Effect of Soil Washing on Diesel Fuel Removal Efficiency and Hydraulic Conductivity

by

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EFFECT OF SOIL WASHING ON DIESEL FUEL REMOVAL EFFICIENCY AND HYDRAULIC CONDUCTIVITY

BY

SALEH A. HAIDAR

A Thesis submitted to the Faculty of Graduate Studies of the University of Manitoba in partial fulfillment of the requirements for the degree of

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ABSTRACT

In porous media that have been inundated with petroleum products or organic chemicals, large concentrations of residual oils typically exist after gravity drainage. Due to the high concentrations of these residual oils and the low solubility of the individual constituents of the oils, residual oils often behave as long-term sources of ground water contamination. Excluding technologies relying on excavation, limited means exist to remediate subsurface soils contaminated with residual oils. An option not relying on excavation is chemically enhanced *in situ* soil washing.

Chemically enhanced *in situ* soil washing is an adaptation of enhanced oil recovery techniques commonly applied in the petroleum industry. Current research has demonstrated that this technique can reduce residual oil concentrations at laboratory scale. However, little is known about the interactive effect of such variables as temperature, grain size and flow rate.

This study consists of a series of one dimensional leaching column experiments of soil washing for various combinations of soils contaminated by diesel fuel to investigate the effect of various parameters on recovery efficiency and hydraulic conductivity. These parameters include: (1) normal and hot water injection, (2) normal and hot water injection enhanced by a surfactant, (3) different soil-grain-size distribution, (4) different time limits. In this particular study the well-known, fairly dramatic effect of the first one or two pore volumes sweeps by the soil washing liquid is of secondary interest. Instead, it is the longer ten or hundreds of pore volume sweeps that is studied in detail.

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LIST OF SYMBOLS AND ABBREVIATIONS

A	Area (m^2)
a	Constant
BTEX	(benzene:toluene:ethylbenzene:xylene)
b	slope or trend of regression line
CMC	Critical micelle concentration
CRE	Cumulative removal efficiency (%)
C	Approximate correction factor based on the bulk hydrocarbon viscosity
C_c	Coefficient of concavity
C_e	Organic chemical concentration (mg)
C_i^n	Concentration of component i in phase n (moles/m^3)
C_i^{of}	Concentration of component i in fast oil phase within the contaminated zone
C_i^{os}	Concentration of component i in slow oil phase within the contaminated zone
C_i^a	Concentration of component i in aqueous oil phase within the contaminated zone
C_i^o	Concentration of component i in initial phase
C_u	Coefficient of uniformity
C_s	Soil organic chemical concentration (mg chemical/mg soil)
C_w	Concentration of chemical in water (mg/L)

c	Chemical concentration (mg/L)
c_o	Source chemical concentration (mg/L)
D	Maximum depth of penetration (m)
D	longitudinal dispersion coefficient (m^3/day)
D_A	Diffusion coefficient of the chemical in air (m^2/day)
D_t	Diffusion time (days)
D_{SA}	Diffusion coefficient of a chemical in soil air (cm^2/day)
D_w	Diffusion coefficient of the chemical in the water (m^2/day)
D_{10}	Grain diameter at 10% passing
D_{30}	Grain diameter at 30% passing
D_{50}	Grain diameter at 50% passing
D_{60}	Grain diameter at 60% passing
EDB	Ethylene dibromide
E.D.T.A.	Ethylene diamino-tetra-acetic acid
e	Void ratio (decimal)
f^{oc}	Fraction of organic carbon in the soil (kg/kg soil)
G_s	Relative density (dimensionless)
I_D	Index density
i	Hydraulic gradient
K	Hydraulic conductivity (m/s)
K_d	Distribution coefficient (m^3/kg)
K_H	Henry's law constant (dimensionless)

k_i	Effective permeability (cm/s)
K_i^{oc}	Aqueous-organic carbon partion coefficient for component i (kg water/kg organic carbon)
K_m	Mass exchange coefficient ($mg/m^2/s$)
K_{oc}	Soil adsorption coefficient normalized for soil organic content
K_{om}	Soil adsorption coefficient normalized for soil content
k	Intrinsic permeability (cm/s)
k_{ri}	Relative permeability (cm/s)
k_{orw}	Effective permeability of water at the residual water concentration
k_{wro}	Effective permeability of water at the residual oil concentration
K_i^{HC}	Partion coefficient of the contaminant i between the aqueous and hydrocarbon phase (kg water/kg hydrocarbon)
LNAPLs	Light nonaqueous-phase liquids
l	Distance transvered by the chemicals (m)
M^{HC}	Total mass of residual hydrocarbon phase (kg)
M^{soil}	Total mass of soil (kg)
M^a	Mass of water in the contaminated zone at any time t
MW	Average gram molecular weight of the non-aqueous phase liquid hydrocarbon
MW^a	Molecular weight of the aqueous phase
m	Measurements
NDIR	Non-dispersive infra-red detector

N.T.A.	Nitrolotriacetic acid
n	Individuals
OC	Soil organic carbon (mg organic carbon/ mg soil)
OM	Soil organic matter content (mg organic matter/ mg soil)
P	Soil porosity
P_t	Soil total porosity
P_{sa}	Soil air content (m^3/m^3)
PV	Pore volumes
p	Pressure (atmosphere)
Q	Flow volume (ml)
q	Flow rate (m^3/s)
R^2	Coefficient of determination
R	Soil retention capacity
RS	Residual saturation capacity
S	Source strength ($mass/t/m^2$)
S_i	Pure component i aqueous solubility ($moles/m^2$)
S_v	Volumetric saturation
SW	Soil washing
TOC	Total organic carbon
TPH	Total petroleum hydrocarbon
t	Time (day)
V	Average linear velocity of groundwater (m/s)

V_a	Volume of air (m^3)
V_b	Bulk volume (m^3)
V_c	Velocity of the chemical at the point at which $c/c_o = 0.5$
V_{HC}	Volume of discharge of hydrocarbon (in barrels)
V_S	m^3 of soil required to attain residual saturation
V_{sw}	Amount of soil water percolating through the unsaturated zone (mm/year)
V_p	Vapour pressure of the chemical
V_T	Total volume of soil sample (m^3)
V_s	Volume of solids (m^3)
V_v	Volume of void (m^3)
V_w	Volume of water (m^3)
v	Variable
WC	Soil water content (m^3/m^3)
W_T	Total mass of soil (kg)
W_s	Mass of soil solids (kg)
W_w	Mass of soil water (kg)
W+D	Water plus detergent
w_i^a	Weight fraction of contaminant i in the solvent effluent (kg/kg solvent)
w_i^{HC}	Weight fraction of component i in the residual hydrocarbon phase (kg/kg residual free-phase hydrocarbon)
x	Flow distance (cm)

z	Longitudinal coordinate (m)
α	Longitudinal dispersivity (m)
γ_i^a	Activity coefficient of component i in the aqueous phase
γ_i^{of}	Activity coefficient of component i in the fast oil phase
γ_i^{os}	Activity coefficient of component i in the slow oil phase
γ_i^s	Activity coefficient of component i in the sorbed phase
γ_w	Unit weight (kN/m^3)
τ	Fluid mobility
μ	Fluid viscosity
μ_o	Viscosity of oil
μ_w	Viscosity of water
ρ_b	Dry bulk density (kg/m^3)
ρ_w	Wet density (kg/m^3)

CHAPTER 1

GENERAL DESCRIPTION

1.1 Introduction

Large amounts of petroleum and petroleum products are produced, refined, and handled on land every year. Despite careful handling and containment, there is the possibility that some hydrocarbon may enter the soil environment. There are three main potential sources of such hydrocarbons. The principal two sources involve continuous, low-level inputs: the residue from domestic wastes, and slow seepage from old underground storage tanks. Sudden accidental spillage is the third source. "There have been no clear estimates of the total input of petroleum into the soil environment." (Newton, 1990).

Experience of major oil pollution incidents in recent years has highlighted the difficulties in dealing with large amounts of oil and oil-soaked debris. The most serious threat posed by a major oil spill is the potential damage it can cause to the ground water. The risk of explosion and fire is also a serious threat.

In the past, contingency plans have generally neglected the disposal of contaminated debris. Sometimes methods were suggested, but there was often no indication of which measures were practical or what was the scope of application of such measures. Difficulties with handling contaminated debris are sometimes mentioned in the case histories of individual spills. A local solution may be described, but a systematic overall appraisal is lacking, and little attention appears

to have been paid to the transportation and storage of the contaminated material.

When an oil spill does occur, there is often a tendency to take hasty action on clean-up and disposal, perhaps with inadequate consideration or consultation. There may be an unwillingness to make local disposal sites available, and much time may be lost before suitable sites can be identified. Furthermore, inappropriate methods of transportation and disposal may be chosen because of the lack of information on the techniques and facilities which are available.

The problem of combatting accidental oil spills is most vexing because it does not permit unique and universal solutions. Instead, one must consider a spectrum of solutions that hopefully overlap to cover the entire problem range. During the past few years, a number of methods for the in-place restoration of oil-contaminated soil have been proposed. These methods employ various processing schemes, and may conveniently be categorized as either thermal, physical, chemical or biological in nature.

Cleaning up a release from an underground storage tank (UST) requires both short-term emergency measures and long-term corrective actions. Short-term emergency measures involve taking immediate steps to abate safety and health hazards, including potential explosions. They include notifying appropriate government agencies, stopping the release, removing hazardous substances as necessary, taking steps to prevent further releases, and inspecting and repairing the tank system.

The focus of this work is on long-term remediation and site restoration. A

variety of corrective actions can be used at a UST site to remove contaminant from the vadose zone. The approach presented below involves on-the-spot treatment, without excavation of the soil. The approach allows cleaning the contaminated zone without incurring the risk of damaging the neighbouring environment. However, the main reason for undertaking this work is to see if during a field *in situ* soil washing campaign we can learn "how we are doing" from measuring the rate of circulation of the washing fluid. In the field the procedure is: 1) plot any increase in flow rate with time and relate this to a decrease in contaminant, and 2) compare the measured circulation rate with the theoretical flow rate that would be if the soil were clean. The goal is to save money by not drilling and sampling and having chemical tests run until it is certain that the ground is clean. At the same time, the aim is not to over treat the ground. Therefore, the idea is to stop the field program just as soon as the ground is clean, because every day past this point is money wasted.

1.2 Health-Based Soil Quality Guidelines

1.2.1 Scientific Derived Guidelines

Health and Welfare Canada, in association with Environment Canada and provincial environment agencies, has now initiated work toward deriving scientifically defensible, health-based soil quality guidelines. The department has been involved for several years in the setting of health-based guidelines for drinking water, indoor air, as well as ambient air quality. However, the setting of guidelines for contaminated soil presents a unique difference in that a variety of land uses present

unique exposure scenarios. Land use is an important determinant of the nature and extent of human exposure to contaminated soil, and is an essential element in setting cost-effective soil clean up objectives. The wide variety of land use and the significant differences in the nature and extent of exposure associated with those uses requires that guidelines be developed for these different possibilities. Guidelines will be developed for three primary land uses: agriculture, residential/parkland, and commercial/industrial. The nature and extent of exposure from these three land uses is fundamentally different.

1.2.2 Interim Guidelines

The Canadian National Contaminated Site Remediation Program (NCSRP) has recently released Interim Environmental Quality Criteria for contaminated sites through the auspices of the Canadian Council of Ministers of the Environment. The interim guidelines, presented in Table 1.1,have been adopted from various provincial agencies across Canada (Calabres et al., 1989). In most cases, these interim guidelines have not been derived in a wholly scientific or defensible manner. Many have been adopted from other agencies, are based solely on professional judgment or may be simple multiples of analytical detection limits.

To ensure that these interim soil guidelines provided some health protection, Health and Welfare Canada subject them to a limit assessment for potential health significance.

1.3 Description of Treatment System

The soil washing process, which is also referred to as soil extraction or soil flushing, originated from a very common observation: the washing of oily dishes with hot soapy water resulted in the oil being dissolved and clean dishes. From this down-to-earth observation the idea of soil washing was born.

Soil washing is used for removal of a number of organic and inorganic material from the vadose zone. A variation of soil flushing, referred to as chemical extraction, may be used to remove non-water-soluble organics from the saturated zone. Soil washing involves the addition of a solvent or surfactant to the contaminated soil to enhance contaminant mobility (U.S.EPA, 1991). The contaminants are then recovered by strategically placed extraction wells and pumped to the surface for treatment. Soil washing is most applicable when soil must be remediated, but other technologies such as vacuum extraction or physical removal (i.e., excavation) are not feasible. High water tables, deep contamination, and high-permeability soil that require dewatering are conditions in which these other technologies would be less feasible. Soil washing is not feasible for soils with low-hydraulic conductivities (e.g., less than $4x10^{-3}$ mm/sec) and for strongly adsorbed contaminants (e.g., PCBs, dioxin). The addition of chemicals to the flushing solution that will increase contaminant mobility is necessary to reduce the interfacial tension between the petroleum constituents and water, if strongly adsorbed, hydrophobic contaminants are present in the soil (Newton, 1990). (The extraction of strongly adsorbed contaminants may not be desirable, however, unless there is an imminent

threat to human health and the environment.) The more permeable the soil, the more water that can be flushed through the soil and the more practicable is this technology (EPA, 1990a). Soil washing strategies can be incorporated into pump and treat or containment systems to accelerate the contaminant removal processes. Soil washing can be accomplished using sprinkling systems or, more aggressively, by flooding the contaminated area. The liquid removed from the soil is then discharged either directly to a bioreactor or to a filtration treatment process for recycling the water. "Chemical extraction involves extracting ground water, amending it with solvents and/or other chemicals, and reinjecting it at strategic locations into the aquifer" (U.S. EPA, 1990b). With any soil washing system, proper controls must be incorporated to prevent migration of extractant-contaminant mixtures.

Key factors involved in soil washing (SW) include but are not limited to :

. Contaminate distribution at site,

. Hydrogeology,

. Contaminate properties; and

. Site physical properties.

Extensive studies of water injection have been reported in the oil recovery literature, but applications to *in situ* soil washing remediation have been limited.

Some of the knowledge and techniques developed in petroleum engineering for enhanced oil recovery by steam/water injection and enhanced oil recovery with surfactant (e.g., Willman et al., 1961; Gogart, 1977) are useful to the problem of *in situ* soil washing for remediation of heavy hydrocarbon contaminated soil.

However, there is a distinct difference between these two applications. In enhanced oil recovery, the objective is to continue to remove oil from the reservoir for as long as it is economically feasible. Small amounts of oil left in the formation are usually ignored. In contrast, the purpose of remediation efforts is to remove as much of the contaminant as possible, at least until the required cleanup levels are achieved.

The process of *in situ* soil washing for subsurface remediation involves several complex interacting phenomena at the pore level that are not considered in petroleum reservoir engineering. The process is characterized by heat and mass transfer in multiphase flow (air, water, heavy and/or light hydrocarbon) in which the mass transfer of components between the phases is significant. Important mechanisms include air-phase mass transfer and contaminant advection in the liquid due to a large pressure gradient. These complexities limit the general application of analytical methods to *in situ* soil washing problems.

Early exploratory experiments with soil washing for soil remediation were carried out by the United State Environmental Protection Agency by Nash (1985). Hunt et al. (1988) performed laboratory experiments to study the fundamental aspects and to demonstrate the feasibility of hot water injection as an *in situ* remediation technique for soil contaminated by light nonaqueous-phase liquids (LNAPLs). Hunt et al. (1988) found in some cases that only one pore volume of fluid had to be displaced by hot water injection to achieve cleanup standards. Simplified measurements of recovery efficiency of kerosene and gasoline in one-dimensional experiments of vacuum-assisted water stripping were conducted by

Treweek (1988) and Kao (1989), who also performed observations of two-dimensional water front movement. Castle et al. (1989) later extended the work to include experiments to measure the recovery efficiency of vacuum-assisted water stripping of several single compound chemicals, and of gasoline and kerosene in soils containing various amounts of silt, clay, and organic material.

Several field demonstration projects related to soil remediation by soil washing were conducted (Castle et al., 1989; Baker et al., 1986; Laney, 1988; Smarkel, 1988; Ellis, 1991). Castle (1989) performed field measurements to identify the dominant mechanisms responsible for displacement and recovery of NAPLs from soils, using combined water injection and vacuum extraction. In a field demonstration study of steam and hot water injection (under the U.S. Environmental Protection Agency (EPA) Superfund innovative technology evaluation (SITE) program, 1989), Castle et al. found that more than 80% of the organic compounds were recovered by chemically-enhanced soil washing.

1.4 Objectives

In all the studies reported so far, the effect of *in situ* soil washing (enhanced chemically) has not been studied systematically. The main objective of the present study was to conduct laboratory experiments of chemically-enhanced soil washing for various combinations of soils contaminated by nonaqueous-phase liquid (NAPLs) in order to investigate the effects of various parameters on NAPL recovery efficiency and the hydraulic conductivity. These parameters include (1) normal and hot water

injection, (2) normal and hot water injection enhanced by a surfactant, (3) different soil-grain-size distribution, (4) different time limits.

Other goals of this study were to answer the following questions:

- Is it possible to predict, by comparing the measured circulation rate with the theoretical rate, that the soil is clean ?
- What processes govern soil washing in the longer term ?
- What are the limitations / advantages of these processes ?
- Can remediation by soil washing attain target cleanup levels ?
- What information / data is needed to answer these questions ?

It was envisioned that answers to these questions could be used in the development of an approach to (a) identify sites at which soil washing could be practised effectively, and (b) design efficient soil washing systems.

Table 1.1 Canadian Interim Remediation Criteria for Soil

	Agricultural	Residential Parkland	Commercial Industrial
Monocyclic Aromatic Hydrocarbon			
Benzene	0.05	0.5	5
Chlorobenzene	0.1	1	10
1,2-Dichlorobenzene	0.1	1	10
1,3-Dichlorobenzene	0.1	1	10
1,4-Dichlorobenzene	0.1	1	10
Ethylbenzene	0.1	5	50
Styrene	0.1	5	50
Toluene	0.1	3	30
Xylene	0.1	5	50
Phenolic Compounds			
Nonchlorinated (each)	0.1	1	10
Chlorophenols (each)	0.05	0.5	5
Polycyclic Aromatic Hydrocarbons (PAHs)			
Benzo(a)anthracene	0.1	1	10
Benzo(a)pyrene	0.1	1	10
Benzo(b)fluoranthene	0.1	1	10
Benzo(k)fluoranthene	0.1	1	10
Dibenz(a,h)anthracene	0.1	1	10
Indeno(1,2,3-c,d)pyrene	0.1	1	10
naphthalene	0.1	5	50
Phenanthrene	0.1	5	50
Pyrene	0.1	10	100
Chlorinated Hydrocarbons			
Chlorinated aliphatics (each)	0.1	5	50
Chlorobenzenes (each)	0.05	2	10
Hexachlorobenzene	0.05	2	10
Hexachlorocyclohexane	0.01	-	-
PCBs	0.5	5	50
PCDDs and PCDFs	0.00001	0.001	-
Miscellaneous Organic Parameters			
Nonchlorinated aliphatics (each)	0.3	-	-
Phthalic acid esters (each)	30	-	-
Quinoline	0.1	-	-
Thiohene	0.1	-	-

All values in microgram/gram dry weight.
Source: Calabres, et al., 1989.
- = Value not established.

CHAPTER 2

FUNDAMENTAL TECHNICAL CONCEPTS OF SOIL WASHING

2.1 Introduction

The discovery of petroleum products in soils has led to one of the most comprehensive and widespread environmental investigation and mitigation efforts this country has experienced. Attention has been focused primarily on gasoline because of its universal usage by the ever-present automobile. On the other hand, certain segments of the private sector, such as hydro and railroad industries, depend heavily on diesel fuel as their source of energy.

The successful investigation and mitigation of a release of diesel fuel and other petroleum products are substantially affected by the understanding by scientists and engineers of how diesel fuel and other petroleum products migrate and degrade in soil systems.

This chapter presents a general review of the physical and chemical reactions that govern the fate of diesel fuel and other petroleum products in the soil system.

2.2 Characteristics of petroleum

Petroleum liquids are a complex mixture of organic compounds called hydrocarbons. Hydrocarbons contain the elements hydrogen and carbon, sometimes with minor amounts of nitrogen, oxygen, and sulphur. The transfer of these compounds from the liquid phase to other phases, and the migration potential of

each phase, are largely dependent on the physical and chemical properties of the specific hydrocarbon compounds and blends. A general knowledge of such properties for the pertinent hydrocarbon compounds is useful when performing a site assessment (NWWA/API Conference, 1987).

2.2.1 Types of Petroleum

Crude oil is refined into petroleum products through several processes, including fractional distillation. The resulting petroleum products are mixtures of as many as several hundred compounds, which can be assigned to one of the following general groups:

a. Gasolines.

b. Middle distillates - diesel fuel, kerosene, jet fuel, and lighter fuel oils.

c. Heavier fuel oils and lubricating oils.

d. Asphalt and tars.

The refining process may also selectively produce pure compounds termed petrochemicals. This group includes compounds such as butane, benzene, toluene, xylene, and hexane. These materials are used as solvents, as raw materials in the chemical manufacturing industry, or for reblending into fuel (Goodger, 1975).

2.2.1.1 *Gasoline*

Gasoline and finished oils are blends of petroleum-derived chemicals plus additives that improve fuel performance and engine longevity, assist in wear

reduction, and color code the product. The bulk of chemical compounds in petroleum are classed as either aliphatic or aromatic. Aliphatic compounds are organic compounds in which the carbon atoms exist as either straight or branched chains. Examples include pentane, hexane, and octane. Aromatic compounds contain carbon molecular ring structures and include compounds such as benzene, toluene, ethylbenzene, and xylene (BTEX = 1:1:1:1). These compounds are somewhat soluble, volatile, and mobile in the subsurface environment and are useful indicators of contaminant migration (Morrison, 1973; Goodger, 1975; Petrov, 1987).

Oxygenated compounds (oxygenates) such as alcohols (methanol) act as octane boosters. These compounds are the most soluble components in gasoline, being present in some gasolines in concentration as high as 10 percent by volume.

Ethylene dibromide (EDB) is present in some leaded gasolines and, along with lead, may be used as an indicator of a leaded gasoline release. The presence of EDB in the subsurface can also be due to the application of agricultural chemicals, and should be used with caution as an indicator of petroleum hydrocarbon contamination. Lead must also be used with caution as a contamination indicator because native earth materials commonly contain lead. Some laboratories analyze and report total lead content, which includes inorganic lead. Also, the use of lead as an indicator of contamination will decrease in the future as the production of leaded gasoline is phased out (Petrov, 1987).

2.2.1.2 *Middle Distillates*

The middle distillate group includes diesel fuel, kerosene, jet fuel, and lighter fuel oils. Middle distillate materials may contain as many as 500 individual compounds; however, these compounds tend to be more dense, less volatile, less mobile, and less water soluble than gasoline-boiling-range material. Also, middle distillate materials usually contain low percentages of lighter-end aromatic compounds such as BTEX. Commonly, in older releases, the concentrations of BTEX compounds will have degraded to minimal or undetectable levels or will have been transported away. (Rossini, 1960; Petrov, 1987)

The BTEX compounds, either singularly or in various combinations, are present in many materials other than petroleum hydrocarbons. Hence the presence of one or two of the BTEX compounds without other evidence is not necessarily an indicator of a petroleum hydrocarbon release (Petrov, 1987).

2.2.1.3 *Heavier Fuel Oils and Lubricating Oils*

Heavier fuel oils and lubricants are similar in composition and characteristics to the middle distillates. These types of fuels are relatively viscous and insoluble in groundwater and are relatively immobile in the subsurface. As discussed above, in older releases, the lighter end components may have been degraded or transported away (Petrov, 1987).

2.3 Physical Properties of Petroleum

Fluid density and dynamic viscosity are two properties that can affect the mobility of liquid-phase hydrocarbons. The fluid density is the mass per unit volume. Most petroleum hydrocarbons have a density less than that of water (that is, 10^3 kg/m^3). Dynamic viscosity is a measure of the resistance of a fluid to flow. Table 2.1 (Nelson, 1958) presents typical density and viscosity data for selected liquid hydrocarbons and water. In general, as the density increases, the viscosity of a petroleum products increases, and the ability of products to move through the subsurface decreases. However, this relationship does not hold for all products. The densities and viscosities of crude oils vary widely but are between the ranges shown for refined products. Densities and viscosities tend to decrease in most hydrocarbons with increasing temperature (Nelson, 1958).

The tendency for hydrocarbons to transfer from the liquid hydrocarbon phase to dissolved phase in water is controlled primarily by their solubilities in water and the degree of contact and mixing.

Solubility values for particular hydrocarbon compounds in distilled water are available in the literature. These data can be misleading because the concentration and water solubility of a specific compound as part of a blend tend to be significantly less than the concentration and solubility of the compound alone in water. However, as the relative concentration of a particular compound in a hydrocarbon blend increases, the concentration and solubility of the compound in water is also greater. (Brookman et al., 1985)

2.4 Characterization of Hydrocarbon Phase

2.4.1 General

Hydrocarbons can be present in the subsurface in solid, liquid, dissolved, and vapour phase or in combinations of several phases. Solid phases include substances like asphalt and bitumen, which will remain solid and essentially immobile unless the temperature rises above their melting points. Such temperatures are rare in shallow groundwater regimes; thus, the solid hydrocarbon phase will not be further discussed.

2.4.2 Liquid-Phase Hydrocarbon

Liquid-phase hydrocarbon can exist in the subsurface in the following forms (see Figure 2.1):

a. Immobile residual liquids in the unsaturated zone and capillary fringe.

b. Free mobile liquids that migrate near the top of the capillary fringe.

c. Immobile residual liquids trapped in the saturated zone.

The particular form taken is determined by degree of hydrocarbon saturation in the void spaces and by the wetting characteristics of the earth materials (see Figure 2.1). In the unsaturated zone a thin film of water will normally coat the solid surfaces of most minerals and rocks, there by acting as a wetting fluid. Liquid hydrocarbons can also behave as a wetting fluid and coat the water film and mineral grain as migration occur towards the water table through the unsaturated zone and capillary fringe . The approximate range of residual hydrocarbon concentrations in the unsaturated zone for different hydrocarbons and earth materials is presented in

Table 2.2 (API Proceeding, 1977).

2.4.3 Dissolved-Phase Hydrocarbons

Dissolved-phase hydrocarbons exist in the following subsurface areas (see Figure 2.1):

a. In infiltrating water in the unsaturated zone.

b. In the residual films of groundwater covering the surfaces of solid minerals in the capillary fringe and liquid hydrocarbon plume zones.

c. In groundwater within the saturated zone.

2.4.4 Vapour-Phase Hydrocarbons

Vapour in the subsurface exists in two areas. Most vapour exists in void spaces in the unsaturated zone not occupied by water or liquid hydrocarbons and is considered mobile (see Figure 2.1). Vapour can also be present as small bubbles trapped in either the liquid hydrocarbon plume or the underlying water-bearing zone. The bubbles are relatively immobile but may be dissolved in the groundwater or be released into the soil air (API Proceeding, 1977).

2.5 Migration of Bulk Diesel Fuel in Soil System

2.5.1 Unsaturated zone

2.5.1.1 *Infiltration*

The knowledge about the infiltration of diesel fuel is relatively qualitative and

based upon general knowledge on the infiltration of hydrocarbon.

The knowledge can be summarized as follows: similar to water, bulk hydrocarbons which are released at the soil surface will penetrate through the soil surface via the most permeable path. Bulk hydrocarbon may temporarily pond on the soil surface if the soil has a very high clay content and a low permeability. On the other hand, a sandy soil may allow rapid infiltration. Bulk hydrocarbon viscosity also affects infiltration rates; heavy oils will infiltrate slowly relative to gasoline and kerosene.

2.5.1.2 *Deep Percolation*

Again, the knowledge about the deep percolation of diesel fuel is relatively qualitative and based upon general knowledge regarding the percolation of hydrocarbon.

Diesel fuel will migrate downward in the unsaturated zone due to gravity and capillary forces. If the volume of released diesel fuel is large, such as those related to catastrophic spills, maximum lateral spreading and downward flow occurs with all soil pores being saturated with hydrocarbon. The downward migration of diesel fuel will eventually cease because (a) the diesel fuel content decreases, or (b) it will encounter an impermeable bed, or (c) it will reach the capillary fringe.

The volume of soil required to immobilize a volume of diesel fuel depends upon the oil wetting characteristics of the soil and the physical properties of the diesel fuel. The number of cubic meters of soil required to immobilize a volume

of bulk hydrocarbon, V_{HC} can be grossly estimated: (adapted from Testa, 1991)

$$V_S = 0.2 \frac{V_{HC}}{P\ (RS)} \tag{2.1}$$

where

V_{HC} = Volume of discharge hydrocarbon, m^3

V_S = of soil required to attain residual saturation, m^3

P = soil porosity, dimensionless

RS = residual saturation capacity, dimensionless

In general, the residual saturation capacity of soil is about 0.33 of its water-holding capacity (Bossert, 1984). The maximum residual saturation for light oil and gasoline is 0.1; for diesel and light fuel oil, 0.15; for lube and heavy fuel oil, 0.20.

