
TP	15	0.444	706	1.063	291

* Values of RSS are in $(\mu\text{mole}\cdot\text{g}^{-1})^2$

† Values of RSS are in $(\text{mmole}\cdot\text{g}^{-1})^2$

‡ RSS = Residual Sum of Squares

To obtain the values of $\psi_{i,j}$, plots of $\frac{C_i}{C_j}$ against $\frac{\beta_i}{C_j}$ ($i \neq j$) for two-component isotherms should give a linear fit with slope = 1. The intercept then would be at $-\psi_{i,j}$. The intercept has to be a negative number, so that the interaction parameter $\psi_{i,j}$ turns out to be positive [196-198].

The results obtained from modelling for the multicomponent Freundlich type isotherm were uniformly bad. In order to obtain the values of ψ , plots of $\frac{C_i}{C_j}$ against $\frac{\beta_i}{C_j}$ ($i \neq j$) were made and fitted with a straight line. The slopes and intercepts obtained from these are given in Table 51. As can be seen from the values reported in the table, the intercept was negative in only two cases, and in those cases the slope was not unity. A slope of 1.06 and an intercept of 0.0003 for the case where component j was THQ and component i was Phenol was the closest that any of the situations came to satisfying the requirements of the model. Indeed, the slope was not close to unity in any other case (except perhaps that of 0.92 in the case where component j was TP and component i was THQ, and then the intercept was positive). The model was, therefore, abandoned as being unsuitable for the present system.

Results with the Simplified IAS Theory

The simplified IAS theory (SIAS) presented by DiGiano *et al.* proved to be the most interesting one from the point of view of predictive ability. Briefly recapitulating, the SIAS theory assumes that “sorption of the solutes can be described by either identical Freundlich equations or by Freundlich equations with equal n values” for the model to be in exact correlation with the IAS theory [58]. However, the concepts of the IAS theory can be applied via the SIAS model to systems where the values of n are not equal [58]. The model is as given below:

Table 51. Results of modelling with the multicomponent Freundlich type isotherm — slopes and intercepts from bicomponent plots

Compounds	<i>j</i>	Slope	Intercept
Phenol & HN	Phenol	0.44	-2.36
	HN	0.80	0.04
Phenol & THQ	Phenol	0.30	-17.48
	THQ	1.06	0.0003
Phenol & TP	Phenol	0.05	3.75
	TP	0.71	0.04
HN & THQ	HN	0.48	0.51
	THQ	0.12	0.62
HN & TP	HN	0.71	0.08
	TP	0.41	0.67
TP & THQ	TP	0.92	0.06
	THQ	0.09	0.25

$$q_i = k'^{(n'-1)/n'} (k_i C_i^{n_i})^{1/n'} \left[\sum_{j=1}^N \left(\frac{k_j}{k'} C_j^{n_j} \right)^{1/n'} \right]^{(n'-1)} \quad (16)$$

The terms k' and n' are the geometric and the arithmetic means of the individual k s and n s, respectively.

Since the simplified IAS theory reduces to the Freundlich isotherm when there is only one sorbate, it was used to model all the single sorbate and the multi-sorbate experimental data. It was to be expected that the SIAS theory would successfully predict the single-sorbate data, since the Freundlich parameters were derived from these. More interesting was the prediction of the SIAS theory for the multi-component mixtures based on the single-component derived parameters.

In general, the predictive modelling was not good. In most cases the model either overpredicted or underpredicted the sorbate concentrations on shale. However, this might have been acceptable were it not for the fact that in the majority of cases the residual concentrations on shale (i.e., measured minus predicted concentration on shale) were greater than 100% of the predicted concentrations.

It was then thought that rather than attempting to predict from the single-solute information, a parameter estimation of the coefficients for the individual components should be performed, and that the results from these might prove to be better. Of course, this implied that instead of being used in a predictive sense, the model was used as a curve-fitting tool. The SYSNLIN procedure for estimating a system of non-linear equations from the SAS/ETS software package was used for this purpose.

A vast number of plots were generated due to the modelling efforts mentioned above. However, in view of the fact that some degree of success was achieved in only a few cases, only those cases will be presented.

Single Solute Estimation According to the SIAS Model

In the case where there is only one solute, the SIAS model — Equation (16) — reduces to the Freundlich equation. This can then be solved using the NLIN procedure of SAS, and the results are identical to those given in Table 49 (for the Freundlich isotherm) in the previous section titled 'Calculation of Langmuir and Freundlich Isotherm Constants'.

Bisolute Predictions and Parameter Estimation According to the SIAS Model

Among the bisolute systems the most success with the prediction of q values was obtained in the Phenol cum 2-Hydroxynaphthalene and Phenol cum 1,2,3,4-Tetrahydroquinoline systems. In addition to the residual plots, three-dimensional plots of the generated surface were also made and compared with the 3D plots of the data. A complete set of 3D and residual plots is given for the Phenol cum 2-Hydroxynaphthalene system (Figures 62 through 65), whereas only residual plots are given for the Phenol cum 1,2,3,4-Tetrahydroquinoline system (Figures 66 and 67). The x- and y-axes of the stacked 3D plots do not have the same range. This is due to the limitations of SAS, wherein the user has no control over the range of the axes (except the z-axis). This author has tried to choose the range of the generated data to be as close to the range of the original data. However, the axes of the actual data plot may not start at zero, and have an uneven range.

A look at the 3D plots for Phenol in the Phenol cum IIN system shows that Phenol has a negative trend with increasing equilibrium concentration of IIN. As the equilibrium concentration of IIN increases, the sorbate concentration on shale of Phenol (q_{phenol}) decreases. The 3D plots for IIN

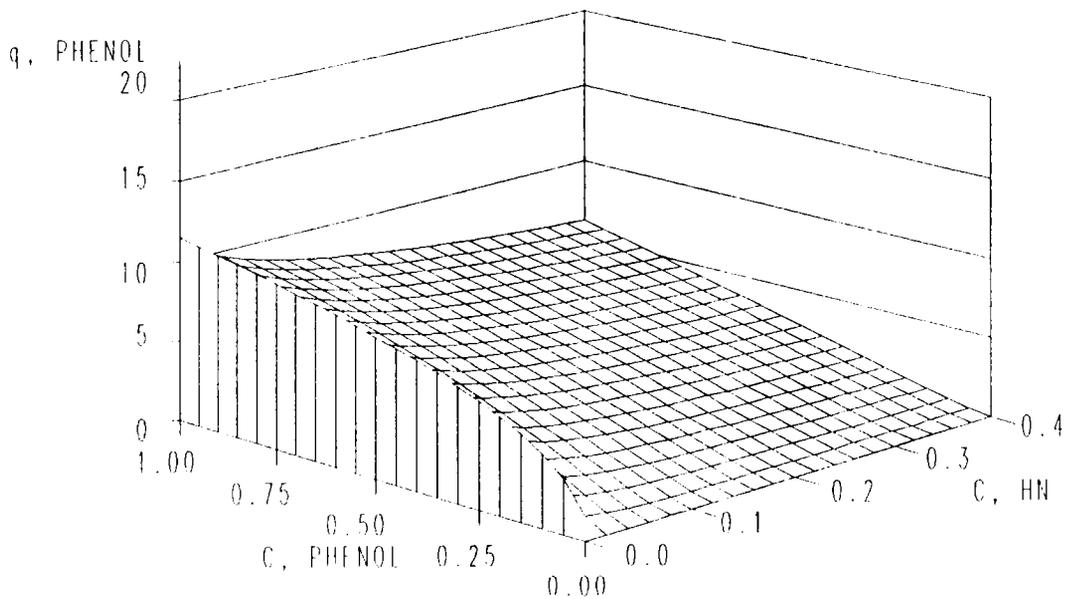
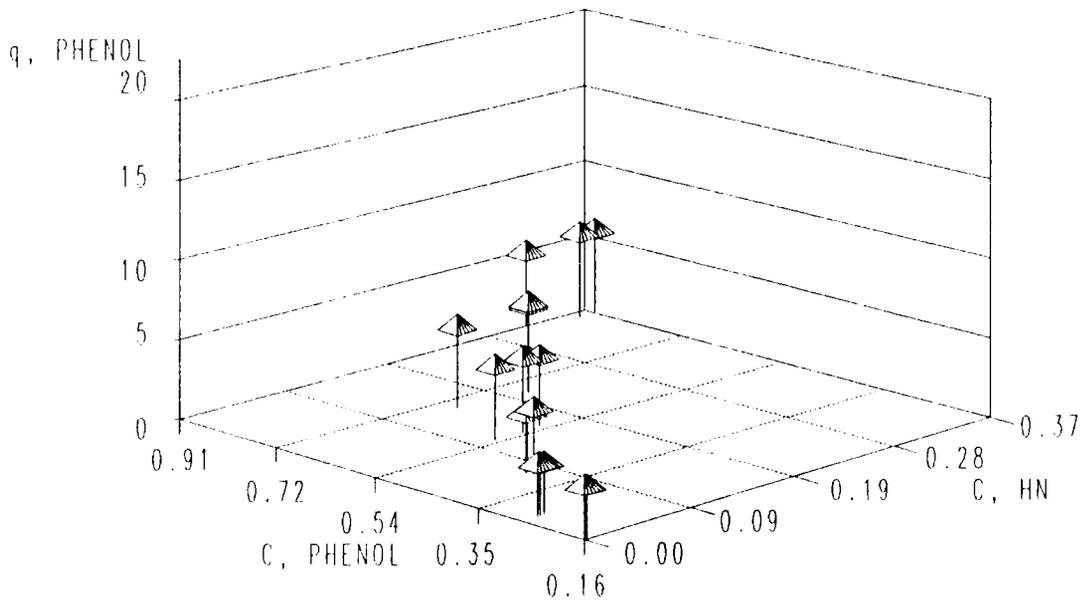


Figure 62. Bisolute predictions of the SIAS model for Phenol in the Phenol cum 2-Hydroxynaphthalene system: The upper plot represents the actual (experimental) data, whereas the lower surface is generated by the model. C in $\text{mmole}\cdot\ell^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

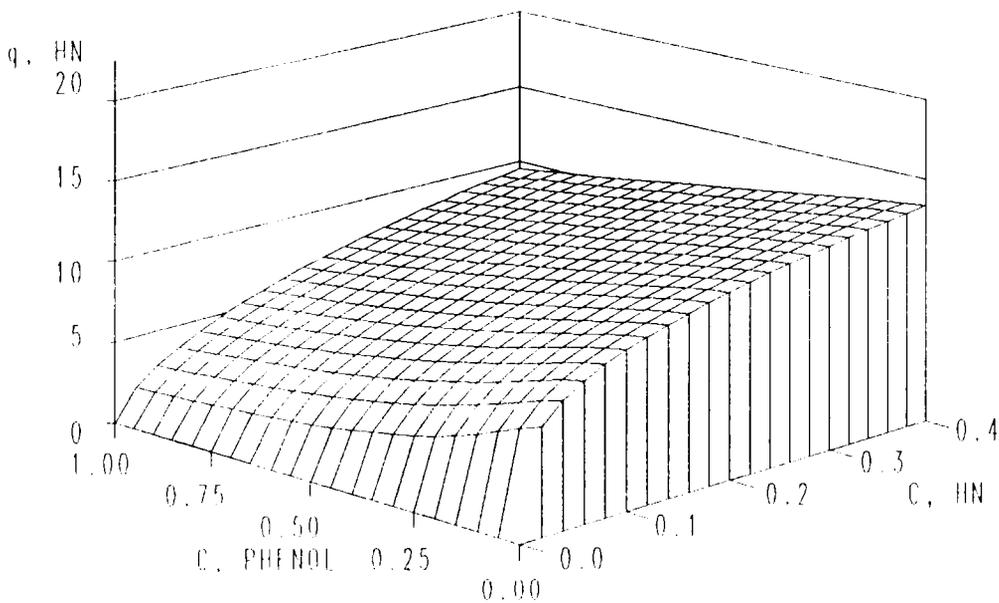
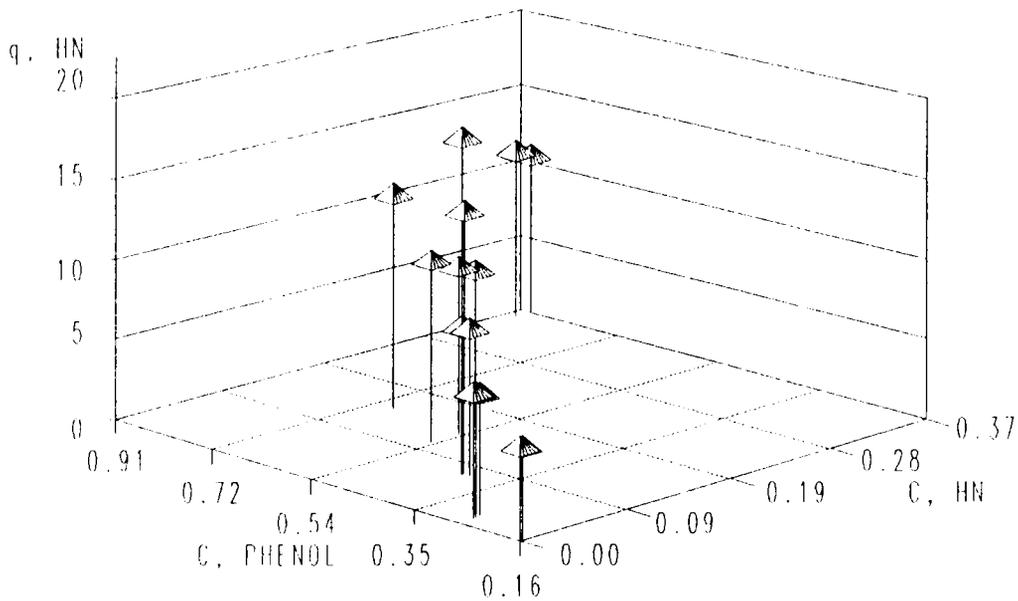


Figure 63. Bisolute predictions of the SIAS model for 2-Hydroxynaphthalene in the Phenol cum 2-Hydroxynaphthalene system: The upper plot represents the actual (experimental) data, whereas the lower surface is generated by the model. C in $\text{mmole}\cdot\ell^{-1}$, q in $\mu\text{mole}\cdot\text{g}^{-1}$.

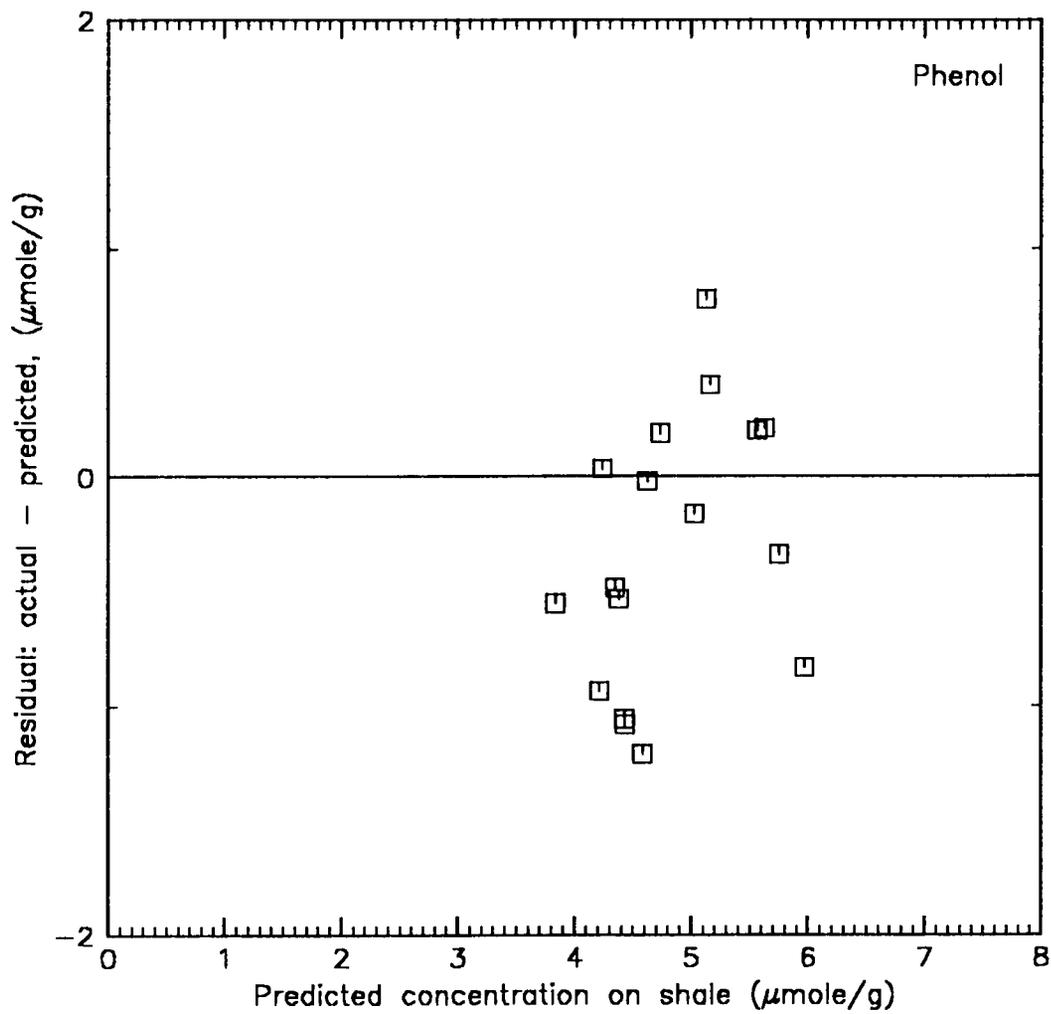


Figure 64. Residual plot for the predictions of the SIAS model for Phenol in the Phenol cum 2-Hydroxynaphthalene bisolute system

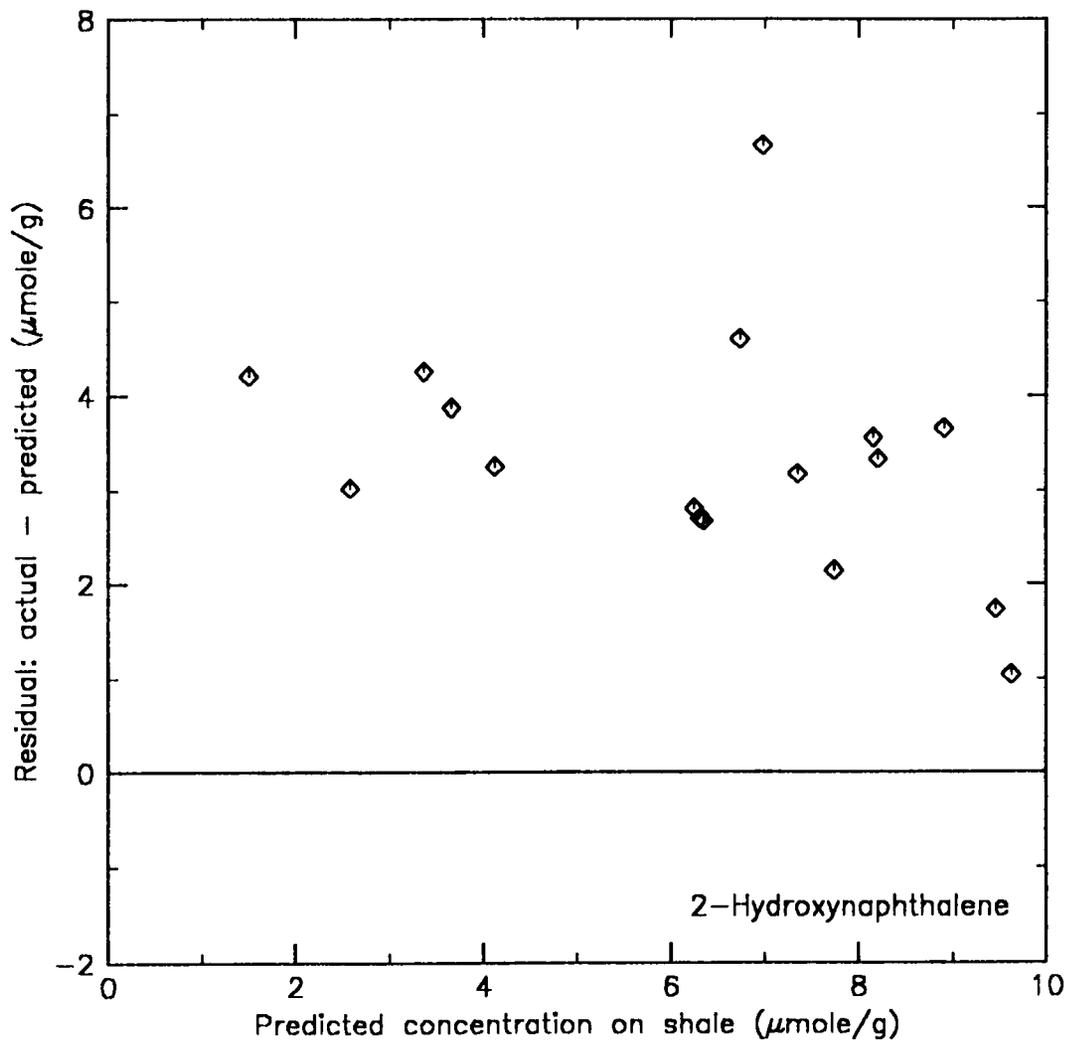


Figure 65. Residual plot for the predictions of the SIAS model for 2-Hydroxynaphthalene in the Phenol cum 2-Hydroxynaphthalene hisolute system

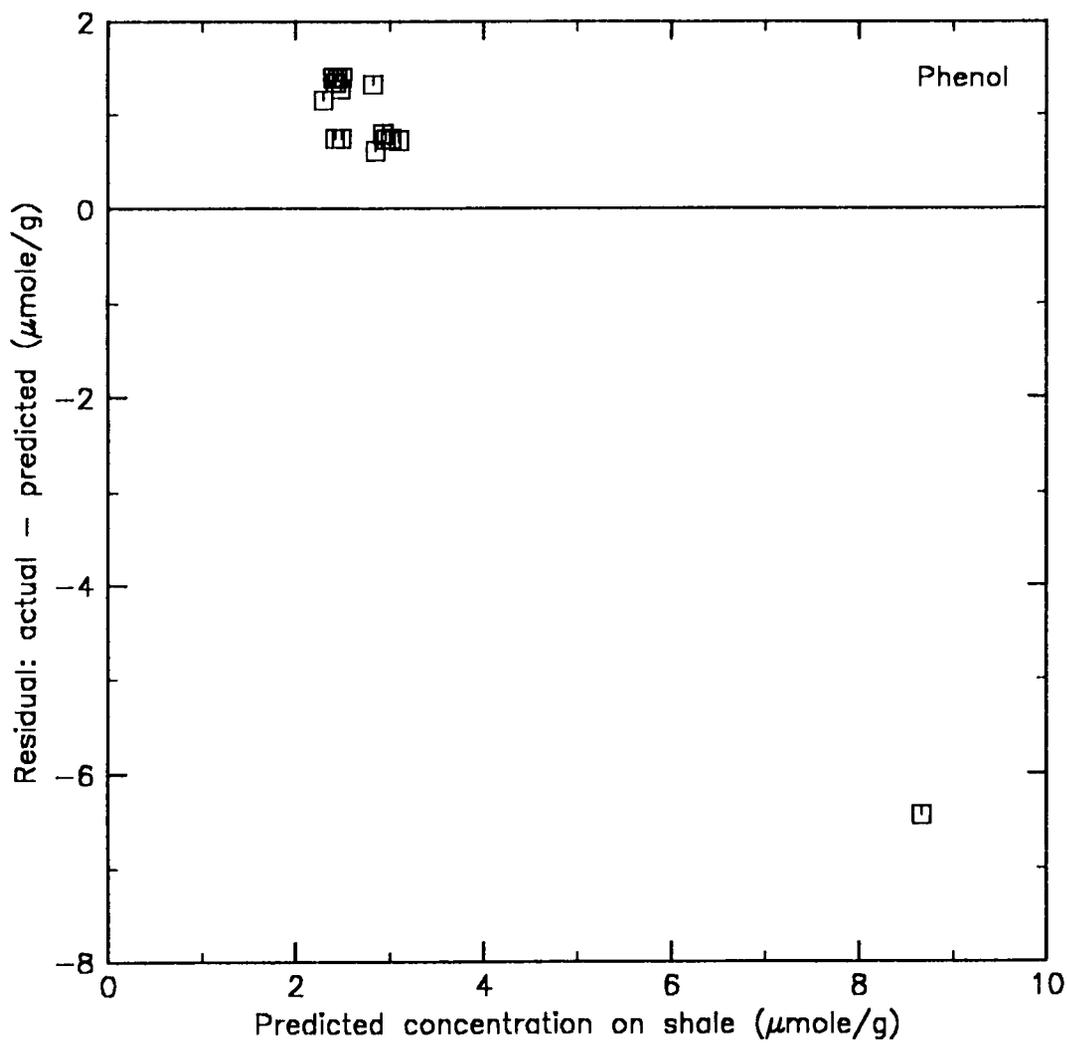


Figure 66. Residual plot for the predictions of the SIAS model for Phenol in the Phenol cum 1,2,3,4-Tetrahydroquinoline bisolute system

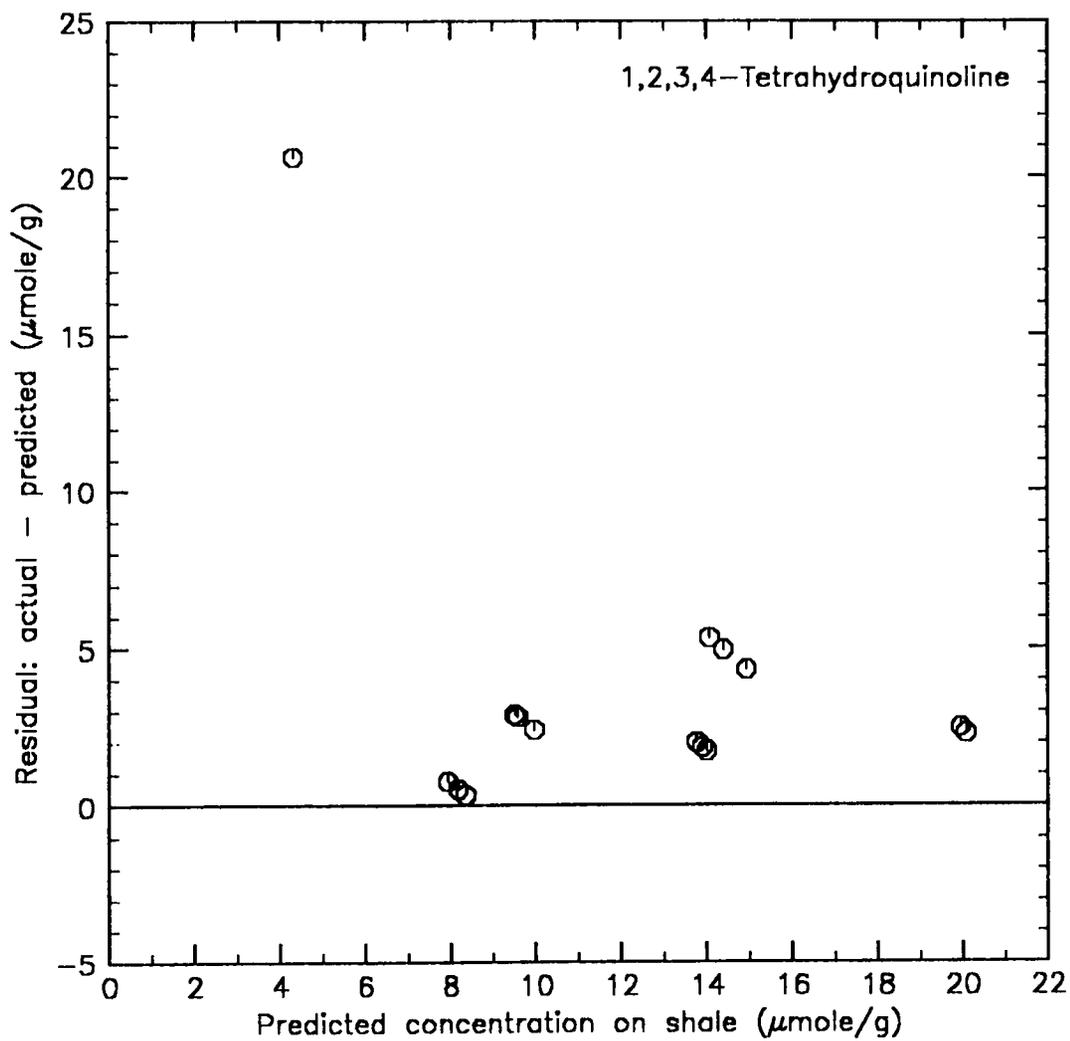


Figure 67. Residual plot for the predictions of the SIAS model for 1,2,3,4-Tetrahydroquinoline in the Phenol cum 1,2,3,4-Tetrahydroquinoline bisolute system

show a similar trend inasmuch as q_{IIN} decreases when the equilibrium concentration of Phenol increases. This seems to contradict the results of the computed α_i s shown for the same system in Figure 49, wherein the ratios of the q values do not change with increasing equilibrium concentrations. Perhaps the reason for this is that the actual data lie in a relatively flat portion of the 3D domain, and hence the α_i values would be constant. However, the other possibility is that the model could be erroneous in prediction. The residual plots show that Phenol is predicted quite well, but that IIN is consistently underpredicted. In the case of a few data points, the residuals for IIN are more than 100% of the predicted value (i.e., the actual value is more than 200% of the predicted value).