The maximum possible depth of penetration, D, in metres, can be grossly estimated using the equation developed by Van Dam (1967), and modified by Dietz (1970), which states that

$$D = \frac{V_S}{A} \tag{2.2}$$

where A is the area of infiltration in m^2. There is an alternative equation that has been stated at CONCAWE, 1974 which grossly estimates the maximum depth of penetration of a volume of bulk hydrocarbon released on a soil (Testa, 1991);

$$D = a \frac{V_{HC}}{A} \tag{2.3}$$

where a is a constant that depends on the soil's retentive capacity for oil and the oil's viscosity. Typical a values for medium to fine sand: for gasoline 80, kerosen 40, and 20 for light gas oil.

Another nonrigorous formula for grossly estimating the maximum depth of penetration of a volume of bulk hydrocarbon into the unsaturated zone is: (Testa, 1991)

$$D = 1000 \frac{V_{HC}}{A\ (R * C)} \tag{2.4}$$

where

R = soil retention capacity

C = approximate correction factor based on the bulk hydrocarbon viscosity (0.5 for gasoline to 2.0 for light fuel oil)

Recommended values of R in litres per cubic meter are 15 for coarse to medium sand, 25 for medium to fine sand, and 40 for fine sand to silt. For dry soils, R will be greater than the values listed above.

2.6 Diesel Fuel and Soil Hydraulic Conductivity

Many bulk hydrocarbons, including diesel fuel, can change the hydraulic conductivity of soils. In one study, diesel fuel caused a 1800 times decrease in the hydraulic conductivity of a 26% mica-sand mixture, 1400 times hydraulic conductivity decrease of a 16% bentonite-sand mixture, and a 40 times hydraulic conductivity

decrease of a 10% bentonite sand mixture as compered to water (Brown, 1984a). In another study, the hydraulic conductivity of compacted unsaturated micaceous soil to diesel fuel was 1 to 1.5 orders of magnitude less than the corresponding hydraulic conductivity to water (Brown, 1984b).

Dragun (1988) explains two mechanisms by which bulk hydrocarbons may cause hydraulic conductivity to increase in soils containing a significant amount of clay (35 to 90%). One involves the dielectric constant of the bulk hydrocarbon. The dielectric constant represents the ability of a liquid to transmit charge. Since most bulk hydrocarbons possess dielectric constants which are less than the dielectric constant of water, the entry of a bulk hydrocarbon into the interparticle space forces water and ions out, and may act as an insulator between electrostatic repulsion forces emanating from two adjacent particles. As a result of the lack of ions and the presence of an insulator, the interparticle spacing could significantly decrease. This would results in the formation of major cracks and fissures to occupy the space previously occupied by clay soil particles. These cracks and fissures would act as preferrential flow channels for bulk hydrocarbons and result in substantial soil hydraulic conductivity increases.

The second mechanism involves the effect of bulk hydrocarbon on the structure of water in the interparticle space. When bulk hydrocarbon enters the interparticle space, it pushes dipolar water, via mass action, out of the interparticle space and destroys the water structure which extends out from the surface of the particle. If the bulk hydrocarbon has a very low dielectric constant, it exhibits no

propensity to align with surface oxygens molecules of clay minerals. As a result, no solvent structure extends out from the particle surface, and the interparticle spacing can be very small.

As the dielectric constant increases, the solvent structure emanating from the particle surface will extend out further; the larger the dielectric constant, the greater is the ability for the bulk hydrocarbon to align and the farther the solvent structure will extend into the interparticle space. As a result, the original significant interparticle spacing remains and major cracks and fissures do not form.

Under either mechanism, the ability of diesel fuel to replace water via mass action will be the factor limiting it from increasing hydraulic conductivity in many clay soils.

2.7 Migration of Dissolved Organics From Diesel Fuel

2.7.1 Dissolution of Dissolved Organics from Bulk Diesel

Diesel fuel is not miscible with water. However, diesel fuel is comprised of numerous individual chemicals that are soluble to some extent in water. When percolating surface water and groundwater came in contact with bulk hydrocarbons, some of the chemicals are released from the bulk hydrocarbon to the soil or groundwater. Very few studies have been published addressing the source strength of bulk hydrocarbons; one study has addressed diesel fuel. Source strength has been defined as the intensity with which dissolved chemicals are released from a bulk

hydrocarbon to water over time, expressed as mass/time per unit contact area: (Pfannkuch, 1984)

$$S = K_m A \qquad (2.5)$$

where

S = source strength, mg/time

K_m = mass exchange coefficient, mg/m^2/sec

A = contact area, m^2

The contact area, A, is the interface across which mass exchange occurs. It governs the actual mass that is exchanged in a given period of time. Due to the complexity of hydrocarbon distribution in soil pores, the quantification of A is, at best, exceedingly difficult. As a result, studies have focused on quantifying K_m using several approaches.

Mass exchange coefficients were estimated to be 1.0 mg/meter^2/sec for gasoline and tar oil, 0.01 for fuel oil, diesel oil and kerosene, and 0.001 for lube oils and heavy fuel oil (Pfannkuch, 1984).

2.7.2 Migration of Dissolved Organics in the Unsaturated & Saturated Zones

As stated earlier, when percolating soil water and groundwater contact bulk hydrocarbon, some of the chemicals are released from the bulk hydrocarbon to the soil or groundwater. The foundation of our knowledge of how the organic chemicals comprising diesel fuel migrate in a soil system is based on decades of pesticide research.

The most commonly accepted and used equation for grossly estimating the migration rate of one of the dissolved organic chemicals in a soil-groundwater system is the retardation-equation: (Domenico and Schwartz, 1990)

$$V_c = V\,[1 + K_d\,(\frac{\rho_b}{P})]^{-1} \qquad (2.6)$$

where

V_c = the velocity of the chemical at the point at which $c/c_o = 0.5$

c = chemical concentration (mg/l)

c_o = source chemical concentration (mg/l)

V = average linear velocity of groundwater (mm/s)

K_d = distribution coefficent (m^3/kg)

ρ_b = soil bulk density (kg/m^3)

P = soil porosity

The term $[\,1 + K_d\,(\rho_b/P)\,]$ is known as the retardation factor. The retardation equation can be modified for use in estimating the migration rate, V_c, of a dissolved organic chemical in the unsaturated zone soil (Baes, 1983):

$$V_c = V_{sw}\,[WC + (\rho_b * K_d)]^{-1} \qquad (2.7)$$

where

V_{sw} = amount of soil water percolating through the unsaturated zone ($mm^3/mm^2/year$)

WC = Volume water content (m^3/m^3)

ρ_b = soil bulk density (kg/m^3)

This and many other derivations of this approach have been utilized successfully to estimate the velocity of organic chemicals in soil-groundwater systems.

The distribution coefficient , K_d, is, in most cases, the coefficient that exerts the greatest effect on the migration rate. Adsorption is defined as the accumulation of a chemical over the soil surface. The coefficient K_d, is defined as the ratio:

$$K_d = \frac{C_s}{C_e} \tag{2.8}$$

where

C_s = soil organic chemical concentration (mg chemical/mg soil)

C_e = organic chemical concentration (mg)

The greater the extent of adsorption (i.e. $C_s >> C_e$), the greater the magnitude of K_d.

In general, the factors that affect organic chemical adsorption on to a soil surface include molecular size, hydrophobicity, molecular charge, hydrogen bonding, and the arrangement and interaction of molecular fragments. Several researchers have found that if K_d is normalized on the basis of the soil's organic matter or organic carbon content, much of the variation observed among the K_d values for different soils can be eliminated. Normalized K_d values are expressed as either K_{om} or K_{oc}; where

$$K_{om} = \frac{K_d}{OM} \tag{2.9}$$

and

$$K_{oc} = \frac{K_d}{OC} \qquad (2.10)$$

where

K_{om} = soil adsorption coefficient normalized for soil water content.

K_{oc} = soil adsorption coefficient normalized for soil organic content.

OM = soil organic matter content (mg organic matter/mg soil)

OC = soil organic carbon (mg organic carbon/mg soil)

The relationship between OM and OC is assumed typically to be constant:

$$K_{oc} = 1.7\ K_{om} \qquad (2.11)$$

Many K_{oc} and K_{om} values, which have been measured for a wide variety of organic chemicals and soils, are listed in Dragun's work 1988.

In many cases where it is not feasible to obtain an accurate measurement of K_d, K_{om}, or K_{oc}, it may be necessary to settle for a reasonable estimate. Several researchers have found that the extent of adsorption of nonionic organic chemicals on a soil particle surface was well-correlated with two empirical measurements of organic chemical hydrophobicity: the water solubility, S, and the octanol-water partition coefficient, K_{ow}. Dragun (1988) lists 14 equations which utilize either S or K_{ow} to estimate K_{oc} or K_{om}.

It is most important to recognize that these equations are not universally applicable to all organic chemicals in all soils systems. The estimation equations

should not be overextended or used without regard to their limitations. The limitations are discussed extensively by Dragun (1988).

2.8 Diffusion of Diesel Fuel Organic in Air-Filled Soil Pores

Once again, the foundation for the knowledge of how organic chemicals comprising diesel fuel migrate in soil systems is decades of pesticide research.

The rate at which an organic chemical will move through soil air and volatilize into the atmosphere is controlled by the following equilibria:

Chemical adsorbed onto soil particles	----->	Chemical in soil water	(2.12)
Chemical in soil water	-----> (air in soil pores)	Chemical in soil air	(2.13)
Chemical in soil air	----->	Chemicals in atmosphere	(2.14)

An analysis of equations 2.12, 2.13, and 2.14 will reveal that in order for a chemical to volatilize from a soil surface two events must occur. First, the chemical within the soil must move to the soil surface. Second, the chemical must move away from the soil surface into the atmosphere above the soil. These two events directly depend upon diffusion.

Diffusion in this context is defined as the average rate of migration velocity of a chemical in air and/or water. When mass flow by convection is small or negligible, a chemical is able to move through the soil only by liquid or vapour diffusion. A characteristic diffusion time for a chemical to migrate in a soil system can be expressed as (Jury, 1984):

$$D_t = \frac{l^2}{DE} \qquad (2.15)$$

where

D_t = diffusion time (days)

l = distance transversed by the chemicals (meters)

$$DE = [(D_A\ K_H\ P_{sa}\ \frac{3.33}{P^2})] * [(D_w\ \rho_b\ K_d + WC + P_{sa}\ K_H) - 1] \qquad (2.16)$$

where

D_A = diffusion coefficient of the chemical in air (m^2/day)

K_{II} = Henry's law constant (dimensionless)

P_{sa} = soil air content (m^3/m^3)

P = soil total porosity

D_W = diffusion coefficient of the chemical in water (m^2/day)

WC = soil water content (m^3/m^3)

ρ_b = soil bulk density (kg/m^3)

K_d = distribution coefficient (m^3/kg)

2.8.1 Water Solubility

The water solubility of the organic chemical is utilized in Equation 2.17 as a component of the Henry's Law constant, which is described below. The magnitude of Van der Waal's forces and dipole-dipole interactions determines the solubility of a chemical in water and in organic solvents. The solubility of a chemical will affect

the diffusion and volatilization of a chemical from water into air. The greater the water solubility of a chemical, the greater the propensity for that chemical to exist in the water phase instead of in air which is in equilibrium with it.

2.8.2 Henry's Law

The distribution of a chemical between water and air can be mathematically described through Henry's Law. In other words, the propensity for a chemical to volatilize from an aqueous phase and exist in atmospheric or soil air can be estimated through Henry's Law. Henry's Law states that when a solution becomes very dilute (i.e. mole fraction less than 0.001), the vapour pressure of a chemical should be proportional to its concentration:

$$V_p = K_H C \qquad (2.17)$$

where

V_p = vapour pressure of the chemical

C = concentration of the chemical in water (mg/L)

K_H = Henry's law constant (atm.m^3/mole)

In general, chemicals having K_H values less than 5×10^{-6} atm.m^3/mole encounter resistance to mass transfer primarily in the gas phase; in other words, these chemicals should be present only in negligible amounts in the atmosphere or in soil air. Also, chemicals having K_H values greater than 5×10^{-3} atm.m^3/mole encounter resistance to mass transfer primarily in the aqueous phase; in other words, volatilization and diffusion in soil should dominate. Chemicals possessing K_H values

and $5x10^{-6}$ encounter resistance to mass transfer in both the gas and aqueous phases.

2.8.3 Soil Bulk Density and Porosity

In general, as bulk density increases, porosity decreases. The general overall effect of increasing soil bulk density is to decrease D_{SA} (Guenzi, 1974). The equation developed to estimate the effect of varying soil porosity on the D_{SA} of hexachlorobenzene (Farmer, 1978) can be utilized to derive a general understanding of the variation of bulk density on D_{SA}:

$$D_{SA} = D_A (P_{SA}) \frac{3.33}{P^2} \qquad (2.18)$$

where

D_{SA} = diffusion coefficient of a chemical in soil air (cm^2/day)

D_A = diffusion coefficient of a chemical in air (cm^2/day)

P_{SA} = soil air content (m^3/m^3)

P = soil porosity

2.8.4 Soil Water Content

The soil water content also affects air diffusion. At higher soil moisture content, the cross-sectional area where air diffusion can occur will be relatively smaller. As a result, the air diffusion coefficient must also decrease, which is opposite to water diffusion.

2.9 Theory of Hydrocarbon Leaching

2.9.1 Introduction

A general mathematical model is proposed by Borden and Piwoni (1989) to describe the dissolution and transport of water-soluble and water-plus-surfactant-soluble aromatic components. The model assumes that the equilibrium concentration of individual hydrocarbons in the aqueous phase is proportional to both the compound solubility and the mole fraction in the soil phase. Mass transfer between the oil and water is described, assuming the oil phase consists of two parts: a fast fraction in equilibrium with the aqueous phase and a slow fraction in which mass transfer is limited. A simple procedure is also presented for estimating the number of pore volumes of water required to flush individual hydrocarbon components from the sand.

Diesel and other petroleum products are complex mixture of insoluble and sparingly soluble organic compounds. These compounds have individual physical and chemical characteristics which interact to form three distinct phases during their migration through soil and contact with water: (1) a non-aqueous phase liquid hydrocarbon (NAPL); (2) a dissolved phase; and (3) a vapour phase.

If the pollutant is a hydrocarbon, it retains its basic identity in the subsurface. It may be transported with the water flow or it may be trapped interstitially above and below the water table. Spilled oil is trapped in the sand as separate immobile globules and is not removed by conventional methods of separate phase hydrocarbon recovery. Typically, only a small fraction of spilled hydrocarbon is removed by

conventional methods such as pumping or water flooding. As water flows past trapped oil globules, the more soluble components of oil will exchange with the water and form a plume of dissolved hydrocarbon typically containing components such as tertiary butylalcohol and methyl tertiary butylether.

In a previous study, Borden and Piwoni (1989) demonstrated that dissolution of low concentrations of residual hydrocarbon (less than 0.1% relative saturation) could be modeled using a linear equilibrium relationship. The objective of this work is to examine the dissolution and transport of hydrocarbon in sandy materials containing high levels of residual oil (greater than 10% relative saturation).

2.9.2 Mathematical Modelling Development

In their study, Borden and Piwoni (1989) evaluated two different models of hydrocarbon dissolution: (1) an equilibrium model; and (2) a mass transfer limited model. Both of these models assumed that all of the residual oil was equally available for dissolution by water flow. In their work it was found that effluent hydrocarbon concentrations, during the initial equilibrium and rapid drop-off period, could be represented adequately using an equilibrium model.

A general mathematical model is proposed for simulating the dissolution of hydrocarbons which assumes the non-aqueous phase liquid hydrocarbon (oil) is composed of two fractions: (a) "fast oil" which readily exchanges with the flushing fluid; and (b) "slow oil" which for some currently unknown reason is not readily available for dissolution by the flushing fluid. The model allows for n individual

hydrocarbon components which may be present in the four phases: (1) an aqueous phase; (2) a fast oil phase which is in chemical equilibrium with the aqueous phase; (3) a slow oil phase in which mass transfer between the aqueous and oil phases is relatively slow and can be modeled as a first order reversible reaction; and (4) a sorbed phase which is in equilibrium with the aqueous phase. For brevity, the aqueous, fast oil, slow oil, and sorbed phases will be identified by the superscripts *a*, *of*, *os*, and *s* respectively. Governing equations are developed by writing material balances for each phase and compound. Units of moles, metres and days have been adopted in developing these equations to simplify data analysis and interpretation. All concentrations are written in units of moles per m^3 of pore water. The final governing equations, in one dimension, for the aqueous, fast oil, slow oil, and sediment phases are written as (Borden and Piwoni, 1989)

$$[1+\frac{\Sigma C_i^{of}\gamma_i^a}{S_i\gamma_i^{of}}+K_i^{oc}]\frac{\delta}{\delta t}C_i^a=\frac{\delta}{\delta z}[D\frac{\delta}{\delta z}C_i^a]-\frac{\delta}{\delta z}(VC_i^a)-Km\frac{[C_i^a-S_i\gamma_i^{os}C_i^{os}]}{\Sigma C_i^{os}\gamma_i^a} \quad (2.19)$$

$$\frac{\delta}{\delta t}C_i^{os} = Km\ \frac{[C_i^a - S_i\ \gamma_i^{os}\ C_i^{os}]}{\Sigma C_i^{os}\ \gamma_i^a} \quad (2.20)$$

and

$$\frac{\delta}{\delta t}C_i^{of} = \frac{[\Sigma C_i^{of}\ \gamma_i^a]}{S_i\ \gamma_i^{of}}\frac{\delta}{\delta t}C_i^a \quad (2.21)$$

where

where

C_i^n = concentration of component i in phase n (moles/m^3)

C_i^o = concentration of component i in initial phase (moles/m^3)

D = longitudinal dispersion coefficient (m^3/day) = αV

α = longitudinal dispersivity (m)

V = non reactive transport velocity (m/day)

t = time (day)

z = longitudinal coordinate (m)

S_i = pure component i aqueous solubility (moles/m^3)

K_i^{oc} = aqueous-organic carbon partition coefficient for component i

γ_i^a = activity coefficient of component i in the aqueous phase

γ_i^{of} = activity coefficient of component i in the fast oil phase

γ_i^{os} = activity coefficient of component i in the slow oil phase

γ_i^s = activity coefficient of component i in the sorbed phase

These equations assume that the equilibrium concentrations of the hydrocarbon components can be obtained by equating the activities in the oil and aqueous phase (Stumm and Morgan, 1981)

$$C_i^a \gamma_i^a = S_i \gamma_i^o X_i^o \qquad (2.22)$$

where X^o_i is the mole fraction of compound i in the oil phase. This approach assumes a Raoult's Law definition of ideal conditions. Equilibrium partitioning between the sorbed and aqueous phases is assumed to follow a linear isotherm.

$$C_i^s = K_i^{oc}\ C_i^a \tag{2.23}$$

In cases where all of the oil is in equilibrium with the aqueous phase, a rough estimate of the number of pore volumes required to flush a given hydrocarbon (say diesel fuel) from the subsurface would be very useful. The number of pore volumes (PV) required to flush a given compound from a contaminated sample can be estimated using Equation 2.24 under the following conditions: (1) mass transfer effects are negligible; (2) the activity coefficient ratio (γ_i^o/γ_i^a) is equal to 1.0, and (3) the majority of hydrocarbon is essentially insoluble.

$$PV = 1 + K_i^{oc} + \frac{\Sigma C_i^o}{S_i} \tag{2.24a}$$

If we define total petroleum hydrocarbon (TPH) as $TPH = \Sigma C_i\ MW\ P/\rho b$ where MW is the average gram molecular weight of the non-aqueous phase liquid hydrocarbon, P is the porosity and ρb is the sediment bulk density, equation 2.24a can be rewritten

$$PV = 1 + K_i^{oc} + \frac{(TPH)\ \rho_b\ (MW_i)}{S_i\ P\ MW} \tag{2.24b}$$

where S_i is the aqueous solubility in mg/L and MW_i is the molecular weight of component i.

Table 2.1 - Densities and Viscosities of Selected Fluids

Fluid	Density (gm/ml)			Viscosity (centipoise)		
	0 C	15 C	25 C	0 C	15 C	25 C
Water	1.000	0.998	0.996	1.790	1.140	0.800
Gasoline	0.746	0.729		0.75	0.62	
Diesel Fuel	0.838	0.827		3.90	2.70	
Kerosene	0.842	0.839	0.835	3.40	2.30	2.20
No. 5 Jet Fuel		0.844				
No. 2 Fuel Oil	0.874	0.866	0.840	7.74		4.04
No. 4 Fuel Oil	0.914	0.904	0.898	7.20		22.70
No. 5 Fuel Oil	0.932	0.923	0.917		215.00	122.00
No. 6 Fuel Oil	0.986	0.974	0.964	7.35E+07		3180.00
Lubricating Oil	0.882	0.873		350.00	144.00	
Lubricating Oil, Used	0.883	0.874		359.00	154.00	
Insulating Oil	0.892	0.882		37.80	18.80	
Insulating Oil, Used	0.878	0.867		35.80	18.10	
Norman Crude Oil	0.845	0.832	0.829	8.76	5.05	3.93
Avalon Crude	0.846	0.839	0.834	575.00	11.40	25.60
Alberta Crude	0.850	0.840	0.832	17.60	6.43	4.22

Note: gm/ml = grams per milliliter; C = Celsius.
Source: Modified from Nelson, 1958

Table 2.2 - Ranges of Residual Liquid Hydrocarbon in the Unsaturated Zone

Earth Material	Gasoline			Middle Distillate			Fuel Oil		
	(gal/ft^3)	(l/m^3)	(mg/kg)	(gal/ft^3)	(l/m^3)	(mg/kg)	(gal/ft^3)	(l/m^3)	(mg/kg)
Coarse Gravels	0.02	2.5	950	0.04	5.00	2,200	0.07	10.00	4,800
Coarse Sand	0.06	7.5	2,800	0.1	15.00	6,500	0.22	30.00	15,000
Fine Sand/Silt	0.15	20.00	7,500	0.3	40.00	17,000	0.60	80.00	39,000

Note: gal/ft^3 = gallons per cubic feet; l/m^3 = liters per cubic meters;
mg/kg = milligrams per kilogram
Sourse: Modified from API Proceeding, 1977.

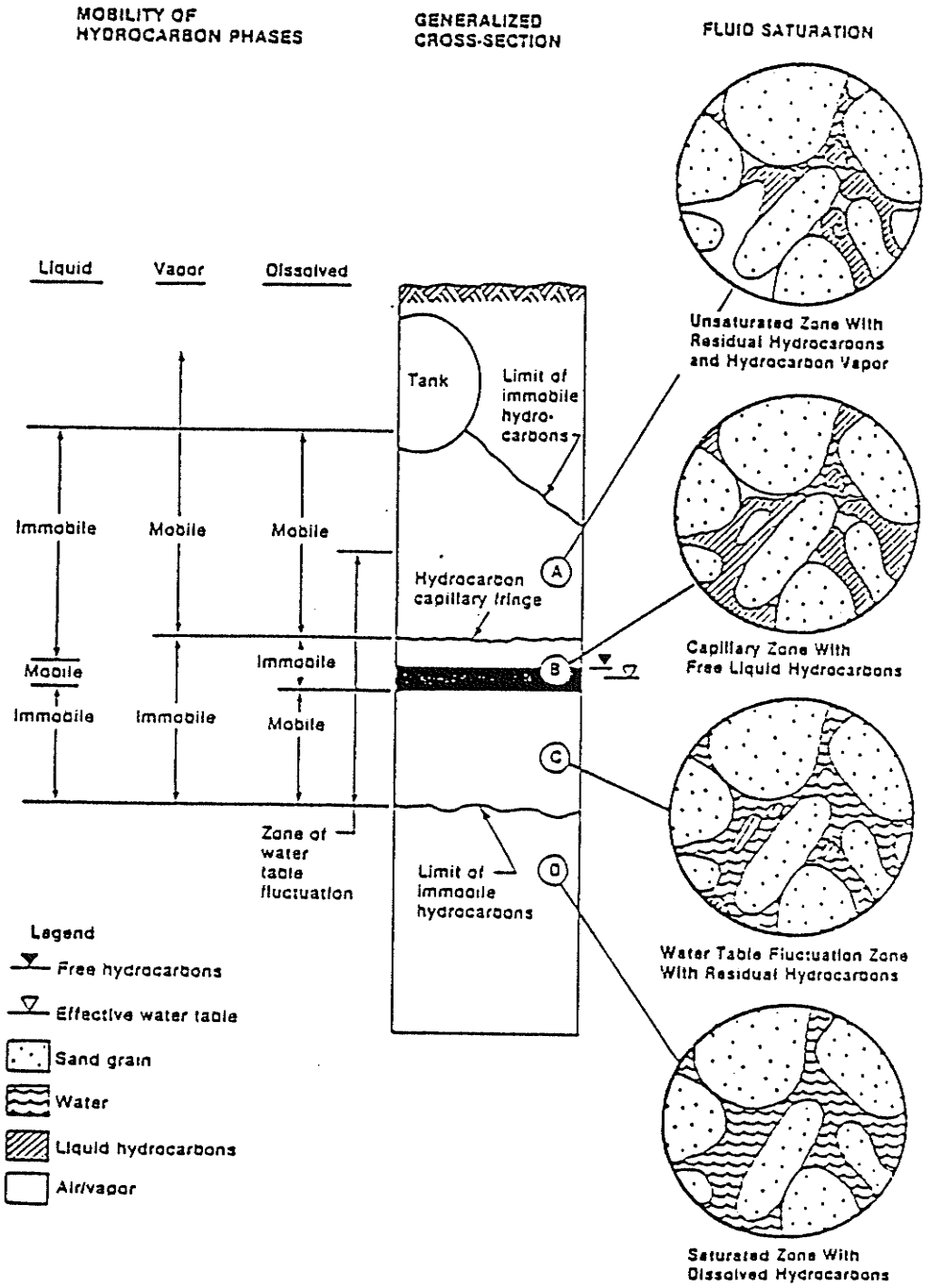


Figure 2.1 Vertical distribution and degree of mobility of hydrocarbon phase in earth materials (NWWA/API, 1987).

CHAPTER 3

MECHANICS OF CHEMICALLY ENHANCING OIL REMOVAL

3.1 Overview

To understand the methods by which the recovery of free-phase oils can be enhanced, one must first understand the physical distribution of fluids in porous media and the forces that lead to that distribution.

3.2 Fluid-Transmitting Properties

Two physical properties of earth materials that most affect fluid movement are porosity and permeability.

3.2.1 Porosity

Porosity, or total porosity, is the ratio of the volume of void space in the earth material to the total volume of material. Porosity is expressed as a percentage and is dependent upon factors such as grain size and shape, the manner in which the earth materials are packed together, and sorting. The porosity of unconsolidated sediments comprised of well-rounded particles of equal size will be greater than the porosity of sediments containing either angular or well-rounded particles of variable sizes. In the latter case the small particles can fill in void spaces between the larger particles. The wider the range of grain size, the lower the porosity. (Bears and Verruijt, 1992)

Porosity is also affected by the shape of grains in the earth material. Spherically shaped grains pack together more tightly and exhibit less porosity than particles of other shapes, such as plates or rods. Clay particles, for example, are of plate or rod shape and do not tend to pack closely together. Thus general ranges of porosity that can be expected for typical sediments are listed as follows:

Well-sorted sand or gravels	25 - 40 percent
Sand and gravel, mixed	20 - 35 percent
Glacial till	10 - 20 percent
Clay	33 - 60 percent

These ranges presuppose that all the void spaces of material are interconnected, which is usually not the case.

Effective porosity is the ratio of the volume of interconnected voids through which fluid can flow to the total volume of material. Although clays and some organic soils can have large porosities, they generally have smaller intergranular voids and smaller effective porosities compared with coarser-grained materials. (Bears and Verruijt, 1992)

Fractures can develop in finer-grained clayey soils and sediments because of shrinkage caused by drying. This phenomenon is known as secondary porosity. Secondary porosity can also develop from animal burrows and root spreading.

3.2.2 Permeability

The permeability of a geological material is a measure of its ability to transmit fluid. Hydraulic conductivity is also a measure of the ability of a geological material to transmit fluid but is dependent on the type of fluid passing through the material (Freeze and Cherry, 1979). For example, the hydraulic conductivity of soil to water is greater than the conductivity of more viscous fluids such as crude oil or diesel fuel. Although the two terms (permeability and hydraulic conductivity) have in the past been used interchangeably, the term permeability is technically more fundamental, because it relates to the porous medium regardless of the characteristics of the fluid.

Table 3.1 (Freeze and Cherry, 1979) shows that the range of hydraulic conductivity for various earth materials to water is very broad. Hydraulic conductivities for fractured rock materials are generally less than for materials having intergranular voids, but the possible overlap of values is significant.