It should be noted that the prediction of any one component when the other components are at a concentration of 0.0 is exactly the same as the Freundlich isotherm for that component. For example, in Figure 62 the prediction for Phenol when $C_{\text{IIN}} = 0.0$ is the same as for the single solute Freundlich isotherm. This is due to the fact that the predictions are based upon the Freundlich constants, and that Equation (16) reduces mathematically to a single-component Freundlich isotherm when the C_j values for all other components are 0.0.

For the Phenol cum 1,2,3,4-Tetrahydroquinoline system, the q values are generally overpredicted, but not by much (residuals for Phenol are less than $2 \mu\text{mole}\cdot\text{g}^{-1}$ and those for THQ are less than $5 \mu\text{mole}\cdot\text{g}^{-1}$). There is one outlying point in both residual plots (Figures 66 and 67), without which the agreement would be quite good. Of course, what is good agreement and what is not will depend on how one wishes to use the prediction. If it is used for design purposes, then the allowed leeway in the calculations for design could be on the order of 100%, in which case even those residual predictions that are on the order of 100% can be used. Whereas if the design were more stringent, then this margin of error in prediction would need to be reduced. However, it should be noted that frequently there is underprediction at the lower concentrations (i.e., the residual is positive) and this may not be suitable for design purposes without a considerable safety factor.

Figures 68 and 69 display the residuals from the parameter estimation for the Phenol cum HN system. Although the residual values for HN are reasonably small, those for Phenol show a definite bias in the parameter estimation. Indeed, the results obtained from the parameter estimation show that of the two values of k and of n , the value of n for Phenol is equal to 1. Actually, in order to constrain the range of estimated n between 0 and 1, the parameter was transformed as $n = \frac{e^m}{1 + e^m}$, and the value of m was estimated. This means that for relatively large values of m , the value of n approaches close to 1. It was seen that every time that the model parameter estimation provided a biased estimate, the value of n for the biased solute was 1, and the spread of the residual points was as shown in Figure 68, i.e., a linear downward trend from left to right — from under-prediction at lower values of C to overprediction at higher values of C . This may indicate that the model is missing some parameter and is, hence, misspecified. The data in Figure 69 show some heteroscedasticity (inconstant variance).

The Phenol cum HN and Phenol cum THQ systems both were estimated with a bias for Phenol, and in the TP cum THQ system where there was a bias for TP. The results of the residual analysis of the parameter estimation for the Phenol cum TP, HN cum THQ and HN cum TP systems are displayed in Figures 70 through 75.

For the Phenol cum TP system the residuals lie in the 0 to $-2 \mu\text{mole}\cdot\text{g}^{-1}$ range for Phenol and in the -2 to $3.5 \mu\text{mole}\cdot\text{g}^{-1}$ range for TP, whereas those for the HN cum THQ system are in the range -2 to $3.5 \mu\text{mole}\cdot\text{g}^{-1}$ for HN and -3 to $4.5 \mu\text{mole}\cdot\text{g}^{-1}$ for THQ. In the HN cum TP system, the residuals for HN are in the -1 to $2 \mu\text{mole}\cdot\text{g}^{-1}$ range and those for TP are in the -4 to $2.5 \mu\text{mole}\cdot\text{g}^{-1}$ range. The residual data show some vertical spread as the equilibrium concentration of TP increases in the HN cum TP system, although it cannot be clearly said whether or not the data show heteroscedasticity.

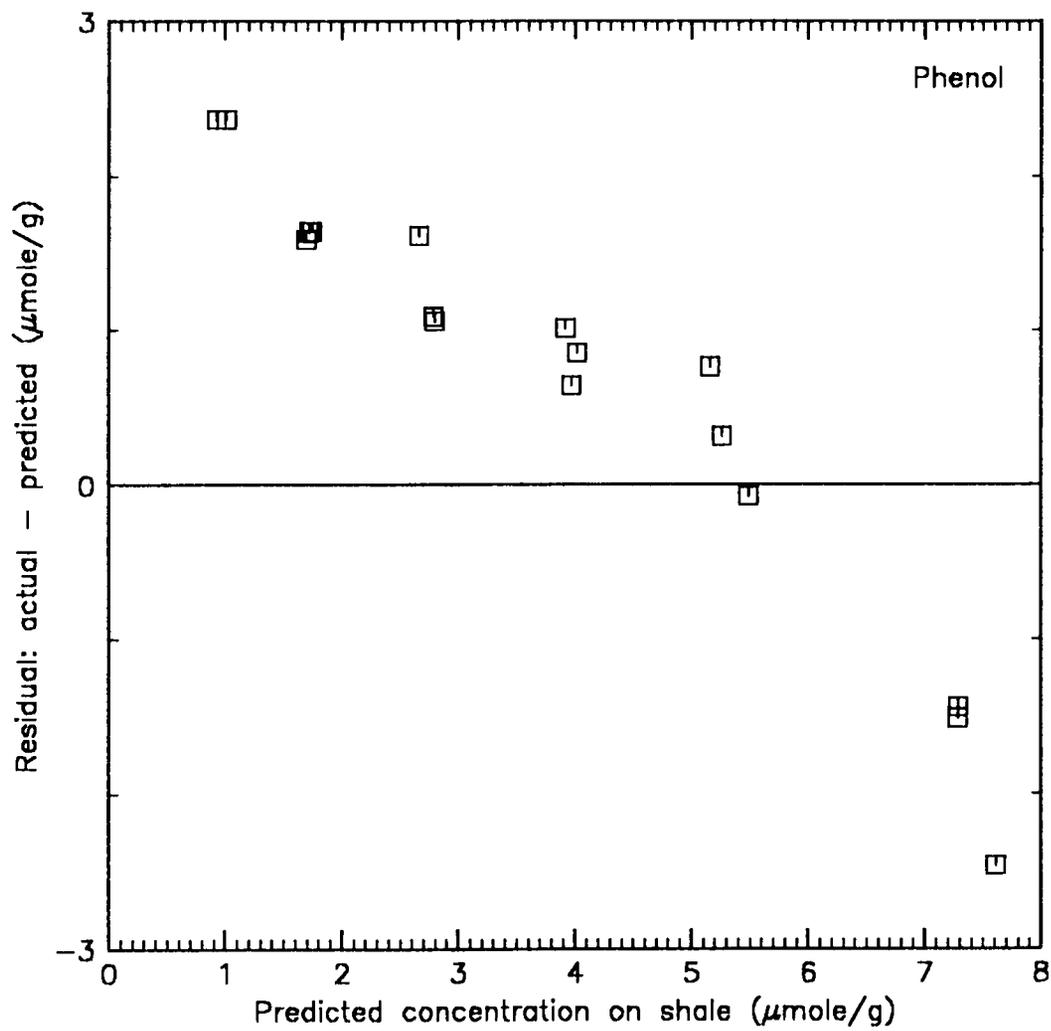


Figure 68. Residual plot for Phenol in Phenol cum 2-Hydroxynaphthalene system computed by parameter estimation

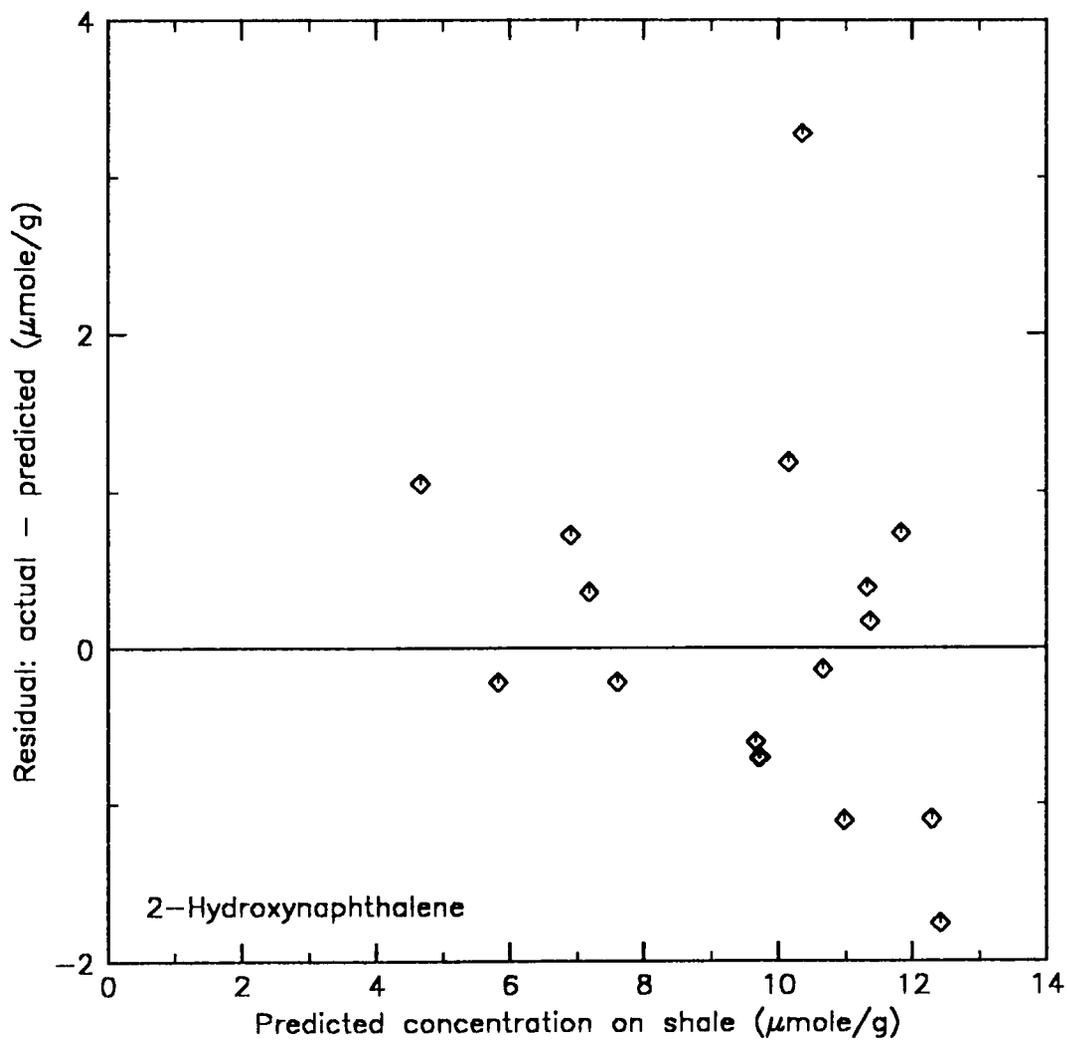


Figure 69. Residual plot for 2-Hydroxynaphthalene in Phenol cum 2-Hydroxynaphthalene system computed by parameter estimation

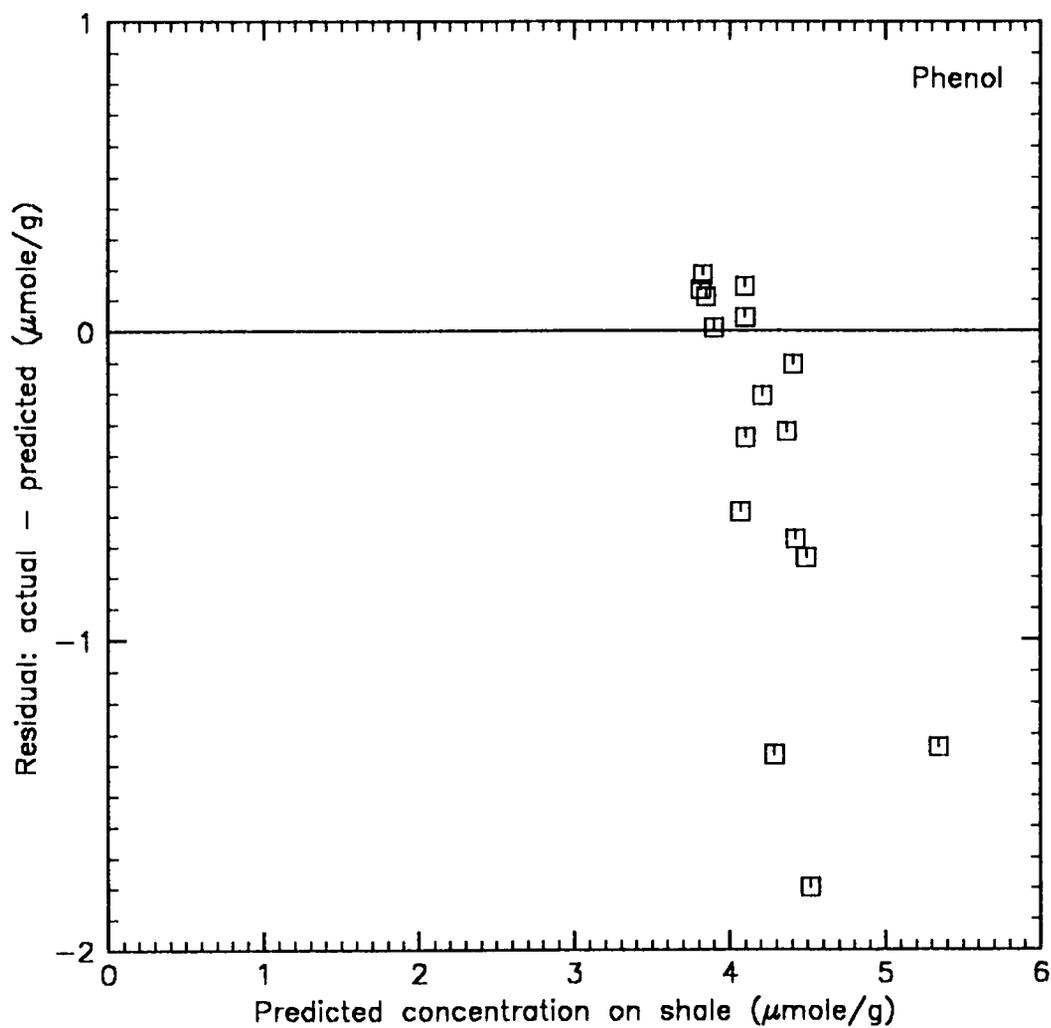


Figure 70. Residual plot for Phenol in Phenol cum 2,3,5-Trimethylphenol system computed by parameter estimation

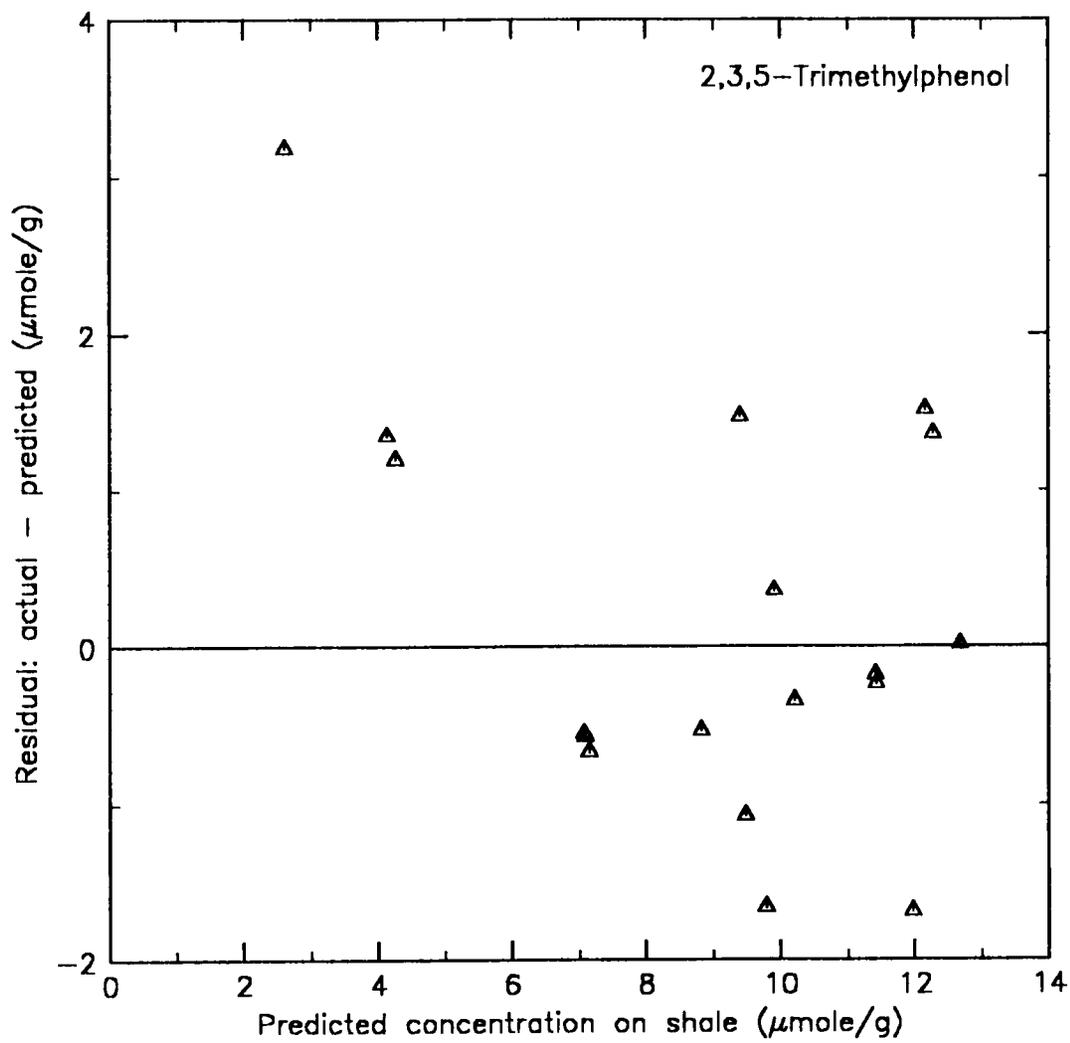


Figure 71. Residual plot for 2,3,5-Trimethylphenol in Phenol cum 2,3,5-Trimethylphenol system computed by parameter estimation

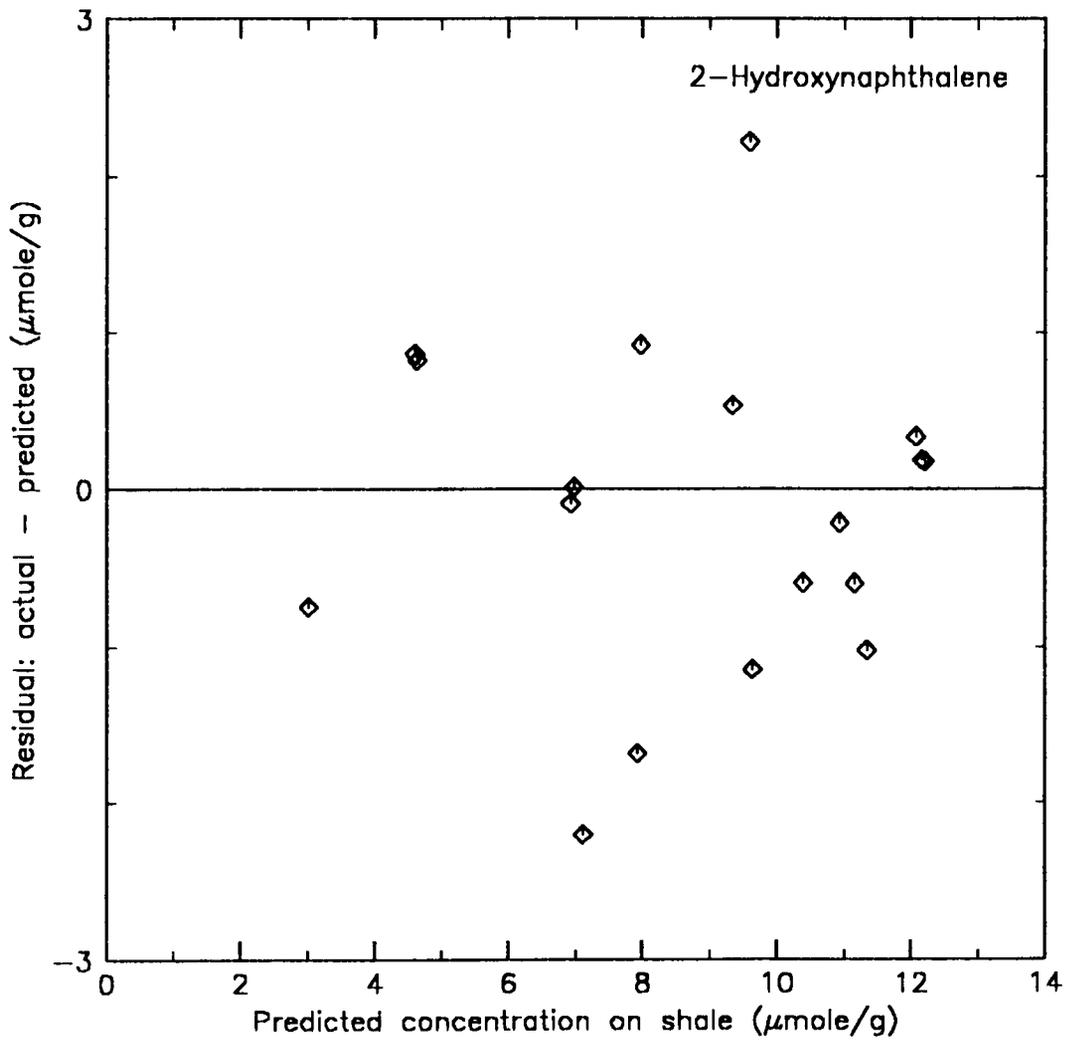


Figure 72. Residual plot for 2-Hydroxynaphthalene in 2-Hydroxynaphthalene cum 1,2,3,4-Tetrahydroquinoline system computed by parameter estimation

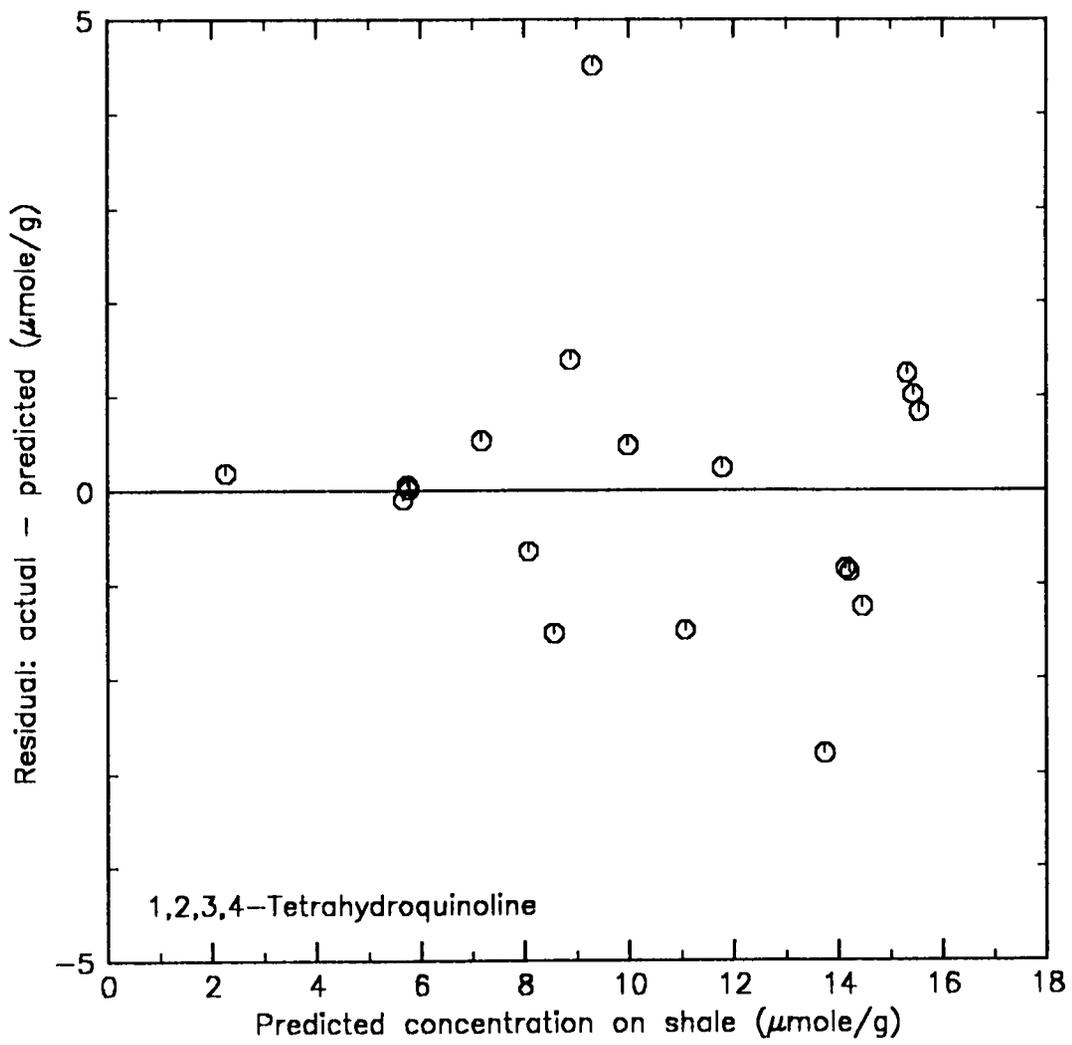


Figure 73. Residual plot for 1,2,3,4-Tetrahydroquinoline in 2-Hydroxynaphthalene cum 1,2,3,4-Tetrahydroquinoline system computed by parameter estimation

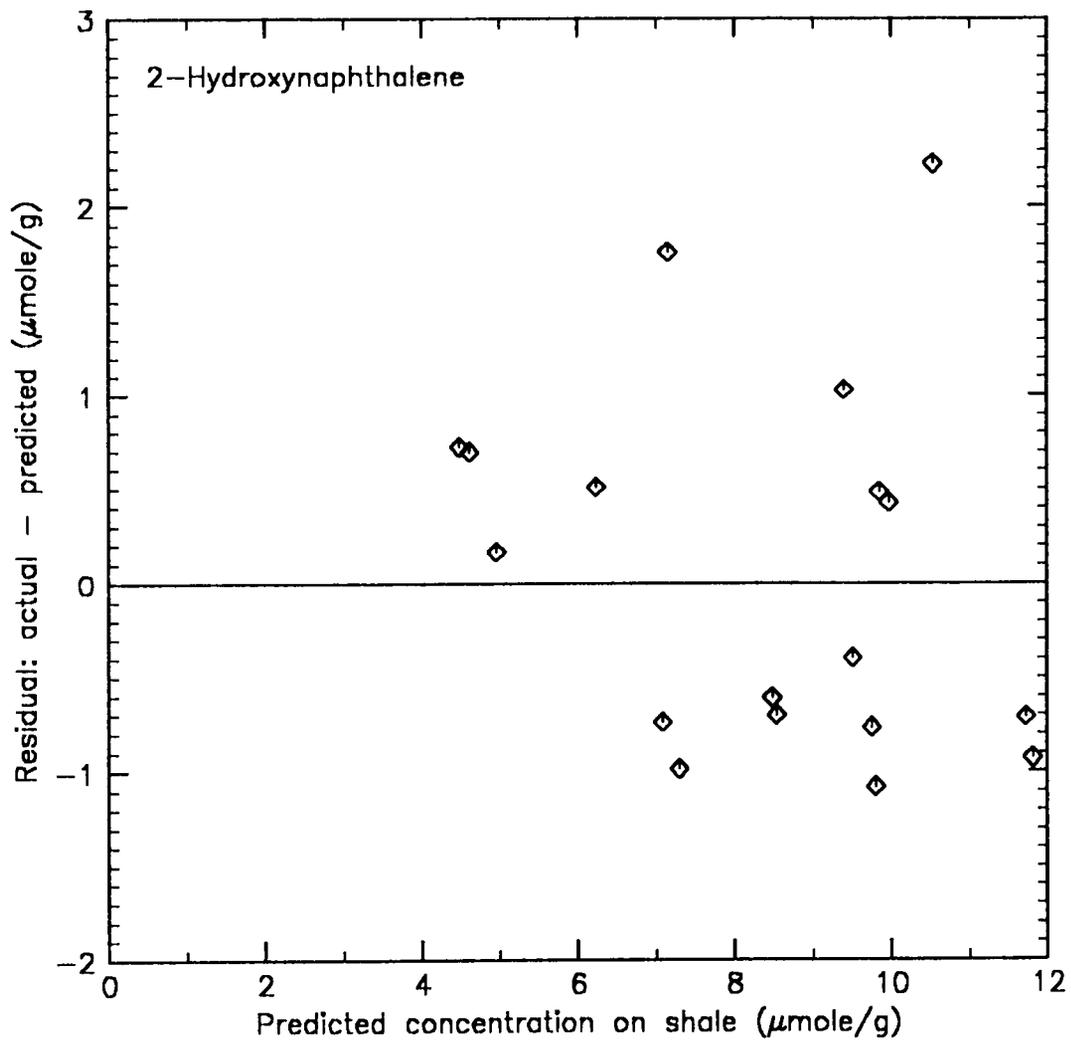


Figure 74. Residual plot for 2-Hydroxynaphthalene in 2-Hydroxynaphthalene cum 2,3,5-Trimethylphenol system computed by parameter estimation