3.3 Relative Permeability and Residual Saturation

Whenever a porous media is saturated with more than one fluid (and the fluids are immiscible), the medium will demonstrate an ability to pass each fluid separately through its pores. According to Marsily, 1986, the effective permeability, k_i, which is a measure of the porous medium's ability to conduct a particular fluid, i, will depend on the volumetric saturation, S_i, of fluid i. The volumetric saturation, S_i, is, in turn, a measure of the proportion of void volume that is occupied by the particular fluid. By definition

$$S_i = \frac{\textit{part of porosity occupied by the fluid } i}{\textit{total porosity}} \qquad (3.1)$$

The greater the value of S_i, the greater the value of k_i linked to the fluid i.

On the other hand, there is a certain value of S_i below which the fluid i is not continuous from one pore to the next. In this range, the value of k_i is zero. It should be noted, therfore, that an effective permeability of zero does not imply that there is none of the particular fluid left in the soil. There could, in fact, be a significant amount of the fluid remaining, significant at least from an environmental clean-up point of view. The amount remaining will depend on such things as the affinity of the porous medium for each phase (the wetting characteristics) and the geometry of the pores (Brown, 1984b, Hunt et al., 1988b). The volumetric saturation at which the particular fluid first becomes discontinuous is sometimes referred to as the "residual saturation".

In the case of oil and water, the effective permeabilities of the two fluids also depend upon whether the mineral grains of soil are oil-wet or water-wet. The most common scenario by which residual oils occur in soils is when a damp or water-saturated soil is inundated with oil. With this scenario, the grains are water-wet. In a less common scenario, dry soil is first inundated with oil and then with water - the water, perhaps, being the result of water flooding in an attempt to displace the oil. In this instance, the soil would be oil-wet.

Figure 3.1 illustrates typical effective permeability curves for oil and water

through sand. In this figure, the relative permeability for each fluid is given depending upon its volumetric saturation. The relative permeability, k_{ri}, for fluid i is defined as

$$k_{ri} = \frac{k_i}{k} \tag{3.2}$$

where k is the intrinsic permeability of the porous medium independent of the fluid. It should be noted that the sum of the two relative permeabilities is often less than unity for the soils which are completely saturated with liquid (in this case, oil and water). It is said (Marsily, 1986) that the two fluids interfere with one another. Relative permeabilities which add up to greater than one have been measured for three immiscible fluids - oil, water, and gas. This may be the case in the ground which is only partially saturated with the liquids oil and water, and the remainder of the pore space contains air.

3.4 Displacement Efficiency

Oil typically has a higher viscosity than water. The viscosity and the effective permeability of each fluid will dictate the ease with which each fluid will flow through the porous medium (Smith, 1966). This relationship is called mobility (τ) and is defined as:

$$\tau = \frac{k_i}{\mu} \tag{3.3}$$

where

k_i = effective fluid permeability

μ = fluid viscosity

The mobility ratio, as defined by Smith (1966), is:

$$\tau = \frac{\textit{mobility of displacing fluid}}{\textit{mobility of displaced fluid}} \tag{3.4}$$

$$\mu = \frac{k_{wro}\ \mu_o}{k_{orw}\ \mu_w} \tag{3.5}$$

where

k_{wro} = effective permeability of water at the residual oil concentration

k_{orw} = effective permeability of oil at the residual water concentration

μ_o = viscosity of oil

μ_w = viscosity of water

A mobility ratio of less than 1 is considered favourable. In this case, the displacement efficiency is usually good, and the displacing fluid effectively moves the displaced fluid through the pore throats in a piston-like fashion. When the mobility

ratio is greater than 1, the displacement efficiency is generally poor. In this case, the displacing fluid bypasses the fluid targeted for displacement.

3.5 Modification of Pore-Level Physical Forces

In environmental applications, the final oil saturation in the ground after waterflooding will be dictated by the residual oil saturation and by the sweep efficiency. Since the residual oil after waterflooding may provide a source of contamination to groundwater, it is often desirable to further reduce the oil saturation to levels below the residual oil saturation. This reduction can be accomplished by adding a variety of chemicals to the displacing water. Surfactant, alkalis, and polymers are chemicals commonly used in the petroleum industry (Clark et al., 1988; Nelson, 1958) to modify the pore-level physical forces that inhibit oil removal.

3.5.1 Surfactant

Surfactant, or surface active agents, are amphiphitic molecules with a hydrophobic (hydrocarbon or fluorocarbon) chain moiety and a hydrophillic (polar or ionic) head group (Figure 3.2). The amphiphilic nature of a surfactant molecule enables it to exist in one or more forms in a biphasic or multiphase system: dissolved in water as a monomer, adsorbed at an interface, or incorporated with other surfactant as part of a micelle. (O'Connell, 1977; Edward et al., 1991)

Micelles Figure 3.3,are colloidal aggregates formed from surfactant monomers

at an aqueous surfactant concentration called the Critical Micelle Concentration (CMC). Surfactant chemistry, temperature, ionic strength, and the presence and types of organic additives determine the CMC (Shah, 1981; Rosen, 1989). At the CMC, abrupt changes in solution properties such as surfactant tension occur, thus increasing the solubility of hydrophobic organic in water.

The unique properties of surfactants give them potential in remedial systems for petroleum contaminated soils. Surfactant may partition between or adsorb to the interfaces of an oil-water-soil system and reduce the interfacial tension. The polar head group interacts strongly with the water phase, and the nonpolar hydrocarbon chain portion interacts very weakly with water molecules, but partitions into hydrophobic organic compounds (HOCs). The HOCs are thus desorbed from the soil, solubilized and/or mobilized, allowing the implementation of pump-and-treat remediation after soil exposure to a surfactant solution (Vigin and Rubin, 1989).

Surfactants are classified according to the nature of the hydrophillic head group (Shah, 1977; Rosan, 1978). Anionic surfactants have a negatively charged head group; cationic surfactants have a positively charged head group. If both positive and negative charges are present in the surface-active head group, the surfactant is known as Zwitterionic. When there is no apparent ionic charge in the head group, the surfactant is nonionic (Shah, 1981).

There are over 12,000 surfactants available. The selection of the most effective surfactant for a particular purpose is a function of the physical-chemical characteristics of the surfactant, the compounds of interest, and the subsurface

environment of the multiphase system. For remediation of petroleum contaminated sites, therefore, the selection of the most effective surfactant(s) is highly site specific. Vigon and Rubin (1989) have outlined guidelines for surfactant selection and dosage optimization for use in remediating contaminated sites. Unsuitable surfactant can cause soil dispersion and pore clogging.

In all cases, surfactant reduces the interfacial tension between the oil and the aqueous phase. This reduction mobilizes the contaminant from the soil surface by reducing the physical forces holding the contaminant to the surface and by altering the shape of the globules trapped in the pore-throat restrictions, allowing the globules to move.

3.5.2 Alkalis

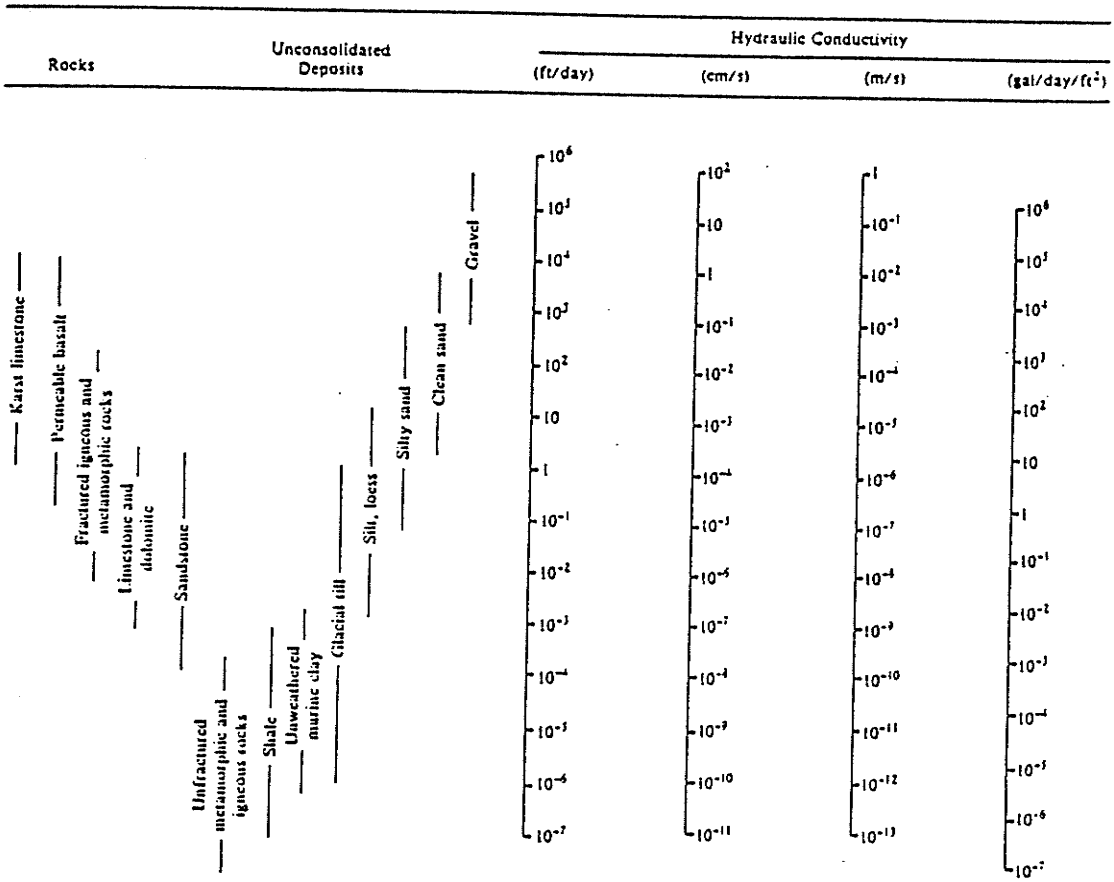
Alkalis can reduce the interfacial tension between the oil phase and the aqueous phase by reacting with amenable components of the oil phase to form a surfactant. In addition, an alkaline agent will neutralize rock and clay surfaces and reduce the amount of exchangeable calcium and magnesium ions present on these surfaces. Both of these functions will reduce surfactant and polymer adsorption into the soil matrix. The alteration of both the soil surface and the contaminant components can change the soil's affinity for oil. In general, alkalis make the matrix surface more water wet. Alkalis also act as a salinity agent to optimize the interaction between the oil and the surfactant added to the soil-washing solution (Clark et al., 1988).

3.5.3 Polymers

The addition of a polymer will increase the viscosity of the soil-washing fluids, providing mobility control to reduce the fingering of the displacing fluid past the fluid to be displaced and helping to ensure that the contaminated area is efficiently contacted by the soil-washing solution. The addition of a polymer to the soil-washing solution is especially important when an interfacial tension-reducing agent is added to reduce the residual oil saturation. This importance becomes apparent when the mobility ratio equation is examined.

If an interfacial tension-reducing agent is added to the water, the effective permeability to water will increase. (See Figure 3.1 and extrapolate the water relative permeability curve to a lower residual oil saturation). The addition of the interfacial tension-reducing agent will have a minimal effect on the soil-washing fluid viscosity, but the mobility ratio will increase due to the change of the effective water permeability. This increased mobility ratio will result in an increase of soil-washing fluid fingering and in poorer sweep efficiency. Looking at the mobility ratio equation, the way to prevent this is to increase the viscosity of the water phase (Van Dam, 1967; Testa, 1991)

Table 3.1 Range of values of hydraulic conductivity.



Note: ft/day = feet per day; cm/s = centimeters per second; m/s = meters per second; gal/day/ft² = gallons per day per square foot.
Source: Modified from Freeze and Cherry, 1979.

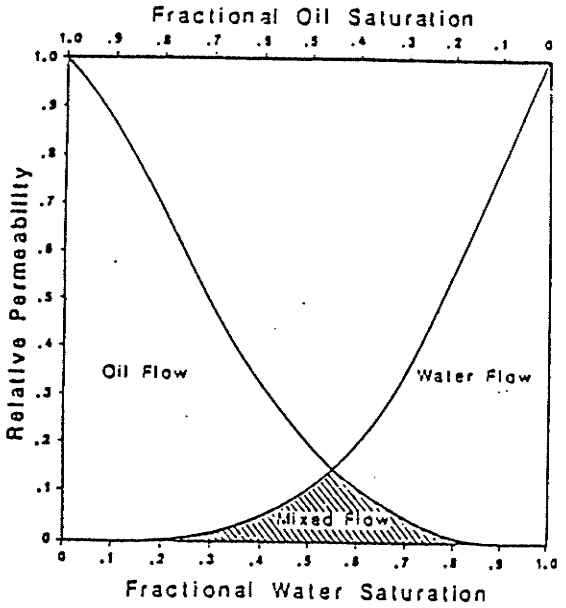


Figure 3.1a Relative permeability of two immiscible fluids in water-wet sand (Testa et al., 1991).

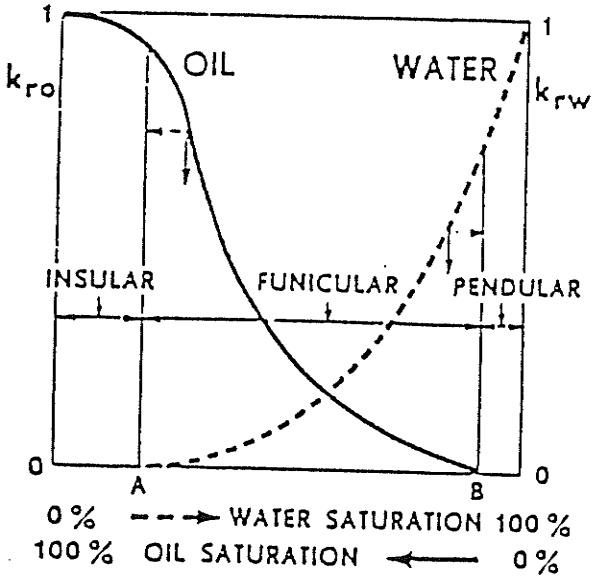


Figure 3.1b Relative permeability of two immiscible fluids in oil-wet sand (Van Dam, 1968).

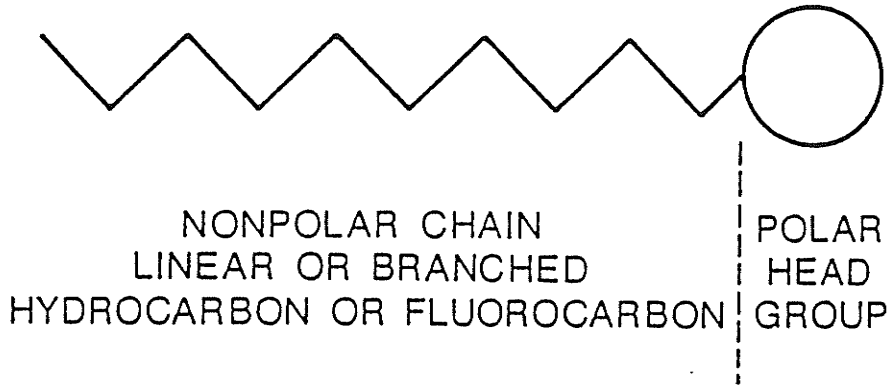


Figure 3.2 Basic structure of surfactant molecule (Rosan, 1978).

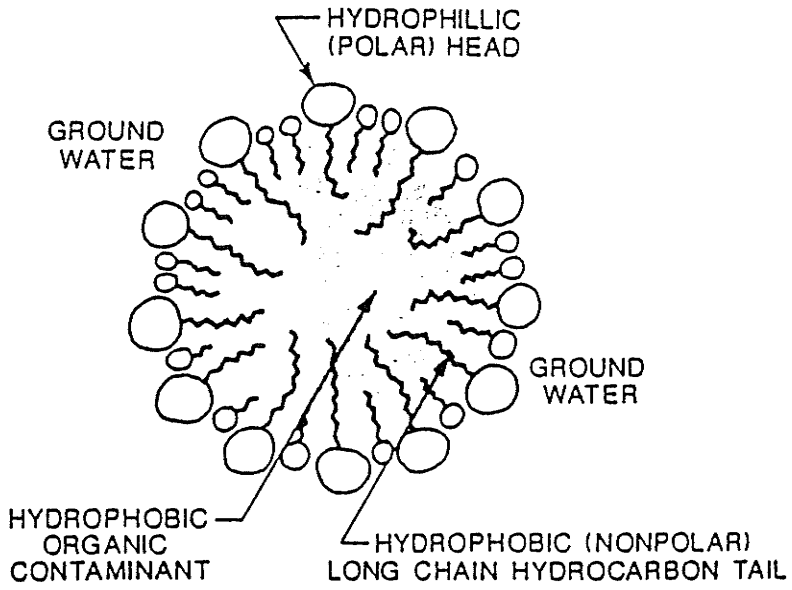


Figure 3.3 Cross section of NAPL -in-water micelle. Polar head groups react with the water phase. The hydrophobic chain tail portion interact with the NAPL (Rosan, 1978).

CHAPTER 4

TEST EQUIPMENT AND PROCEDURE

4.1 Introduction

This chapter presents an experimental program undertaken at the University of Manitoba to examine the behaviour of chemically-enhanced soil washing as an in situ remediation method . Test equipment, test setup, instrumentation, specimen configurations, and the various parameters considered in this program are presented in detail.

4.2 Test Equipment

This section examines the equipment that was designed to test the hydraulic conductivity, and the contaminant removal efficiency at various temperature and grain size distributions. The procedure followed for each test is also reviewed.

4.2.1 Apparatus Compliance Testing

The equipment used in the testing program went through several developmental stages. The main problem which had to be considered was the development of equipment with resistance to both oil and water. Non-corrosive plastic materials were used wherever possible. Teflon lining was used where abrasion was considered to be a problem. Refer to Figure 4.1, for the layout of the testing system.

4.2.1.1 *Permeameter*

The permeameter (Figure 4.2) was the heart of the soil washing testing apparatus. The apparatus was based on an ASTM standard and was a transparent acrylic plastic cylinder of 10 cm diameter. The diameter of 10 cm is about 100 times the maximum particle size of the sands which were tested.

The permeameter was fitted with: (1) a porous reinforced screen at the bottom, with a permeability greater than that of the soil specimen, but with an opening sufficiently small (not larger than D_{10}) to prevent the movement of the soil particles; (2) manometer outlets for measuring the loss of head, h, over a length, l, equivalent to at least the diameter of the cylinder, and (3) a porous reinforced screen at the top. The volume of soil, and the density remained relatively constant during the saturation of the specimen and soil washing.

The constant head tank, as shown in Figure 4.2, was used to supply the fluid to the permeameters. The tank was fitted with suitable control valves to maintain the flow of the fluid. A vacuum was used to remove most of the air inside the soil voids, before flooding the cell with water.

Each permeameter, of which four were used in the test program, was connected to a temperature bath, and a thermometer was used to monitor the sample temperature. The sand specimen was placed inside the permeameter and the remaining space was filled with water. The manometer outlets, as shown in Figure 4.2, monitor the loss in head during flow.

4.2.1.2 *Total Organic Carbon Analyzer*

Quantifying the total organic carbon (TOC) content of soil is essential for understanding the contaminant fate and transport, and the effective treatment methodology.

The DC-80, Figure 4.3, is a modular TOC analysis system for laboratory use. Depending upon configuration, TOC can be measured by either ultra-violet promoted persulfate oxidation or high-temperature combustion, followed by infrared detection. External sparging is routinely used to remove inorganic carbon.

The operating principle can be understood from the following description and flow diagram, Figure 4.4. The acidified persulfate reagent is continuously pumped from an external reservoir to the injection port and then into the bottom of the UV reactor. The reactor is of constant volume design. The excess liquid is pumped to waste from the drain port.

The reactor liquid is continuously sparged and this sparge/carrier gas flows out at the top of the reactor to the non-dispersive infra-red detector (NDIR).

When a sample containing combined carbon is injected, it is carried into the reactor by the reagent flow. The oxidation of organics occurs rapidly, and the resultant carbon dioxide is sparged from the liquid and carried to the NDIR. The NDIR produces an electrical output (peak) which is integrated and scaled by the number processor, and then displayed and printed.

After a suitable standard reagent (400 mg/l of total organic carbon) is injected and the calibrate button is pushed, the display and printer will read directly in

concentration units.

4.2.1.3 *Grain size Analysis*

The grain size analysis is an attempt to determine the relative proportions of the different grain sizes that make up a given soil mass.

There are two types of grain size analyses: mechanical (or sieve) analysis and hydrometer analysis. The mechanical analysis was used in this testing program, to determine the size and the relative distribution for those particles greater than 0.04 mm.

The mechanical (sieve) analysis is accomplished by stacking the sieves, one on top of the other, pouring a known weight of soil into the top sieve on the stack, and shaking the sieves in a certain manner to allow the soil to fall down through the stack. A 20 minute shaking period was used using the machine shown in Figure 4.5.

After weighing the amount retained on each sieve, the percent passing each sieve is calculated and plotted. An indication of the spread or range of grain size is given by the coefficient of uniformity C_u, defined as

$$C_u = D_{60}/D_{10} \qquad (4.1)$$

where

D_{10} = grain diameter at 10% passing

D_{60} = grain diameter at 60% passing

Also, the coefficient of concavity C_c, which is the measure of the shape of the curve between the D_{60} and D_{10} grain sizes can be determined; it is defined as

$$C_c = (D_{30})^2/D_{10}\ D_{60} \quad (4.2)$$

where

D_{30} = grain diameter at 30% passing

The sand which was used for this project fell in these ranges mesh #60 (0.42 mm), mesh #80 (0.24 mm), and mesh #100 (0.17 mm).

4.2.1.4 *Temperature Control*

Three levels of temperature, 4, 22, and 50°C were used in this testing program. A different method of maintaining the required temperature was used for each of the three temperatures: 1) A heating rod was put inside the main reservoir to raise the temperature to 50°C. 2) A tubing coil was put inside the reservoir and the coil was connected to a constant temperature Haake K Refrigerator Bath with a Haake F3 controller to keep the temperature at 4°C. 3) The whole test system, excluding the water supply, was placed inside an environmentally controlled chamber at 22°C. In all cases,temperature variations were kept to within ±1.0°C.

4.3 Index Testing

4.3.1 Relative Density, Void Ratio & Fluid Saturation

The relationships between the basic soil properties of density, moisture content, degree of saturation, relative density, void ratio, and porosity are termed phase relationships (Figure 4.6). The basic equations are:

Dry bulk density, ρ_b:

$$\rho_b = \frac{W_T}{V_T} \quad (\frac{Kg}{m^3}) \tag{4.3}$$

Relative density, G_s:

$$G_s = \frac{W_s}{V_s \, \rho_w} \quad (dimensionless) \tag{4.4}$$

Void ratio, e:

$$e = \frac{V_v}{V_s} \quad (decimal) \tag{4.5}$$

Porosity, P:

$$P = \frac{V_v}{V_T} * 100\% \quad (percent) \tag{4.6}$$

The terms in Equations (3) through (9) are defined as:

$W_T = W_s + W_w$ = total mass of the soil (kg)

W_w = mass of soil water (kg)

W_s = mass of soil solids (kg)

$V_T = V_v + V_s$ = total volume of soil sample (m^3)

V_s = volume of solids (that part of the total volume occupied by the solid soil particles)(m^3)

$V_v = V_w + V_a$ = volume of voids (that part of the total volume not occupied by the soil solids) (m^3)

ρ_w = density of water (usually assumed to be 1000 kg/m^3, but changes with respect to temperature)

V_w = volume occupied by the water in the soil sample (m^3)

V_a = that part of the total volume occupied by air (m^3)

It is sometimes required to compare the density of the aggregate soil solids to the density of the fluid used. This comparison is in the form of a ratio and is termed the relative density, see equation 4.4 above.

By definition, relative density, G_s, is the ratio of the true density, ρ_s, of some material to that of some reference material. By convention, distilled water at 4°C is selected as the reference material (ρ_w). Thus,

$$G_s = \frac{\rho_s}{\rho_w(at\ 4^oC)} \tag{4.7}$$

and

$$\rho_s = \frac{W_s}{V_s} \tag{4.8}$$

4.4 Measurement of Hydraulic Conductivity

4.4.1 Background

Analyses of water flow in saturated locus grained soils such as those used in this program are usually based on Darcy's Law which, in turn, is based on the experimental observation of a linear relationship between the rate of flow and the driving forces. The law has been written in many forms depending mainly on the discipline of the user and the date of usage. The form most commonly encountered is

$$q = - K i \tag{4.9}$$

where q is the flux [length^3/length^2 . time ($L^3/L^2.T$)]; i is the gradient of hydraulic potential (dimensionless); and K is the constant of proportionality (L/T), which is termed the hydraulic conductivity in most disciplines, but is often termed the permeability by civil engineers.

The K of Equation 4.9 is dependent on the properties of both the fluid and the porous media. An alternative form of Darcy's Law is

$$q = - k\frac{\gamma_w}{\mu} i \tag{4.10}$$

where γ_w [units of force/length^3 = F/L^3] and μ [unite of force . time/length^2 = $F.T/L^2$] are the unit weight and viscosity of the fluid, respectively, and k is the

constant of proportionality (L^2). In most disciplines k is termed the coefficient of permeability but sometimes it is termed intrinsic permeability (de Wiest, 1969). A third form of Darcy's Law is

$$q = - \frac{k}{\mu} \frac{dp}{dx} \qquad (4.11)$$

where q is the flux (cubic centimetres per square centimetres per second), μ is viscosity (centipoise), p is pressure (atmospheres), x is flow distance (centimetres), and k is the permeability in units of "darcys" (Bear, 1979).

Because of its simplicity and its general use in soil mechanics, Equation 4.9 will be used. The constant K will be called the hydraulic conductivity.

4.5 Pore Volume Measurement

As stated earlier soils can be either two-phase or three phase composition. In a completely dry soil and a fully saturated soil there are just two phases. The dry soil is composed of solid soil particles and pore air, while the saturated soil is composed of solid soil particles and pore water. Pore volume can be defined as the total volume of the pore space (volume of void). The pore volume of soil was determined by compacting an oven-dry sample in layers in a cylindrical mould, each layer being compacted by means of a vibrating hammer for a period of, say, 1.5 minute. The mass and volume of the compacted sand are measured. The pore volume, *PV*, is given by

$$PV = V_T - \frac{W_s}{G_s \rho_w} \qquad (4.12)$$

where

V_T = bulk volume of the sand

W_s = mass of the sand

G_s = relative density of the soil particles

ρ_w = density of water

To arrive at the number of pore volumes of water, PV, that have passed through the sample at time, t, divide the quantity of flow through the sample (to the particular time t), Q_t, by the volume of void, V_v.

Calculation example for the number of pore volumes;

For sample #60(W+D) 50°C

$V_T = 0.00125\ m^3$ Diam. = 10.0 cm

$W_s = 1.99$ Kg Area = 78.5 cm^2

$\rho_w = 1000\ Kg/m^3$ Hight = 16.0 cm

$G_s = 2.68$

Hence,

$$PV = 0.00125 - \frac{1.99}{2.68 * 1000}$$

$$PV = 0.0005\ m^3 = 500ml$$

which represents a porosity, P, of

$$\frac{0.0005}{0.00125} * 100 = 40\%$$

at t_1 = 1min Flow Volume = Q_1 = 0.124 L

PV = flow Volume/V_v = 0.124/0.5 = 0.25

at t_2 = 180 min Flow Volume = Q_2 = 22 L

PV = Flow Volume/V_v = 22/0.5 = 44

4.6 Cumulative Removal Efficiency

The change in the amount of petroleum in the soil can be detected by the changes in the organic carbon measurements, as well as by other methods. The organic carbon test by itself is not definitive in many clayey or silty soils, because the range of contamination is often within the natural variability of the organic carbon content of these soils. In sandy soils, however, organic carbon can be a good indicator of the amount of petroleum contamination. One reason for choosing the organic carbon analysis is that it is often less than half the cost of direct chemical tests for petroleum hydrocarbons, and because it is an indicator of the partitioning coefficient of the soil, i.e.,the ease with which the petroleum is retained or released by the soil.

Total petroleum hydrocarbon is commonly determined by several test methods. The most common analytical methods in use are Standard Method #503, and EPA-SW-846 methods 9071 and 418.1. These methods are all of comparable sensitivity and reliability.

Method 418.1 is more commonly used to detect the presence of the heavier fraction of diesel oils (see Section 4.2.1.2for details on the TOC DC-80 machine that

was used for measuring the organic carbon).

The LNAPL cumulative removal efficiency was calculated as follows:

$$CRE = \frac{Total\ volume\ of\ LNAPL\ recovered}{Initial\ volume\ of\ LNAPL\ within\ the\ soil} * 100\% \qquad (4.13)$$

Calculation example for CRE:

For sample #60(W+D) 50°C, the effluent from 0 to 1 minute was collected, then mixed thoroughly and was tested for TOC. (all samples were diluted 1000 times)

$TOC_{eff(0-1)}$ = 73.88 * 1000 = 73880 mg/L = 73.88 g/L

Influent TOC (W+D) = 18 * 1000 = 18000 mg/L = 18.0 g/L

Effluent collected = 0.12 L

Gross TOC removed to 1 minute = 73.88 g/L * 0.12 L = 8.86 g.