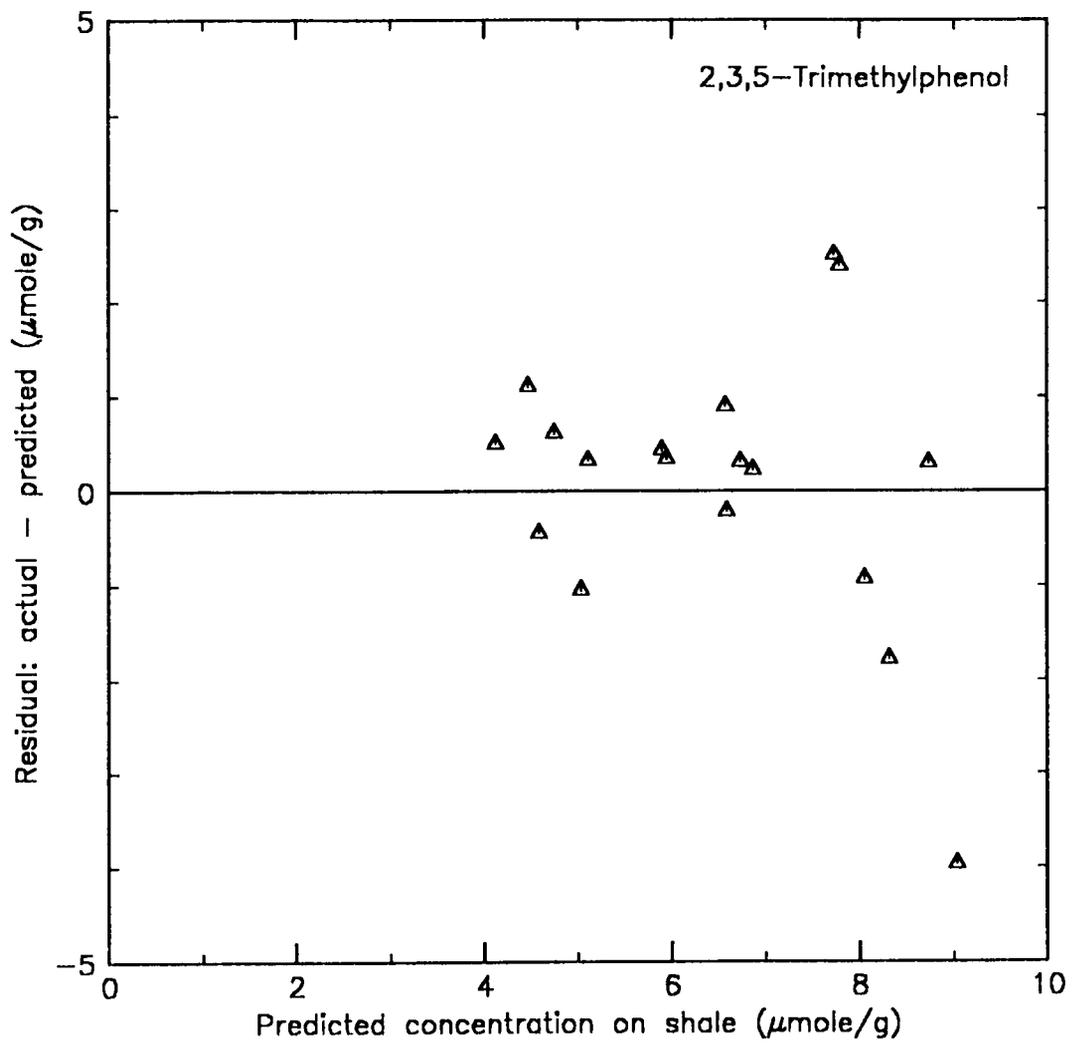


Figure 75. Residual plot for 2,3,5-Trimethylphenol in 2-Hydroxynaphthalene cum 2,3,5-Trimethylphenol system computed by parameter estimation

Parameter Estimation for the Tri- and Tetra-Component Systems

The estimates of parameters for the tri-component system gave residuals in the range of -2 to 2 $\mu\text{mole}\cdot\text{g}^{-1}$ for Phenol equilibrium concentrations between 2.5 and 4 $\mu\text{mole}\cdot\text{g}^{-1}$, for IIN equilibrium concentrations between 4 and 16 $\mu\text{mole}\cdot\text{g}^{-1}$ and for TP equilibrium concentrations between 4 and 10 $\mu\text{mole}\cdot\text{g}^{-1}$. These estimates are considered to be quite good, since the residuals were low in comparison to the predicted values.

The estimates for the tetra-component system produced rather large residuals for Phenol (-7 to 14 $\mu\text{mole}\cdot\text{g}^{-1}$ for C between 2 and 10 $\mu\text{mole}\cdot\text{g}^{-1}$), but otherwise reasonable residuals for the other three compounds. The residuals were in the range -9 to 17 $\mu\text{mole}\cdot\text{g}^{-1}$ for equilibrium concentrations in the ranges 1 to 21 $\mu\text{mole}\cdot\text{g}^{-1}$ for IIN, 1 to 30 $\mu\text{mole}\cdot\text{g}^{-1}$ for THQ, and 1 to 13 $\mu\text{mole}\cdot\text{g}^{-1}$ for TP.

Summary of Modelling Efforts

Because the results with the SIAS predictions were generally not good, and because the parameter estimation method, although improving the results in some cases, is not a predictive method, a final model was tried. This was the multicomponent Langmuir model:

$$q_i = \frac{a_i b_i C_i}{1 + \sum_{j=1}^N b_j C_j} \quad (13)$$

The results from this model for the first few bisolute systems that were analyzed were not good, and it was also abandoned.

In sum, then, the result of quite extensive modelling with the multicomponent data was not satisfactory. Parameter estimation did improve the 'predictions' of the data, but not enough to justify

using it as a standard technique. It is a moot point, however, whether parameter estimation should be tried or not, since the object of modelling is to predict the data so that the actual experiments do not have to be performed. It is felt that the parameter estimations could be improved if the data points were more evenly spread over the equilibrium concentration (C) domain. In the bisolute cases, this would mean generating data in areas other than in the 45° direction along which most of the data points lie.

Column Experiments on Shale

The four compounds used in this study were used in continuous-flow column experiments. The influent feed was at $50 \text{ mg}\cdot\ell^{-1}$, and the experiments were continued until the columns were exhausted, except in the case of THQ where one column was continued almost until exhaustion and the other two replicates were stopped earlier. This last was due to the fact that THQ was removed to a large extent, but the effluent level reached a plateau at $25 \text{ mg}\cdot\ell^{-1}$. The first replicate was continued for 1289 hr (54 days) for a total of 1750 pore volumes; the feed was changed to distilled water at 1640 pore volumes. The results of the first replicates of the column studies are given in Figures 76-79. The other replicates are shown in Appendix E.

It is difficult to completely characterize or model the column studies because of the lack of kinetic data — there is only one replicate of a single-solute kinetic experiment on THQ available in a previous study [19], whereas in the case of HIN and TP the concentration dropped to zero (and Phenol was not studied). However, some general conclusions can be drawn.

The column data confirmed the conclusions drawn from the batch studies that the order of sorbability (from smallest to largest amount) was Phenol < TP < HIN < THQ. The pH of the eluate from the columns usually started at a lower value (around 6.0-6.5) and then gradually increased to

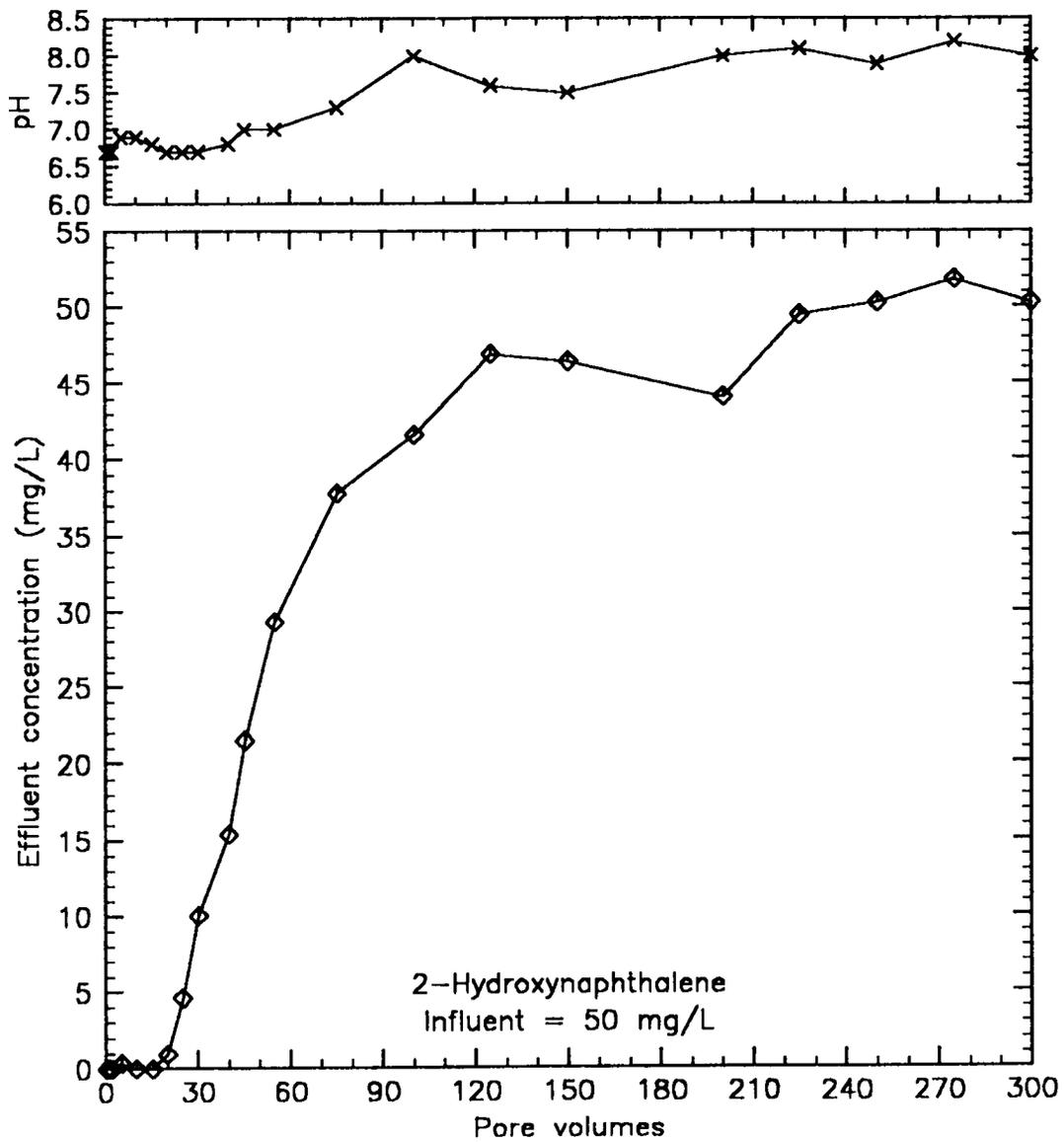


Figure 76. Continuous-flow column sorption trials with 2-Hydroxynaphthalene on shale: First replicate.

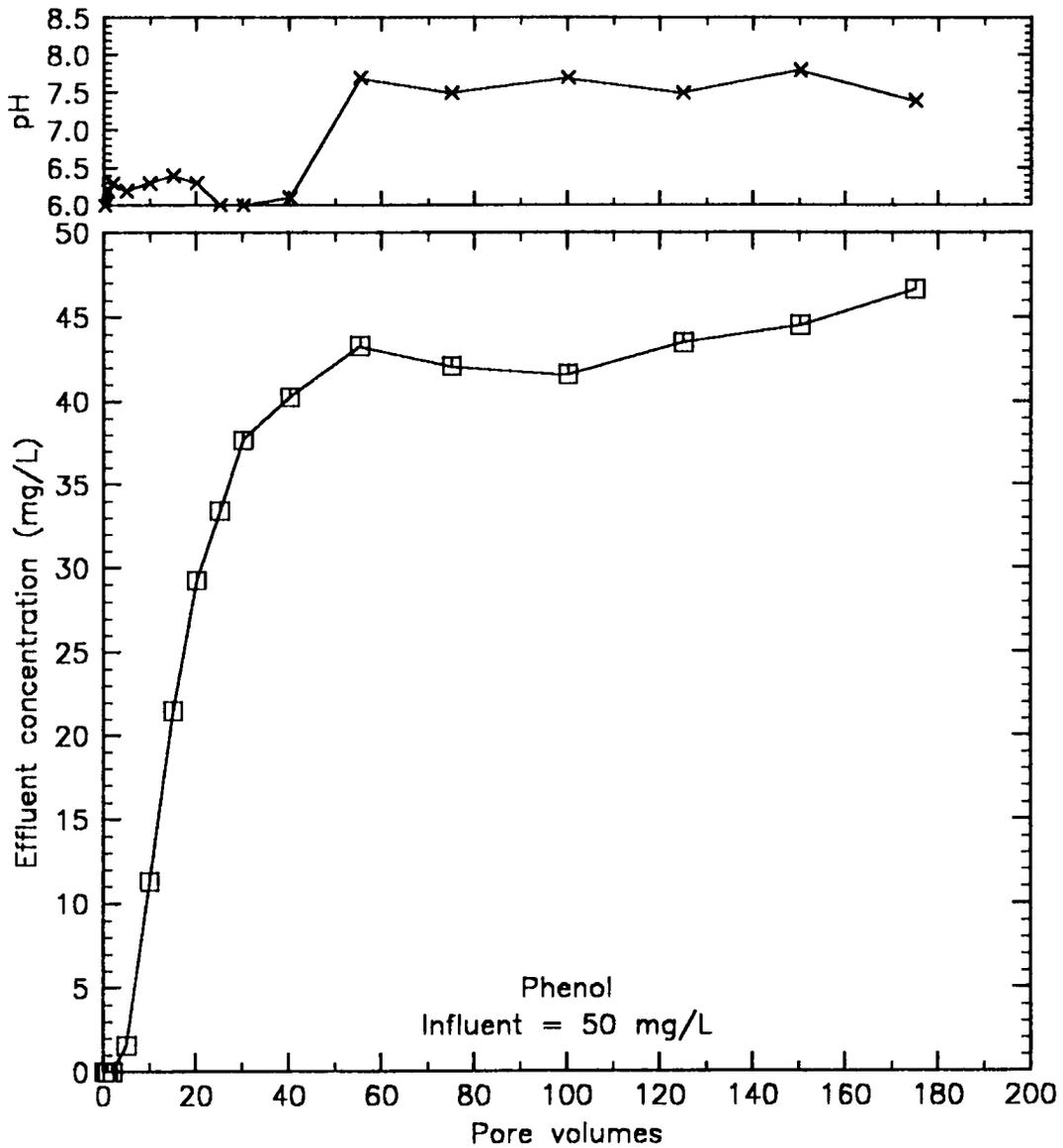


Figure 77. Continuous-flow column sorption trials with Phenol on shale: First replicate.

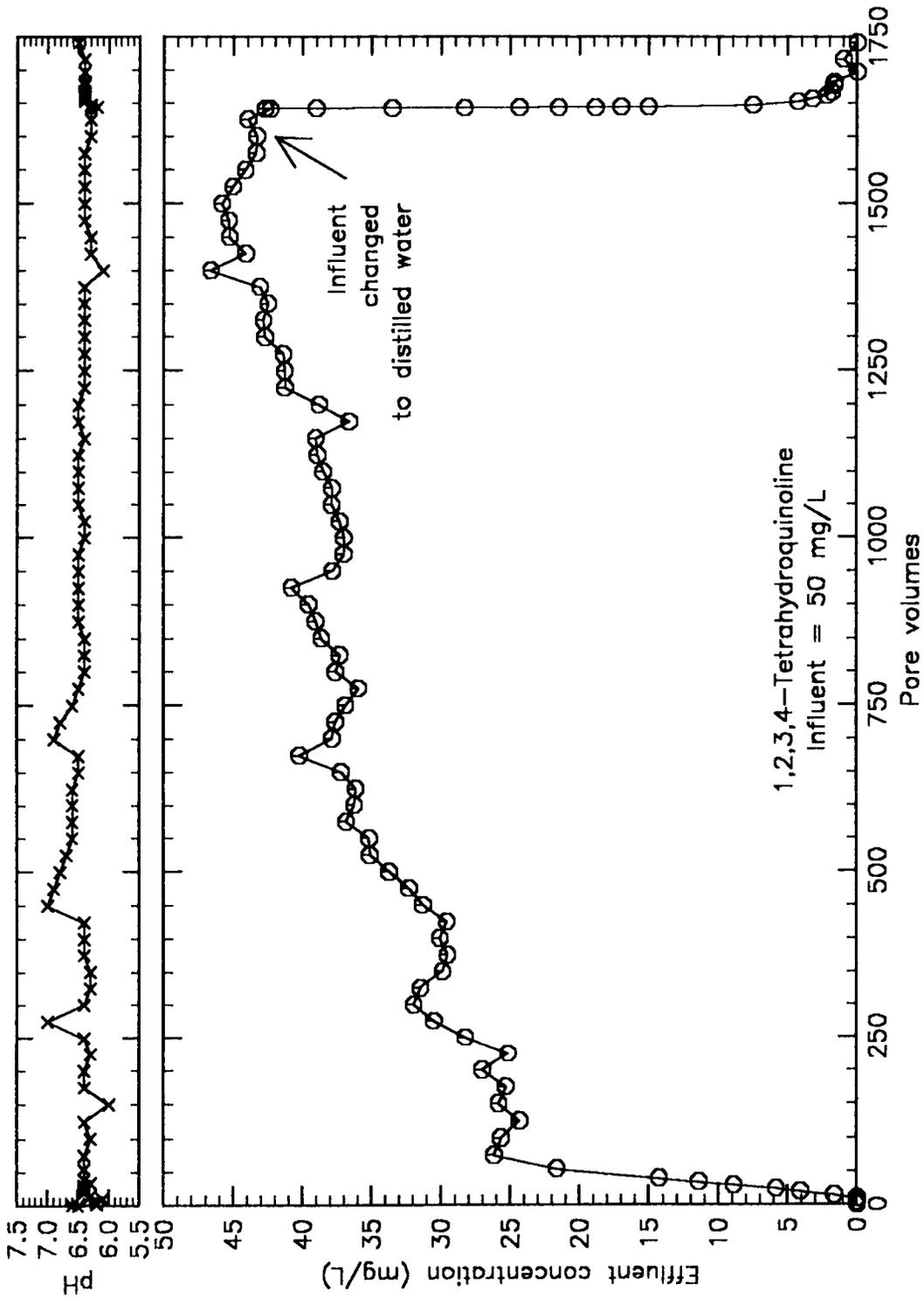


Figure 78. Continuous-flow column sorption trials with 1,2,3,4-Tetrahydroquinoline on shale: First replicate

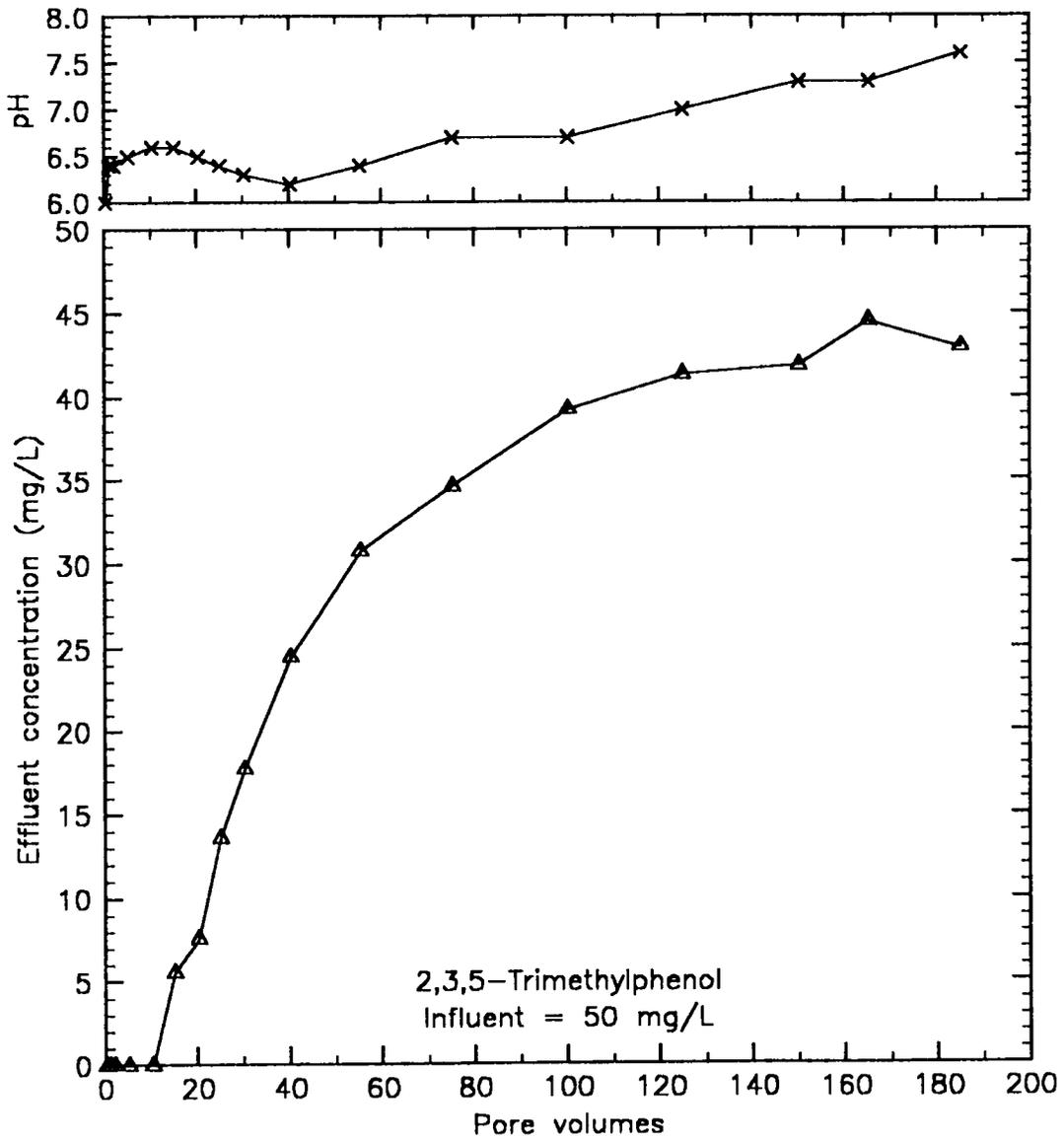


Figure 79. Continuous-flow column sorption trials with 2,3,5-Trimethylphenol on shale: First replicate.

a more neutral value (around 7.0-7.5). This pH range was observed for the batch studies also, and it can therefore be concluded that Antrim shale does not leach any constituents in amounts that would change the pH to a large degree. The leachable materials should leach in the first few pore volumes, and this would indicate that the nature of the materials is slightly acidic.

The previous study by Boardman, *et al.* [18, 19], had determined that the order of breakthrough and exhaustion of columns of Antrim spent shale was with TP first, followed by THQ, followed by HN. In other words, the amounts sorbed were in the order $TP < THQ < HN$. The feed concentration of the experiments performed in that study was $25 \text{ mg}\cdot\ell^{-1}$. All other factors, such as the flow rate and the column jacket temperature, were the same as those used in this study. Although it appears that the positions of THQ and HN were changed in the previous study with respect to the amount sorbed, the difference is not so great. THQ did break through sooner; however, at the time when the column experiments were stopped, the differences in the effluent concentrations of THQ and HN were $1\text{-}2 \text{ mg}\cdot\ell^{-1}$ (at an effluent concentration of about $10 \text{ mg}\cdot\ell^{-1}$) with the concentration of THQ being the higher one. This difference is not significant, since, on the HPLC that was used for that study, the error in analysis could easily account for a $1 \text{ mg}\cdot\ell^{-1}$ difference. Even when a fourth component — 2,6-Dimethylpyridine — was added to the influent, the final difference in the effluent concentration of THQ and HN was about $3 \text{ mg}\cdot\ell^{-1}$ at a level of $14 \text{ mg}\cdot\ell^{-1}$.

Weber and Chakravorti [220] provide a factor for the determination of favorable or unfavorable conditions based upon the Langmuir factor, a , and the initial concentration, C_0 , in batch isotherm studies. This factor is derived based on the shape of the isotherm. If the isotherm is convex with respect to the abscissa on a plot of q against C (i.e., if the initial slope is larger than unity), then it is considered to be a favorable sorption isotherm, and the more convex, the more favorable the sorptive behavior. If the isotherm is concave (initial slope smaller than unity), then the isotherm is considered to be an unfavorable isotherm, and the compound to be unfavorably sorbed. The case when the slope remains unity throughout is called the linear isotherm. This parameter, R , called the constant separation factor or equilibrium parameter, is defined as:

$$R = \frac{1}{1 + aC_0} \quad (20)$$

$R > 1 \Rightarrow$ Unfavorable

$R = 1 \Rightarrow$ Linear

$0 < R < 1 \Rightarrow$ Favorable

$R = 0 \Rightarrow$ Irreversible

Although this parameter was originally derived for batch systems, it should be applicable to column systems in indicating which component will saturate the column first. Such an analysis was done for the four compounds for an initial concentration of $50 \text{ mg}\cdot\ell^{-1}$. This analysis cannot easily be done and will be confusing for the batch experiments used in this study since the initial concentration (C_0) in each flask varied. More than one value of R would, therefore, be obtained for each batch experiment. Table 52 shows the appropriate information.

The values of a derived from the Langmuir fits prove to be quite good indicators of the column performance behavior when applied with the relationship given above. The R factor agrees quite well with the 10% and 50% breakthrough pore volumes. Phenol broke through the earliest (at 10 pore volumes for 10% breakthrough and 20 pore volumes for 50%), and shale columns had the lowest capacity for sorbing it. It also has the highest value for R (0.276). THQ, on the other hand, broke through very slowly, and went into a very long, slightly sloping plateau stage in the first replicate (the one that was continued for a long time), and it has the lowest value for R (0.005, which is derived from the two replicates that agreed, or 0.017 derived from the first replicate). It has a moderately quick 10% breakthrough at 25 pore volumes, followed by 50% breakthrough at 65-100 pore volumes. To check if this were really the case, the first replicate was eluted with distilled water after 1640 pore volumes of THQ feed. As can be seen from Figure 78, there was very little elution, indicating a strong sorption of THQ. Apparently, the sorption was almost irreversible (at least with distilled-water elution) and this is indicated, too, by the low number for R .

IIN, with a value of 0.047 for R broke through at 25-30 pore volumes (10%) and 45-50 pore volumes (50%). The sorption for IIN is very favorable. The sorption for TP is favorable with a value

Table 52. Values of the constant separation factor, R , calculated for the four compounds used in the study in order to correlate column behavior

Compound	a	$R@50 \text{ mg}\cdot\ell^{-1}$	Type*	Pore volume† at breakthrough of	
				10%	50%
HN	58.2	0.047	Very favorable	25-30	45-50
Phenol	4.9	0.276	Favorable	10	20
THQ (two reps.) (first rep.)	549.6	0.005	Extr. favorable	25	65-100
	151.1	0.017	Very favorable	25	65-100
TP	23.7	0.103	Favorable	20	40

a is the Langmuir parameter, derived from batch data.

R is the constant separation factor.

* Refers to sorption type as defined in equation (20).

† Derived from Figures 76-79, and those in Appendix E.

of 0.103 for R , but it had similar breakthrough pore volumes (20 at 10% and 40 at 50%) similar to HN.

All in all, the column trials were a confirmation of the batch results. The behavior of the shale with respect to repeatability of the results was also good. Antrim shale proved to be a good sorbent for the compounds studied. This was also true for the multi-component experiments performed with HN, THQ and TP in an earlier study [19], with breakthroughs ($> 1\%$ in effluent) occurring between 10-20 pore volumes. The feed solution strength used in those studies was $25 \text{ mg}\cdot\ell^{-1}$ — half the strength used in this study.

Chapter VII

Conclusions and Recommendations

As a result of this study, the following conclusions were reached:

1. Antrim spent shale demonstrated a consistent behavior with respect to sorption of Phenol, 2-Hydroxynaphthalene, 2,3,5-Trimethylphenol and 1,2,3,4-Tetrahydroquinoline, although in one case the single-component replicate of 1,2,3,4-Tetrahydroquinoline did not agree with the other replicates. The sorptive capacity of Antrim spent shale was least for Phenol, and greatest for 1,2,3,4-Tetrahydroquinoline, with the order being Phenol < TP < HN < THQ. The single-solute sorptive capacity of spent shale was about two orders of magnitude less than that of Filtrasorb 300 granular activated carbon. The sorptive order (from least to largest amount sorbed) of the four study compounds in multicomponent experiments on shale can be predicted based upon the single-component experiments.
2. Single-solute continuous-flow column experiments on shale could not be better analyzed because of a lack of proper kinetic data. A better experimental design would have avoided this problem. However, the order in which the compounds would reach a 50% breakthrough in the columns could be predicted based upon the single-component batch experiment data. The

order of breakthrough at 10% of influent is not predicted with the same degree of clarity, specially in the case of 1,2,3,4-Tetrahydroquinoline, which displayed an initial region of quicker sorption by the column followed by an extended region of slower sorption.

3. Ratios of the amount sorbed of any one component to the total sorbed amount of all components (α_i) in a multisolute system can be used to quantify and study the data gathered from experiments with multiple solutes. The means of these ratios ($\bar{\alpha}_i$) indicate the partition between species of the amounts sorbed and provide a means of reducing the relative amounts sorbed to one number for each species to facilitate comparisons. This analysis can also be used to determine if the partition of the individual sorbed amounts changes with changing equilibrium concentrations of the compounds, thereby indicating a more favored or less favored capacity when the equilibrium concentration increases or decreases.
4. Predictions of the means sorptive ratios ($\bar{\alpha}_i$) of lower-order multicomponent experiments from the ratios calculated from the tetra-component experiments provided mixed results. Predictions of the $\bar{\alpha}_i$ for 2-Hydroxynaphthalene and 1,2,3,4-Tetrahydroquinoline agreed to within less than 11% of those computed from the lower-order experiments, whereas for Phenol and 2,3,5-Trimethylphenol the predictions were worse, with the maximum deviation being about 19%. The predicted ratios (when compared to the calculated ones) are better predicted for those compounds that sorb to larger extents (HN and THQ) and not as well for those that sorb to a smaller degree (Phenol and TP).
5. Filtrasorb 300 granular activated carbon showed consistent sorptive behavior for the three phenolic compounds, but there were unexplained discrepancies in the sorption of 1,2,3,4-Tetrahydroquinoline. Except for Phenol, which clearly sorbed the least, no apparent order was discernible in the amounts sorbed of the other compounds. This makes it difficult to compare the behavior of the shale with that of the carbon. The carbon cannot be used as an indicator of the order of sorbed amounts upon the shale, but it can be used as an indicator

that the sorbed amounts were in the range of two orders of magnitude larger than those for the shale.

6. Modelling efforts with three models did not provide good results. The most promising model – the simplified ideal adsorbed solution model – provided biased estimates of the parameters in the case of most systems that contained Phenol. The parameter estimates, in general, improved the fit to the data, but these improvements in the estimation of the parameters cannot be in turn estimated without performing multisolute trials. Therefore, although the sorptive order in multicomponent trials (in terms of the amounts sorbed) could be extrapolated based upon the single-solute data, the equilibrium concentrations and loadings could not be so treated.
7. Among the three phenolic compounds studied, the effects on sorption due to ascending the homologous series is more pronounced than that associated with branching. The higher homolog, HN, sorbed to a larger amount than did the branched compound, TP, both of which sorbed better than the native compound, Phenol. In addition, no relationship was found between the amounts sorbed and the octanol-water partition coefficient. The values of this coefficient would have predicted a sorptive order (from least to most sorbed) of Phenol < THQ < HN < TP, whereas the order determined by the study was Phenol < TP < HN < THQ.

The following recommendations are made for future research:

1. The variable sorptive behavior of 1,2,3,4-Tetrahydroquinoline, both on the shale and the carbon, needs further clarification. Perhaps a larger number of experiments might resolve the issue, but the influence of other factors more closely allied to the structure of the compound and the sorbents need also to be considered.

2. In order to obtain better parameter estimates, so that the SIAS model could be better utilized, data that are spread more evenly in the equilibrium concentration (C) domain need to be gathered.
3. Kinetic data need to be gathered before the results obtained from the column experiment can be adequately characterized.
4. The current study has shown that shale has a reasonable capacity for sorbing the types of organic compounds to be found in retort water. However, the strength of sorption needs to be better characterized if the shale is to be used as a sorbent. Desorption studies need to be performed. One column replicate in the present study was desorbed with distilled water and seemed to indicate that 1,2,3,4-Tetrahydroquinoline is retained upon the shale column. The behavior of other solvents and the presence of other compounds as related to desorption needs to be more thoroughly probed.
5. Finally, if the information gathered from single-solute sorption experiments is to be used in a predictive manner such that multicomponent sorption studies can be avoided, then a model needs to be either found or developed to better predict the sorptive behavior.

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Appendix A

Definitions of Terms Related to Sorption

Absorption Refers to the “penetration of particles of one phase deep into the other phase, resembling dissolution to some extent” [171]. Normally this refers to the penetration of a gas into the bulk of a solid, and is akin to the solubilization of a solid in a liquid. It can be thought of as a “solution” of gas in a solid.

Adsorption Physical sorption has been “internationally defined as the enrichment (i.e. positive adsorption or simply adsorption) or depletion (i.e. negative adsorption) of one or more components in an interfacial layer” [98]. Adsorption is essentially a surface phenomenon, whether the surface is an external one or an internal one (e.g. pores in a solid).

Sorption Originally referred to both absorption, adsorption and capillary condensation within pores. However, the term “sorption” is used frequently to refer to adsorption and capillary condensation.

Adsorbent Also termed “sorbent”, it refers to the solid upon which the material in solution or in a mixture sorbs.

Adsorbate Also termed “sorbate”, this refers to the material that is being sorbed onto a solid. Adsorption is the term used when the material is in the gas phase.

Physisorption Sorption due to van der Waals forces and other electrostatic forces (polarization, dipole and quadrupole interactions). These interactions are basically due to weak forces.

Chemisorption Defined to be the phenomenon “where an atom or molecule is bound to a surface through overlapping of one or more of its electron orbitals” [32]. Usually, but not always, the heat of sorption due to chemisorption is higher than that due to physisorption.

Appendix B

Raw Data Files

The three replicates are identified by the dates on which the experiments were terminated. A line contains the headings for the columns. A heading of 'C' indicates the initial concentration (of each component, for multicomponent experiments) in each flask for the batch isotherms. A heading containing just the abbreviation of the name of the compound (e.g., 'HN') indicates the final concentration in each flask, or the effluent concentration in the case of the column experiments. A heading wherein the abbreviation of the name of the chemical is preceded by the letters 'DEL' indicates the difference between the initial and final concentrations (proportional to the uptake). 'PH' refers to the pII of the flask or effluent.

Note: 'P' = Phenol; 'PV' = Pore Volume; 'TUBE' = Tube number from fraction collector.

Table B.1. Single-component isotherm on shale — 2-Hydroxynaphthalene

* FIRST REPLICATE -- 03/22/87

* C	HN	DELHN	PH
0	0.0	0.0	7.0
10	0.0	10.00	7.0
25	0.62	24.38	7.0
35	2.93	32.07	7.0
50	9.24	40.76	6.9
65	22.84	42.16	6.9
80	34.55	45.45	6.9
100	33.69	66.31	7.0

* SECOND REPLICATE -- 03/29/87

* C	HN	DELHN	PH
0	0.0	0.0	6.3
10	1.340	8.660	6.3
25	4.557	20.443	6.4
35	4.222	30.778	6.4
50	8.813	41.187	6.3
65	20.10	44.90	6.3
80	29.22	50.78	6.3
100	46.28	53.72	6.3

* THIRD REPLICATE -- 01/22/88

* C	HN	DELHN	PH
0	0.0	0.0	6.2
10	0.0	10.00	6.2
25	0.51	24.49	6.3
35	2.82	32.18	6.3
50	9.34	40.66	6.2
65	24.56	40.44	6.2
80	35.01	44.99	6.2
100	44.86	55.14	6.3

Table B.2. Single-component isotherm on shale — Phenol

* FIRST REPLICATE -- 04/04/87

* C	P	DELP	PH
0	0.0	0.0	6.9
10	3.068	6.932	6.8
25	12.794	12.206	6.7
35	18.668	16.332	6.7
50	30.222	19.778	6.6
65	41.514	23.486	6.8
80	55.548	24.452	6.7
100	71.214	28.786	6.7

* SECOND REPLICATE -- 04/25/87

* C	P	DELP	PH
0	0.0	0.0	6.6
10	2.572	7.428	6.6
25	11.74	13.26	6.3
35	17.15	17.85	6.5
50	29.61	20.39	6.6
65	40.63	24.37	6.7
80	53.95	26.05	6.5
100	71.63	28.37	6.6

* THIRD REPLICATE -- 12/25/87

* PROBLEMS OF GROWTH IN THIS REPLICATE

* REPLICATE IGNORED FOR DATA ANALYSIS

* C	P	DELP	PH
0	0.0	0.0	7.2
25	0.0	25.0	7.1
35	0.0	35.0	7.2
50	17.11	32.89	7.2
65	17.46	47.54	7.2
80	32.42	47.58	7.3

Table B.3. Single-component isotherm on shale -- 1,2,3,4-Tetrahydroquinoline

* FIRST REPLICATE -- 03/29/87

* C	THQ	DELTHQ	PH
0	0.0	0.0	6.6
10	0.523	9.477	6.7
25	5.082	19.918	6.6
35	12.92	22.08	6.6
50	26.82	23.18	6.6
65	36.91	28.09	6.5
80	58.36	21.64	6.6
100	76.30	23.70	6.6

* SECOND REPLICATE -- 12/18/87

* C	THQ	DELTHQ	PH
0	0.0	0.0	6.9
10	0.0	10.0	6.7
25	0.0	25.0	6.6
35	0.09	34.01	6.7
50	0.42	49.58	6.7
65	3.15	61.85	6.7
80	4.21	75.79	6.8
100	11.63	88.37	6.7

* THIRD REPLICATE -- 03/29/87

* C	THQ	DELTHQ	PH
0	0.0	0.0	6.3
10	0.0	10.0	6.1
25	0.0	25.0	6.2
35	0.28	34.72	6.2
50	0.35	49.65	4.8
65	3.23	61.77	6.0
80	4.48	75.52	6.2
100	10.50	89.50	6.3

Table B.4. Single-component isotherm on shale -- 2,3,5-Trimethylphenol

* FIRST REPLICATE -- 03/22/87

* C	TP	DELTP	PH
0	0.0	0.0	6.2
10	0.0	10.00	6.2
25	2.41	22.59	6.3
35	9.85	25.15	6.3
50	19.62	30.38	6.3
65	28.98	36.02	6.4
80	37.54	42.46	6.5
100	55.39	44.61	6.5

* SECOND REPLICATE -- 03/29/87

* C	TP	DELTP	PH
0	0.0	0.0	6.6
10	1.677	8.323	6.5
25	5.369	19.631	6.5
35	10.40	24.60	6.5
50	21.47	28.53	6.6
65	29.53	35.47	6.6
80	36.68	43.32	6.4
100	58.05	41.95	6.6

* THIRD REPLICATE -- 01/02/88

* C	TP	DELTP	PH
0	0.0	0.0	6.4
10	0.0	0.0	6.4
25	2.00	23.00	6.4
35	9.12	25.88	6.5
50	22.04	27.96	6.4
65	28.14	36.86	6.5
80	35.90	44.10	6.4
100	57.68	42.32	6.4

Table B.5. Bisolute isotherm on shale -- Phenol and HN

* FIRST REPLICATE -- 04/17/87						
* C	P	HN	DELP	DELHN	PH	
0	0	0	0	0	6.4	
10	5.01	0.00	4.99	10.00	6.6	
25	15.53	0.00	9.47	25.00	6.4	
35	25.45	2.03	9.55	32.97	6.5	
50	39.12	10.83	10.88	39.17	6.5	
65	51.99	22.27	13.01	42.73	6.4	
80	64.26	30.10	15.74	49.90	6.4	
100	83.69	53.87	16.31	46.13	6.4	
* SECOND REPLICATE -- 01/22/88						
* C	P	HN	DELP	DELHN	PH	
0	0	0	0	0	6.6	
10	5.34	0.00	4.66	10.00	6.6	
25	15.71	0.77	9.29	24.23	6.6	
35	25.52	2.40	9.48	32.60	6.6	
50	39.07	11.05	10.93	38.95	6.6	
65	51.08	19.47	13.92	45.53	6.6	
80	63.29	29.33	16.71	50.67	6.5	
100	83.49	51.60	16.51	48.40	6.5	
* THIRD REPLICATE -- 02/05/88						
* C	P	HN	DELP	DELHN	PH	
0	0	0	0	0	6.4	
10	5.20	0.00	4.80	10.00	6.5	
25	15.47	0.29	9.53	24.71	6.4	
35	25.73	3.08	9.27	31.92	6.5	
50	37.92	10.96	12.08	39.04	6.5	
65	51.25	15.97	13.75	49.03	6.5	
80	64.70	21.00	15.30	59.00	6.6	
100	85.48	45.64	14.52	54.36	6.6	

Table B.6. Bisolute isotherm on shale — Phenol and THQ

* FIRST REPLICATE -- 04/17/87						
* C	P	THQ	DELP	DELTHQ	PH	
0	0	0	0	0	7.2	
10	4.59	0.00	5.41	10.00	7.2	
25	15.91	0.00	9.09	25.00	7.2	
35	25.27	0.21	9.73	34.79	7.3	
50	40.23	0.52	9.77	49.48	7.2	
65	54.18	2.07	10.82	62.93	7.3	
80	69.41	2.62	10.59	77.38	7.2	
100	89.38	10.29	10.61	89.71	7.2	
* SECOND REPLICATE -- 12/18/87						
* C	P	THQ	DELP	DELTHQ	PH	
0	0	0	0	0	7.1	
10	4.97	0.00	5.03	10.00	7.1	
25	16.14	0.00	8.86	25.00	7.2	
35	26.08	0.20	8.92	34.80	7.2	
50	39.57	0.44	10.43	49.56	7.2	
65	54.42	2.02	10.58	62.98	7.2	
80	68.31	2.97	11.69	77.03	7.2	
100	89.30	10.55	10.70	89.45	7.2	
* THIRD REPLICATE -- 02/05/88						
* C	P	THQ	DELP	DELTHQ	PH	
0	0	0	0	0	7.2	
10	4.81	0.00	5.19	10.00	7.2	
25	16.40	0.00	8.60	25.00	7.2	
35	25.88	0.18	9.12	34.82	7.2	
50	39.49	0.45	10.51	49.55	7.2	
65	54.01	1.94	10.99	63.06	7.3	
80	69.22	2.41	10.78	77.59	7.2	
100	93.69	0.15	6.31	99.85	7.2	

Table B.7. Bisolute isotherm on shale — Phenol and TP

* FIRST REPLICATE -- 04/17/87						
* C	P	TP	DELP	DELTP	PH	
0	0	0	0	0	7.0	
10	3.50	0.00	6.50	10.00	7.0	
25	13.69	1.35	11.31	23.65	7.1	
35	23.82	8.36	11.18	26.64	7.1	
50	25.99	16.86	24.01	33.14	7.1	
65	52.85	20.66	12.15	44.34	7.0	
80	68.30	34.31	11.70	45.69	7.1	
100	92.31	44.18	7.69	55.82	7.1	
* SECOND REPLICATE -- 12/25/87						
* C	P	TP	DELP	DELTP	PH	
0	0	0	0	0	6.9	
10	3.47	0.00	6.53	10.00	7.0	
25	14.41	2.75	10.59	22.25	7.1	
35	23.85	8.53	11.15	26.47	6.9	
50	40.16	16.16	9.84	33.84	7.0	
65	54.38	24.71	10.62	40.29	7.0	
80	68.96	38.04	11.04	41.96	6.9	
100	91.75	48.17	8.25	51.83	6.9	
* THIRD REPLICATE -- 02/05/88						
* C	P	TP	DELP	DELTP	PH	
0	0	0	0	0	7.0	
10	3.47	0.00	6.53	10.00	6.9	
25	14.39	2.63	10.61	22.37	7.0	
35	23.67	8.37	11.33	26.63	7.0	
50	25.94	15.69	24.06	34.31	7.0	
65	53.69	23.10	11.31	41.90	6.9	
80	68.02	34.15	11.98	45.85	7.0	
100	88.58	44.34	11.42	55.66	7.0	

Table B.8. Bisolute isotherm on shale — HN and THQ

* FIRST REPLICATE -- 05/09/87					
* C	HN	THQ	DELHN	DELTHQ	PH
0	0	0	0	0	6.9
10	0.00	0.00	10.00	10.00	7.1
25	1.40	1.83	23.60	23.17	7.1
35	4.74	4.22	30.26	30.78	7.1
50	7.17	8.19	42.83	41.81	7.0
65	13.89	9.77	51.11	55.23	7.1
80	33.64	27.09	46.36	52.91	7.1
100	46.32	34.47	53.68	65.53	7.1
* SECOND REPLICATE -- 01/15/88					
* C	HN	THQ	DELHN	DELTHQ	PH
0	0	0	0	0	6.6
10	0.16	0.19	9.84	9.81	6.6
25	3.75	2.75	21.25	22.25	6.5
35	8.00	6.83	27.00	28.17	6.5
50	11.55	11.66	38.45	38.34	6.6
65	22.27	21.18	42.73	43.82	6.6
80	35.35	26.74	44.65	53.26	6.7
100	46.59	34.18	53.41	65.82	6.8
* THIRD REPLICATE -- 01/29/88					
* C	HN	THQ	DELHN	DELTHQ	PH
0	0	0	0	0	6.7
10	0.00	0.00	10.00	10.00	6.7
25	1.37	1.80	23.63	23.20	6.7
35	5.44	5.31	29.56	29.69	6.7
50	13.26	8.97	36.74	41.03	6.8
65	22.63	16.92	42.37	48.08	6.9
80	34.32	26.61	45.68	53.39	6.9
100	46.45	33.75	53.55	66.25	6.9

Table B.9. Bisolute isotherm on shale — HN and TP

* FIRST REPLICATE -- 05/01/87						
* C	HN	TP	DELHN	DELTP	PH	
0	0	0	0	0	6.7	
10	0.00	0.79	10.00	9.21	6.8	
25	2.49	8.74	22.51	16.26	6.8	
35	7.57	13.12	27.43	21.88	6.7	
50	16.09	24.18	33.91	25.82	6.6	
65	27.25	36.26	37.75	28.74	6.6	
80	34.89	59.30	45.11	20.70	6.6	
100	44.80	63.13	55.20	36.87	6.8	
* SECOND REPLICATE -- 05/09/87						
* C	HN	TP	DELHN	DELTP	PH	
0	0	0	0	0	6.6	
10	0.00	0.00	10.00	10.00	6.6	
25	2.82	8.10	22.18	16.90	6.7	
35	7.71	12.27	27.29	22.73	6.7	
50	15.95	24.35	34.05	25.65	6.5	
65	25.59	36.09	39.41	28.91	6.6	
80	35.04	50.95	44.96	29.05	6.5	
100	52.94	58.23	47.06	41.77	6.7	
* THIRD REPLICATE -- 01/29/88						
* C	HN	TP	DELHN	DELTP	PH	
0	0	0	0	0	6.8	
10	0.00	0.83	10.00	9.17	6.8	
25	2.04	6.11	22.96	18.89	6.9	
35	5.84	12.81	29.16	22.19	6.8	
50	11.47	24.02	38.53	25.98	6.7	
65	26.13	34.52	38.87	30.48	6.7	
80	35.31	53.30	44.69	26.70	6.8	
100	52.35	58.48	47.65	41.52	7.0	

Table B.10. Bisolute isotherm on shale — TP and THQ

* FIRST REPLICATE -- 05/09/87						
* C	TP	THQ	DELTP	DELTHQ	PH	
0	0	0	0	0	6.9	
10	0.60	0.35	9.40	9.65	6.9	
25	3.28	0.65	21.72	24.35	6.9	
35	9.71	1.77	25.29	33.23	7.0	
50	18.71	6.38	31.29	43.62	7.1	
65	27.94	7.46	37.06	57.54	7.1	
80	48.56	15.50	31.44	64.50	7.1	
100	64.86	32.25	35.14	67.75	7.1	
* SECOND REPLICATE -- 01/02/88						
* C	TP	THQ	DELTP	DELTHQ	PH	
0	0	0	0	0	7.0	
10	0.71	0.43	9.29	9.57	7.0	
25	3.45	0.71	21.55	24.29	7.0	
35	7.60	1.80	27.40	33.20	6.9	
50	18.71	6.22	31.29	43.78	7.0	
65	28.82	7.22	36.18	57.78	7.1	
80	50.47	14.94	29.53	65.06	7.0	
100	64.77	31.47	35.23	68.53	7.0	
* THIRD REPLICATE -- 01/29/88						
* C	TP	THQ	DELTP	DELTHQ	PH	
0	0	0	0	0	7.2	
10	0.71	0.29	9.29	9.71	6.9	
25	3.15	0.45	21.85	24.55	6.9	
35	8.91	1.79	26.09	33.21	7.0	
50	18.19	6.43	31.81	43.57	7.0	
65	29.87	7.78	35.13	57.22	7.0	
80	48.74	16.43	31.26	63.57	7.0	
100	62.25	30.41	37.75	69.59	7.0	

Table B.11. Trisolute isotherm on shale – Phenol, HN and TP

* SINGLE EXPERIMENT -- 05/24/87

* C	P	HN	TP	DELP	DELHN	DELTP	PH
0	0	0	0	0	0	0	6.5
10	3.64	0.03	0.0	6.36	9.97	10.00	6.4
25	17.11	0.42	4.66	7.89	24.58	20.34	6.4
35	27.26	1.86	11.59	7.74	33.14	23.41	6.4
50	45.16	7.13	23.14	4.84	42.87	26.86	6.5
65	51.46	8.98	29.26	13.54	56.02	35.74	6.5
80	73.47	19.82	43.97	6.53	60.18	36.03	6.7
100	87.00	22.86	56.41	13.00	77.14	43.59	6.6

Table B.12. Tetrasolute isotherm on shale

* FIRST REPLICATE -- 04/25/87

* C	HN	P	THQ	TP	DELHN	DELP	DELTHQ	DELTP	PH
0	0	0	0	0	0	0	0	0	6.5
10	0.04	4.96	0.11	0.54	9.96	5.04	9.89	9.46	6.5
25	2.91	20.46	5.11	11.58	22.09	4.54	19.89	13.42	6.5
35	5.43	29.45	7.85	18.87	29.57	5.55	27.15	16.13	6.6
50	13.72	46.09	16.46	33.06	36.28	3.91	33.54	16.94	6.6
65	27.08	61.35	23.59	52.00	37.92	3.65	41.41	13.00	6.7
80	32.95	69.39	31.37	62.66	47.05	10.61	48.63	17.34	6.7
100	55.77	97.02	44.31	83.49	44.23	2.98	55.69	16.51	6.7

* SECOND REPLICATE -- 05/24/87

* C	HN	P	THQ	TP	DELHN	DELP	DELTHQ	DELTP	PH
0	0	0	0	0	0	0	0	0	6.9
2	0.0	0.35	0.0	0.0	2.00	1.65	2.00	2.00	6.9
4	0.04	1.60	0.0	0.0	3.96	2.40	4.00	4.00	7.0
8	0.03	4.16	0.0	0.31	7.97	3.84	8.00	7.69	6.8
10	0.09	5.93	0.0	0.0	9.91	4.07	10.00	10.00	6.8
25	1.23	21.12	0.76	7.29	23.77	3.88	24.24	17.71	7.0
35	3.33	31.02	5.54	17.01	31.67	3.98	29.46	17.99	7.0
50	12.92	45.29	16.12	25.67	37.08	4.71	33.88	24.33	6.9
65	24.37	61.54	23.26	39.30	40.63	3.46	41.74	25.70	6.9
80	36.05	73.17	30.48	51.00	43.95	6.83	49.52	29.00	6.9
100	43.99	97.33	41.92	69.84	56.01	2.67	58.08	30.16	6.9
125	65.89	118.39	46.11	91.74	59.11	6.61	78.89	33.26	6.9
150	93.58	133.63	83.81	125.15	56.42	16.37	66.19	24.85	7.0
180	113.01	177.28	99.09	141.44	66.99	2.72	80.91	38.56	7.0
210	155.51	199.61	124.26	178.85	54.49	10.39	85.74	31.15	7.0
250	199.34	244.46	165.51	222.14	50.66	5.54	84.49	27.86	7.1

* THIRD REPLICATE -- 02/12/88

* C	HN	P	THQ	TP	DELHN	DELP	DELTHQ	DELTP	PH
0	0	0	0	0	0	0	0	0	6.8
2	0.00	0.79	0.00	0.00	0.00	1.21	2.00	2.00	6.8
4	0.00	1.83	0.00	0.00	0.00	2.17	4.00	4.00	6.8
8	0.00	4.34	0.00	0.00	0.00	3.66	8.00	8.00	6.8
25	2.47	18.28	2.28	7.17	22.53	6.72	22.72	17.83	6.9
35	5.28	29.73	6.80	17.44	29.72	5.27	28.20	17.56	6.8
50	10.81	38.51	9.49	25.37	39.19	11.49	40.51	24.63	7.0
65	20.79	51.89	14.94	27.53	44.21	13.11	50.06	37.47	6.9
80	16.32	50.98	16.94	24.85	63.68	29.02	63.06	55.15	7.0
100	25.11	58.25	19.90	34.72	74.89	41.75	80.10	65.28	7.2
125	39.63	84.06	36.42	64.22	85.37	40.94	88.58	60.78	7.3
150	58.04	105.69	50.20	93.61	91.96	44.31	99.80	56.39	7.4
180	68.06	124.51	62.25	110.03	111.94	55.49	117.75	69.97	7.4
210	96.85	161.36	89.75	143.49	113.15	48.64	120.25	66.51	7.4
250	107.27	217.83	91.88	148.79	142.73	32.17	158.12	101.21	7.4

Table B.13. Single-component isotherm on carbon — 2-Hydroxynaphthalene

* FIRST REPLICATE -- 04/11/87

* C	HN	DELHN	PH
0	0	0	7.0
20	0.1705	19.8295	7.1
50	0	50	7.0
70	0.1364	69.8636	7.0
100	0.1705	99.8295	7.0
130	0.4434	129.5566	7.0
160	0.4434	159.5566	7.0
200	0.7503	199.2497	7.0

* SECOND REPLICATE -- 05/02/87

* C	HN	DELHN	PH
0	0	0	6.8
50	0.1	49.9	6.8
100	0.2	99.8	6.8
175	1.04	173.96	6.8
250	1.97	248.03	6.7
325	15.47	309.53	6.6
400	60.29	339.71	6.7
500	92.01	407.99	6.8

* THIRD REPLICATE -- 01/15/88

* C	HN	DELHN	PH
0	0	0	7.1
50	0.00	50.00	7.1
100	0.00	100.00	6.9
175	0.00	175.00	6.9
250	0.64	249.36	6.8
325	7.47	317.53	6.8
400	42.92	357.08	6.9
500	81.43	418.57	6.7

Table B.14. Single-component isotherm on carbon — Phenol

* FIRST REPLICATE -- 04/04/87

* C	P	DELP	PH
0	0	0	7.5
20	0	20	7.4
50	0.392	49.608	7.0
70	0.979	69.021	7.1
100	4.178	95.822	7.2
130	8.355	121.645	7.3
160	18.734	141.266	7.0
200	39.621	160.379	7.0

* SECOND REPLICATE -- 12/18/87

* C	P	DELP	PH
0	0	0	7.0
25	0	25	7.0
50	0.19	49.81	6.9
70	0.74	69.26	6.8
100	5.37	94.63	6.8
130	7.82	122.18	6.8
160	19.82	140.18	6.8
200	35.30	164.70	6.9

* THIRD REPLICATE -- 01/22/88

* C	P	DELP	PH
0	0	0	7.3
25	0	25	7.3
50	0.31	49.69	7.3
70	0.93	69.07	7.3
100	5.10	94.90	7.1
130	7.23	122.77	7.1
160	16.22	143.78	7.1
200	35.11	164.89	6.8

Table B.15. Single-component isotherm on carbon -- 1,2,3,4-Tetrahydroquinoline

* FIRST REPLICATE -- 04/11/87

* C	THQ	DELTHQ	PH
0	0	0	6.9
20	0	20	6.9
50	0.0742	49.9258	6.9
70	0.0742	69.9258	6.8
100	0.2967	99.7033	6.9
130	0.8160	129.1840	6.7
160	1.483	158.517	6.9
200	6.231	193.769	7.0

* SECOND REPLICATE -- 04/25/87

* C	THQ	DELTHQ	PH
0	0	0	6.5
50	0.1	49.9	6.5
100	0.9	99.1	6.5
150	3.2	146.8	6.6
200	14.8	185.2	6.6
260	48.45	211.55	6.7
330	83.2	246.8	6.8
400	155.3	244.7	6.6

* THIRD REPLICATE -- 01/02/88

* C	THQ	DELTHQ	PH
0	0	0	7.0
50	0.00	50.00	7.0
100	0.00	100.00	6.8
175	0.00	175.00	6.7
250	2.34	247.66	6.6
325	17.42	307.58	6.6
400	51.62	348.38	6.5
500	108.48	391.52	6.6

Table B.16. Single-component isotherm on carbon -- 2,3,5-Trimethylphenol

* FIRST REPLICATE -- 04/11/87

* C	TP	DELTP	PH
0	0	0	7.0
20	0	20	7.0
50	0.1154	49.8846	6.9
70	0.2309	69.7691	7.0
100	0.4619	99.5381	7.1
130	0.3464	129.6536	6.9
160	0.8083	159.1917	6.8
200	1.1545	198.8455	7.0