Net organic carbon removal = 8.86 g - (18 g/L * 0.12 L) = 6.7 g.

Initial TOC added to the specimen = 77 g (which corresponds to 119 g of diesel added to 2 kg of sand)

CRE = (6.93 g / 77 g) * 100 = 8.7 ≈ 9%

Subsequently, the effluent from 1 to 180 minute was collected, then mixed thoroughly for TOC testing.

$TOC_{eff(1-180)}$ = 20.37 *1000 = 20370 mg/L = 20.37 g/L

Effluent collected = 22 L

Gross TOC removed to 180 minutes = 20.37 g/L x 22 L = 448.14 g.

Net organic carbon removal = 448.14 g - (18 g/L x 22 L) = 52.14 g.

CRE = (6.7 g + 52.14 g / 77 g) x 100 = 76.41 %

4.7 Test Procedure

Laboratory-scale column experiments were designed to evaluate the mobilization and recovery of NAPLs by soil washing. An initial phase of the experimental approach included soil preparation and packing, and evaluation of the soil properties.

In the present work, the selected soils were characterized by their grain size distribution. The tested soil types were three soils of uniform grain size in which several grain sizes were mechanically sieved and then recombined to obtain the required grain size distributions see section 5.2.3.

The soil was injected with a constant amount of diesel fuel (60 g/kg of sand) which represents an average concentration of contaminant. The fuel oil and soil were mixed mechanically to ensure the contaminant distribution was homogeneous.

Soil washing experiments were conducted in an instrumented one dimensional soil column (permeameter cell). Four permeameter cells were used; a pair of them were connected to one column reservoir, as illustrated in Figure 4.1. The soil column was 20.5 cm long and 10 cm in diameter and was packed uniformly with a soil of the selected grain-size distribution. The samples were packed in the acrylic plastic cylinder according to ASTM -D558 standard procedures (American Society for Testing and Materials, 1986). The soils were carefully placed into the cylinder to avoid segregation, density variation, or channelling within the soil column. At both ends of the column, a porous reinforced screen held the soil in place. The screen was sized to serve as filter and to promote uniform axial flow conditions. A

thermocouple was inserted into the column to measure the column centre line temperature. The thermocouple was connected to an automatic signal scanner, and the temperature readings were displayed on a digital thermometer. Air-free water and/or surfactant was piped from the main reservoir to the column reservoir, which maintains a constant head. Then a vacuum pump was connected to the permeameter cell for six hours to remove the air from the sample. It is expected that most of the volatile LNAPL would be removed by this process. However, this procedure likely had little or no effect on the less volatile liquid phase of the TOC. After removing the air from the sample, the vacuum valve, V_2, was shut. Valve V_3 was opened and water flooded the permeameter cell, from the bottom upwards. Generally, water rose to about mid-hight of headspace A. V_3 was closed. Valves V_1 and V_4 were opened next. Water then flowed from Reservoir A into the headspace and out through valve V_4, completely saturating the system.

Valve V_4 was closed, and Reservoir B was lowered to the required level which would create a hydraulic gradient $i=0.75$ or 4.0, as required.

At time zero, valve V_3 was opened to start the flow through the soil. At time equal 1 minute, the overflow from Reservoir B was diverted from the graduated cylinder to a 10 ml flask. Other 10 ml specimens were collected at intervals of three hours.

The quantity of water which was collected between sampling intervals was used to calculate the permeability and the number of pore volumes which passed through the system.

Since no automated recording system was available to measure the flow, fellow graduate students and friends were pressed in service to enable readings and samples to be taken at the three hours intervals, for periods as long as three days.

The coefficient of permeability was measured using the constant-head permeameter method (ASTM, 1984). Two hydraulic gradients were imposed i.e. 0.75 and 4. It was realized that i=4 is not realistic in the field. However, a high gradient such as i=4 might be employed in the lab to shorten the time of testing. In fact, one day tests at i=4 caused about twice the PV to pass through the sample as compared to i=0.75 in three days. A direct method was used to measure the porosity. The volume of the void space (V_v) was determined by compacting an oven- dry sample in layers in a cylindrical mould, each layer being compacted by means of a vibrating hammer for a period of 1.5 minute. The bulk volume (V_b) inside the column was calculated from measurements of the cross-sectional area and length of the soil column. The porosity was then determined simply by dividing the volume of voids by the bulk volume of the sample. The pore volume was calculated, as explained earlier in section 4.5 equation 4.13, by subtracting the volume of the soil particles from the bulk volume of the sand. The mass of the sand divided by the relative density of the soil particles times the density of water gave the volume of the soil particles.

The independent variables involved in the experiment, summarized in Figure 4.7, were as follows: 1) The experiment was conducted with one LNAPL (diesel fuel), and one soil of three different mean grain size, D_{50}, (0.42, 0.24, and 0.17 mm).

2) Three different temperatures (4, 22, and 50°C), and two hydraulic gradients (0.75 and 4). 3) The tests were run for 24 and 72 hours. The water flow rate was determined from the amount of liquid collected in the graduated cylinder in a given amount of time, and the total organic carbon loss was calculated based on the TOC results from the 10 ml samples.

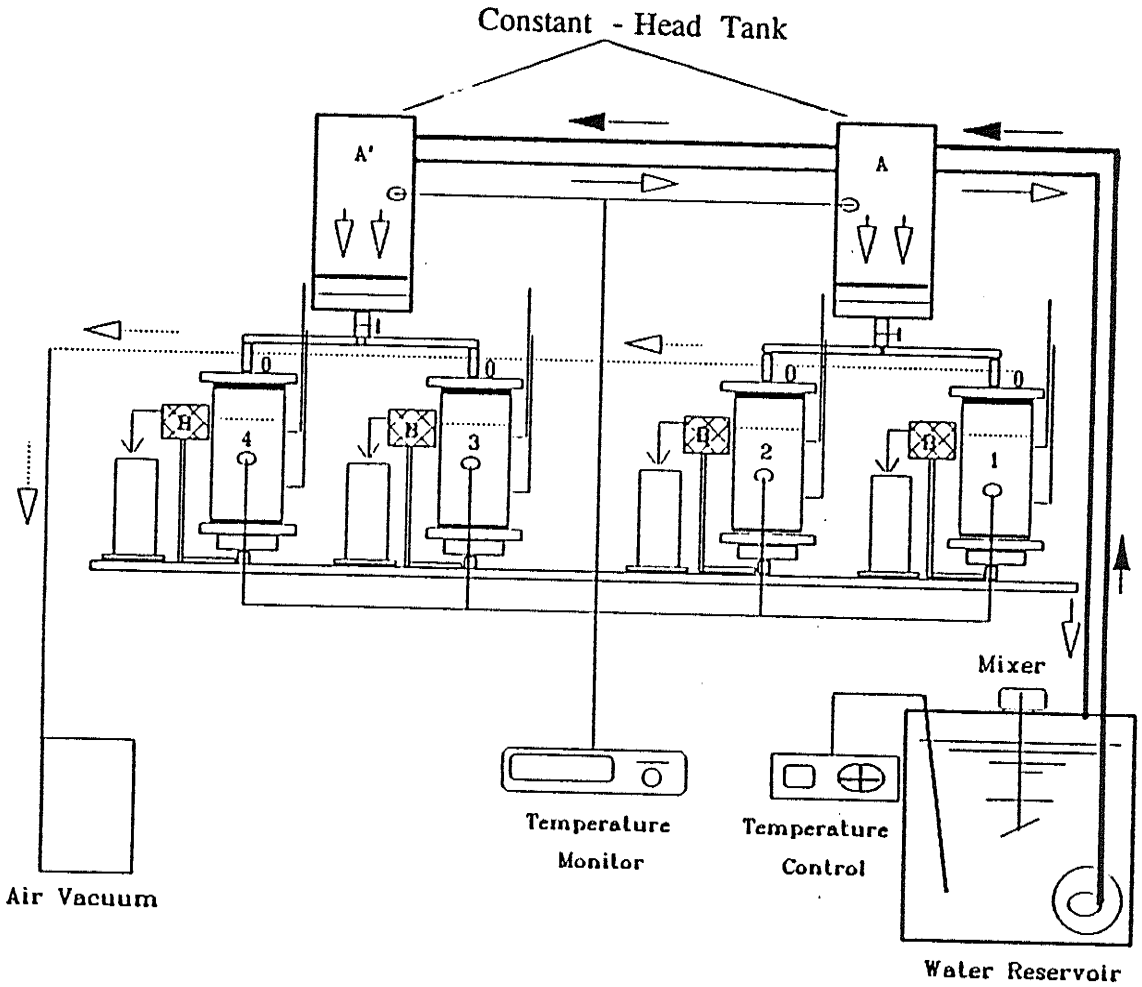


Figure 4.1 Layout of the testing system.

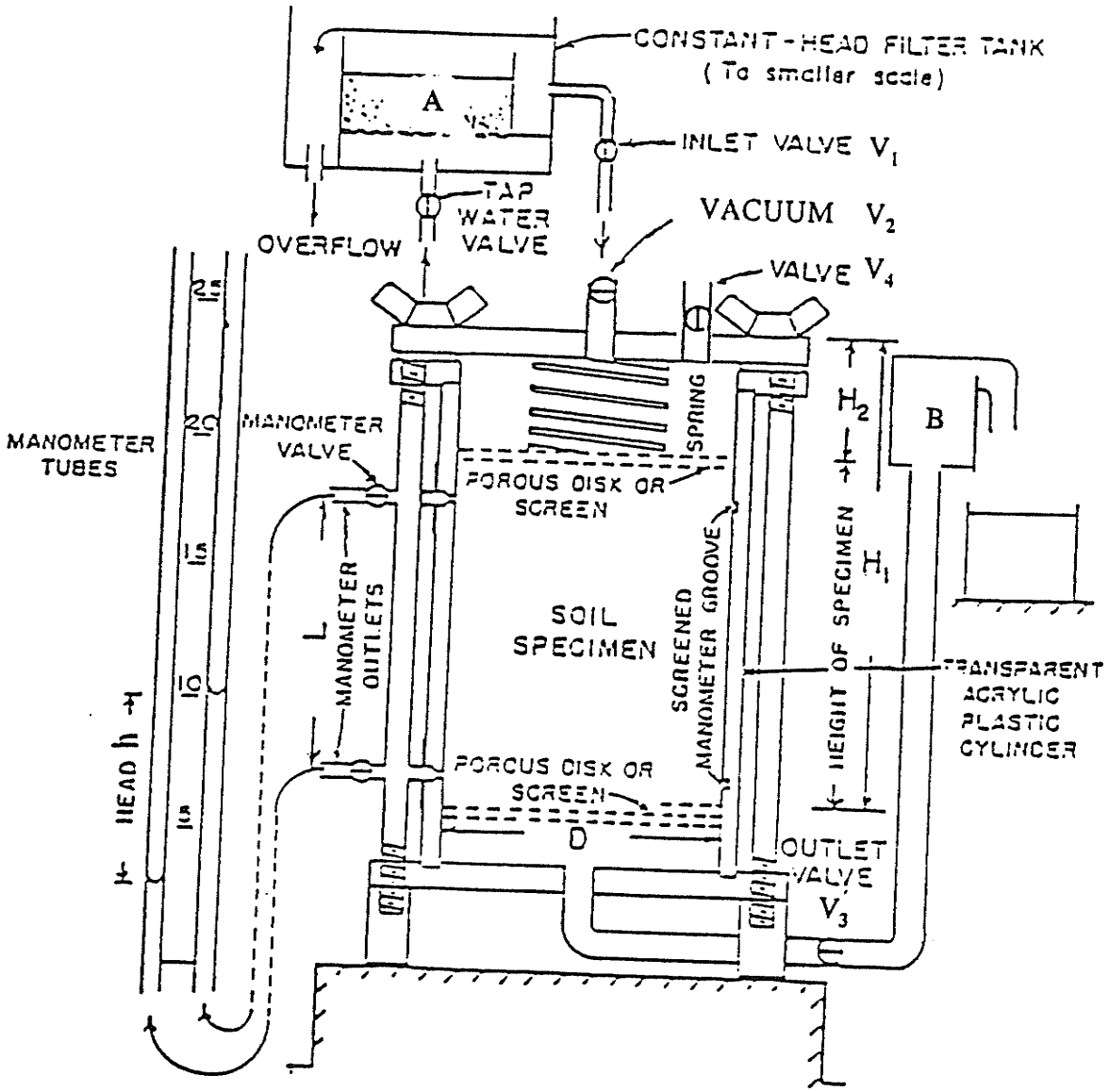


Figure 4.2 Constant-Head Permeameter.

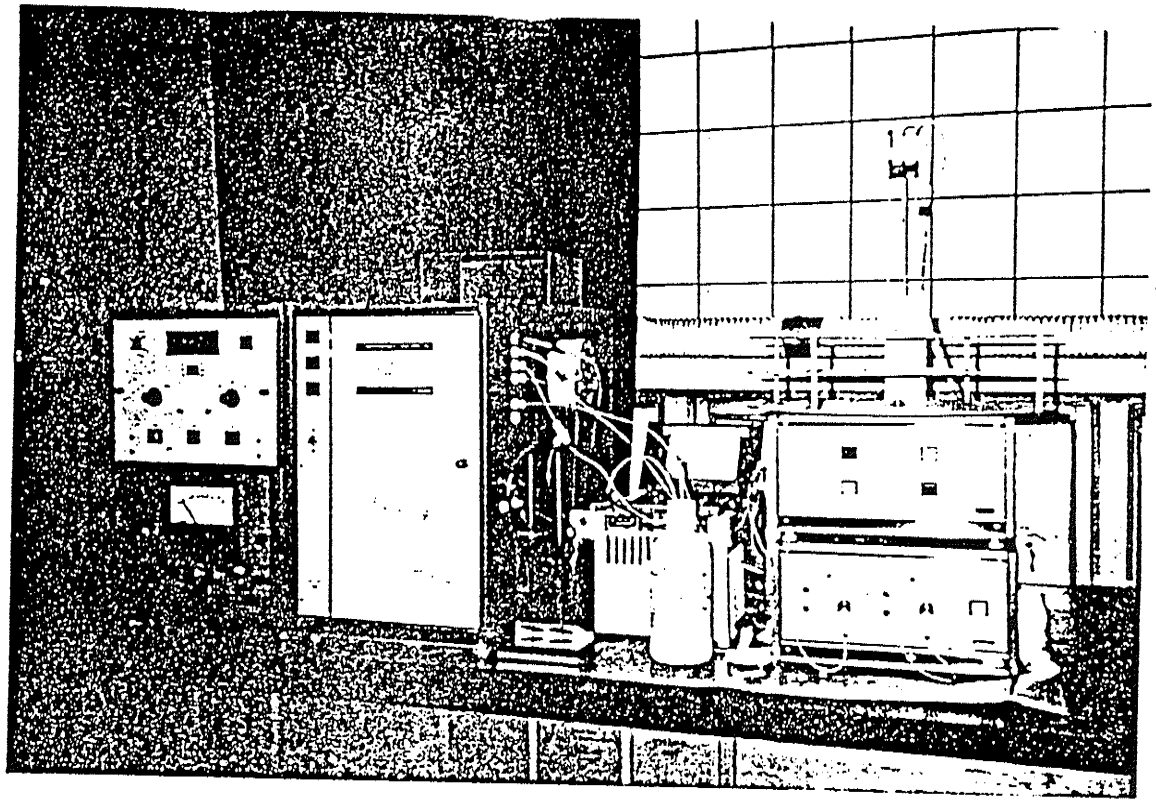


Figure 4.3 The total organic carbon analysis system (DC-80)

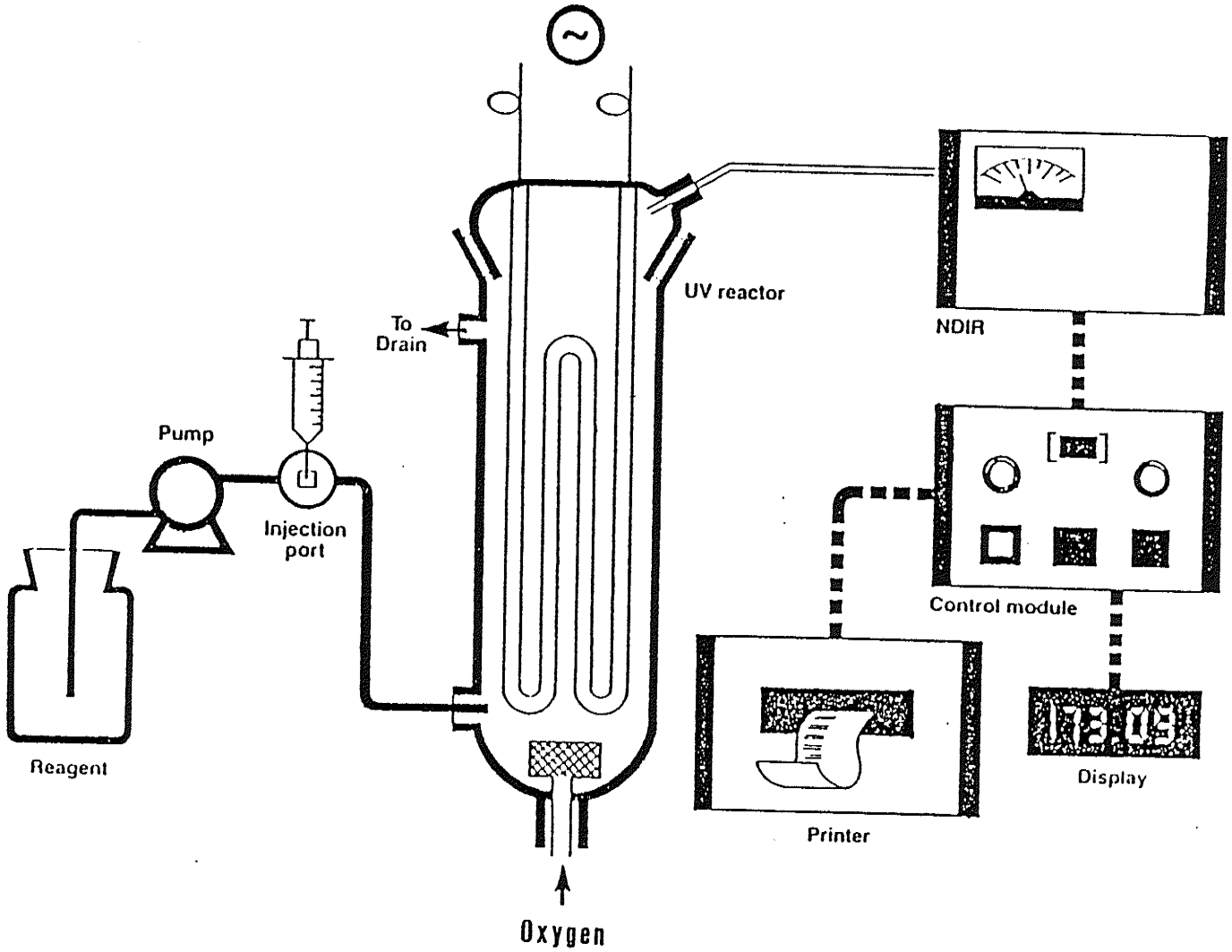


Figure 4.4 Total organic carbon operating principle.

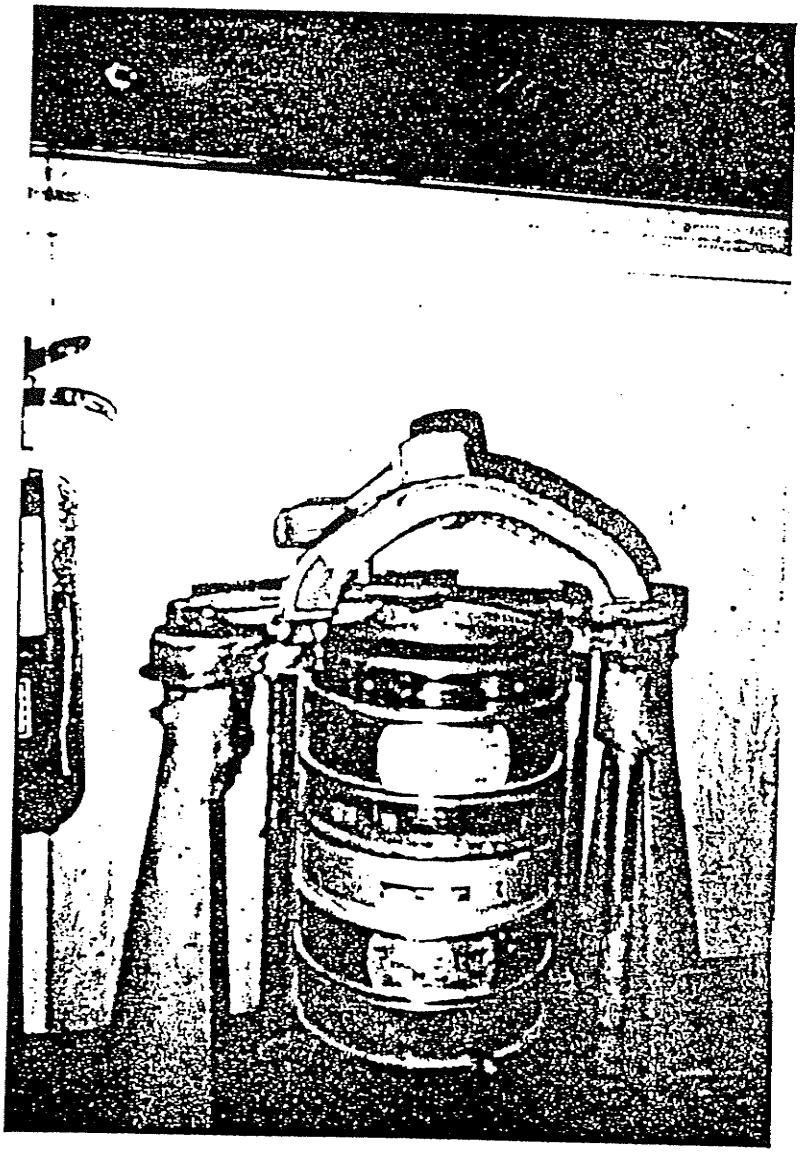
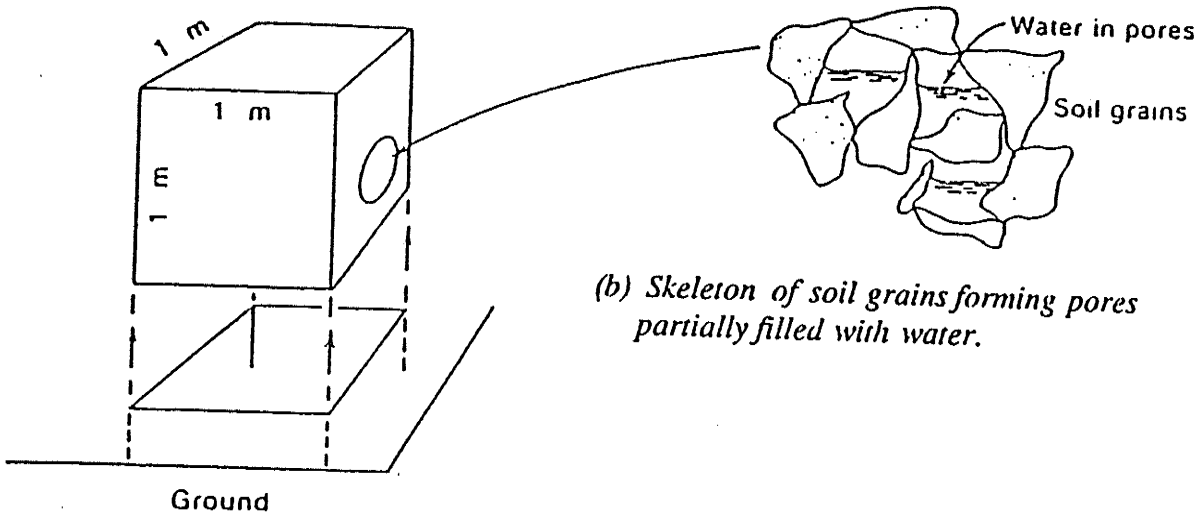
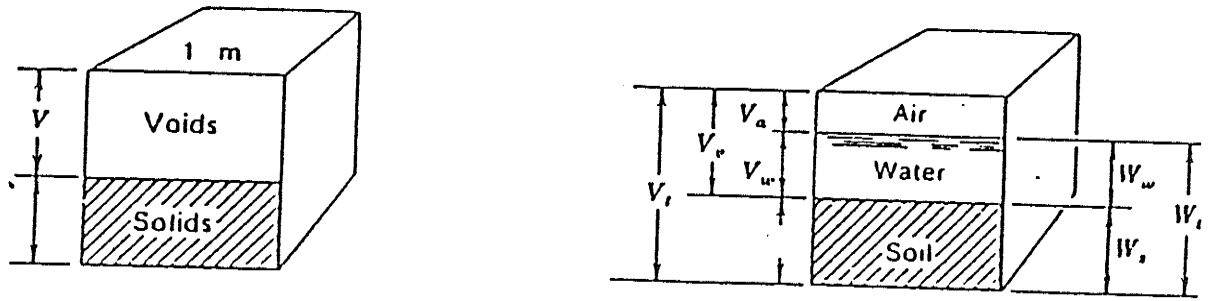


Figure 4.5 The mechanical (sieve) analysis machine



(a) Cube of soil removed from ground.

(b) Skeleton of soil grains forming pores partially filled with water.



(c) Soil solids formed into a nonporous volume of less than 1 m^3.

(d) Block diagram showing volumetric and mass relationships for the original soil mass.

Figure 4.6 Schematic representation of phase relationships (Bowels, 1992).

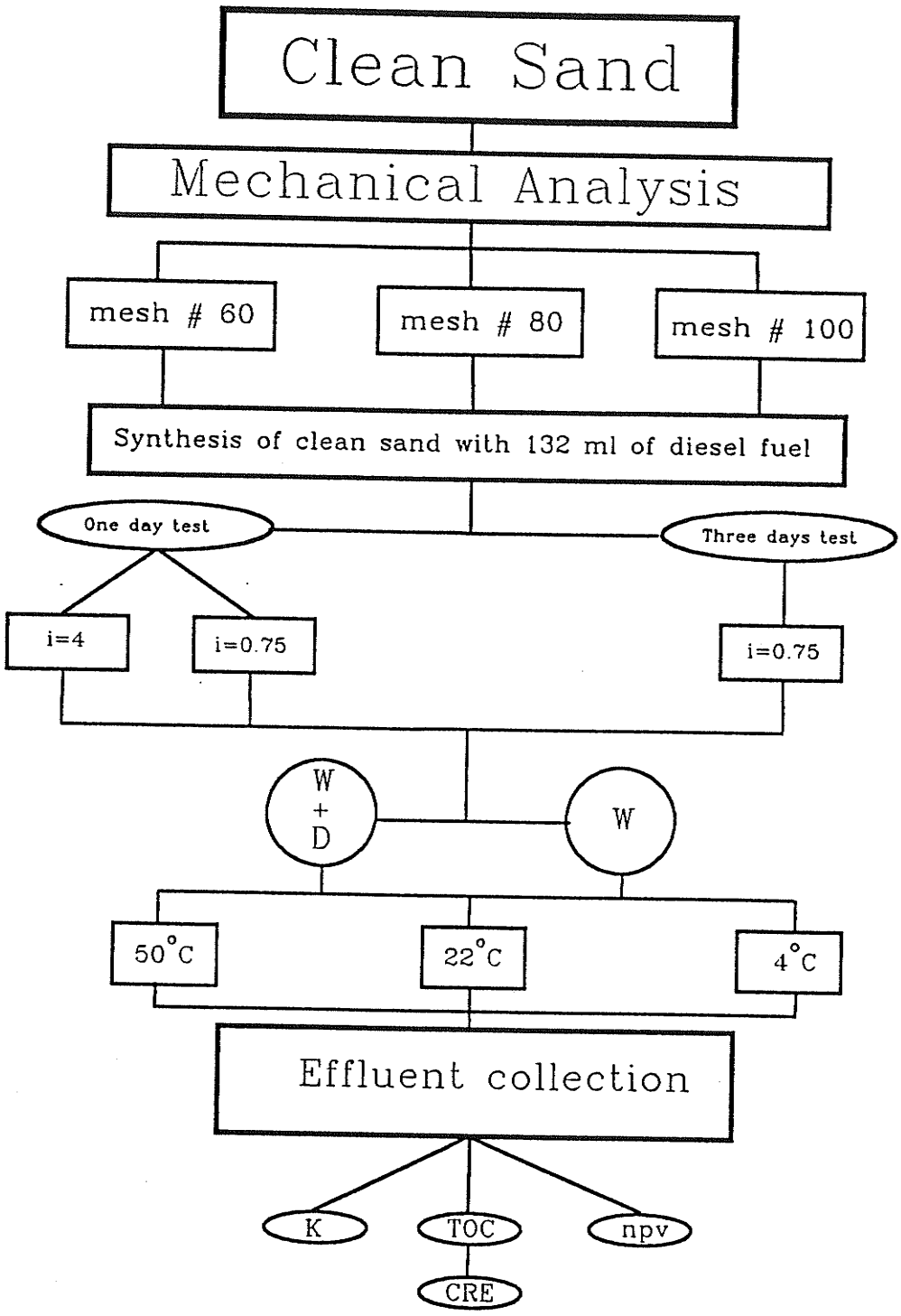


Figure 4.7 Summary of the major steps involved in the experiment.

Chapter 5

Test Results

5.1 Introduction

The results of the soil washing test program are presented here on the basis of whether or not a surfactant was used. The soil properties, changes in hydraulic conductivity and cumulative removal efficiency are discussed.

5.2 Soil Properties

The soil used in the present study had a white crystalline appearance. The soil is described below in terms of mineralogy, density and grain size distribution.

5.2.1 Mineralogy

The soil is 100% crystalline silica quartz, which consists of silicon and oxygen atoms (ions) bonded together in various arrangements. A large number of naturally occurring minerals are silicates, since silicon and oxygen are the two most abundant elements found in the earth crust. Hence the test soil is representative of much of the soil in nature.

5.2.2 Density of Tested Soil

The dry density of the tested soil specimens ranges from 1590 to 1650 kg/m^3. The soil exhibited relatively uniform density characteristics within any particular specimen. The average dry density of all test specimens was 1620 kg/m^3. This

corresponds to a porosity of 0.40 based on an assumed relative density of 2.7. Figure 5.1 shows a chart for finding density index range I_D and using sample data given on the chart. Note that the standard deviation of the densities is less than 1% of the average value.

5.2.3 Grain Size Distribution

The results of the three grain size distribution curves are shown in Table 5.1. For the three grain size distributions the sizes D_{10}, D_{30}, and D_{60} are read from the curves and the values of C_u and C_c are calculated (see Table 5.1). The particle size distribution curves are plotted in Figure 5.2. The curves for the three soils having same distribution slope but different mean grain size, D_{50} (0.42, 0.24, and 0.17mm).

5.3 Biodish® Surfactant

The selection of the most effective surfactant for a particular purpose is a function of the physical-chemical characteristics of the surfactant, the compounds of interest in the soil, and the subsurface environment of the multiphase system.

Le Rue Van Es (1993) showed in her study that Biodish® can solubilize and enhance biodegradability of diesel fuel. Other important reasons for choosing Biodish® as a surfactant in this study include the oil contaminant characteristics, the chemistry of the interstitial water, biodegradability of the surfactant, and the temperature regime.

The viscosity of the oil can influence the soil washing process in several ways.

In general Biodish® is applicable to oils whose viscosities are such that they would be, or have been, candidates for water flushing. The upper limit of viscosity is extended somewhat by Biodish® over that of simple water flushing. As a general rule, the applicable oils are those that exhibit viscosities less than 100 centipoise.

The chemical nature of the oil used in this study (diesel) is important to the extent that it influences the interfacial tension and, consequently the surfactant selection. Biodish® causes a low interfacial tension between the water and oil. Also Biodish® surfactant alters the mobility of the washing solution to minimize by-passing and channelling, and to improve the volumetric coverage of the process.

Certain chemical constituents in the interstitial water can strongly influence the behaviour of the surfactant, and the composition of this water can vary considerably. Both mono valent and divalent metal ions in the water can affect the surfactant solution. The concentration of these ions can influence the interfacial tension, viscosity and phase stability of the solutions. However, Biodish® has the ability to resist reactions with most metal ions.

Srivatana V.J., 1990, developed two techniques to improve the mass-transfer of hydrocarbons, which include the use of biosurfactant and chemical surfactant to solubilized hydrocarbons. Their work showed that biosurfactants were most effective in breaking up the oil and separating it from the soil because they enhance solubility and increase degradation rate. Furthermore, Biodish® is a biosurfactant and easily biodegradable.

The temperature of the contaminated site is another environmental factor that can influence surfactant selection. High temperatures can detrimentally affect the chemical stability of a surfactant solution over the long time period involved in site remediation. However, Biodish® has been proven to be effective at relatively high temperature levels (up to 60°C).

The ingredients used in Biodish® are environmentally friendly. The active ingredients are: 1) silicates and soda chemical components (derived from salt, quartz and limestone), 2) natural food-grade citrus, 3) surfactant (non toxic and readily biodegradable), and 4) glaubersalt (made from natural mirabilite). Biodish® is 100% free of phosphates, nitrogen, chlorine, synthetic perfumes, toxic surfactant, and N.T.A. & E.D.T.A. (nitrolo-triacetic acid and ethylene diamino-tetra-acetic acid).

After several trials, 5 mg/l Biodish® was chosen because this was the minimum concentration needed to emulsify 132 ml of diesel fuel, the amount of diesel fuel in a sand column. The trials were made by adding lesser and greater amounts of Biodish® to 132 ml of diesel fuel in one litre of tap water, mixing well, and visually observing whether the diesel emulsified or floated to the top after a waiting period of at least two hours.

The Biodish® volume, represents only a small fraction of the pore volume filled by the mixture of water and surfactant. Ideally, displacement of the diesel oil by Biodish® surfactant flushing approaches a miscible displacement.

5.4 Hydraulic conductivity and TOC testing program

A series of hydraulic conductivity and TOC tests were performed on both clean sand and sand contaminated with diesel fuel in the permeameter test cells. The testing program is summarized in Table 5.2. A simple linear regression analysis by the method of least squares was used to estimate the relationship of K and CRE with respect to time and CRE as a function of pore volumes. The K and CRE were taken as the dependent variables and the time and pore volumes were taken as the independent variables. In performing this linear regression analysis, it is assumed that the data fit an equation of the following form:

$$y=a+bx \tag{5.1}$$

where

a = constant

b = slope or trend of regression line.

However, regarding the CRE tests an objective procedure was developed as follows. Sequential linear regression analysis were performed on the most recent consecutive data records (e.g., subset of the first two data points, then the last eight data points).

The a and b parameters and the coefficient of determination, R^2, were calculated for each soil type and all variables tested. The reliability of the regression equation can be judged by the b and R^2 parameters. The closer R^2 is to 1, the greater the verification of the theory by experiment. The coefficient of determination R^2, is a measure of suitability of the experimental equation in relating the dependent

and the independent variables.

5.4.1 Hydraulic Conductivity Tests on Oil-Free Sand

Hydraulic conductivity tests were performed on 72 oil-free sand samples. Figures 5.3 through 5.5 show the laboratory hydraulic conductivity results for the three grain size distributions, tested at three different temperatures, over a period of one day. The results show a slight increase in the hydraulic conductivity with time for all distribution types. Tests were repeated for three days in an attempt to measure the maximum value of K. The results are shown in Figures 5.6 through 5.8. The curves show that K generally became constant after few hours, which indicates that the sand samples require a few hours to reach steady state. This time requirement is probably due to imperfect de-airing of the specimens and to a loss of fines.

Laminar flow was observed for flow rates up to approximately 115 ml per minute. The effect of the temperature on the hydraulic conductivity for the three grain size distributions is shown in Table 5.3. As the temperature increases, the hydraulic conductivity increases due to the decrease in the viscosity of the fluid passing through the soil sample. The value of the hydraulic conductivity was in the range of 1.75×10^{-4} to 3.5×10^{-4} m/sec; these are values that are typical for fine to medium, clean sand.

5.4.2 Hydraulic Conductivity Tests on Oil-Rich Samples

Seventy set of tests were conducted on oil-rich sand with four samples each. The samples were prepared synthetically by mixing 132 ml of diesel fuel into 2 kg of clean sand; the mechanical mixing was carried out long enough to ensure the contaminant distribution was homogeneous. The initial bulk density of the samples was approximately 1544 kg/m^3 ±10 kg/m^3, at an initial porosity of 0.42 ±0.04. Three different grain size samples were subsequently tested under three different temperatures. Influent containing either water or water plus surfactant was circulated through the samples. The contaminant removal and the effective permeability (hydraulic conductivity) were measured as the contaminant (diesel fuel) saturation decreased from 98% ±2 to 39% ±2.

5.4.2.1 *Water Flushing*

Curves (a) of Figures 5.9 through 5.35 show the hydraulic conductivity of samples using water as an influent. The values of the hydraulic conductivity vary from 1.77×10^{-4} to 2.57×10^{-4} m/sec depending on three major variables: grain size, temperature, and time. Figures 5.9 through 5.17 show the results of one day test of samples with mesh number 60, 80, and 100 performed at temperatures of 4, 22, and 50°C. At a given temperature, the smaller the grain size, the lower is the hydraulic conductivity. The results indicate, as well, that as temperature increases the value of hydraulic conductivity increases. The hydraulic conductivity was shown to increase linearly with time over the one day. For this reason, three day tests were conducted

in order to determine the values of hydraulic conductivity over a longer period. Figures 5.18 through 5.26 show the results from the three day tests. The maximum hydraulic conductivity values obtained from flushing the contaminated sand with water for three days range from 1.93×10^{-4} to 2.5×10^{-4} m/sec. This represents approximately a 5% increase in hydraulic conductivity relative to the initial values.

It is clear that the values of the hydraulic conductivity for the contaminated sand are substantially below the values for the clean sand even at the end of three days. This must be due to the presence of some unwashed free-phase hydrocarbon in the pore space.

Another series of permeability tests was conducted with a higher hydraulic gradient (i=4 instead of i=0.75) for one day, as shown in Figures 5.27 through 5.35, to determine the effect of velocity and the increase in pore volumes on the hydraulic conductivity. The hydraulic conductivity values obtained from the higher hydraulic gradient tests over one day were close to those from the lower hydraulic gradient tests performed for three days. This is in spite of the fact that the number of pore volumes that pass through the specimen in one day at i=4 equals 1.8 times the number that pass through in 3 days at i=0.75.

5.4.2.2 *Surfactant Flushing*

Tests with water plus surfactant were run to determine the enhancement in contaminant removal. Curves (a) of Figures 5.36 through 5.62 show the hydraulic conductivity of contaminated samples using water and surfactant (biodish 5 mg/L of

water) as an influent. The maximum hydraulic conductivity values vary from $1.92x10^{-4}$ to $3.22x10^{-4}$ m/sec, depending on the grain size distribution and the temperature.

Figures 5.36 through 5.44 show the results of a one day test with hydraulic gradient equal to 0.75. The data shows that the hydraulic conductivity increases linearly with time. Again a series of three day tests were conducted and the results are presented in Figures 5.45 through 5.53. They show that the maximum values of the hydraulic conductivity range from $2.07x10^{-4}$ to $3.1x10^{-4}$ m/sec. The data represent only 1 to 3% increase in K relative to the one day tests.

Another set of tests was performed with a higher hydraulic gradient (i=4) to indicate any changes in the hydraulic conductivity values. The results of these tests are presented in Figures 5.54 through 5.62. The data indicate that the major effect of increasing the velocity, and therefore the number of pore volumes that pass through in a given time, is that it took less time to flush the contaminant out of the pores. The time needed to wash out 90% of the contaminant was 72 hours with i=0.75, while for i=4, it took only 24 hours. But the number of pore volumes used with i=4 was nearly two times the number with i=0.75, hence increasing i proved not to be efficient in terms of surfactant demand. (In the field it would be very difficult to achieve an i=4.)

5.4.3 Cumulative Removal Efficiency

The results of the TOC obtained in this study are presented as a cumulative removal efficiency (CRE) in curves (b) and (c) through Figures 5.9 to 5.62.

The results of the recovery efficiency were divided into two sections. Section One deals with tests conducted with water as the influent, while Section Two deals with the tests conducted with water plus surfactant as the influent.

The results of Section One are presented in curves (b) and (c) of Figures 5.9 through 5.35. Curves (b) represent the cumulative removal efficiency (CRE) versus time, while curves (c) represent the cumulative removal efficiency (CRE) versus number of pore volumes. Figures 5.9 through 5.17 show the results of one day tests for the three grain size distributions (mesh #60, 80 and 100 mesh) performed at three different temperatures (4, 22, and 50°C). The removal efficiency varies widely from 36 to 73%, with the corresponding number of pore volumes ranging from 121 to 160, depending on the grain size and temperature.

Another set of tests was conducted for a 3 day period to predict the removal efficiency over a longer period. The results are shown in figures 5.18 through 5.26. The maximum removal efficiency that was measured varies from 38 to 74%, which represents an additional 2% increase in CRE relative to the one day test. However, the number of pore volumes used ranges from 372 to 512 , which is approximately 3 times the number used for the one day test. (The ratio of 3 simply reflects the fact that the test were run 3 times longer.)

Since there was a slight increase in CRE between the one day and three day tests, another set of tests was performed for one day with a higher hydraulic gradient (i=4), to determine if a higher velocity, and an even greater number of pore volumes passing through in a day, would affect the removal efficiency. Figures 5.27 through

5.35 represent the results of these tests. The maximum removal efficiency ranges from 43 to 80% with the corresponding number of pore volumes used varying from 643 to 850, depending on the grain size distribution and the temperature.

Section Two results are presented in curves (b) and (c) of Figures 5.36 through 5.62. Curves (b) show CRE versus time, while curves (c) show the number of pore volumes used. The CRE for one day tests, with i=0.75, for the surfactant flushing experiment, is shown in Figures 5.36 through 5.44. The results show a removal efficiency that varies from 42 to 83%, with the corresponding number of pore volumes used ranging from 132 to 233, depending on the grain size distribution and temperature.

To measure the CRE over a longer period, the same type of tests was repeated, but this time for a three day period. The results are presented in Figures 5.45 through 5.53. The data shows maximum removal efficiencies ranging from 43 to 85%. There was approximately a 2% increase compared to the one day test even though the number of pore volume used varies from 438 to 735, 3 times the number used for the one day test.

Again a one day test with a higher hydraulic gradient (i=4) was performed to determine the effect of an increase in liquid velocity and in the number of pore volumes per day on the removal efficiency. The results are shown in Figures 5.54 through 5.62. The maximum removal efficiency varies from 47 to 94% with the corresponding number of pore volumes ranging from 700 to 1235. This represents 5% increase compared to the one day test with i=0.75, and a 3% increase over the

three days tests with i=0.75. Since nearly twice as much surfactant was used over one day at i=4, as compared to three days at i=0.75, it is arguable whether or not efficient use was being made of the surfactant at the high hydraulic gradient.

5.5 Contaminated Sand Microfabric and Mineralogy Studies

5.5.1 Textural and Mineralogic Alteration

An optical microscope study was conducted with the aim of identifying mineralogic or textural alternations resulting from the washing of contaminated sand at normal and elevated temperatures. The study was also useful in comparing the microfabric of the soil particles before and after the removal of the contaminant.

5.5.2 Optical Microscope Study

The mineral grain fabric and texture of seventeen oil sand specimens were studied and photographed using a optical microscope (Model S-4) before and after the soil washing treatment. Intact specimens of sand contaminated with diesel fuel were carefully taken from larger samples using a sharp knife. The specimens were spread on a square piece of glass.

A summary of the specimens studied and photographed in the scanning electron microscope is listed in Table 5.4. Figures 5.63 and 5.64 inclusive show typical examples of microfabric and grain texture for intact samples before contamination. It is of interest to note that quartz sand grains with unclassified flocculated minerals adhering to their surface have not lost their interpenetrative

microstructural arrangement and are in "tangent-to-tangent" contact. By contrast, an oil rich contaminated sample, as shown in Figure 5.65 through 5.68 appears to have lost its flocculated minerals that normally adhere to the surface. The grains are intact, rest on top of each other but are separated by oil. However, after the samples have been washed, the grain adherent surface was in between "two ranges intact" and "tangent-to-tangent" contact as shown in Figures 5.69 and 5.70.

Table 5.1 The results of particle size analysis for three grain size.

	Percentage smaller		
BS sieve	mesh #60	mesh #80	mesh #100
1.0 mm	100		
0.9 mm	98		
0.7 mm	95	100	
0.6 mm	90	98	100
0.5 mm	80	95	97
0.4 mm	35	88	91
0.3 mm	20	80	88
0.2 mm	5	30	75
0.15 mm	0	10	40
0.1 mm		0	15
0.08 mm			0

For the three grain size D10, D30 and D60 are read from Figure 5.2 and the values of Cu and Cc are calculated:

mesh #	D10	D30	D60	Cu	Cc
60	0.23	0.37	0.45	1.2	1.3
80	0.15	0.2	0.27	1.35	0.98
100	0.09	0.14	0.18	1.28	1.2

Table 5.2 List of test results - fuel oil contaminated sand.

Tests with Water only					Final Reading		
Figure	i	days	T ^ C	mesh#	CRE(%)	PV	K (m/s)
5.9	0.75	1	4	60	41	124	1.82E-04
10				80	37	123	1.80E-04
11				100	36	121	1.77E-04
12			22	60	57	143	2.09E-04
13				80	55	141	2.05E-04
14				100	54	138	1.99E-04
15			50	60	73	160	2.38E-04
16				80	72	148	2.19E-04
17				100	67	142	2.12E-04
18	0.75	3	4	60	56	384	1.99E-04
19				80	39	380	1.95E-04
20				100	38	372	1.93E-04
21			22	60	62	450	2.22E-04
22				80	61	443	2.20E-04
23				100	60	437	2.10E-04
24			50	60	74	512	2.50E-04
25				80	73	465	2.35E-04
26				100	70	441	2.24E-04
27	4.00	1	4	60	48	658	1.88E-04
28				80	47	654	1.81E-04
29				100	43	643	1.78E-04
30			22	60	59	763	2.10E-04
31				80	57	752	2.09E-04
32				100	55	733	2.00E-04
33			50	60	80	850	2.57E-04
34				80	78	787	2.33E-04
35				100	77	756	2.14E-04

Table 5.2 Contd

Tests with Water plus Surfactant					Final Reading		
Figure	i	days	T ^ C	mesh#	CRE(%)	PV	K (m/s)
5.36	0.75	1	4	60	45	139	2.00E-04
37				80	44	135	1.92E-04
38				100	42	132	1.92E-04
39			22	60	64	152	2.10E-04
40				80	61	150	2.10E-04
41				100	61	145	2.10E-04
42			50	60	83	233	3.10E-04
43				80	82	226	2.80E-04
44				100	78	180	2.66E-04
45	0.75	3	4	60	47	443	2.18E-04
46				80	46	482	2.08E-04
47				100	43	438	2.07E-04
48			22	60	66	469	2.33E-04
49				80	66	472	2.31E-04
50				100	65	458	2.27E-04
51			50	60	85	735	3.10E-04
52				80	84	630	2.98E-04
53				100	81	580	2.82E-04
54	4.00	1	4	60	51	738	2.03E-04
55				80	49	714	1.97E-04
56				100	47	700	1.93E-04
57			22	60	72	808	2.25E-04
58				80	67	800	2.19E-04
59				100	65	772	2.15E-04
60			50	60	94	1238	3.22E-04
61				80	84	1205	3.02E-04
62				100	82	959	2.78E-04

Table 5.4 Asymptotic values of hydraulic conductivity for three mean grain size at three different temperature - clean sand, pure water.

Grain-Size mesh #	Hydraulic Conductivity (m/sec) 4°C	22°C	50°C
60	2.02×10^{-4}	2.55×10^{-4}	3.35×10^{-4}
80	1.87×10^{-4}	2.40×10^{-4}	3.20×10^{-4}
100	1.80×10^{-4}	2.30×10^{-4}	2.92×10^{-4}

Table 5.5 Summary of the specimens studied and photographed

Figure #	mesh #	Influent	Type
5.64	60	None	Clean
5.65	100	None	Clean
5.66	60	None	Contaminated
5.67	100	None	Contaminated
5.68	60	Water + Surfactant	After washing
5.69	100	Water + Surfactant	After washing
5.70	60	Water	After washing
5.71	100	Water	After washing

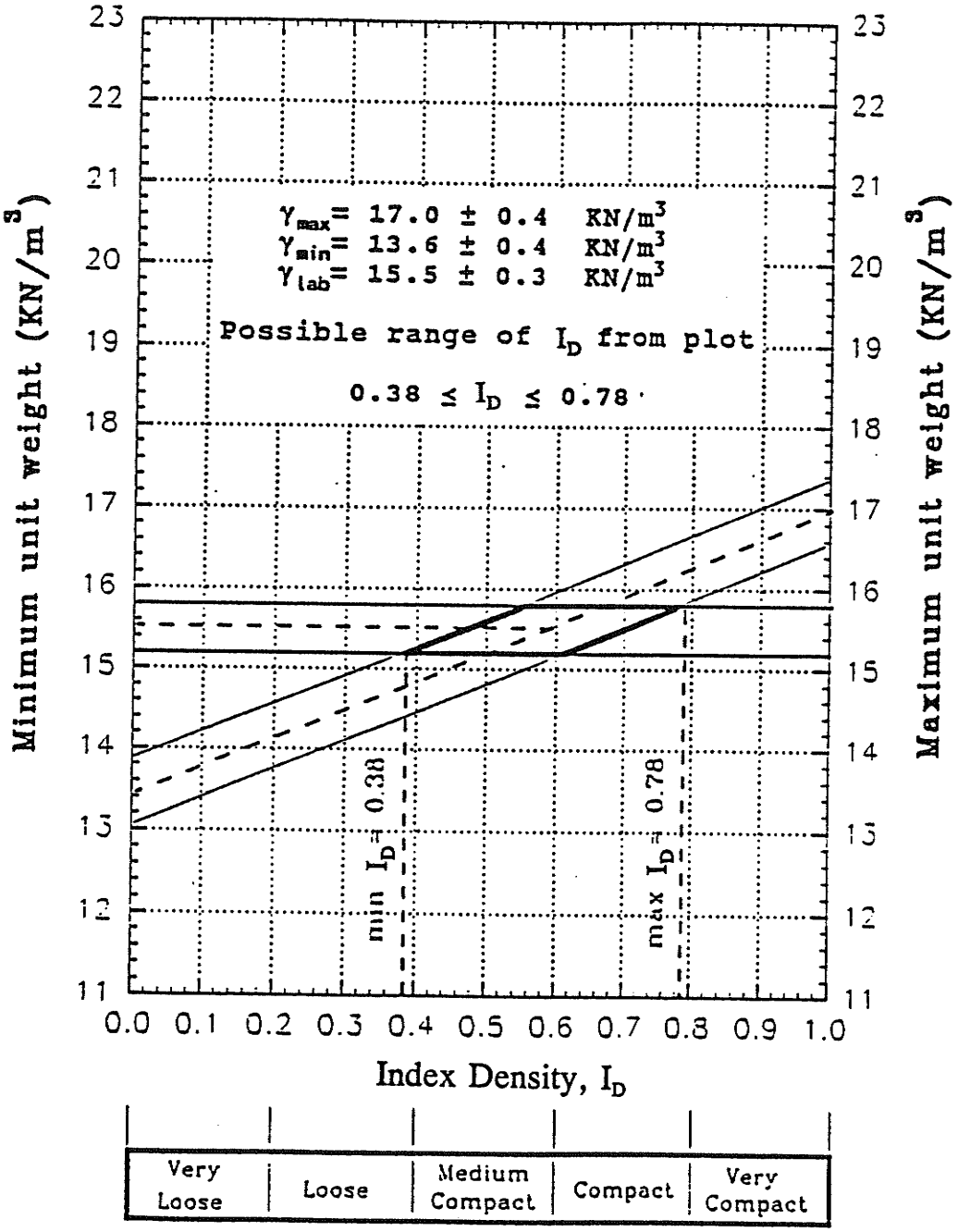


Figure 5.1 Chart for finding index density range I_D and using sample data given above. Value range plotted solid and given values are dashed.

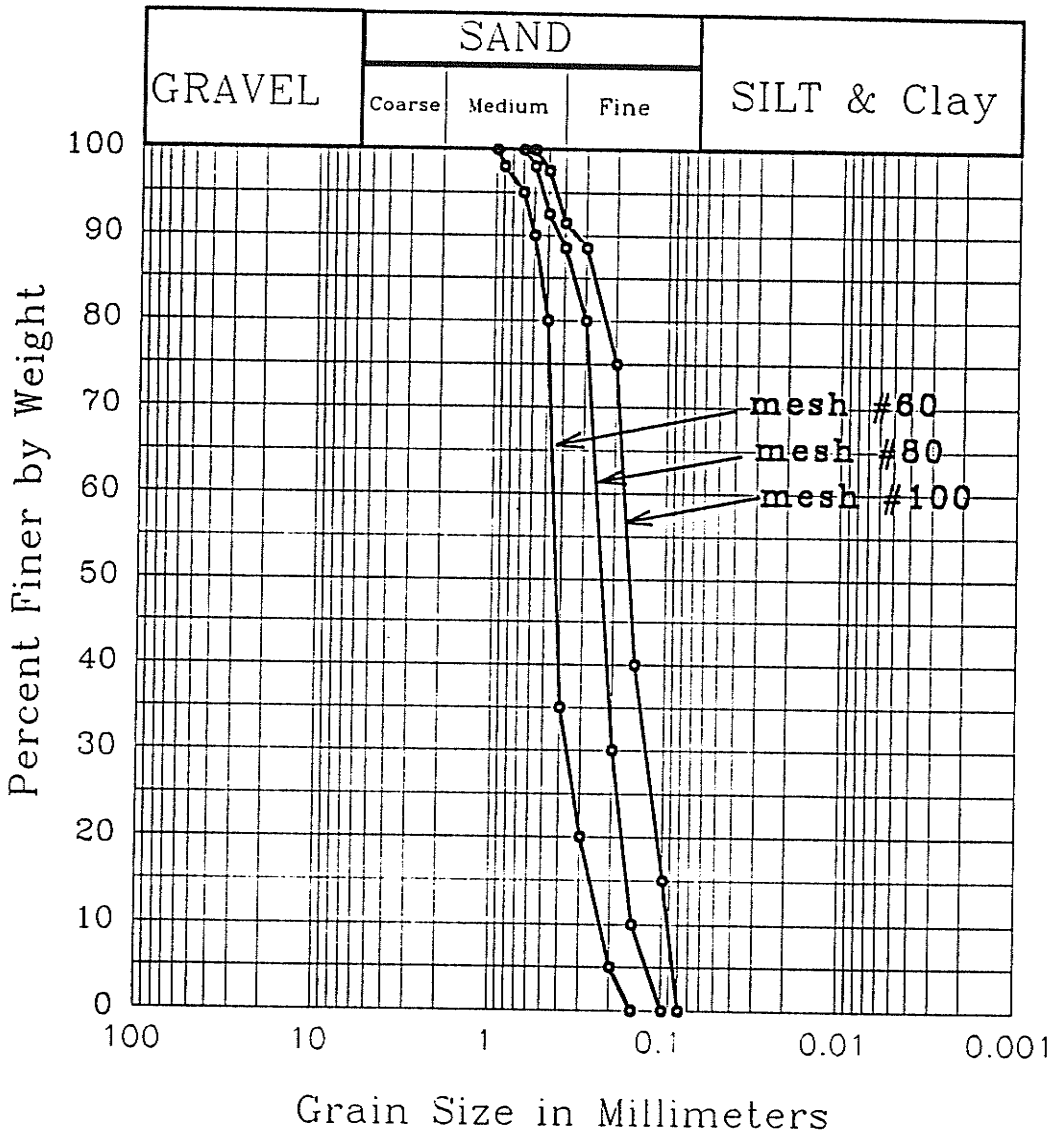


Figure 5.2 Grain size distribution of the sand samples.