* SECOND REPLICATE -- 05/02/87

* C	TP	DELTP	PH
0	0	0	6.8
50	0.0	50.0	6.8
100	0.0	100.0	7.0
175	0.47	174.53	7.2
250	3.18	246.82	6.9
325	36.20	288.80	7.0
400	75.12	324.88	7.0
500	138.68	361.32	7.0

* THIRD REPLICATE -- 12/25/87

* C	TP	DELTP	PH
0	0	0	7.6
50	0.00	50.00	7.7
100	0.00	100.00	7.6
175	0.00	175.00	7.5
250	1.99	248.01	7.4
325	20.30	304.70	7.4
400	77.63	322.37	7.4
500	133.16	366.84	7.3

Table B.17. Column experiments on shale — 2-Hydroxynaphthalene

* FIRST REPLICATE				* SECOND REPLICATE				* THIRD REPLICATE			
* PV	HN	PH	TUBE	* PV	HN	PH	TUBE	* PV	HN	PH	TUBE
0.348	0	6.7	1	0.333	0	6.3	1	0.352	0	6.0	1
1.045	0	6.7	3	1.332	0	6.5	4	1.056	0	6.3	3
2.090	0	6.7	6	2.330	0	6.7	7	2.112	0	6.3	6
5.226	0.36	6.9	15	5.327	0	6.9	16	5.280	0	6.6	15
10.103	0	6.9	29	10.320	0	7.1	31	10.207	0	6.7	29
15.329	0	6.8	44	15.314	0	7.1	46	15.135	0	6.8	43
20.206	0.95	6.7	58	20.308	0.78	7.1	61	20.062	0.39	6.8	57
25.084	4.61	6.7	72	25.301	4.15	7.2	76	25.342	1.66	6.8	72
30.309	10.05	6.7	87	30.295	10.01	7.2	91	30.270	5.11	6.8	86
40.064	15.38	6.8	115	40.283	22.03	7.2	121	40.125	17.82	7.0	114
45.290	21.49	7.0	130	55.264	32.20	7.5	166	55.260	26.87	7.1	157
55.045	29.32	7.0	158	75.238	39.35	7.9	226	75.322	35.25	8.4	214
75.251	37.80	7.3	216	100.207	40.87	8.0	301	100.312	39.12	8.2	285
100.335	41.57	8.0	288	125.176	45.39	7.7	376	125.302	41.94	8.0	356
125.070	46.87	7.6	359	150.144	46.51	7.5	451	150.292	42.88	7.7	427
150.154	46.40	7.5	431	175.113	50.09	7.7	526	175.282	46.85	8.0	498
200.321	44.08	8.0	575	200.081	50.40	8.2	601	200.272	48.65	7.7	569
225.057	49.46	8.1	646	225.050	51.18	8.3	676	225.262	48.97	7.8	640
250.140	50.28	7.9	718								
275.224	51.83	8.2	790								
300.308	50.29	8.0	862								

Table B.18. Column experiments on shale — Phenol

* FIRST REPLICATE				* SECOND REPLICATE				* THIRD REPLICATE			
* PV	P	PH	TUBE	* PV	P	PH	TUBE	* PV	P	PH	TUBE
0.335	0	6.0	1	0.344	0	6.4	1	0.341	0	6.2	1
1.006	0	6.2	3	1.032	0	6.5	3	1.022	0	6.4	3
2.012	0	6.3	6	2.063	0	6.7	6	2.044	0	6.4	6
5.030	1.58	6.2	15	5.158	0	6.8	15	5.111	1.27	6.4	15
10.059	11.30	6.3	30	10.316	5.46	6.9	30	10.222	9.23	6.5	30
15.089	21.49	6.4	45	15.130	17.76	6.9	44	15.333	19.48	6.6	45
20.118	29.24	6.3	60	20.288	25.53	6.8	59	20.103	25.11	6.5	59
25.148	33.40	6.0	75	25.102	31.79	6.7	73	25.214	30.67	6.4	74
30.178	37.66	6.0	90	30.260	35.24	6.7	88	30.325	33.23	6.4	89
40.237	40.25	6.1	120	40.232	39.63	6.9	117	40.207	41.02	6.5	118
55.326	43.30	7.7	165	55.018	45.02	8.3	160	55.119	43.13	7.9	162
75.109	42.09	7.5	224	75.305	42.85	7.9	219	75.302	43.11	7.5	221
100.257	41.60	7.7	299	100.063	40.72	8.1	291	100.176	43.44	7.4	294
125.070	43.50	7.5	373	125.165	42.95	7.8	364	125.050	44.84	7.7	367
150.218	44.53	7.8	448	150.267	42.27	7.6	437	150.264	46.36	7.5	441
175.031	46.63	7.4	522	175.025	42.57	7.9	509	175.138	47.31	7.3	514

Table B.19. Column experiment on shale — 1,2,3,4-Tetrahydroquinoline; first replicate

* FIRST REPLICATE							
* PV	THQ	PH	TUBE	* PV	THQ	PH	TUBE
0.317	0	6.5	1	975.161	37.02	6.5	3079
1.267	0	6.6	4	1000.181	37.02	6.4	3158
2.217	0	6.2	7	1025.201	37.34	6.4	3237
5.067	0	6.2	16	1050.222	37.91	6.5	3316
10.135	0	6.1	32	1075.242	37.87	6.5	3395
15.202	1.64	6.3	48	1100.262	38.52	6.5	3474
20.270	4.08	6.4	64	1125.283	38.93	6.5	3553
25.020	5.84	6.4	79	1150.303	39.05	6.4	3632
30.088	8.90	6.4	95	1175.007	36.63	6.5	3710
35.155	11.42	6.3	111	1200.027	38.81	6.5	3789
40.223	14.27	6.4	127	1225.048	41.26	6.4	3868
55.108	21.64	6.4	174	1250.068	41.29	6.4	3947
75.061	26.17	6.4	237	1275.088	41.40	6.4	4026
100.081	25.66	6.3	316	1300.109	42.72	6.4	4105
125.102	24.32	6.4	395	1325.129	42.85	6.4	4184
150.122	25.85	6.0	474	1350.149	42.50	6.4	4263
175.143	25.31	6.4	553	1375.170	43.09	6.4	4342
200.163	27.00	6.4	632	1400.190	46.63	6.1	4421
225.183	25.15	6.3	711	1425.210	44.12	6.3	4500
250.204	28.22	6.4	790	1450.231	45.29	6.3	4579
275.224	30.51	7.0	869	1475.251	45.32	6.4	4658
300.244	31.97	6.4	948	1500.271	45.84	6.4	4737
325.265	31.46	6.3	1027	1525.292	45.04	6.4	4816
350.285	29.89	6.3	1106	1550.312	44.14	6.4	4895
375.305	29.52	6.4	1185	1575.016	43.37	6.4	4973
400.009	30.08	6.4	1263	1600.036	43.30	6.3	5052
425.029	29.57	6.4	1342	1625.057	43.95	6.3	5131
450.050	31.29	7.0	1421	1640.892	42.34	6.3	5181
475.070	32.30	6.9	1500	1641.209	42.73	6.3	5182
500.090	33.73	6.8	1579	1641.526	42.70	6.3	5183
525.111	35.13	6.7	1658	1641.842	39.03	6.3	5184
550.131	35.19	6.6	1737	1642.159	33.55	6.3	5185
575.152	36.85	6.6	1816	1642.476	28.33	6.3	5186
600.172	36.26	6.6	1895	1642.793	24.36	6.3	5187
625.192	36.15	6.6	1974	1643.109	21.55	6.3	5188
650.213	37.22	6.5	2053	1643.426	18.88	6.3	5189
675.233	40.22	6.5	2132	1643.743	17.05	6.3	5190
700.253	37.89	6.9	2211	1644.059	15.06	6.2	5191
725.274	37.63	6.8	2290	1647.226	7.52	6.3	5201
750.294	36.90	6.6	2369	1652.294	4.27	6.4	5217
775.314	35.97	6.5	2448	1657.045	3.23	6.4	5232
800.018	37.62	6.4	2526	1662.112	2.19	6.4	5248
825.038	37.33	6.4	2605	1667.179	1.82	6.4	5264
850.059	38.66	6.4	2684	1677.314	1.69	6.4	5296
875.079	39.07	6.5	2763	1682.065	1.63	6.4	5311
900.100	39.57	6.5	2842	1697.267	0	6.4	5359
925.120	40.80	6.5	2921	1717.202	0.99	6.4	5422
950.140	37.86	6.5	3000	1742.241	0	6.5	5501

Table B.20. Column experiments on shale -- 1,2,3,4-Tetrahydroquinoline; two replicates

* SECOND REPLICATE				* THIRD REPLICATE			
* PV	THQ	PH	TUBE	* PV	THQ	PH	TUBE
0.375	0	6.0	1	0.359	0	6.3	1
1.126	0	6.3	3	1.077	0	6.6	3
2.253	0	6.3	6	2.154	0	6.6	6
5.256	0	6.1	14	5.027	0	6.7	14
10.137	0	5.9	27	10.054	0	6.1	28
15.018	0	6.2	40	15.081	1.92	6.3	42
20.274	0	5.9	54	20.107	4.98	6.3	56
25.155	7.12	6.0	67	25.134	8.54	6.4	70
30.036	9.03	6.0	80	30.161	10.48	6.5	84
35.292	11.55	6.1	94	35.188	12.26	6.5	98
40.173	13.76	6.0	107	40.215	14.68	6.1	112
55.191	17.47	6.2	147	55.296	19.55	6.3	154
75.090	22.42	6.0	200	75.044	22.77	7.3	209
100.245	25.31	6.4	267	100.178	25.86	7.0	279
125.025	25.73	5.6	333	125.313	26.22	6.9	349
150.181	22.35	5.9	400	150.088	26.37	6.0	418
175.336	25.30	6.0	467	175.222	26.40	6.4	488
200.116	24.52	6.1	533	200.357	25.46	6.4	558
225.271	26.11	6.0	600	225.132	25.81	6.1	627
250.051	26.89	6.1	666	250.266	25.93	6.3	697
275.206	27.17	5.8	733	275.042	26.38	7.1	766
291.726	26.32	6.0	777	300.176	21.42	7.0	836
325.141	25.11	6.2	866	325.310	24.72	6.1	906
350.296	25.52	6.1	933	350.086	25.53	6.1	975
375.076	27.36	6.1	999	375.220	26.61	6.2	1045
400.231	29.40	6.1	1066	400.354	27.52	6.3	1115
425.011	27.71	6.1	1132	425.130	27.38	6.4	1184
450.166	30.47	6.2	1199	450.264	28.94	6.5	1254
475.321	27.89	6.2	1266	475.039	28.15	6.6	1323
500.101	28.20	6.3	1332	500.174	29.15	6.6	1393
525.256	30.43	6.4	1399	525.308	30.54	6.5	1463

Table B.21. Column experiments on shale — 2,3,5-Trimethylphenol

* FIRST REPLICATE				* SECOND REPLICATE				* THIRD REPLICATE			
* PV	TP	PH	TUBE	* PV	TP	PH	TUBE	* PV	TP	PH	TUBE
0.343	0	6.0	1	0.321	0	6.4	1	0.298	0	6.9	1
1.030	0	6.4	3	1.282	0	6.6	4	1.192	0	6.9	4
2.061	0	6.4	6	2.244	0	6.6	7	2.085	0	6.9	7
5.152	0	6.5	15	5.129	0	6.6	16	5.064	0	6.8	17
10.305	0	6.6	30	10.258	0	6.6	32	10.128	1.95	6.8	34
15.114	5.58	6.6	44	15.067	3.51	6.5	47	15.192	5.08	6.8	51
20.266	7.59	6.5	59	20.196	12.24	6.5	63	20.256	12.08	6.7	68
25.075	13.61	6.4	73	25.004	15.40	6.5	78	25.022	17.33	6.7	84
30.228	17.73	6.3	88	30.133	23.78	6.5	94	30.085	23.44	6.8	101
40.189	24.49	6.2	117	40.071	26.93	6.6	125	40.213	29.16	6.8	135
55.303	30.77	6.4	161	55.137	33.36	6.6	172	55.107	37.00	7.0	185
75.226	34.63	6.7	219	75.012	38.59	6.9	234	75.065	39.52	7.1	251
100.301	39.23	6.7	292	100.016	42.21	7.1	312	100.086	43.62	7.4	336
125.033	41.33	7.0	364	125.020	41.95	7.4	390	125.108	42.13	7.3	420
150.108	41.85	7.3	437	150.024	46.67	7.3	468	150.130	48.48	7.1	504
165.222	44.50	7.3	481	165.091	46.84	7.2	515	160.257	43.51	7.2	538
185.143	42.96	7.6	539								

Appendix C

Third Tetra-Component Batch Isotherm Replicate

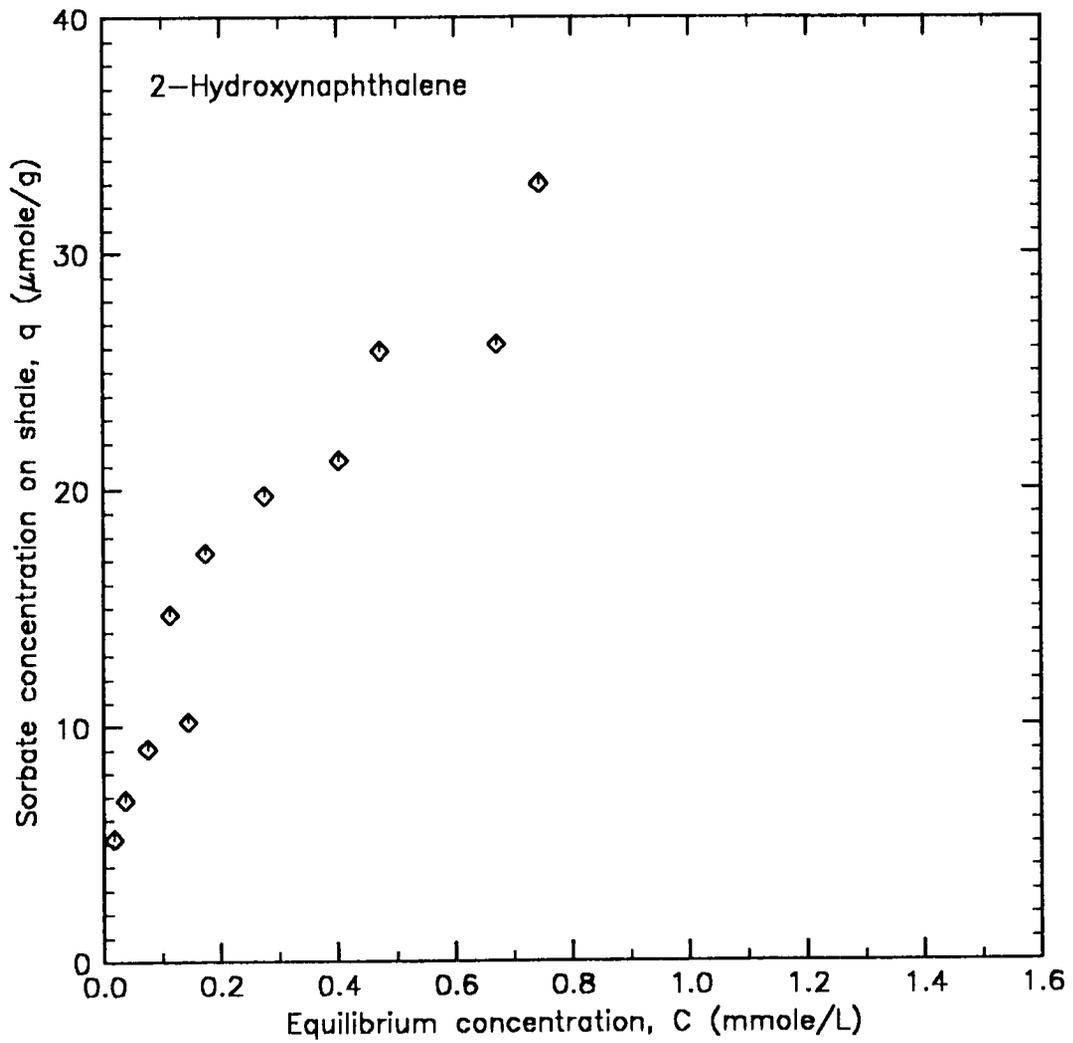


Figure C.1. Isotherm of 2-Hydroxynaphthalene from third replicate of tetra-sorbate trials

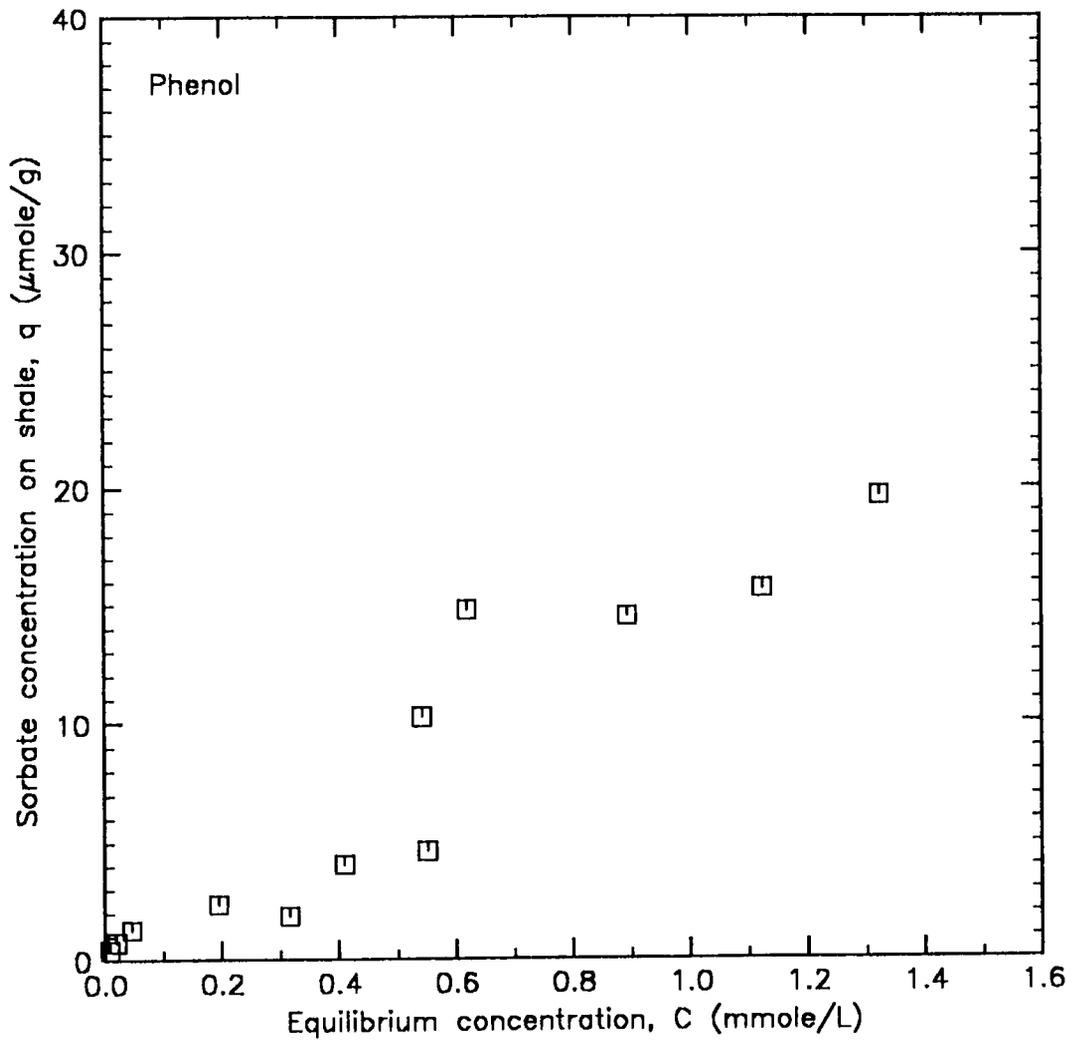


Figure C.2. Isotherm of Phenol from third replicate of tetra-sorbate trials

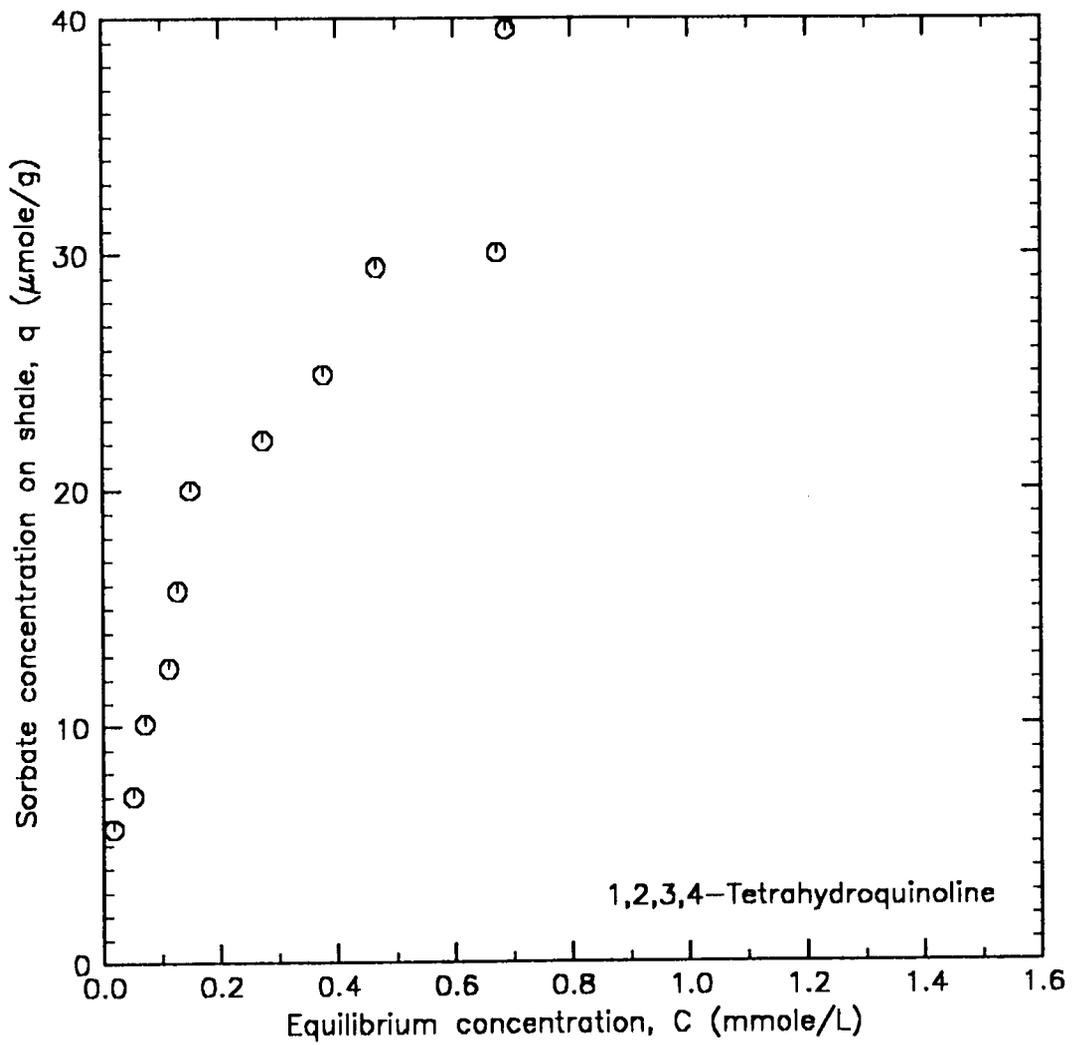


Figure C.3. Isotherm of 1,2,3,4-Tetrahydroquinoline from third replicate of tetra-sorbate trials

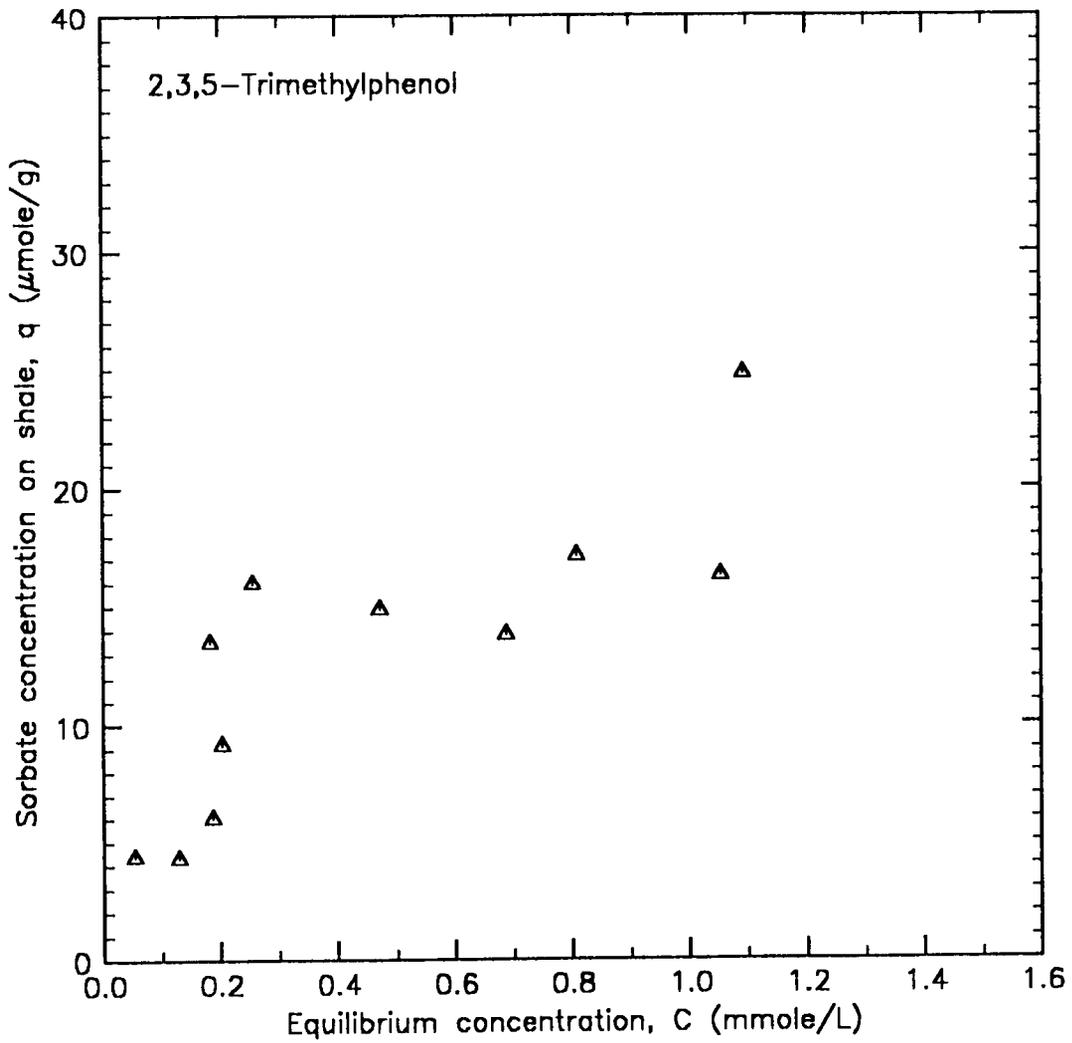


Figure C.4. Isotherm of 2,3,5-Trimethylphenol from third replicate of tetra-sorbate trials

Appendix D

Freundlich and Langmuir Plots for Monocomponent Experiments Upon Shale and Carbon

Note: The Freundlich and Langmuir plots for 2-Hydroxynaphthalene upon shale are reproduced in the text (Figures 59 and 60, respectively).