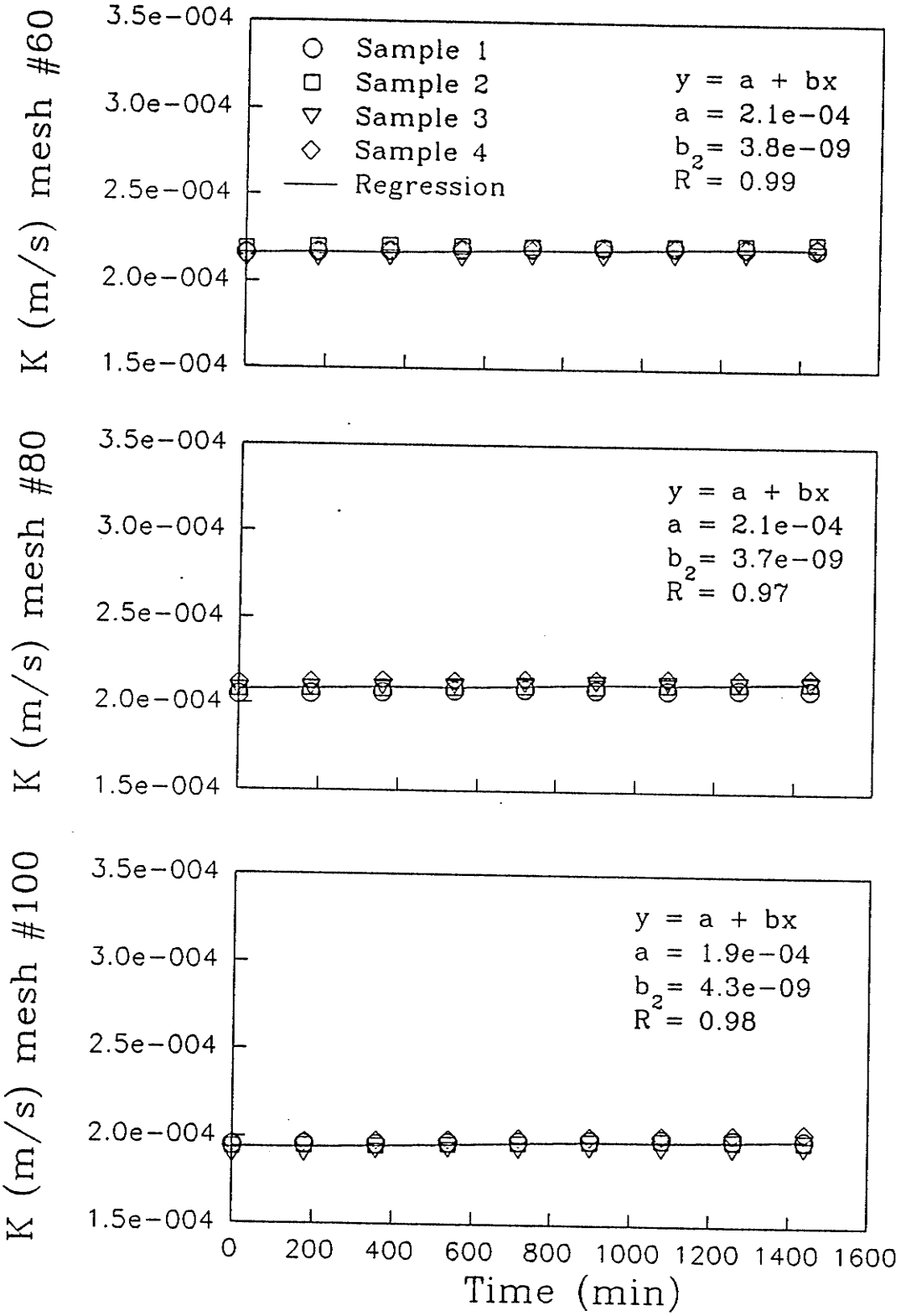


Figure 5.3 One day test results of hydraulic conductivity versus time at 4°C for various mesh sizes–clean sand, water.

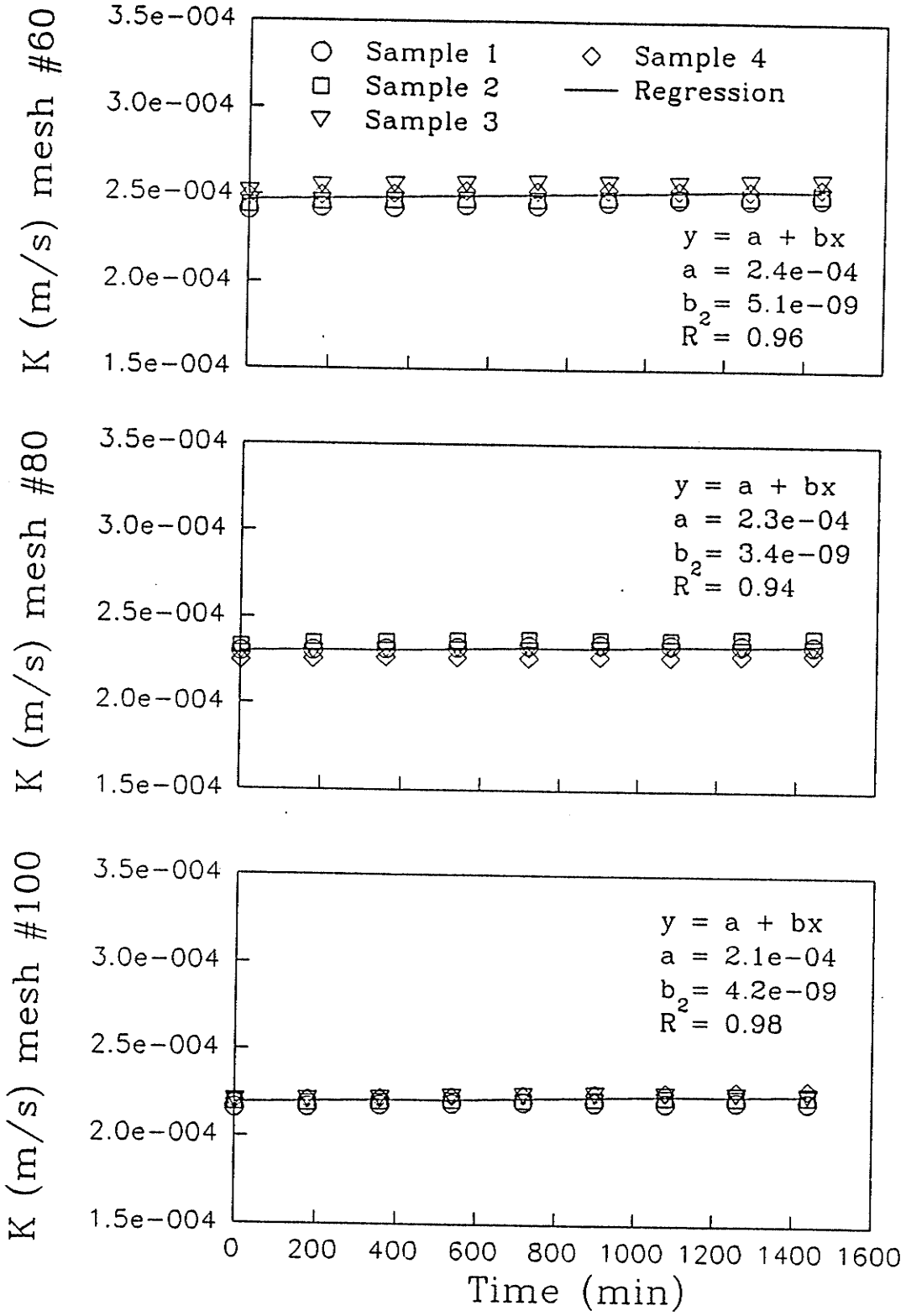


Figure 5.4 One day test results of hydraulic conductivity versus time at 22°C for various mesh sizes–clean sand, water.

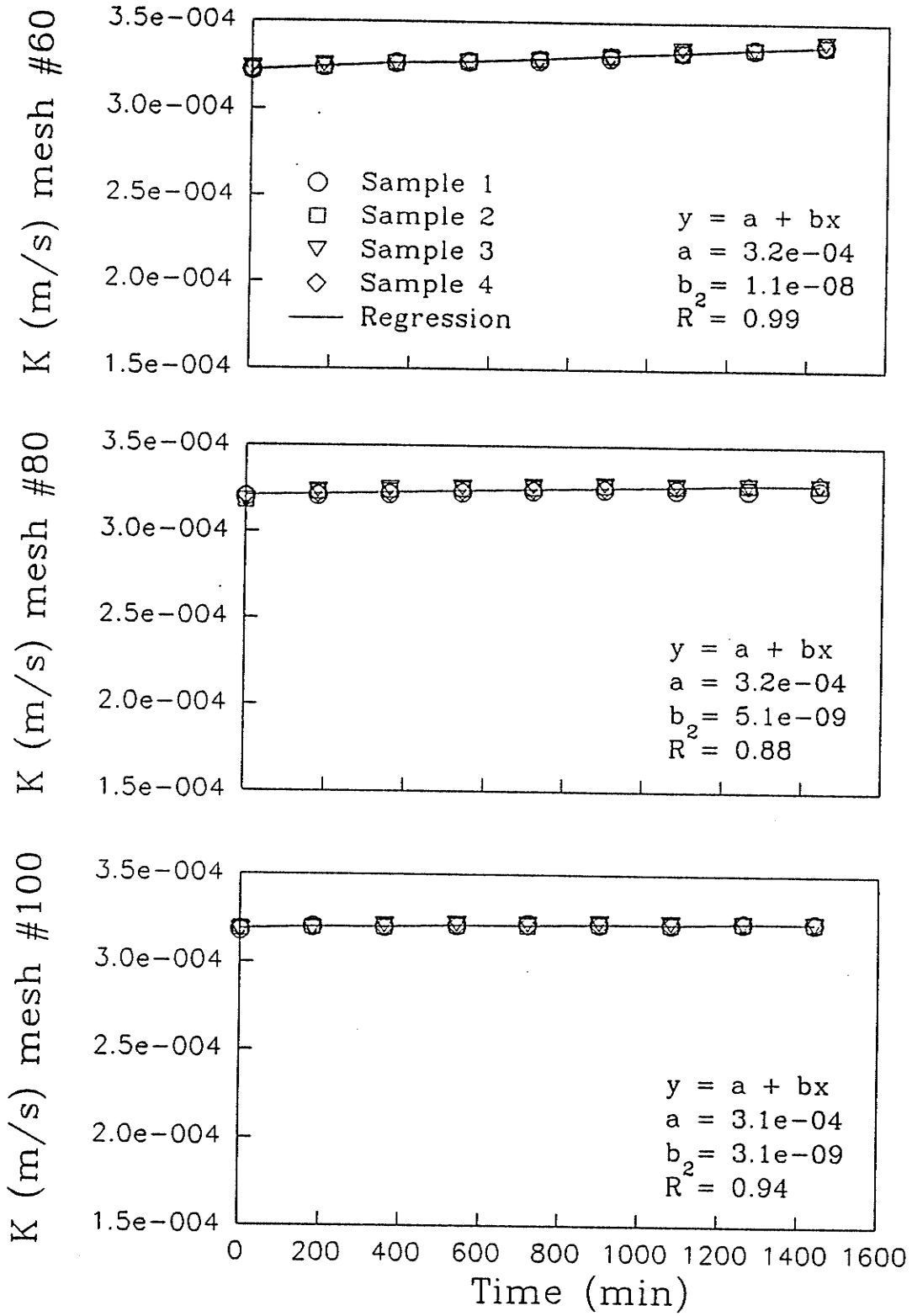


Figure 5.5 One day test results of hydraulic conductivity versus time at 50°C for various mesh sizes–clean sand, water.

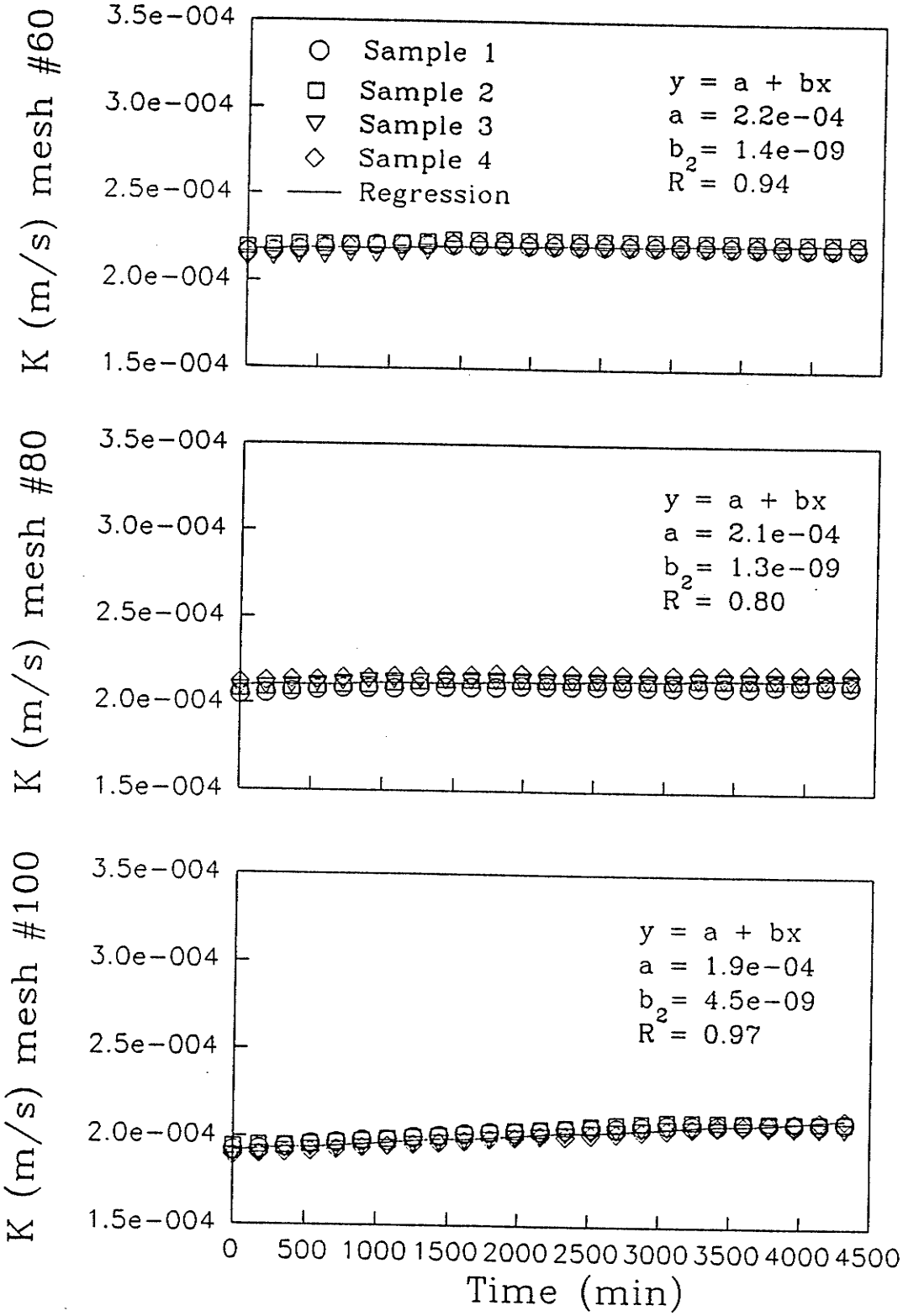


Figure 5.6 Three days test results of hydraulic conductivity versus time at 4°C for various mesh sizes–clean sand, water and detergent.

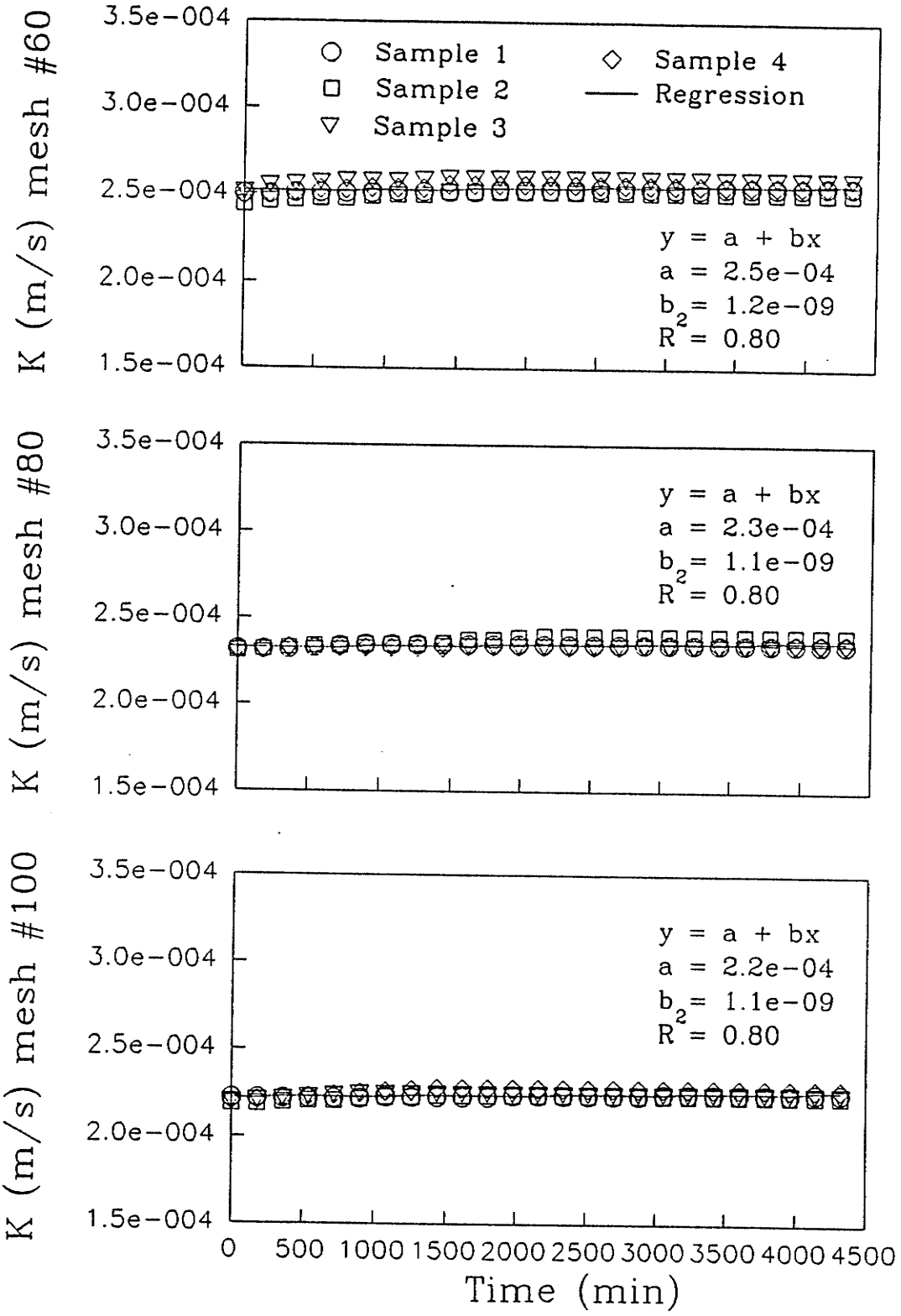


Figure 5.7 Three days test results of hydraulic conductivity versus time at 22°C for various mesh sizes–clean sand, water and detergent.

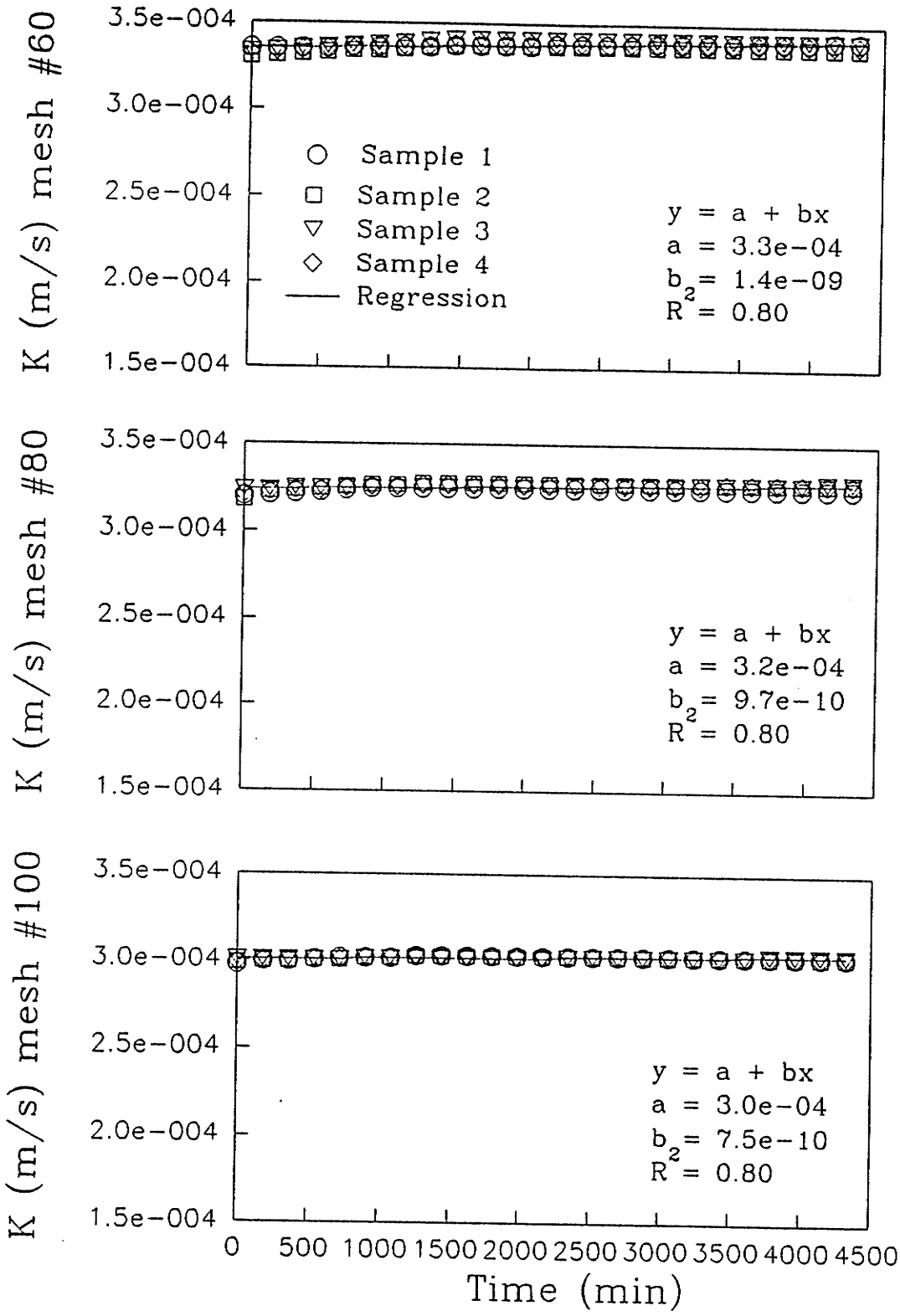


Figure 5.8 Three days test results of hydraulic conductivity versus time at 50°C for various mesh sizes–clean sand, water and detergent.

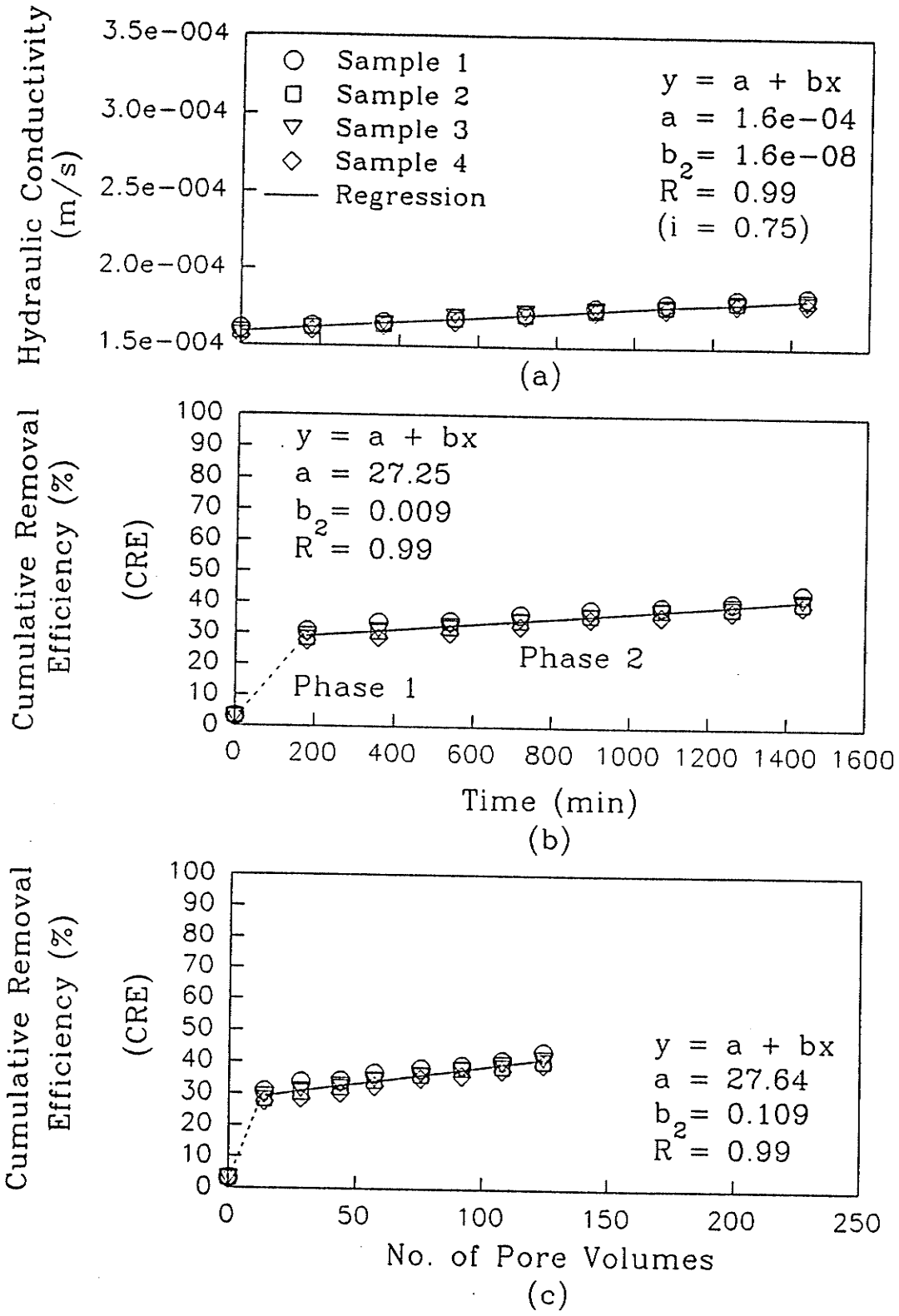


Figure 5.9 One day test results: mesh #60 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

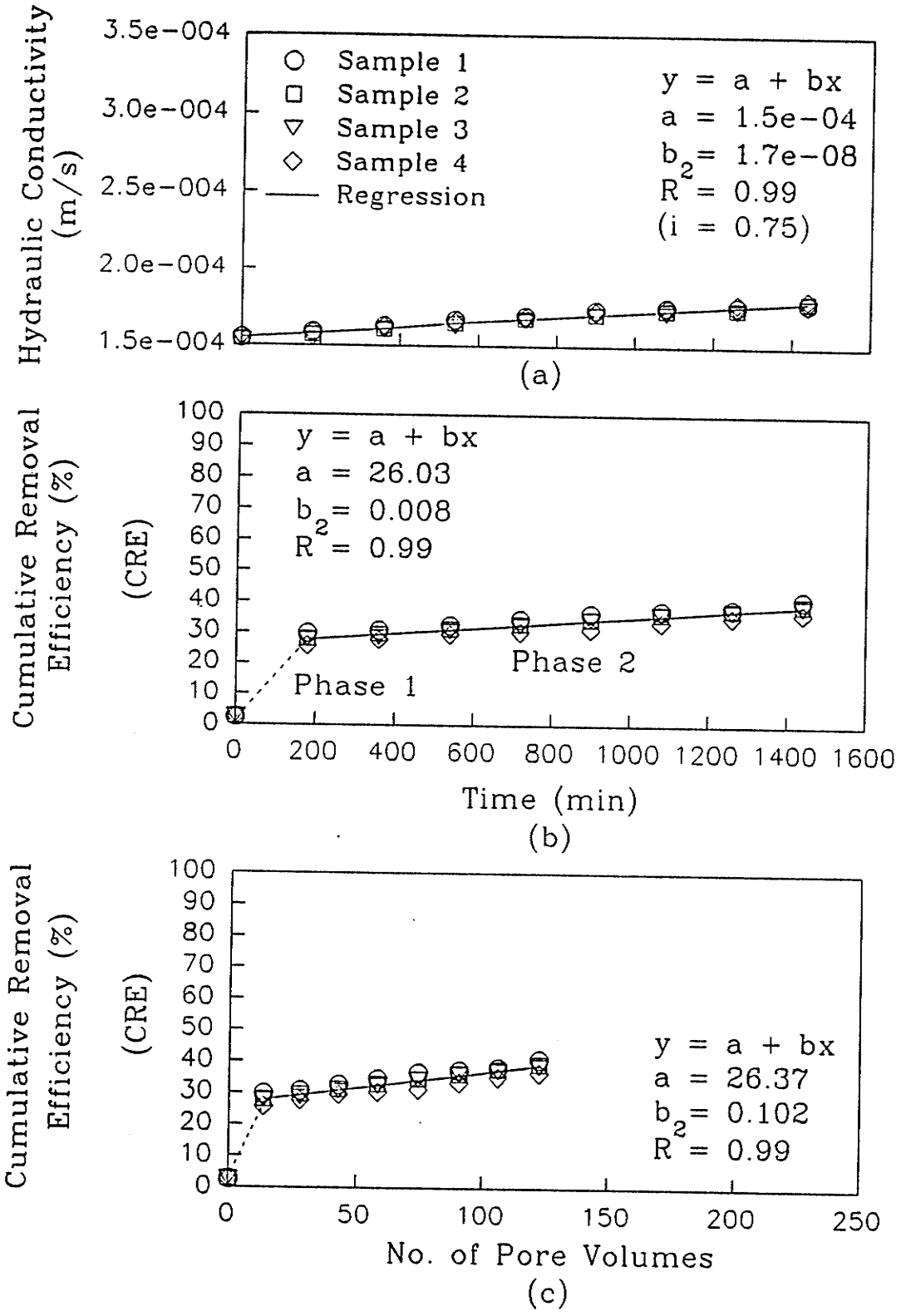


Figure 5.10 One day test results: mesh #80 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

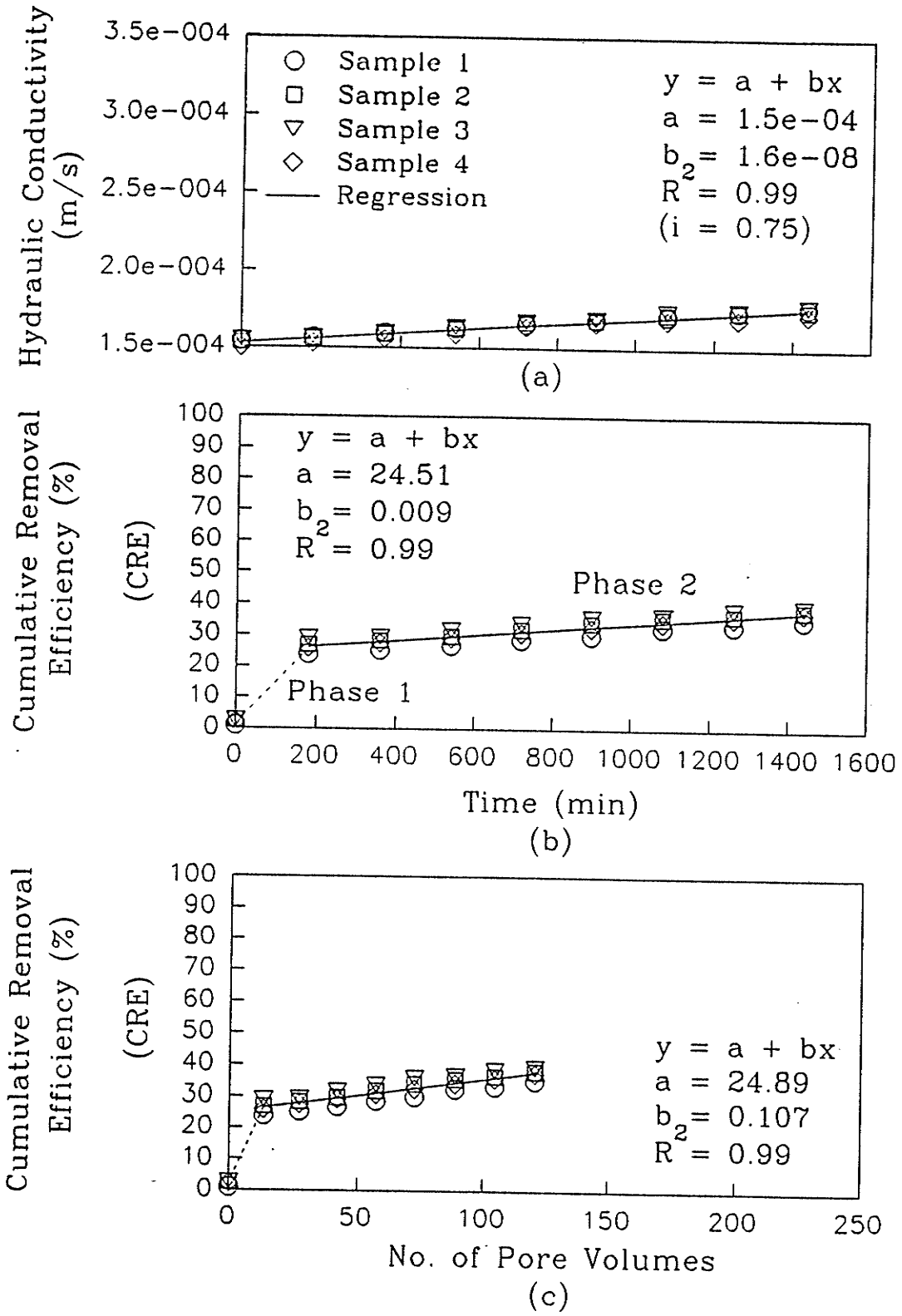


Figure 5.11 One day test results: mesh #100 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

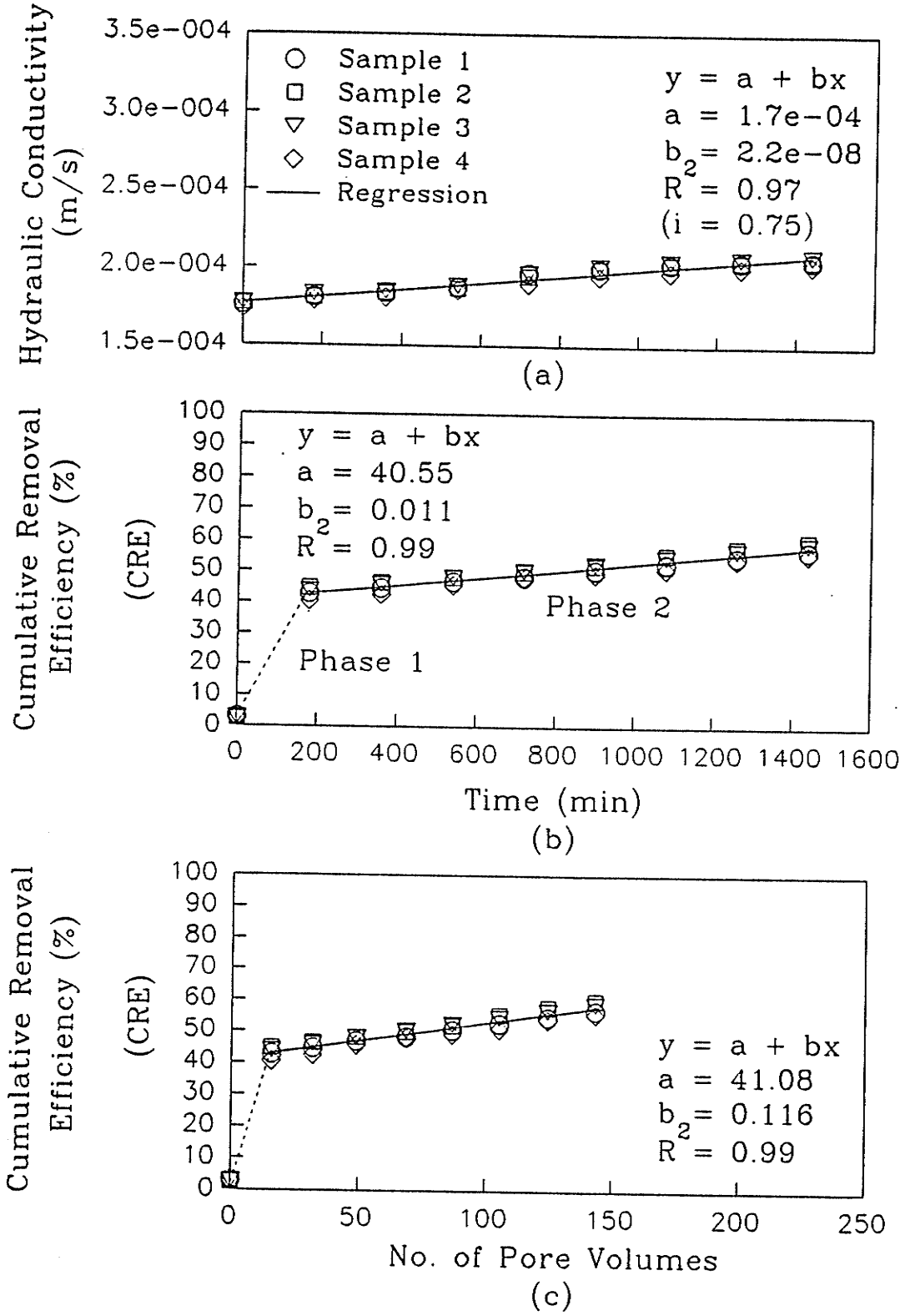


Figure 5.12 One day test results: mesh #60 contaminated sand, water at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

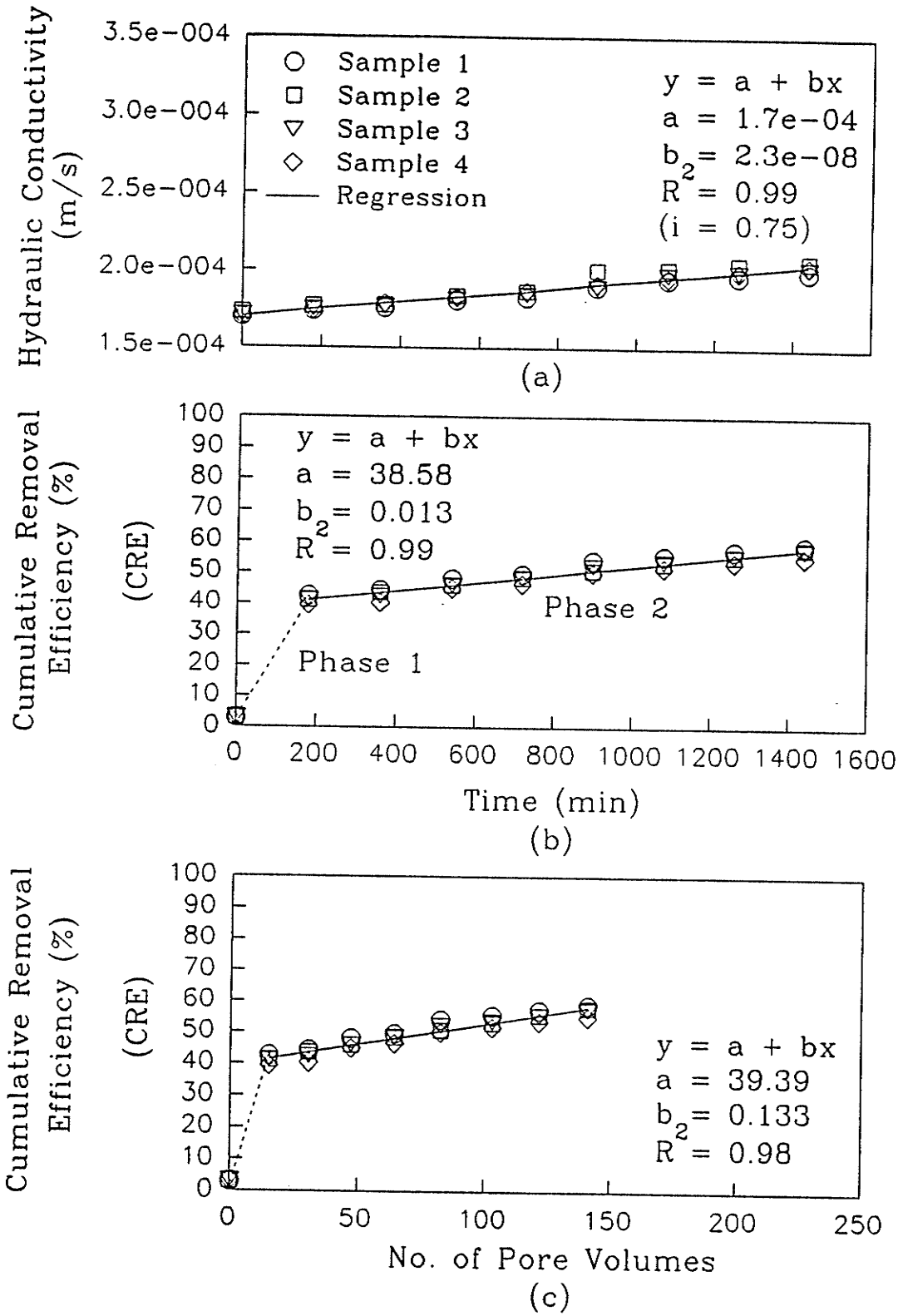


Figure 5.13 One day test results: mesh #80 contaminated sand, water at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

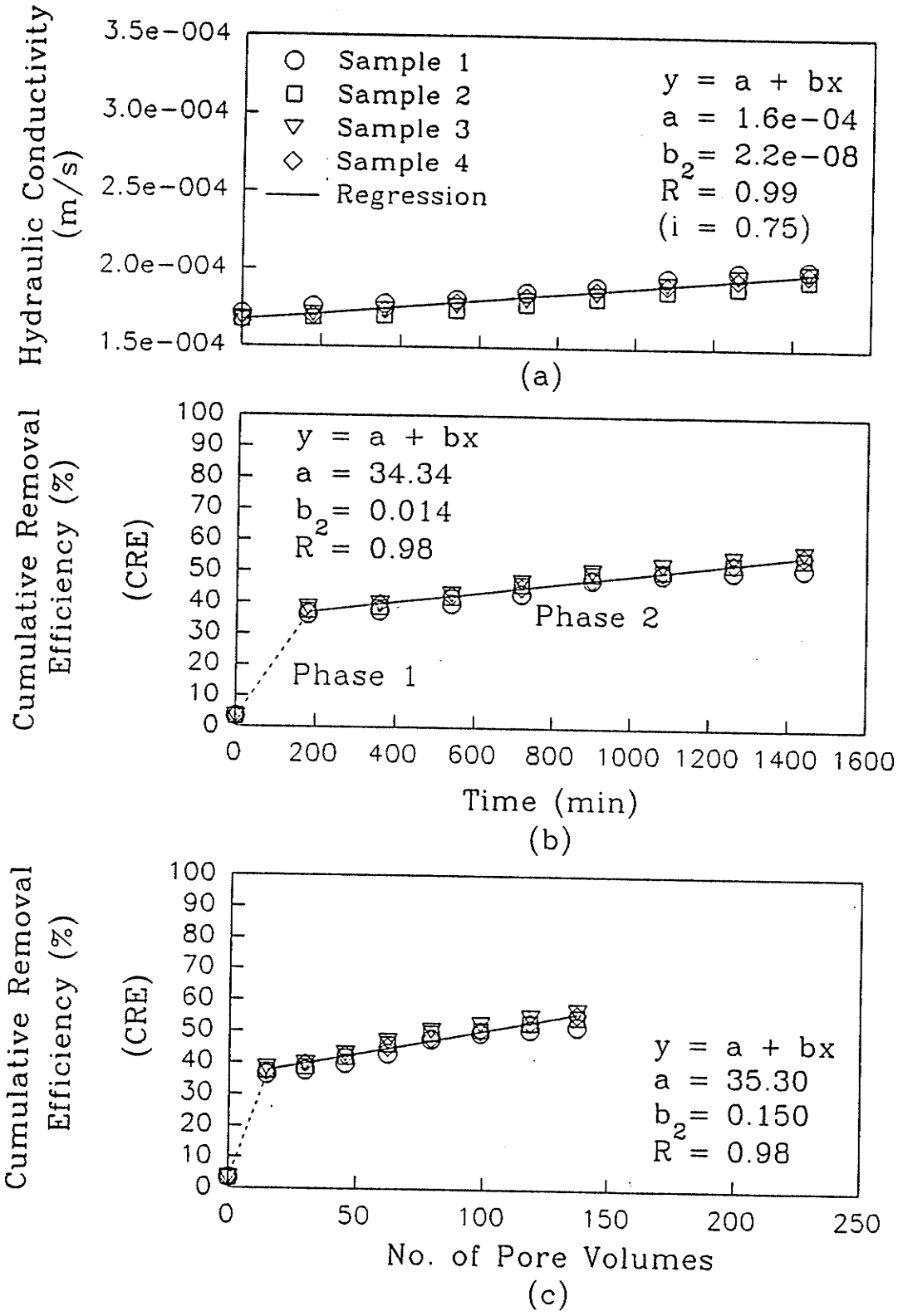


Figure 5.14 One day test results: mesh #100 contaminated sand, water at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

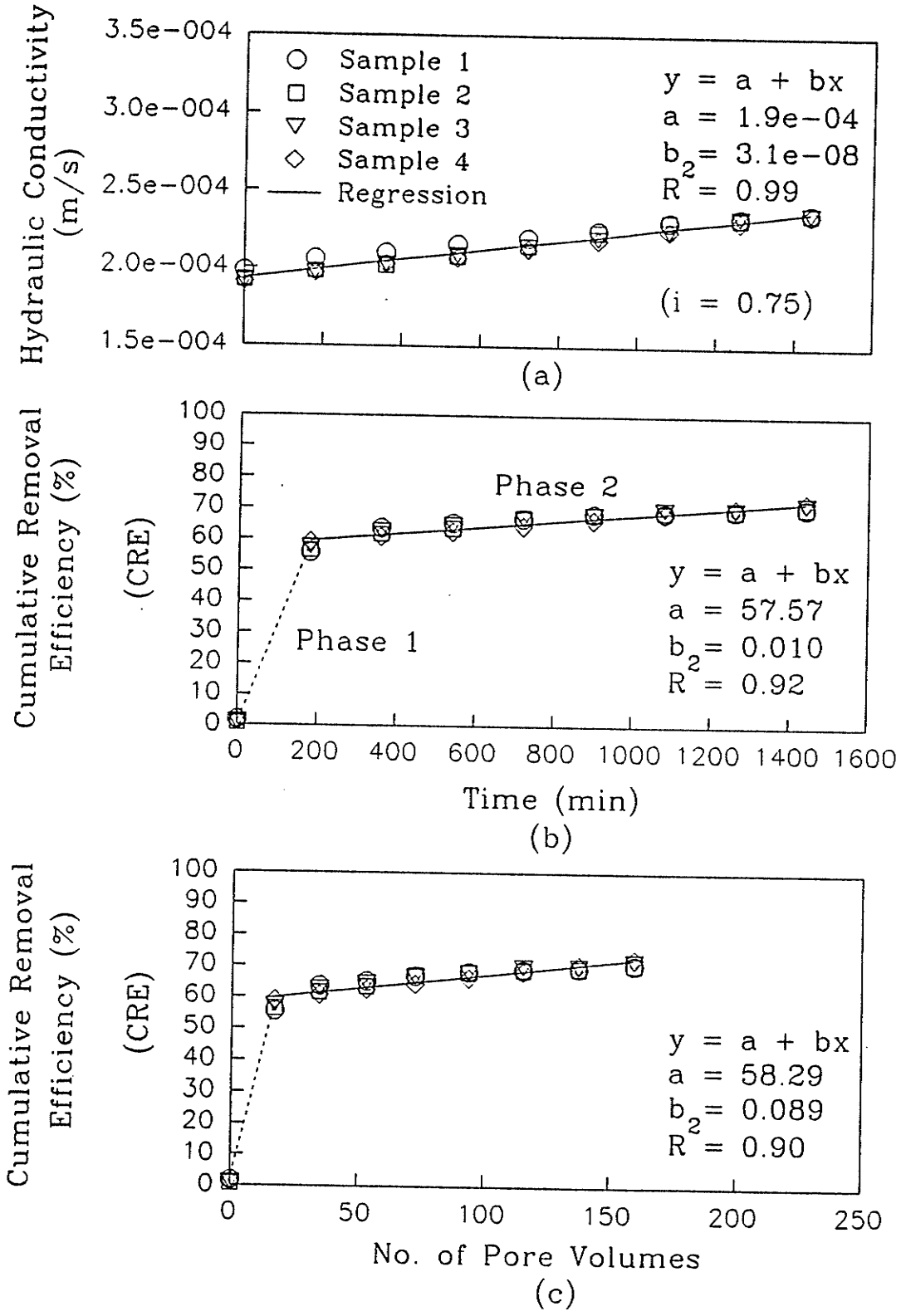


Figure 5.15 One day test results: mesh #60 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of Pore Volumes.

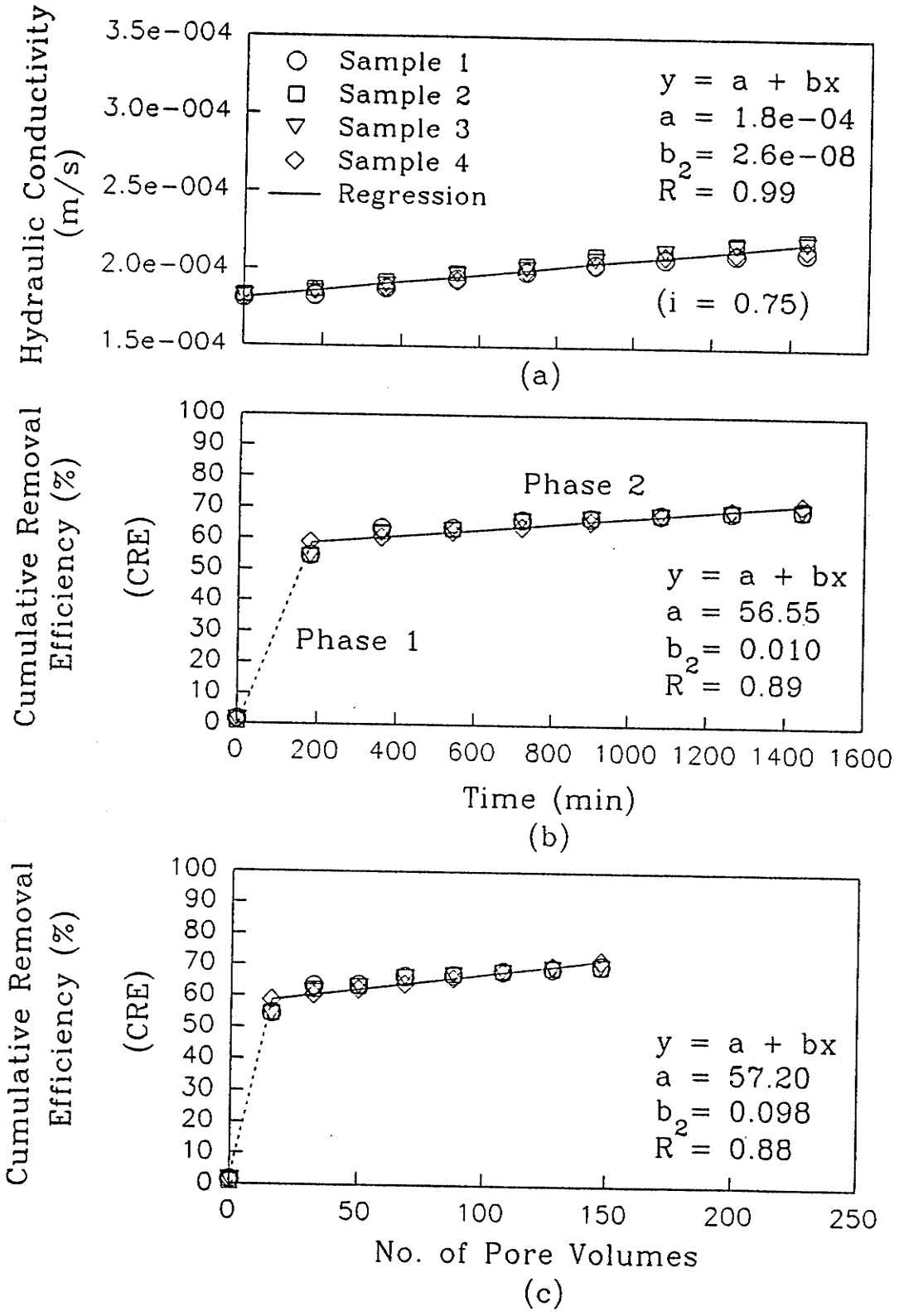


Figure 5.16 One day test results: mesh #80 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of Pore Volumes.

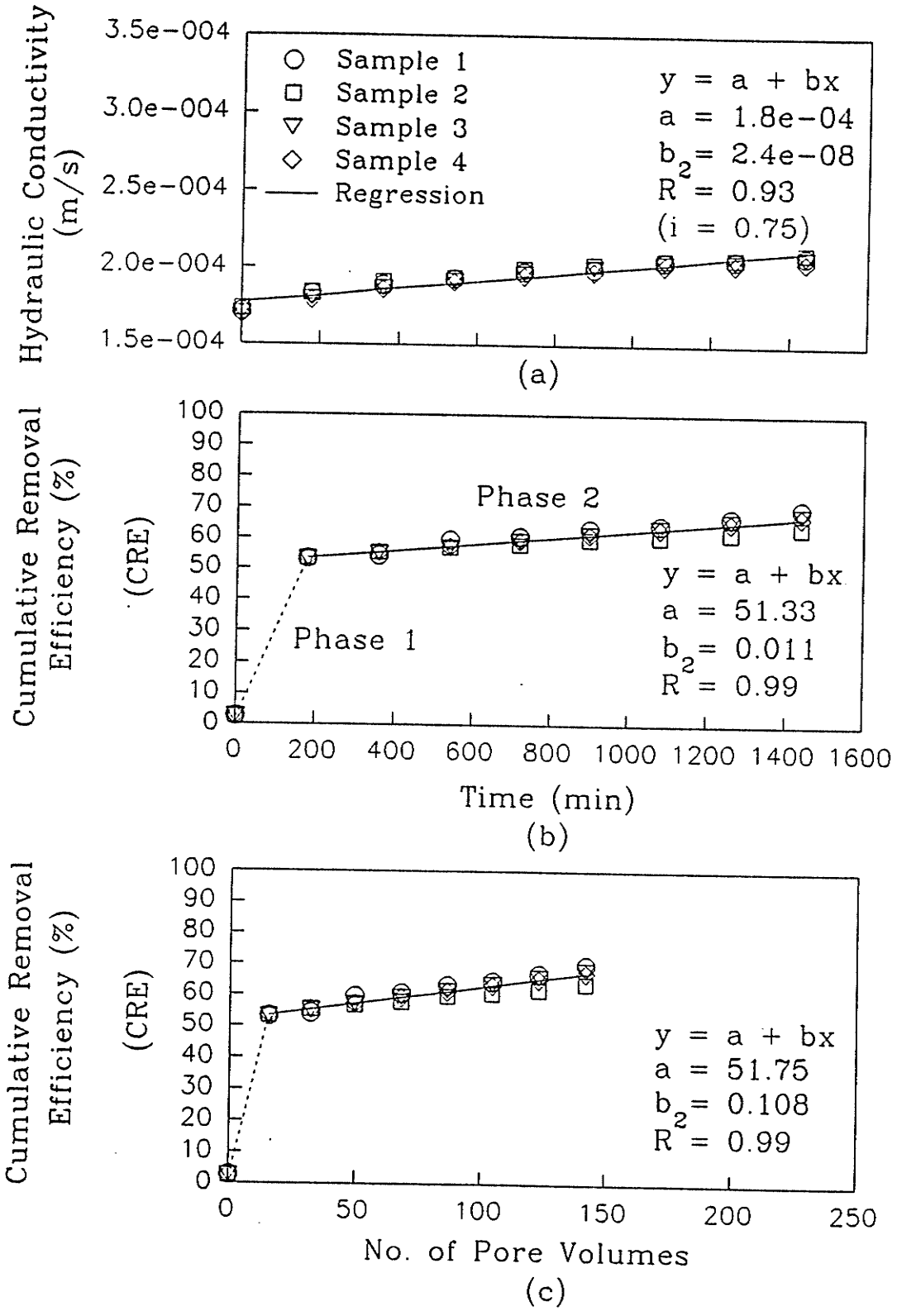


Figure 5.17 One day test results: mesh #100 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of Pore Volumes.