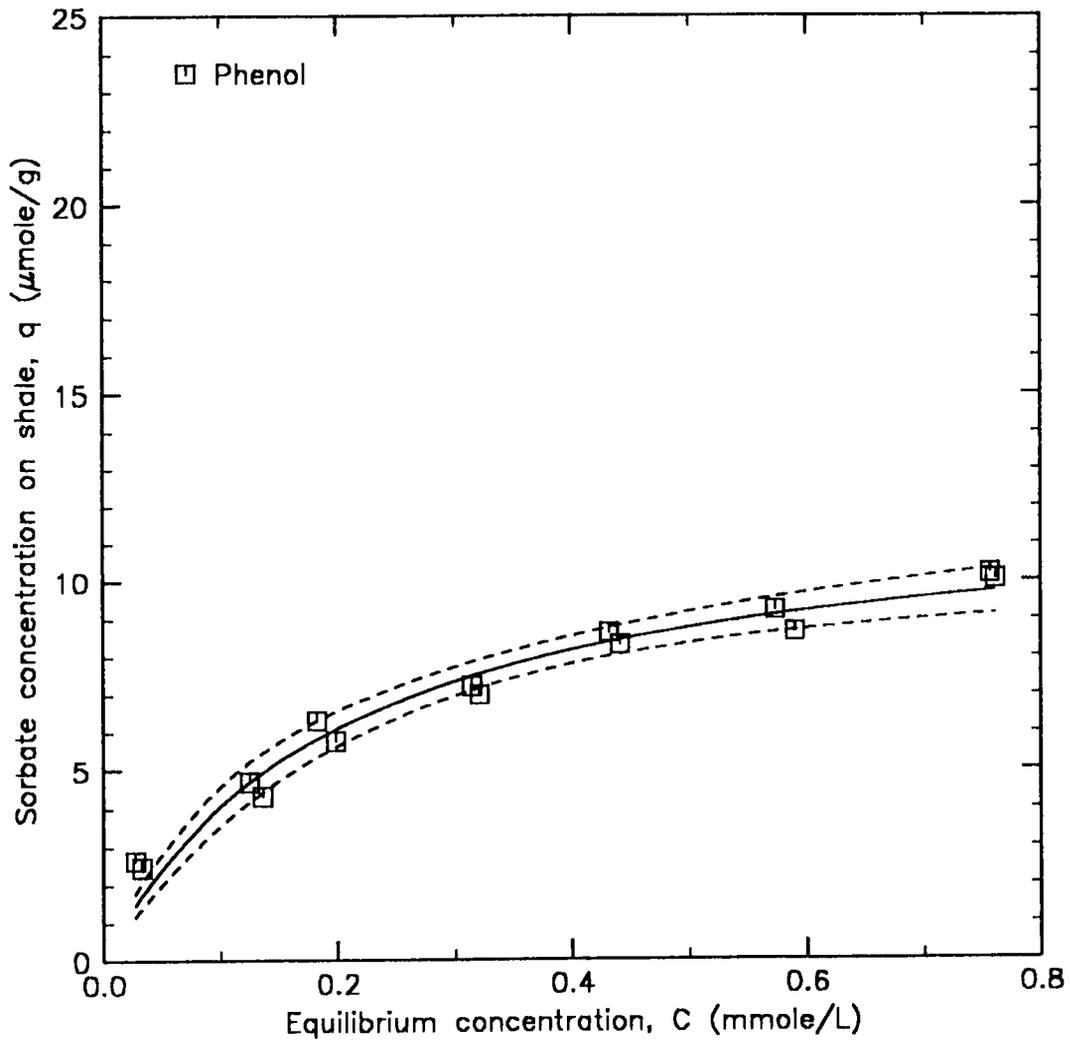


Figure D.1. Nonlinear least squares fit to Phenol data using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

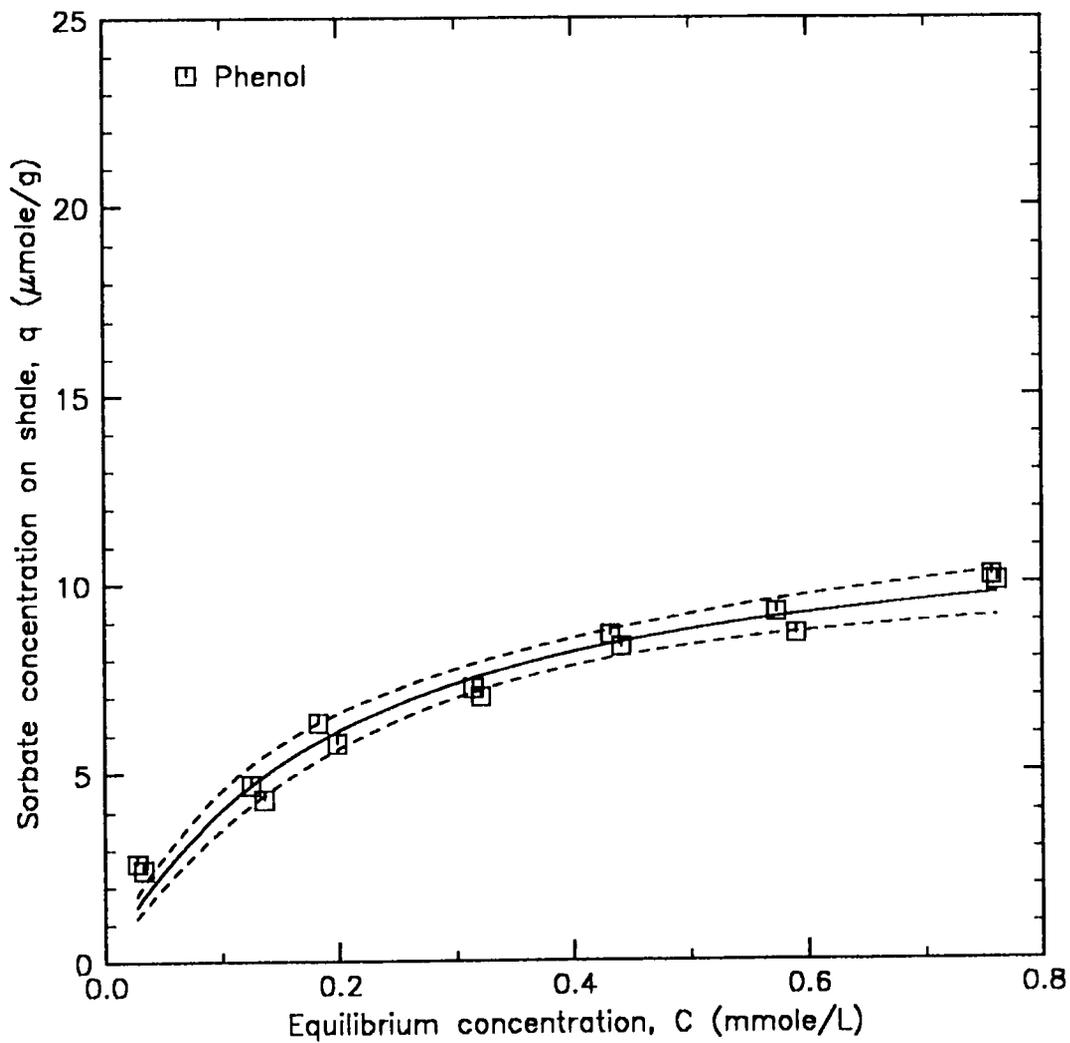


Figure D.2. Nonlinear least squares fit to Phenol data using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

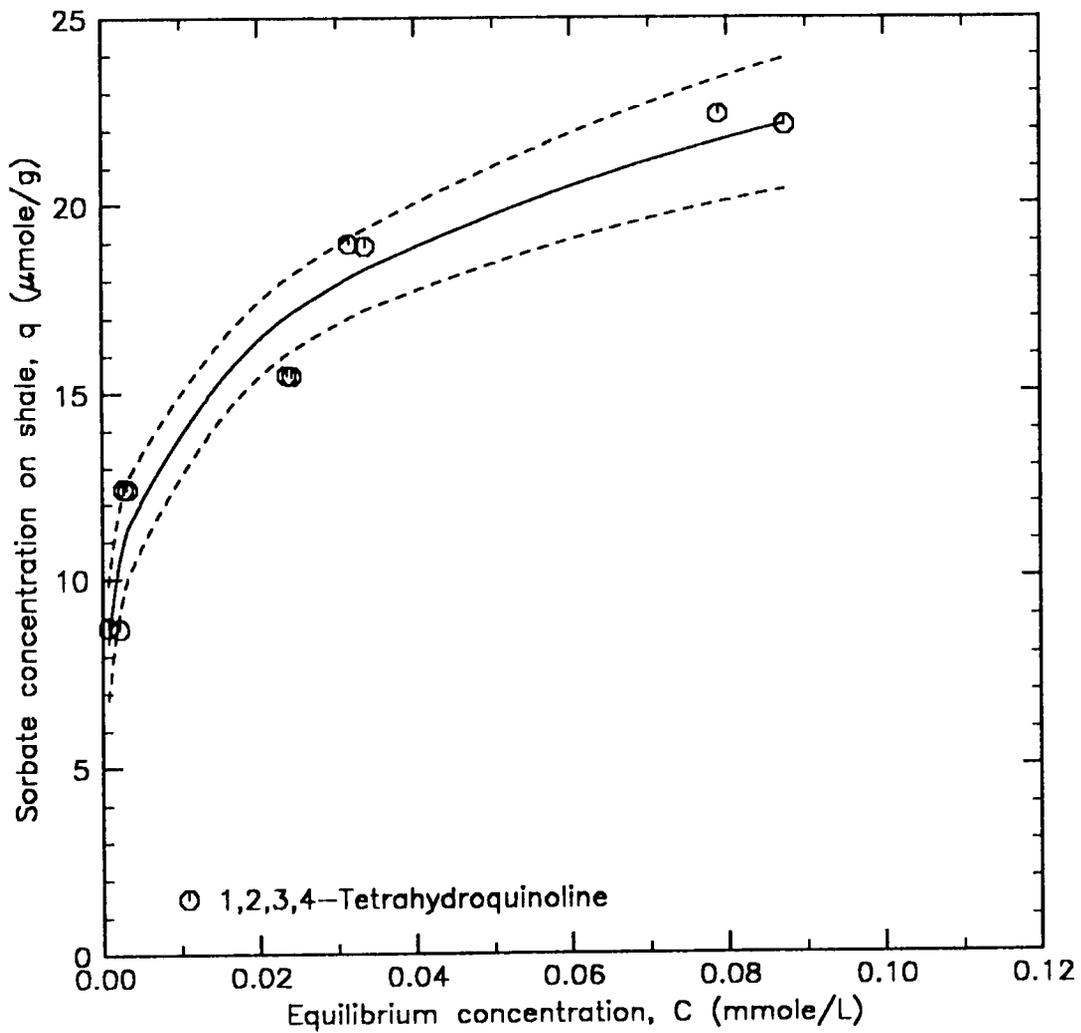


Figure D.3. Nonlinear least squares fit to 1,2,3,4-Tetrahydroquinoline data (two replicates) using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

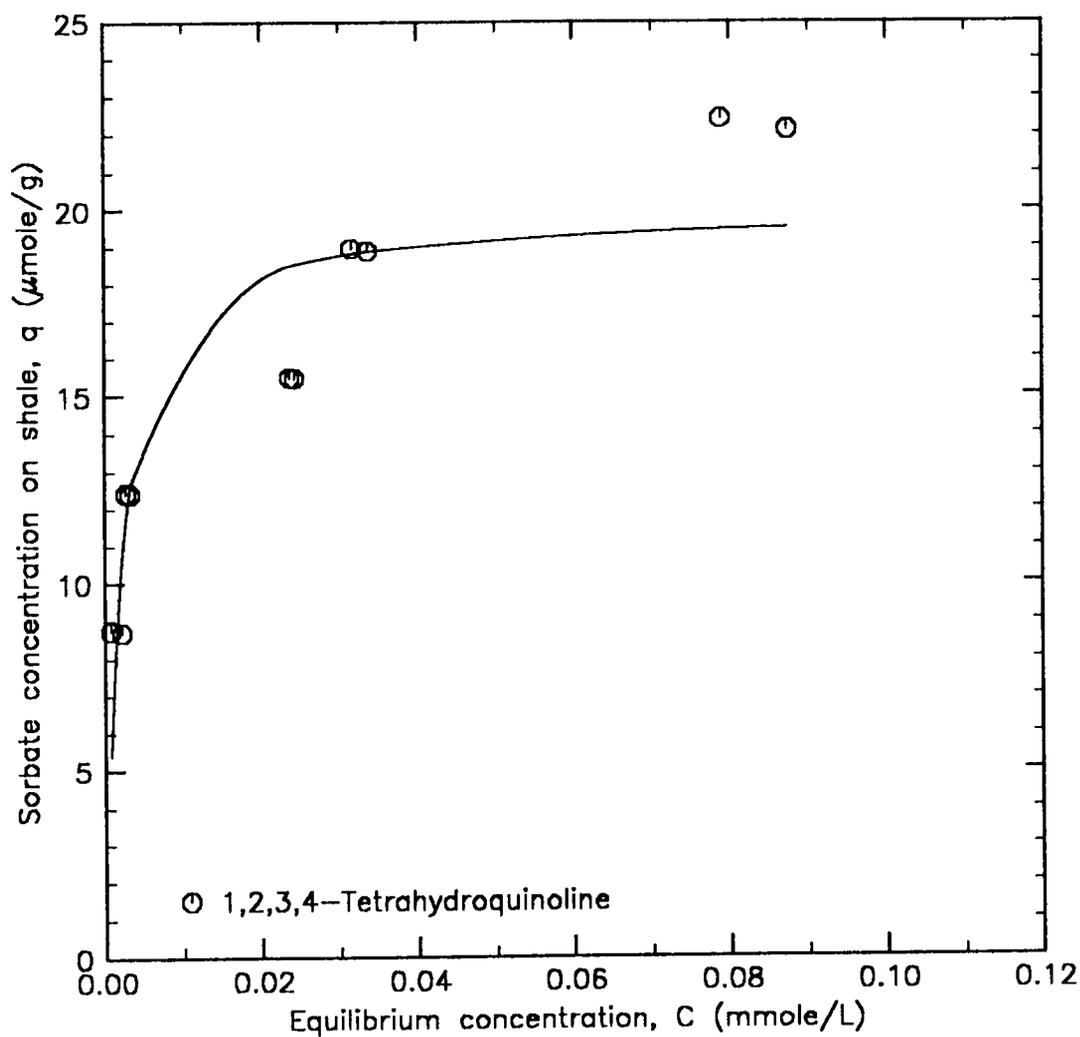


Figure D.4. Nonlinear least squares fit to 1,2,3,4-Tetrahydroquinoline data (two replicates) using the Langmuir isotherm: Confidence limits could not be drawn because the DUD method of the NLIIN procedure does not provide confidence limit data.

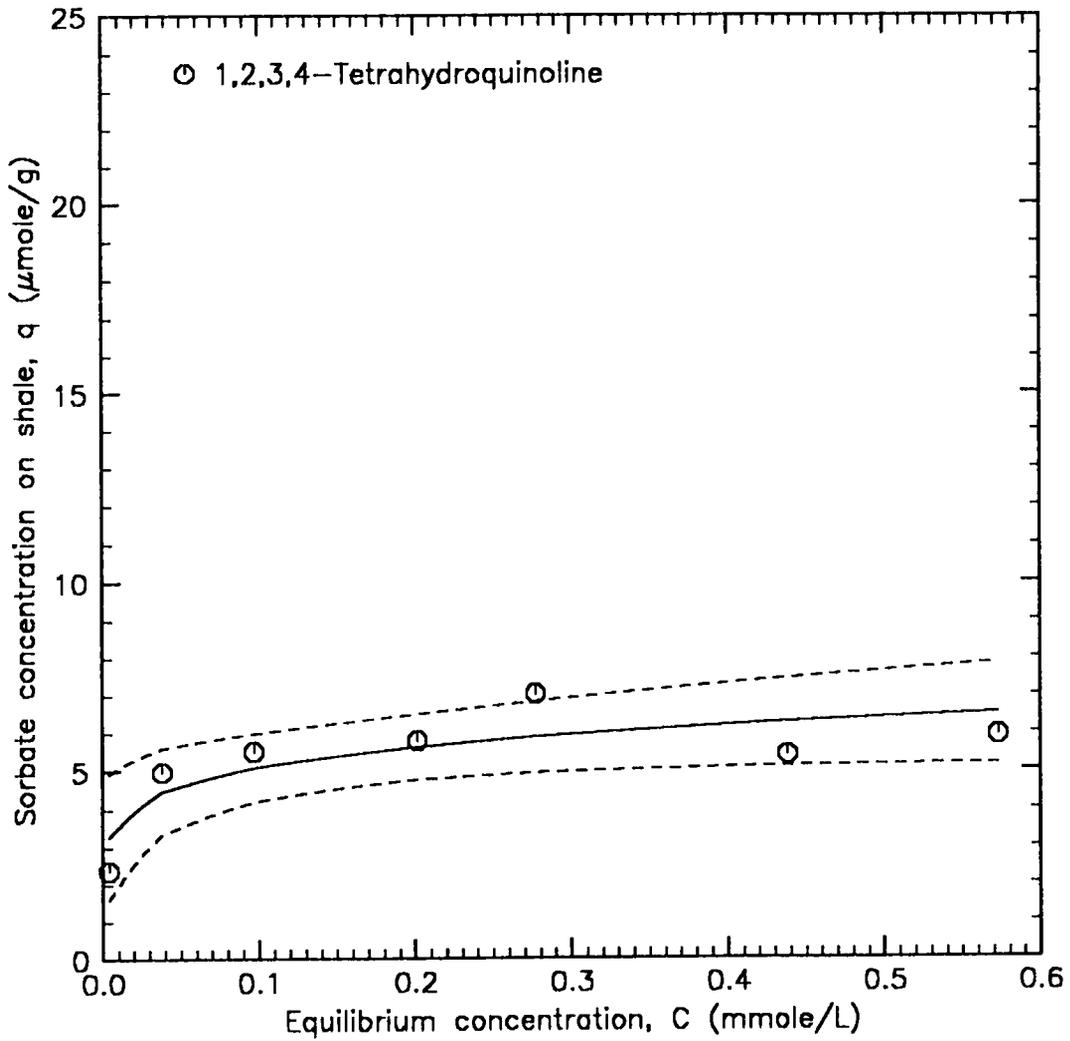


Figure D.5. Nonlinear least squares fit to 1,2,3,4-Tetrahydroquinoline data (first replicate) using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

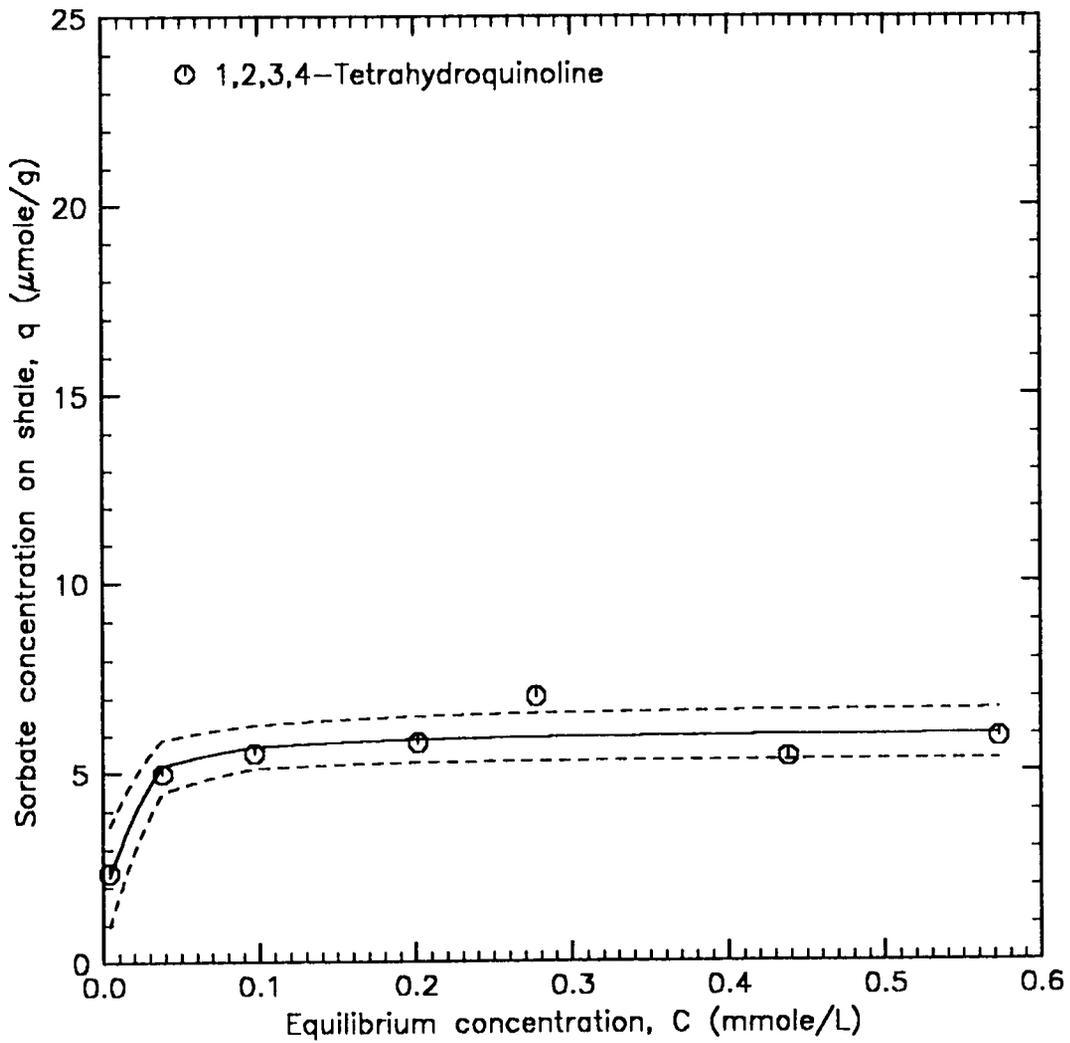


Figure D.6. Nonlinear least squares fit to 1,2,3,4-Tetrahydroquinoline data (first replicate) using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

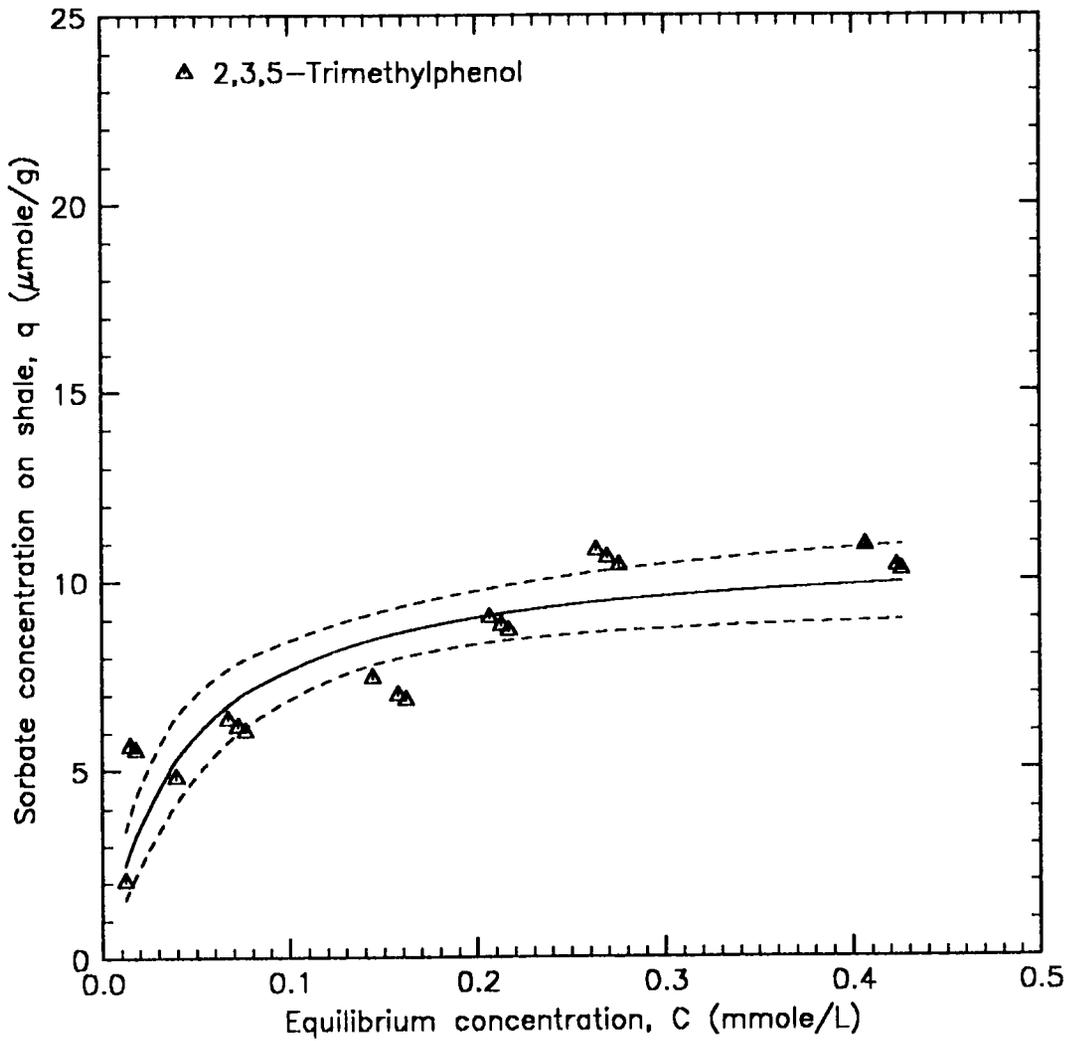


Figure D.7. Nonlinear least squares fit to 2,3,5-Trimethylphenol data using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

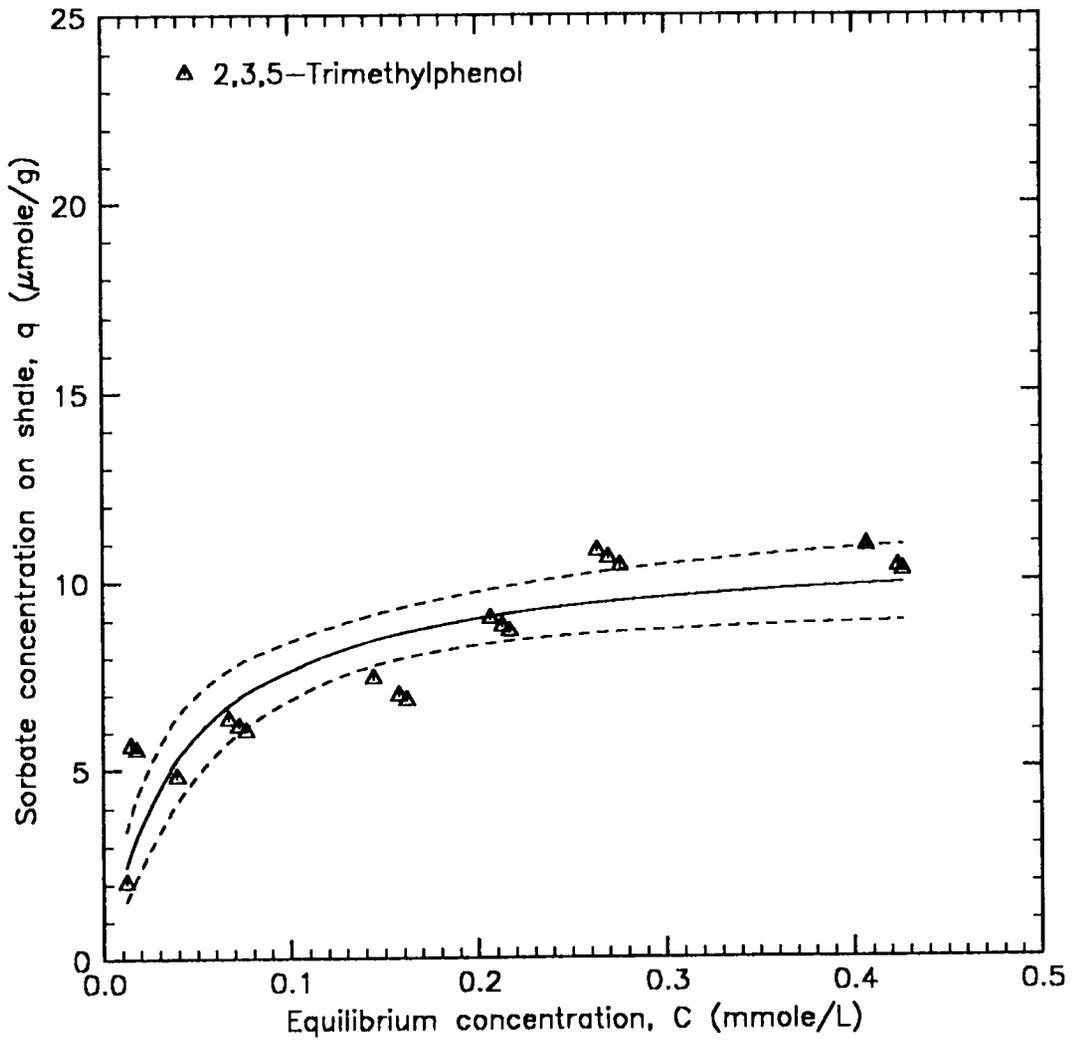


Figure D.8. Nonlinear least squares fit to 2,3,5-Trimethylphenol data using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

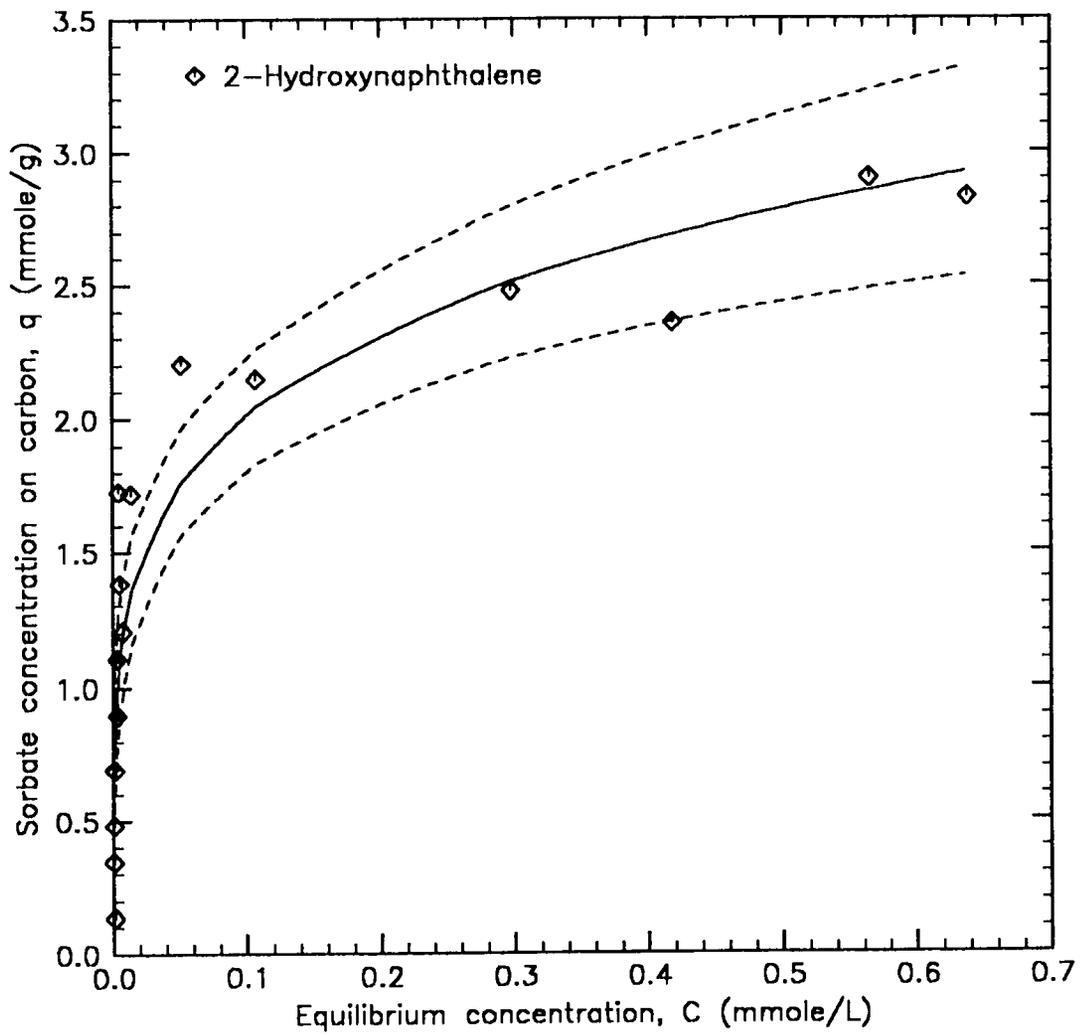


Figure D.9. Nonlinear least squares fit to 2-Hydroxynaphthalene data using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

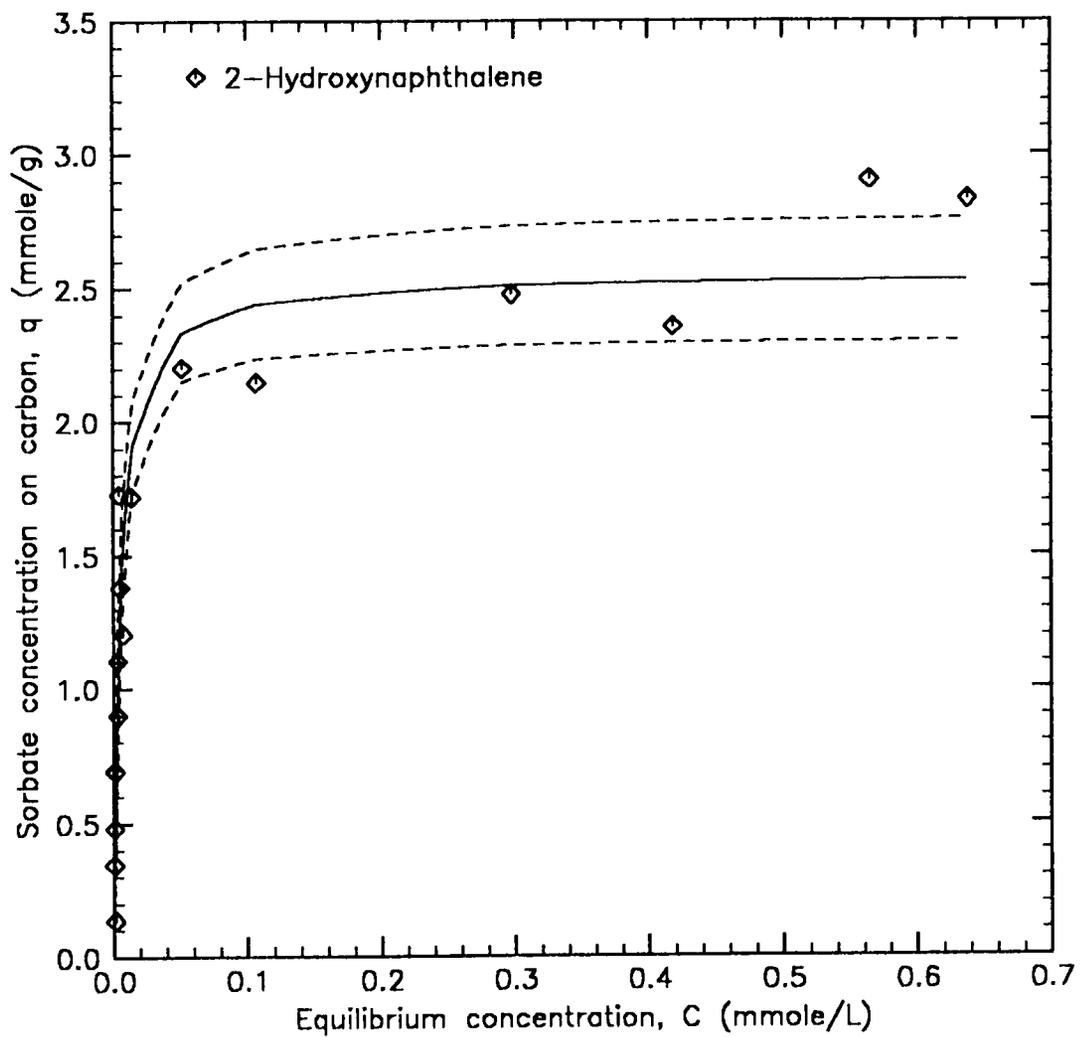


Figure D.10. Nonlinear least squares fit to 2-Hydroxynaphthalene data using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

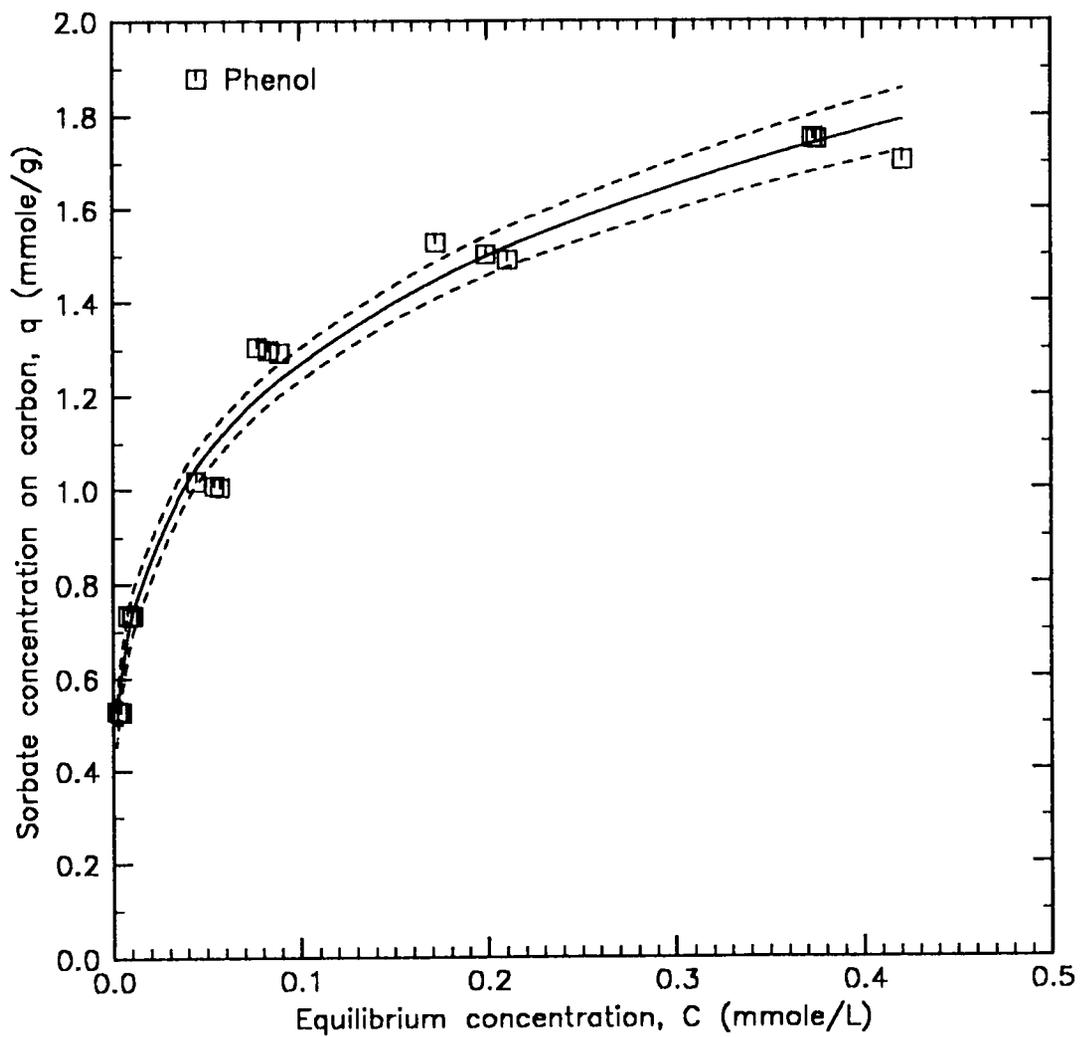


Figure D.11. Nonlinear least squares fit to Phenol data using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

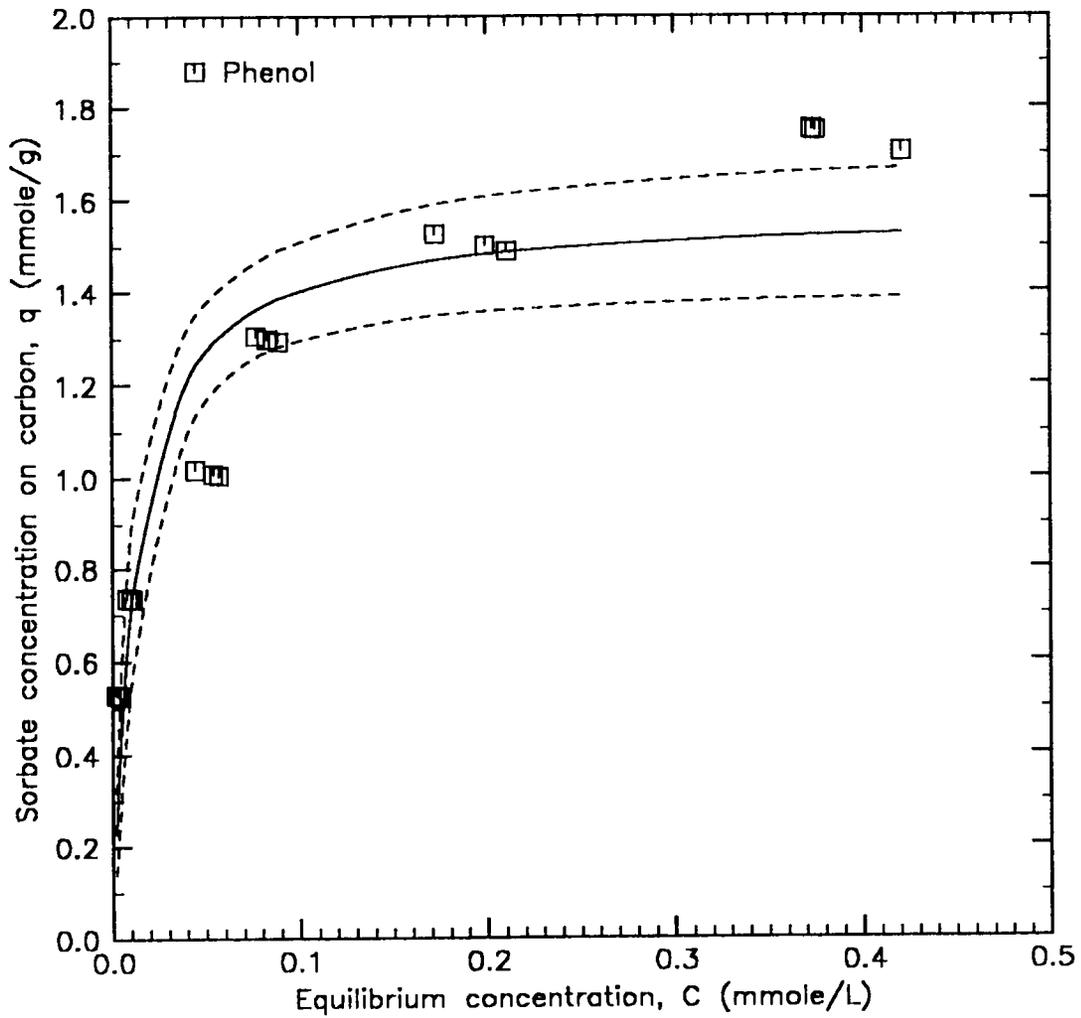


Figure D.12. Nonlinear least squares fit to Phenol data using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

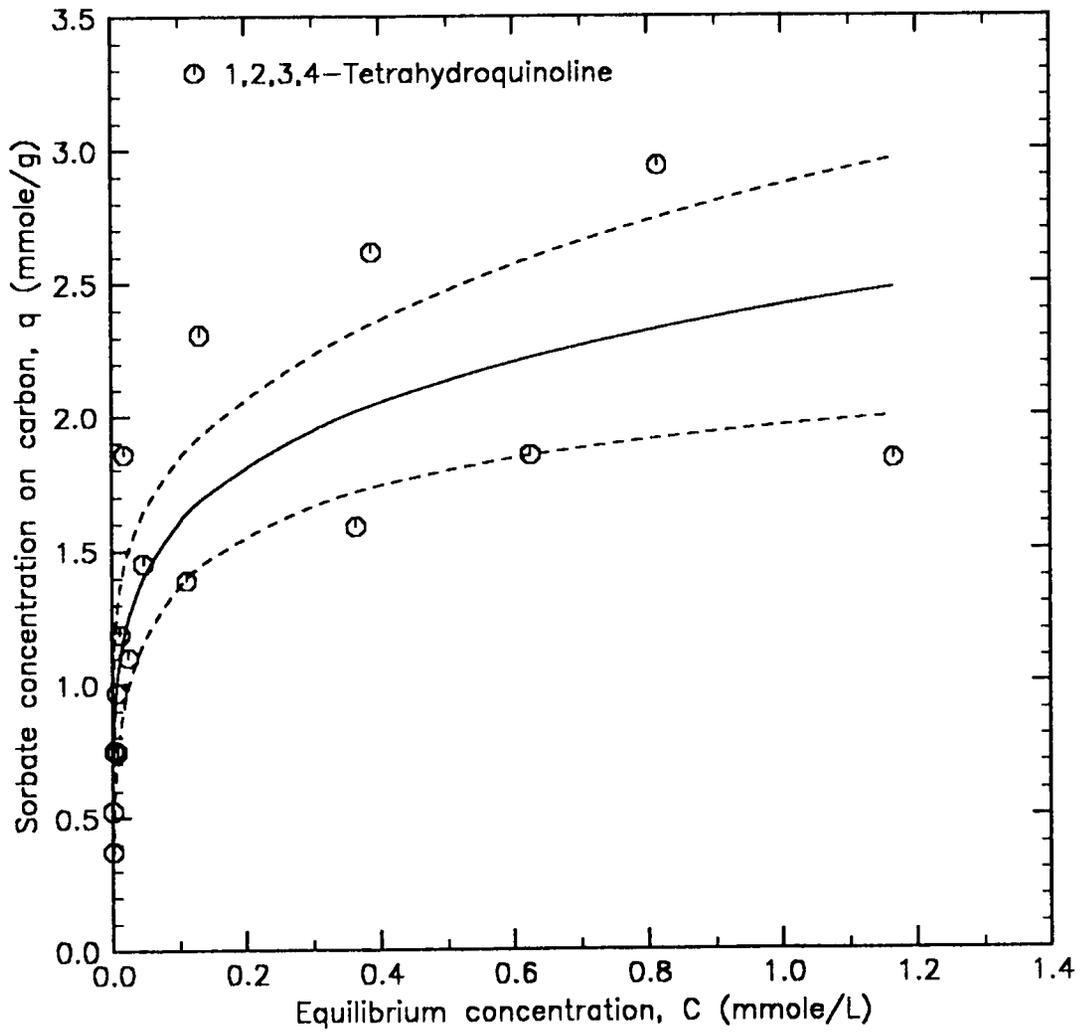


Figure D.13. Nonlinear least squares fit to 1,2,3,4-Tetrahydroquinoline data using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

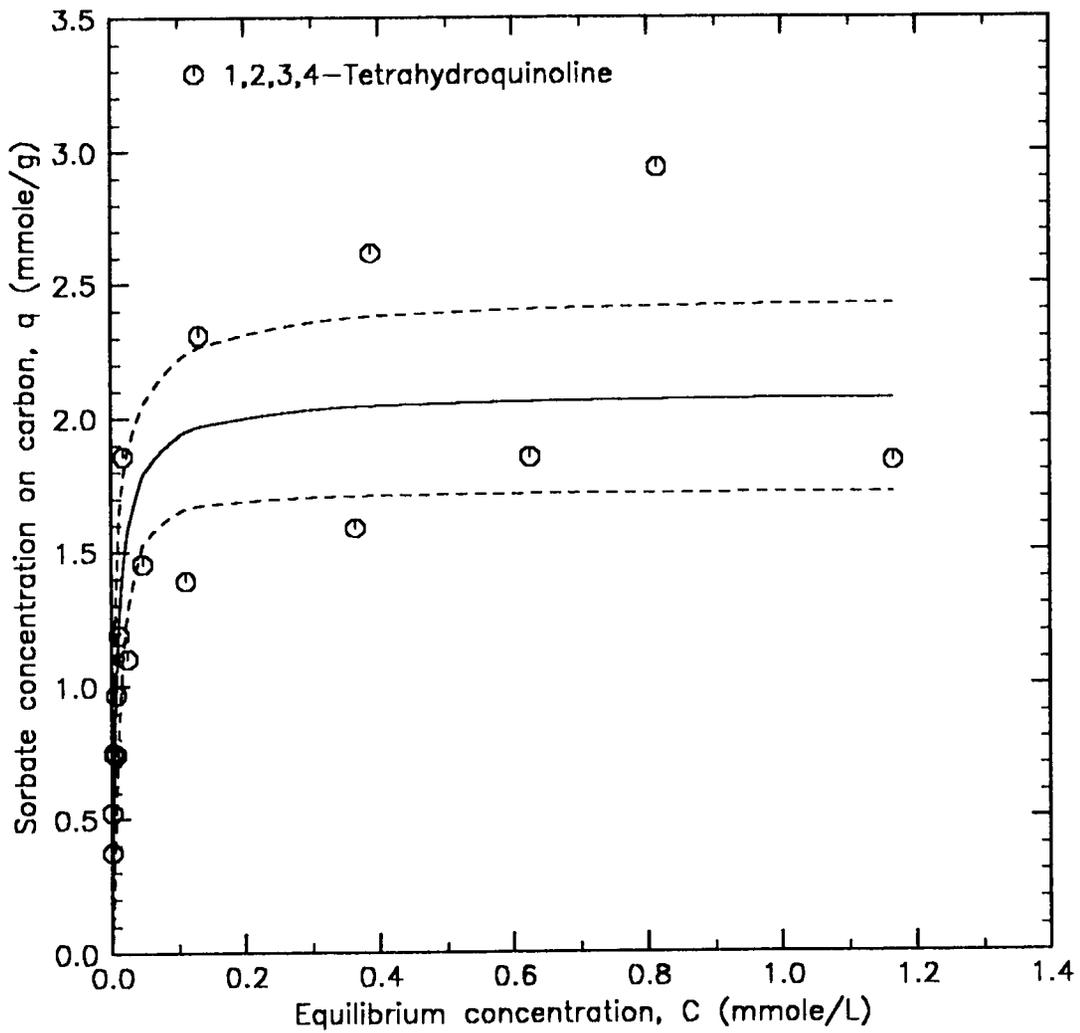


Figure D.14. Nonlinear least squares fit to 1,2,3,4-Tetrahydroquinoline data using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

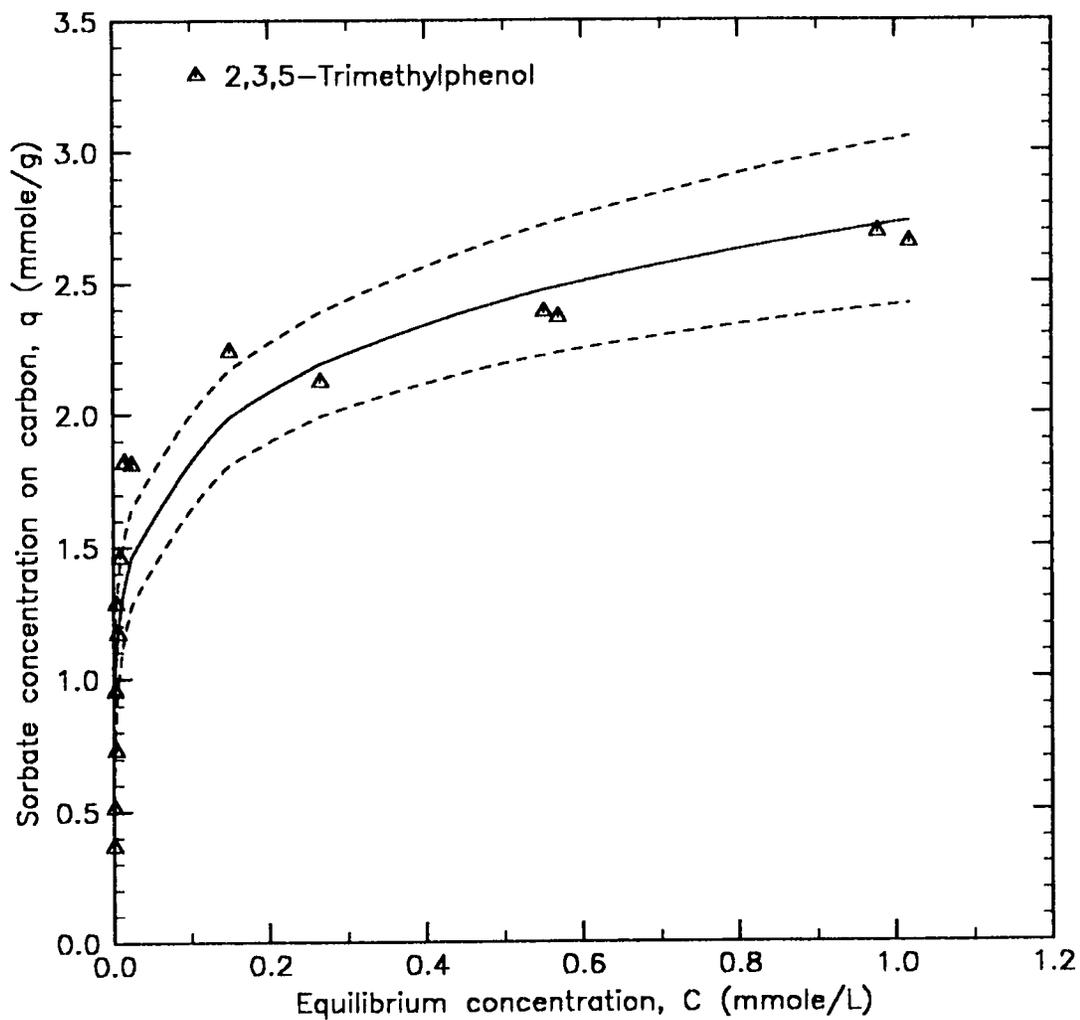


Figure D.15. Nonlinear least squares fit to 2,3,5-Trimethylphenol data using the Freundlich isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

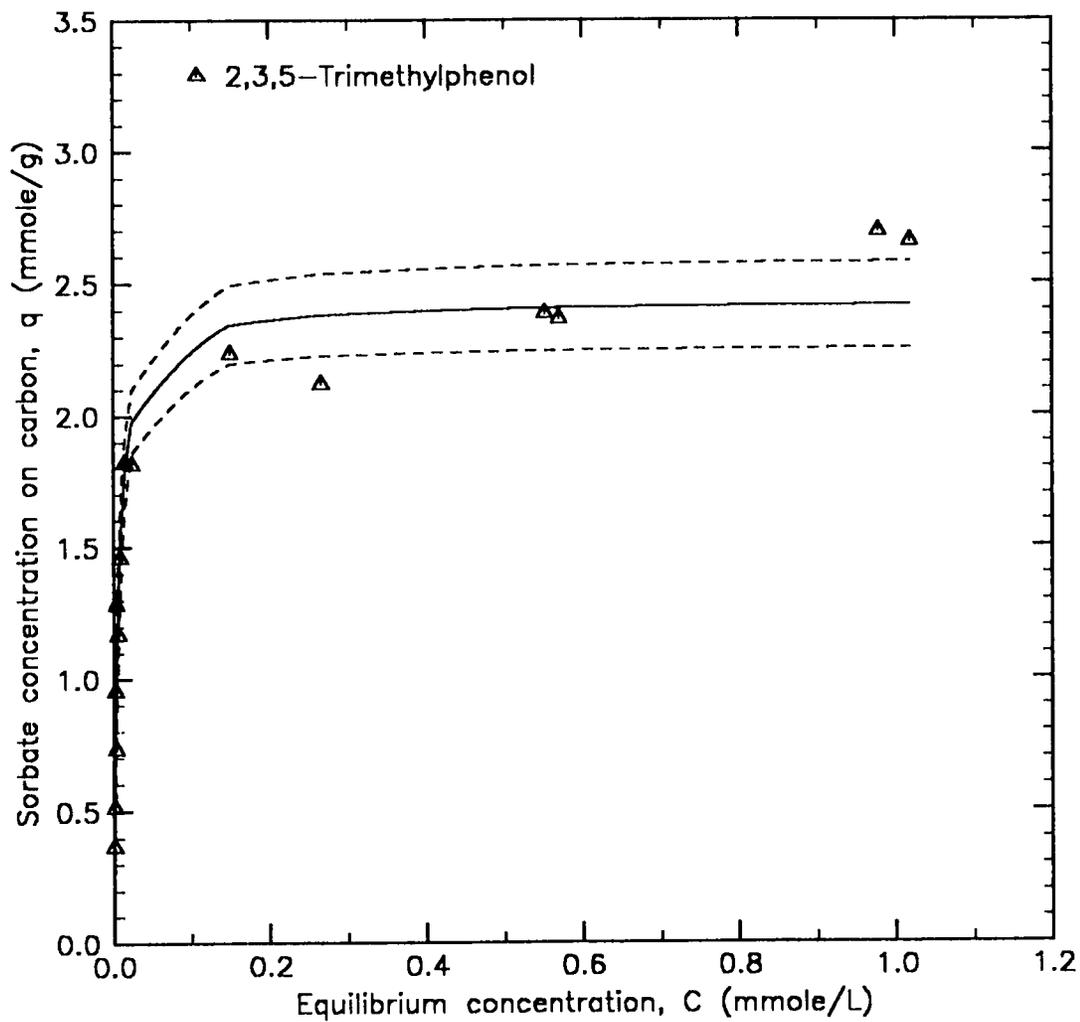


Figure D.16. Nonlinear least squares fit to 2,3,5-Trimethylphenol data using the Langmuir isotherm: The dashed lines represent the 95% confidence limits of the fitted line.

Appendix E

Replicates of Continuous-Flow Column Sorption

Experiments

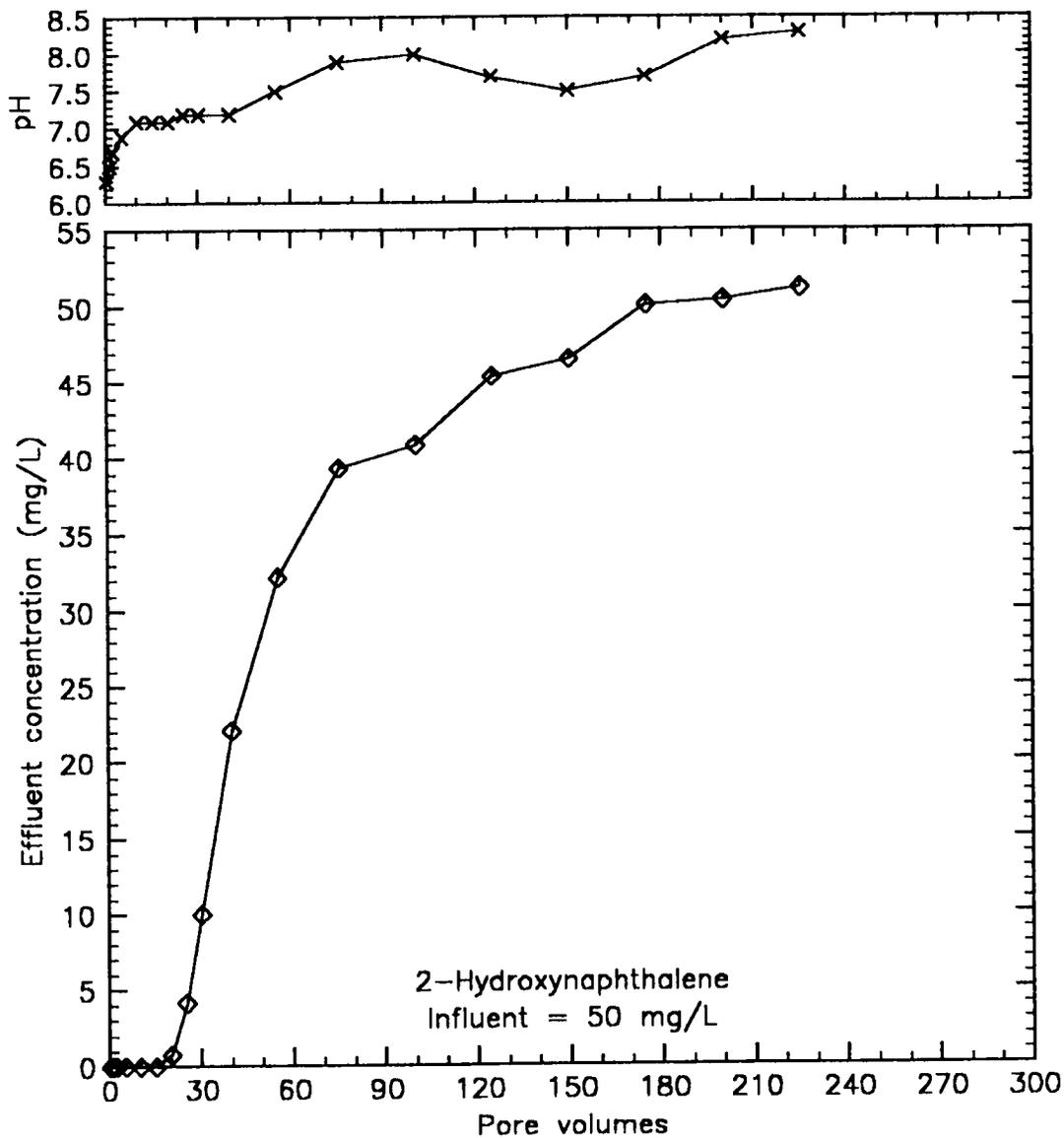


Figure E.1. Continuous-flow column sorption trials with 2-Hydroxynaphthalene on shale: Second replicate.

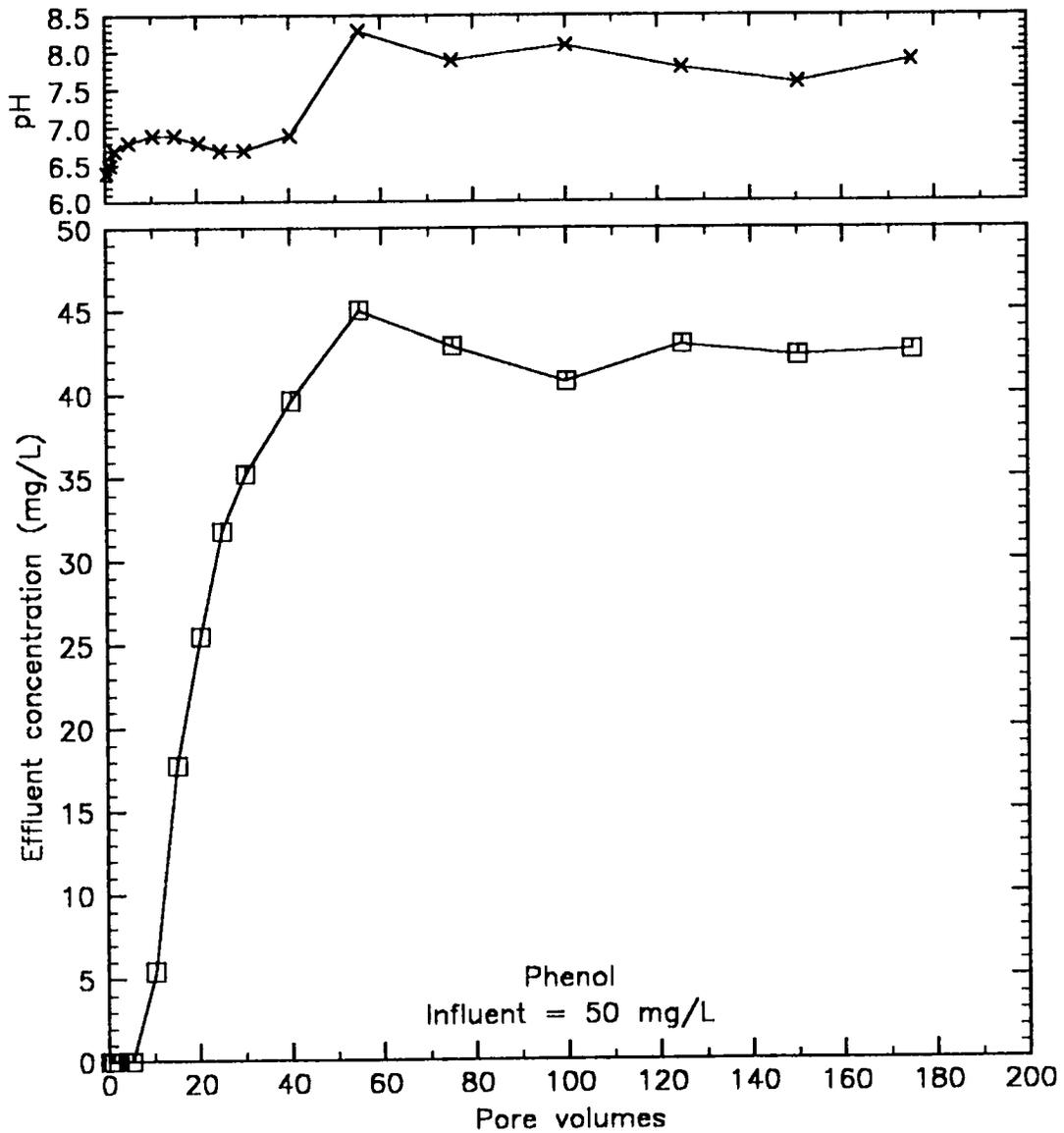


Figure E.2. Continuous-flow column sorption trials with Phenol on shale: Second replicate.

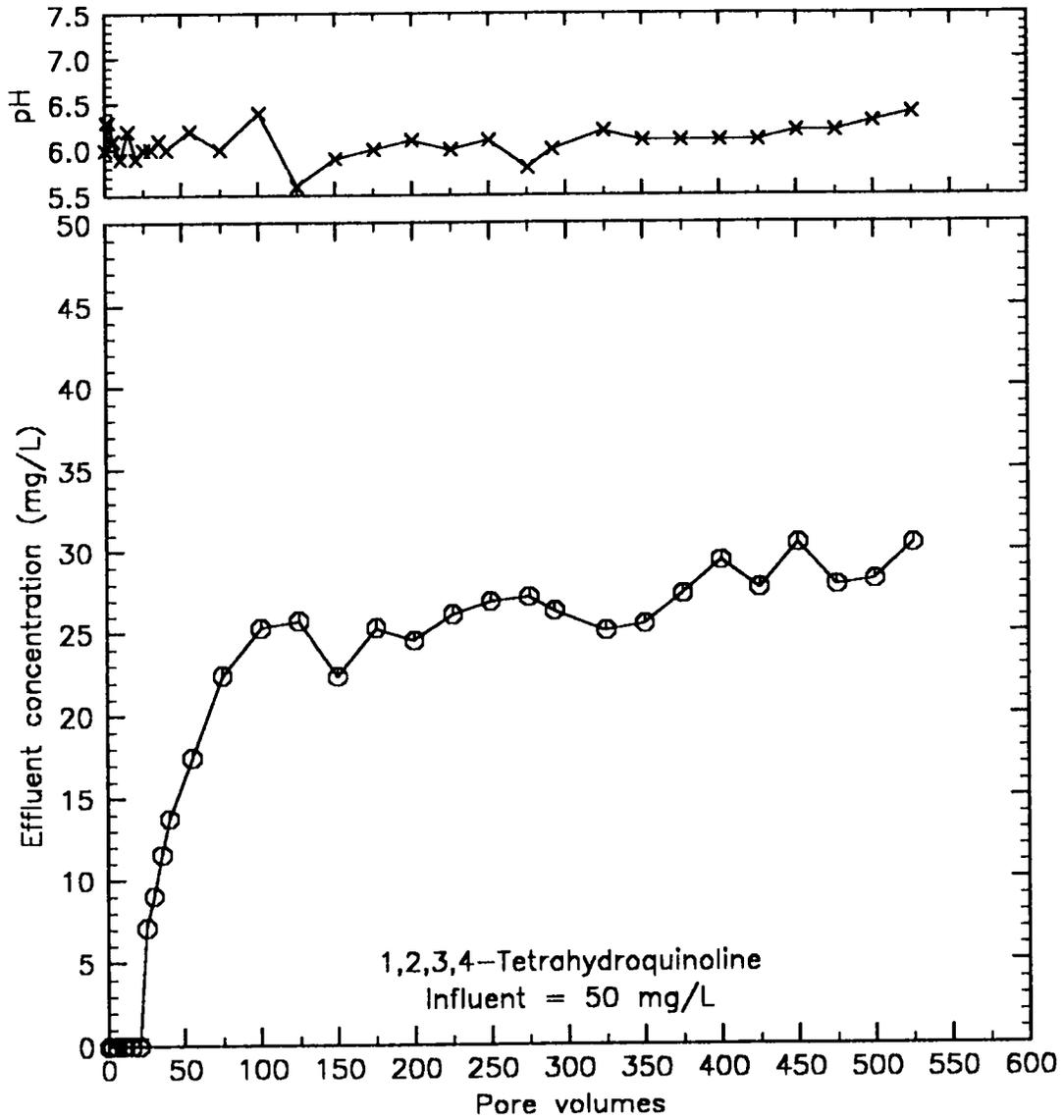


Figure E.3. Continuous-flow column sorption trials with 1,2,3,4-Tetrahydroquinoline on shale: Second replicate.

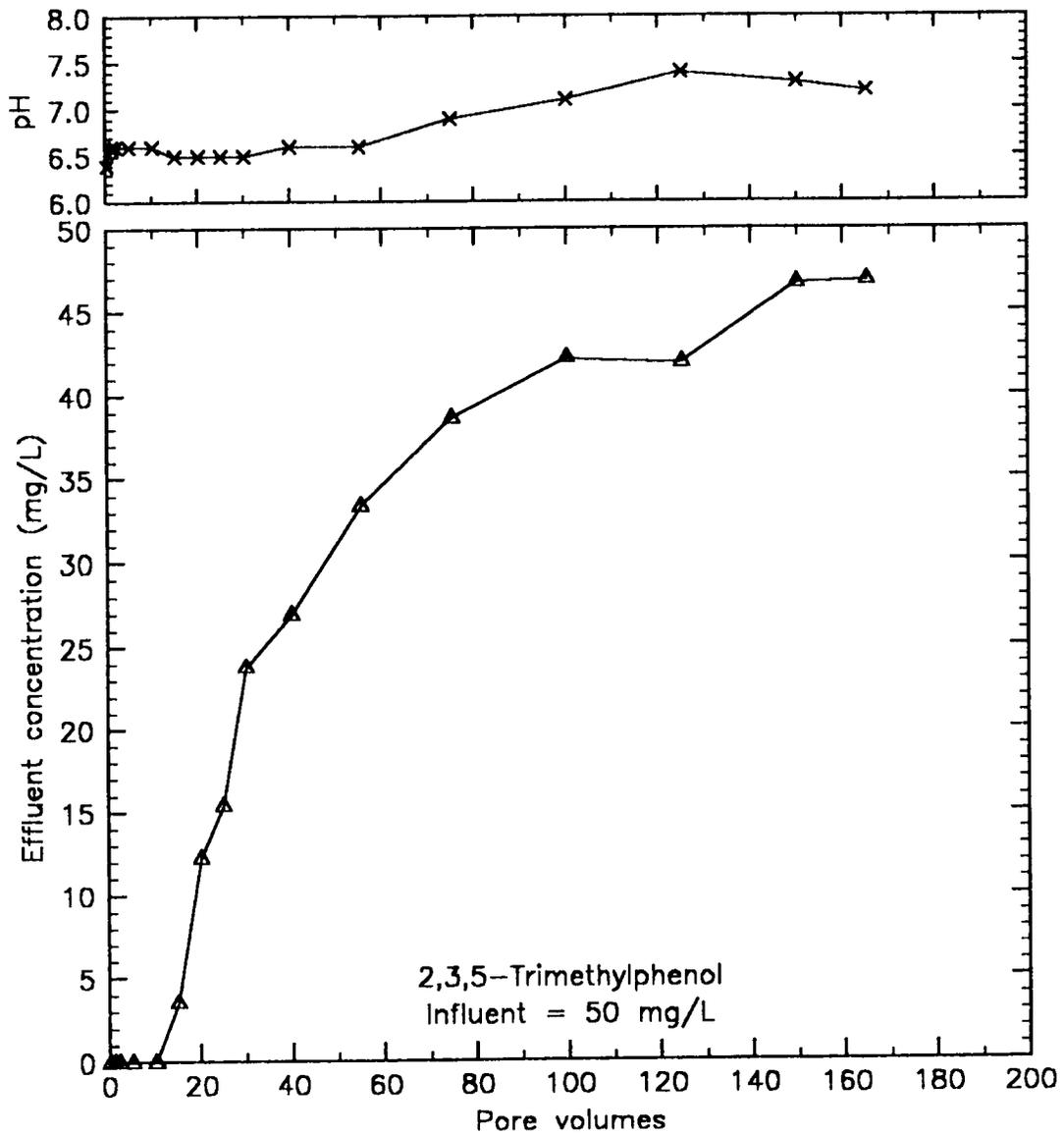


Figure E.4. Continuous-flow column sorption trials with 2,3,5-Trimethylphenol on shale: Second replicate.

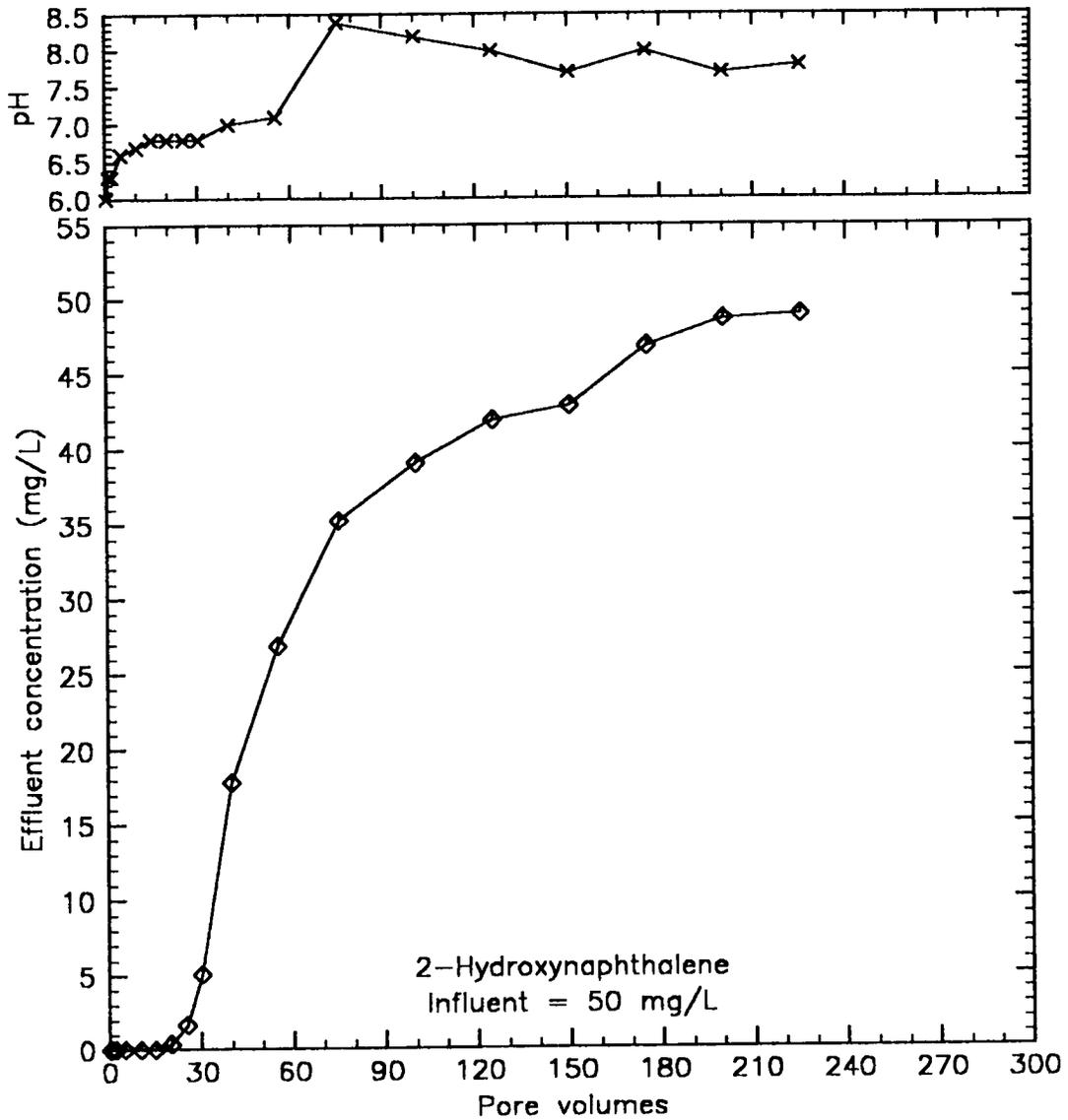


Figure E.5. Continuous-flow column sorption trials with 2-Hydroxynaphthalene on shale: Third replicate.

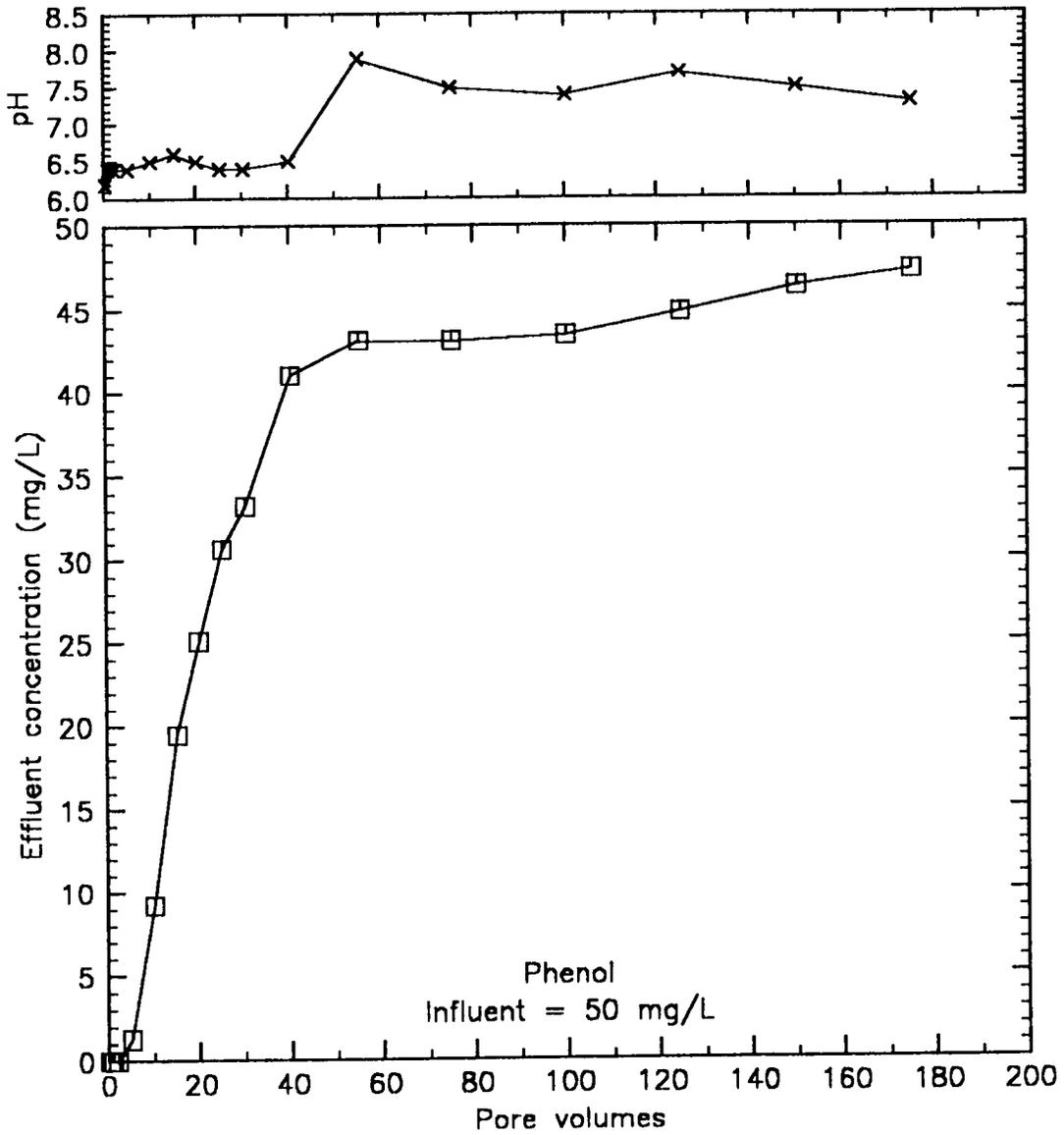


Figure E.6. Continuous-flow column sorption trials with Phenol on shale: Third replicate.

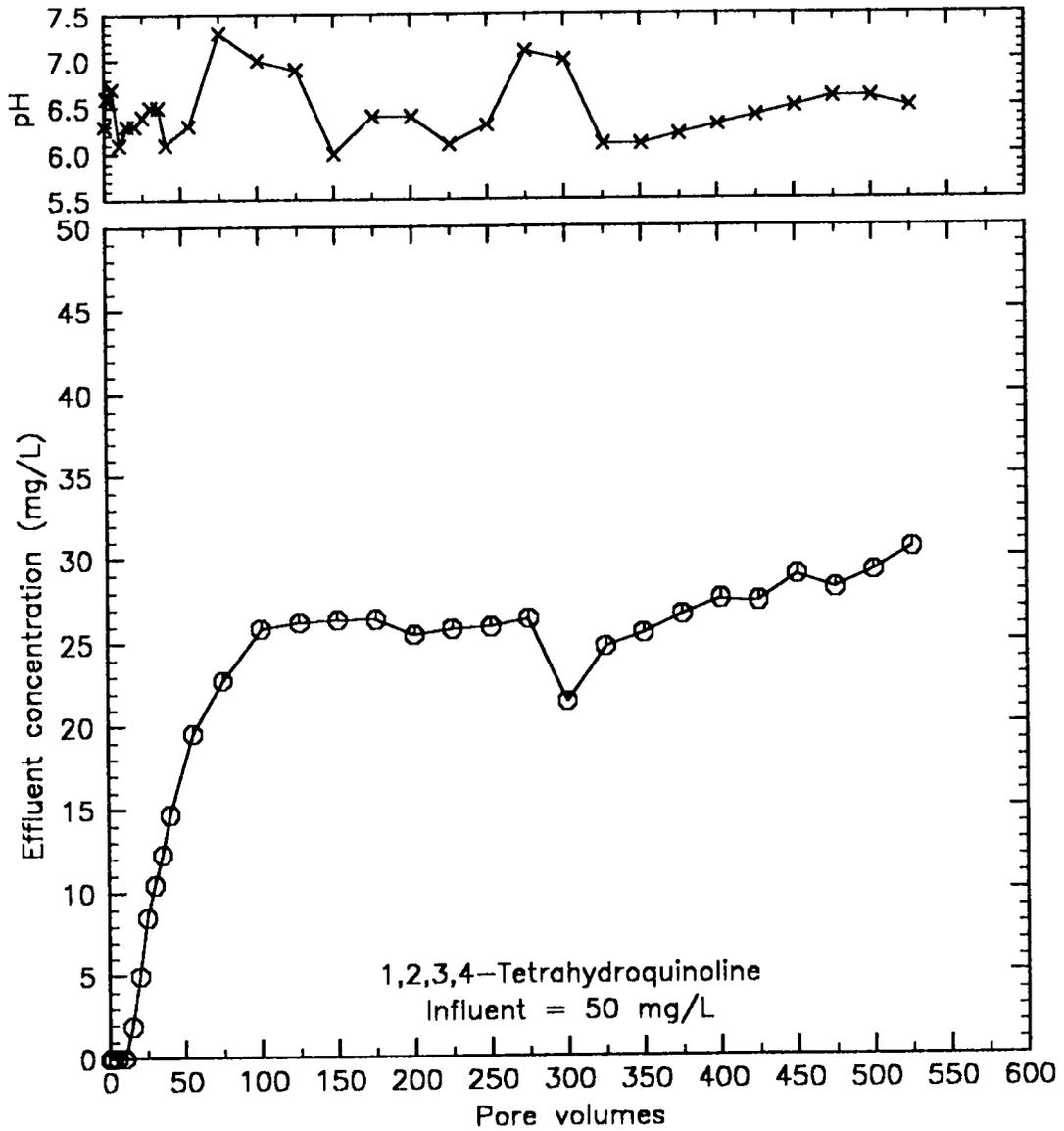


Figure E.7. Continuous-flow column sorption trials with 1,2,3,4-Tetrahydroquinoline on shale: Third replicate.

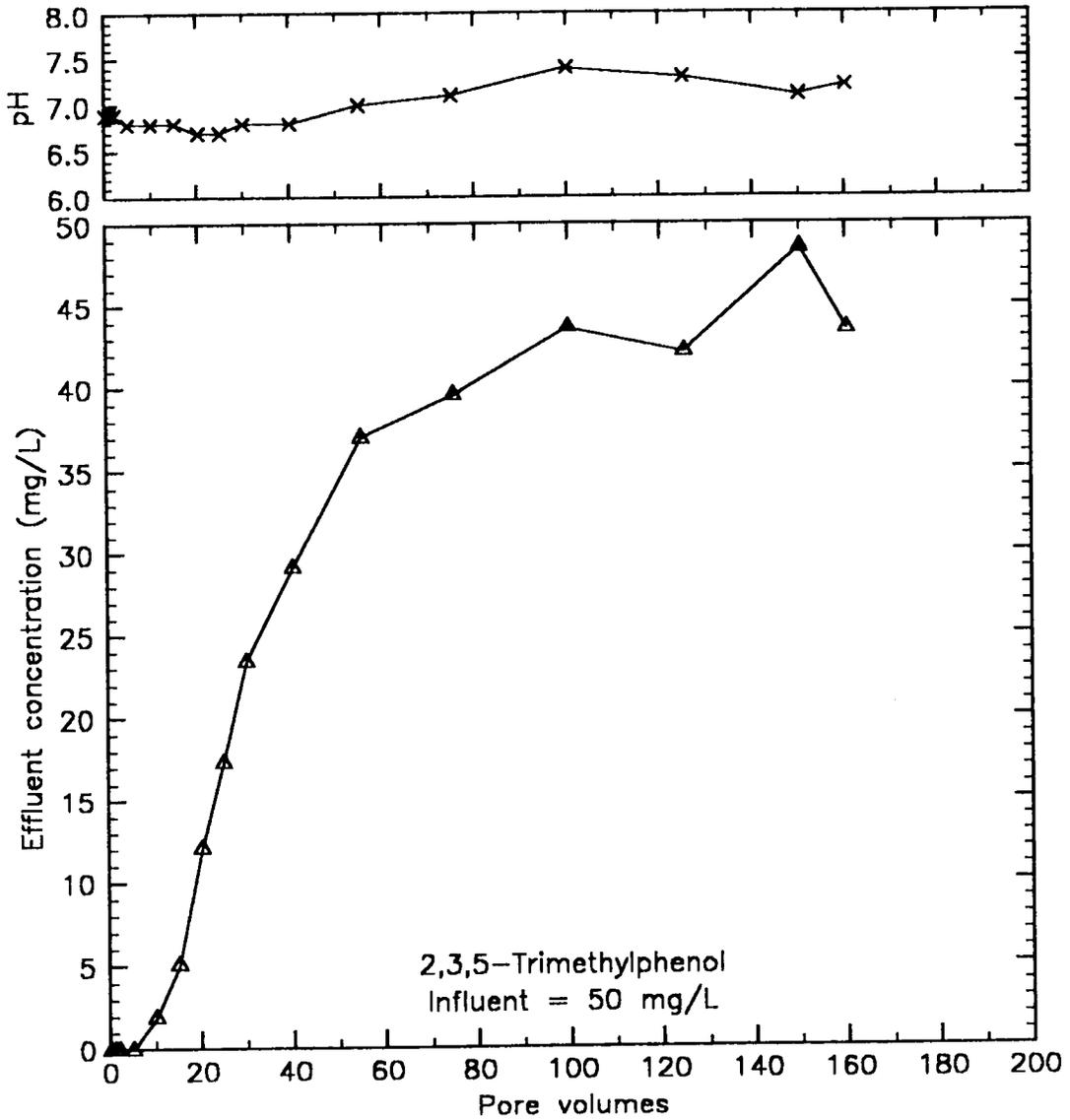


Figure E.8. Continuous-flow column sorption trials with 2,3,5-Trimethylphenol on shale: Third replicate.

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