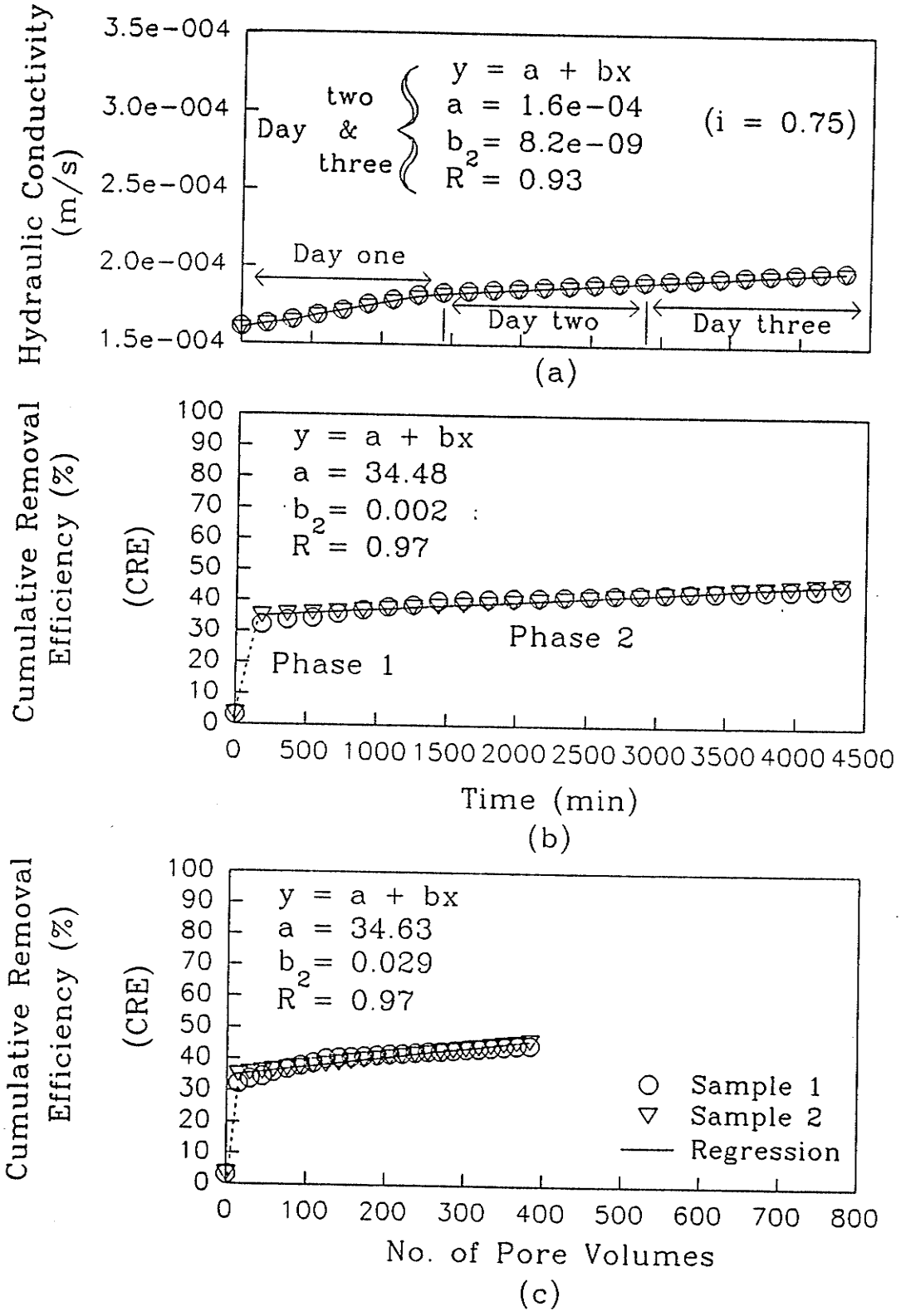


Figure 5.18 Three days test results: mesh #60 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No of pores. volumes.

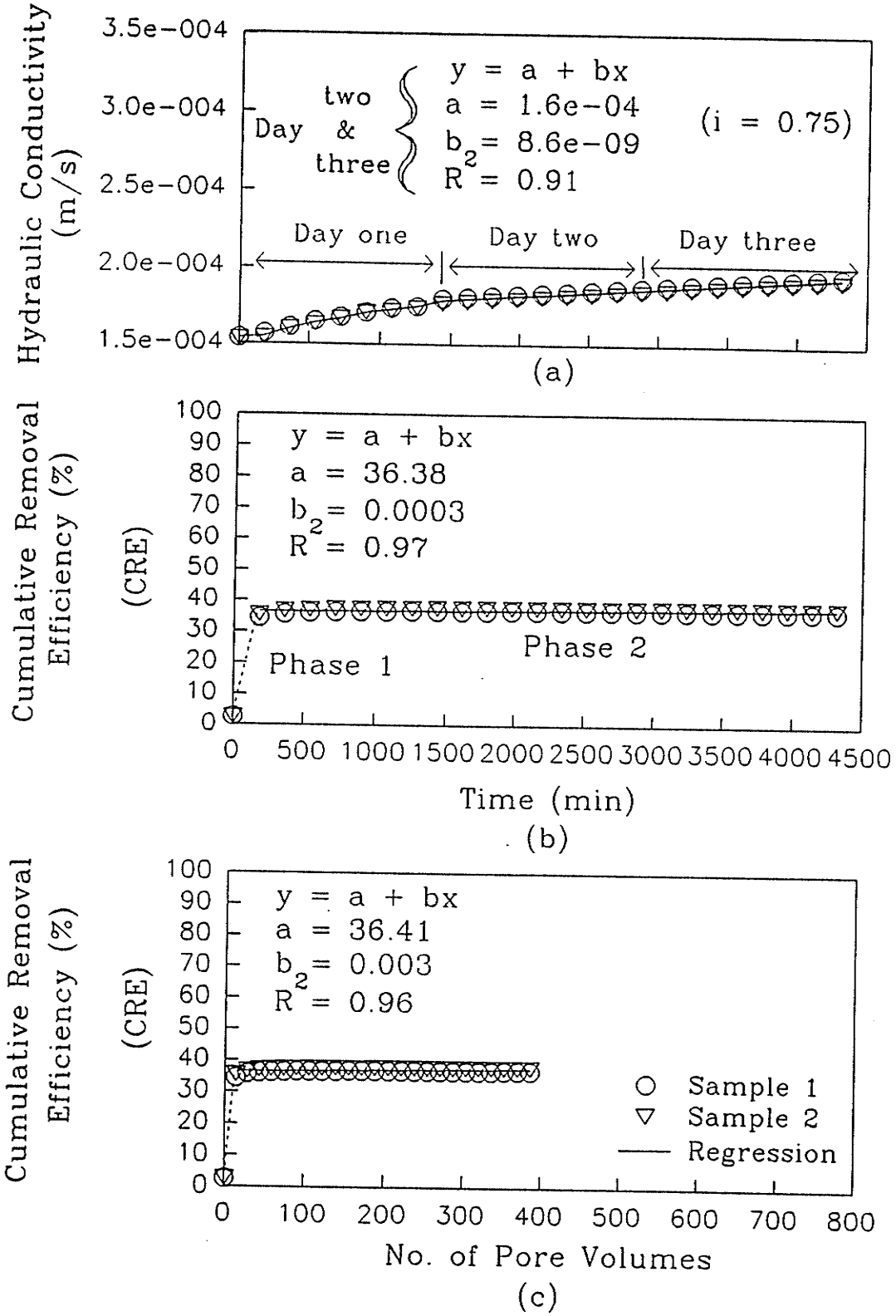


Figure 5.19 Three days test results: mesh #80 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No of pores. volumes.

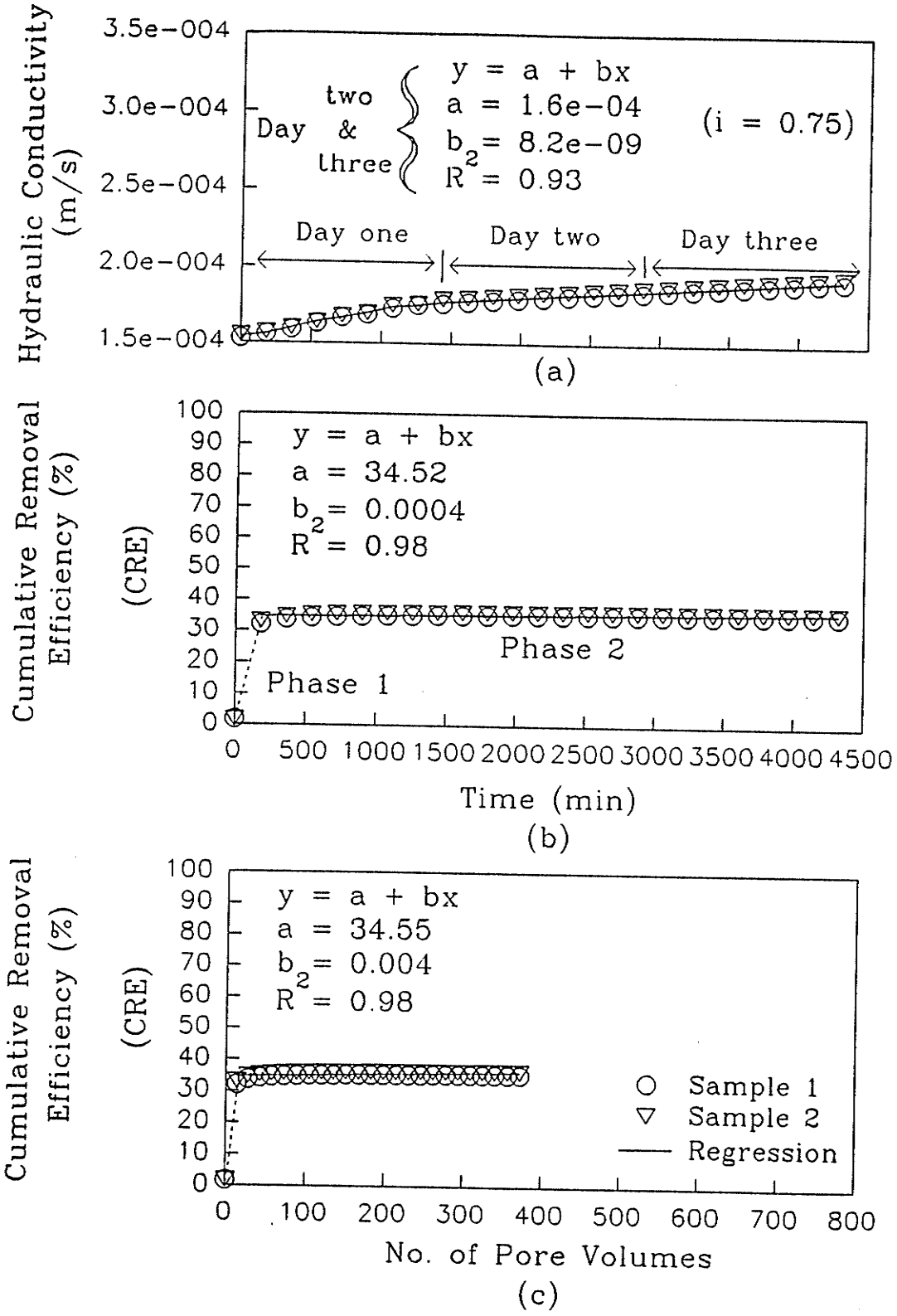


Figure 5.20 Three days test results: mesh #100 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No of pores volumes.

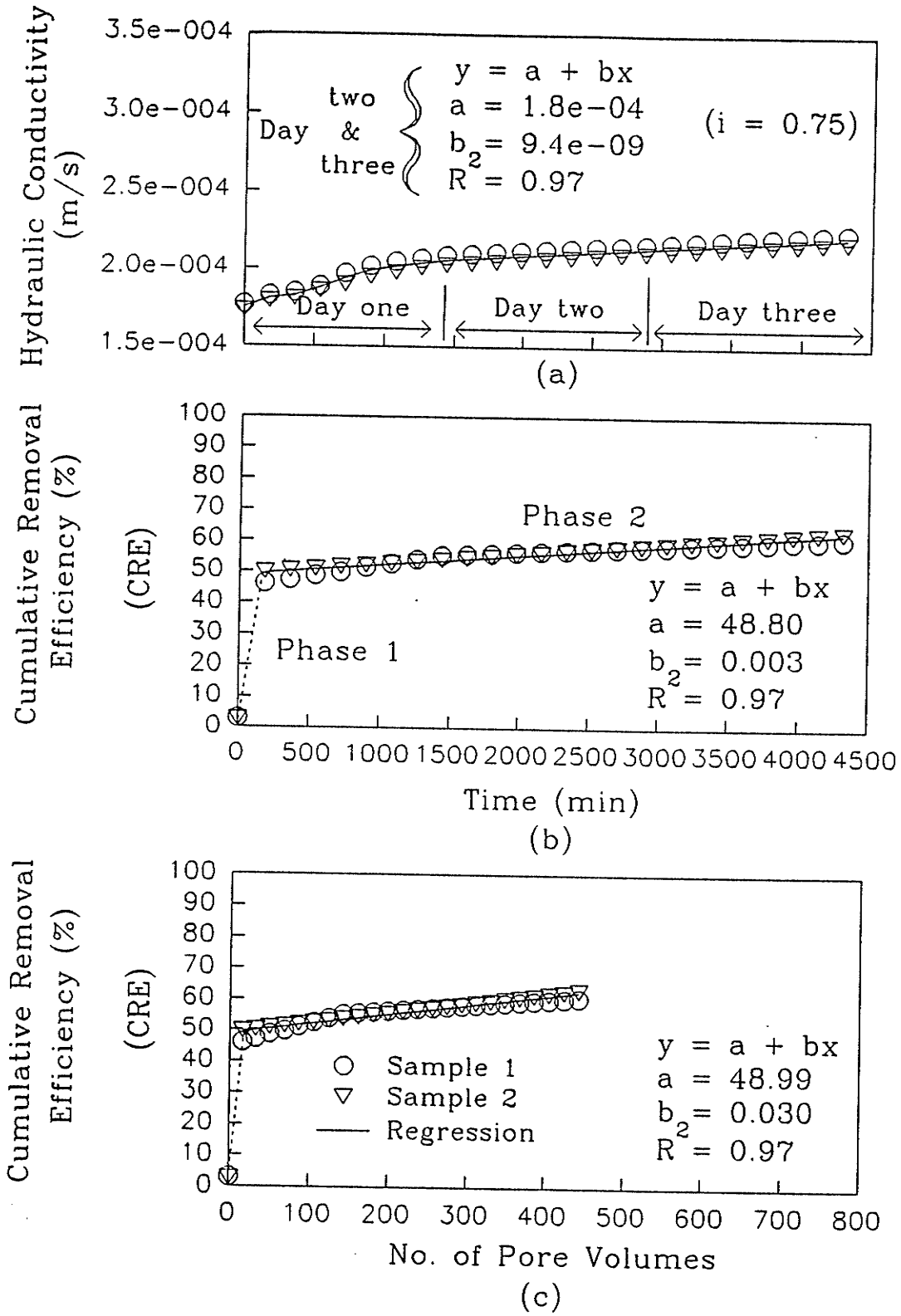


Figure 5.21 Three days test results: mesh #60 contaminated sand, water at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No of pores. volumes.

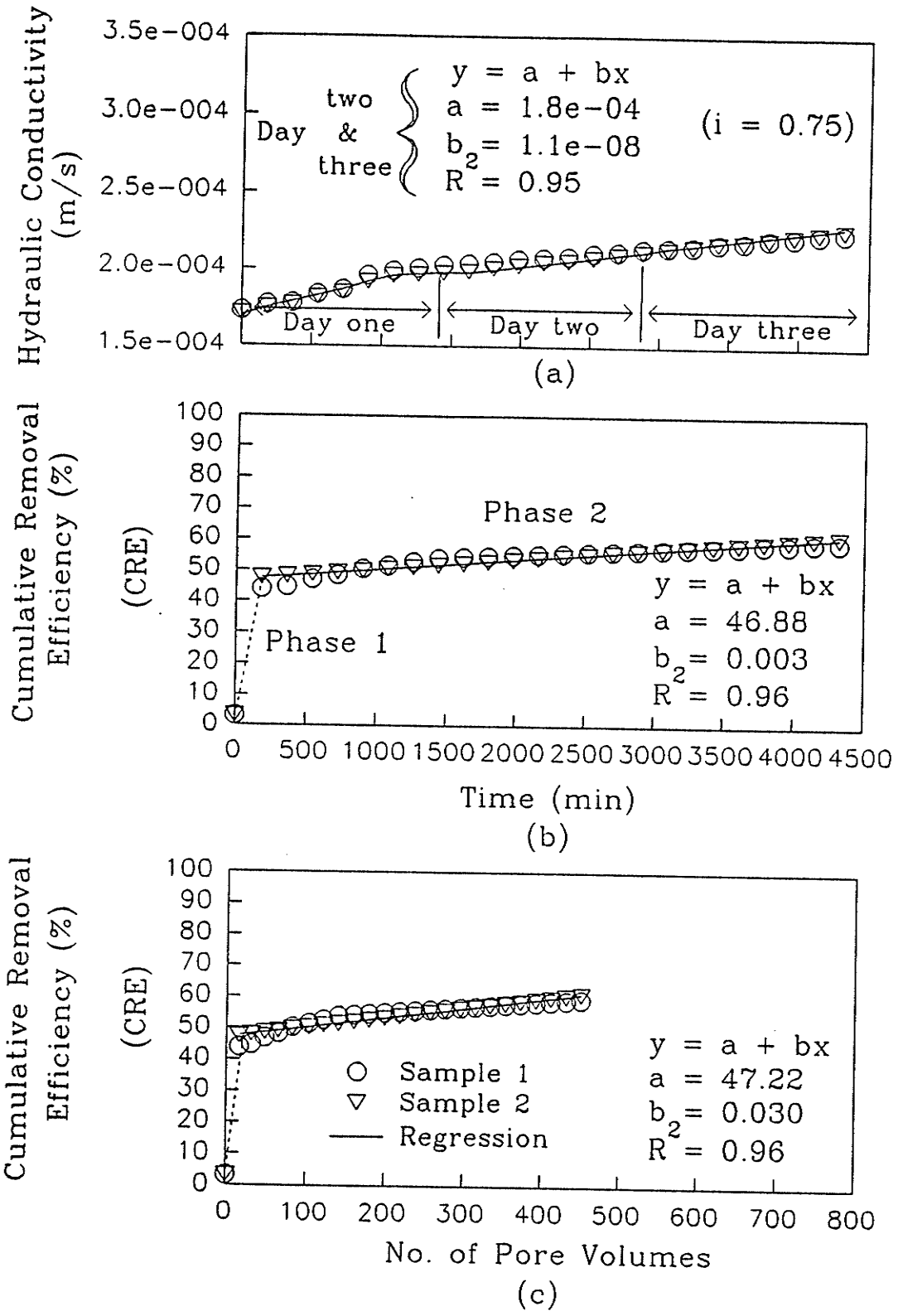


Figure 5.22 Three days test results: mesh #80 contaminated sand, water at 22°C,(a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

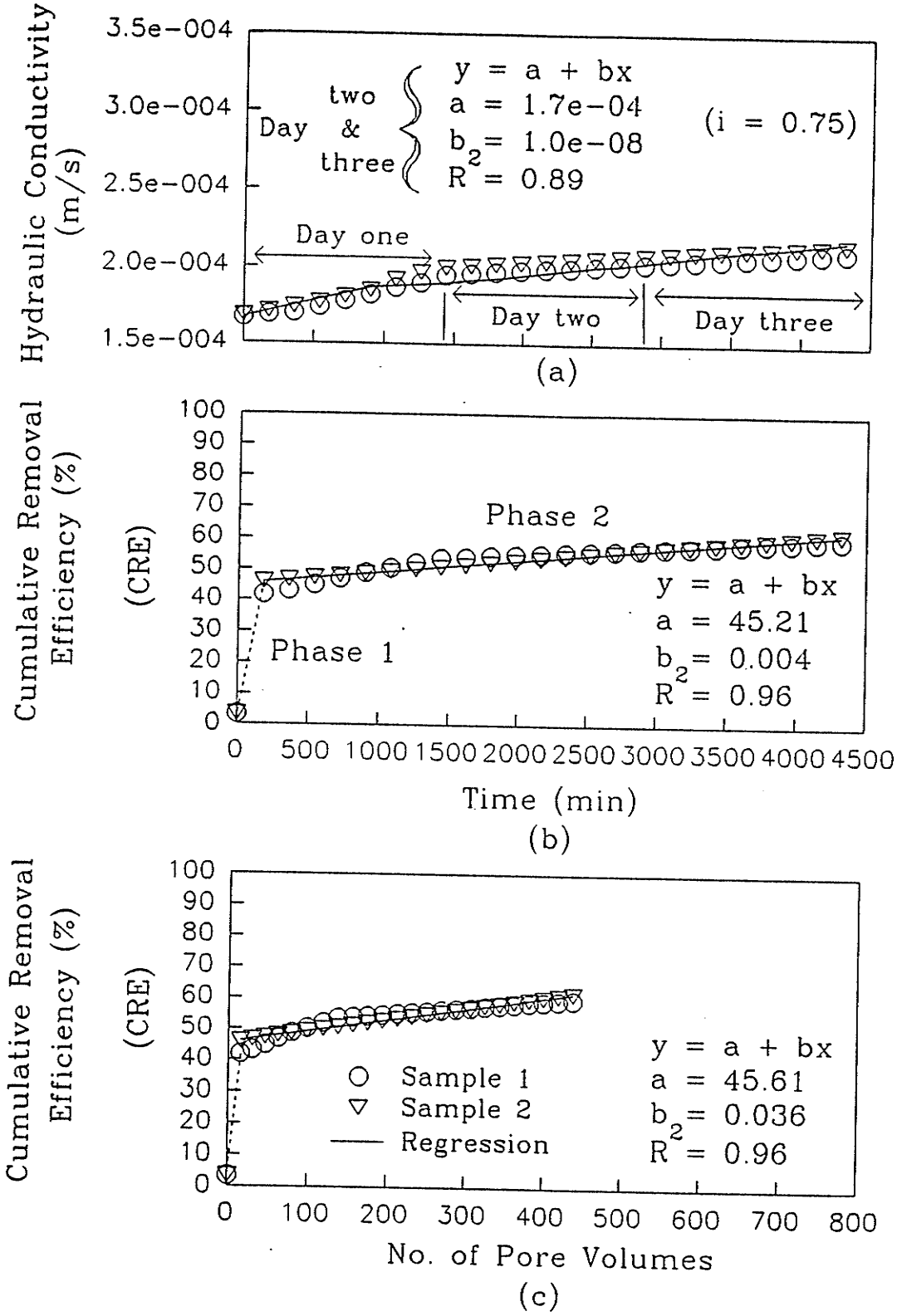


Figure 5.23 Three days test results: mesh #100 contaminated sand, water at 22°C,(a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

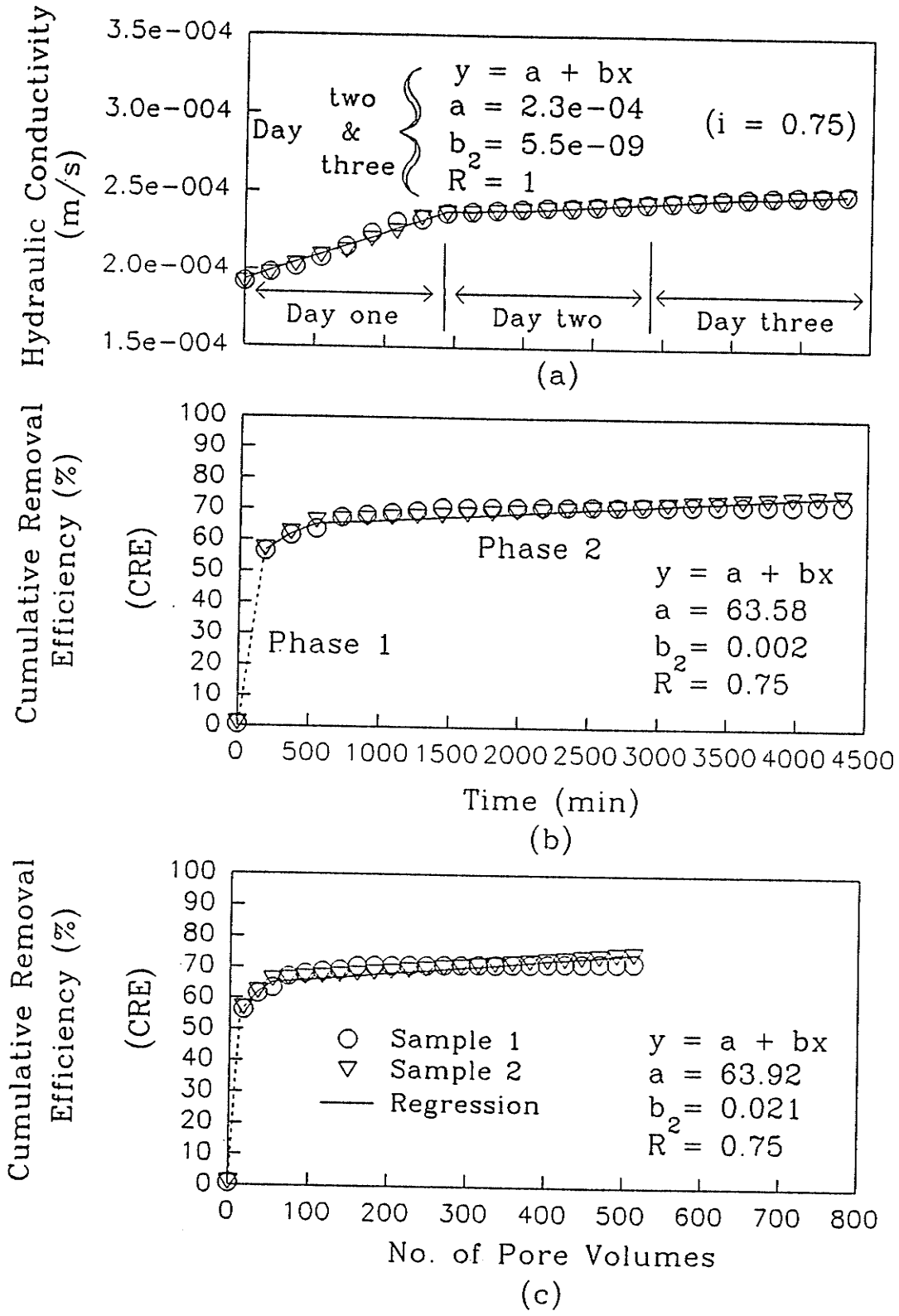


Figure 5.24 Three days test results: mesh #60 contaminated sand, water at 50°C (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

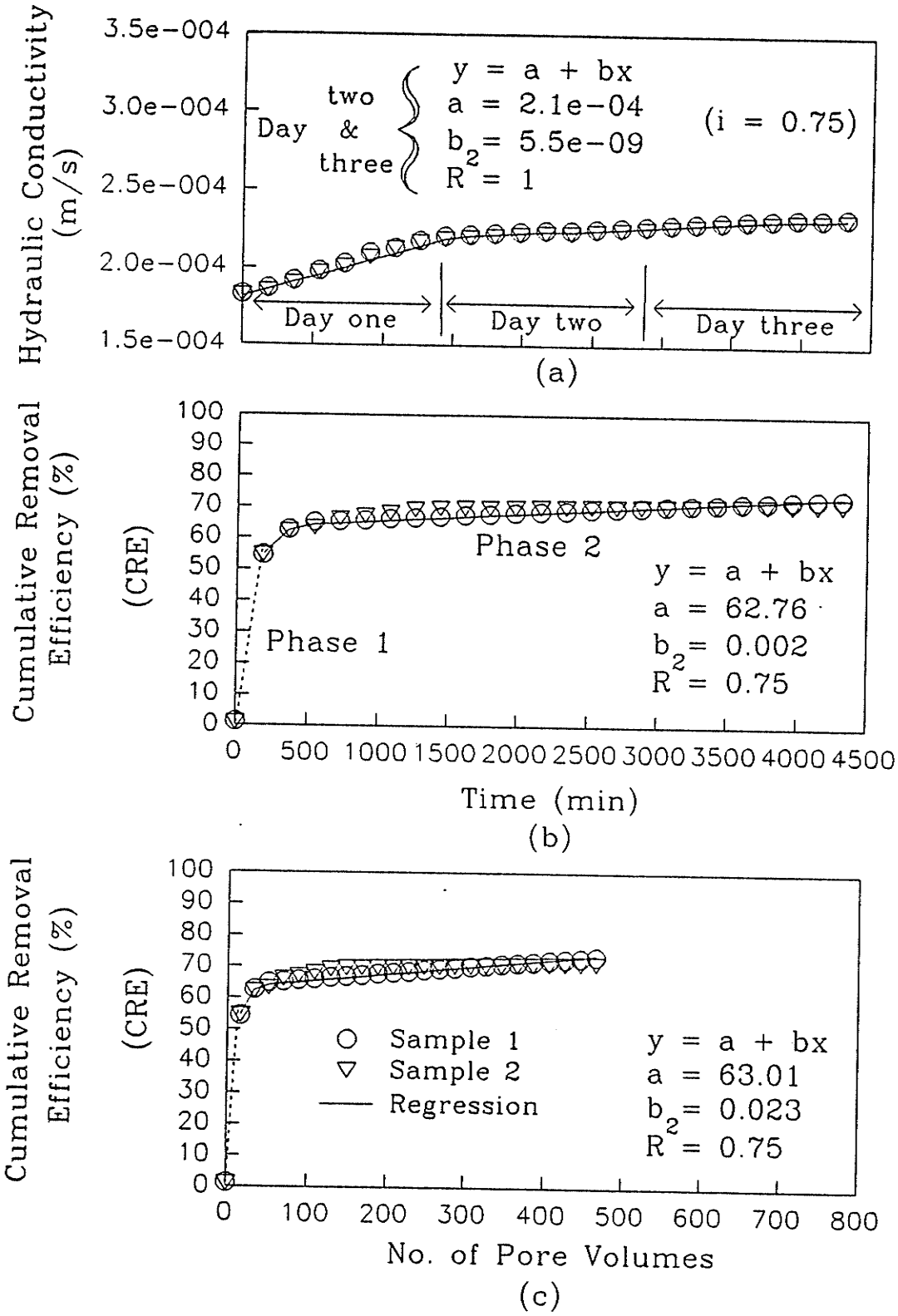


Figure 5.25 Three days test results: mesh #80 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

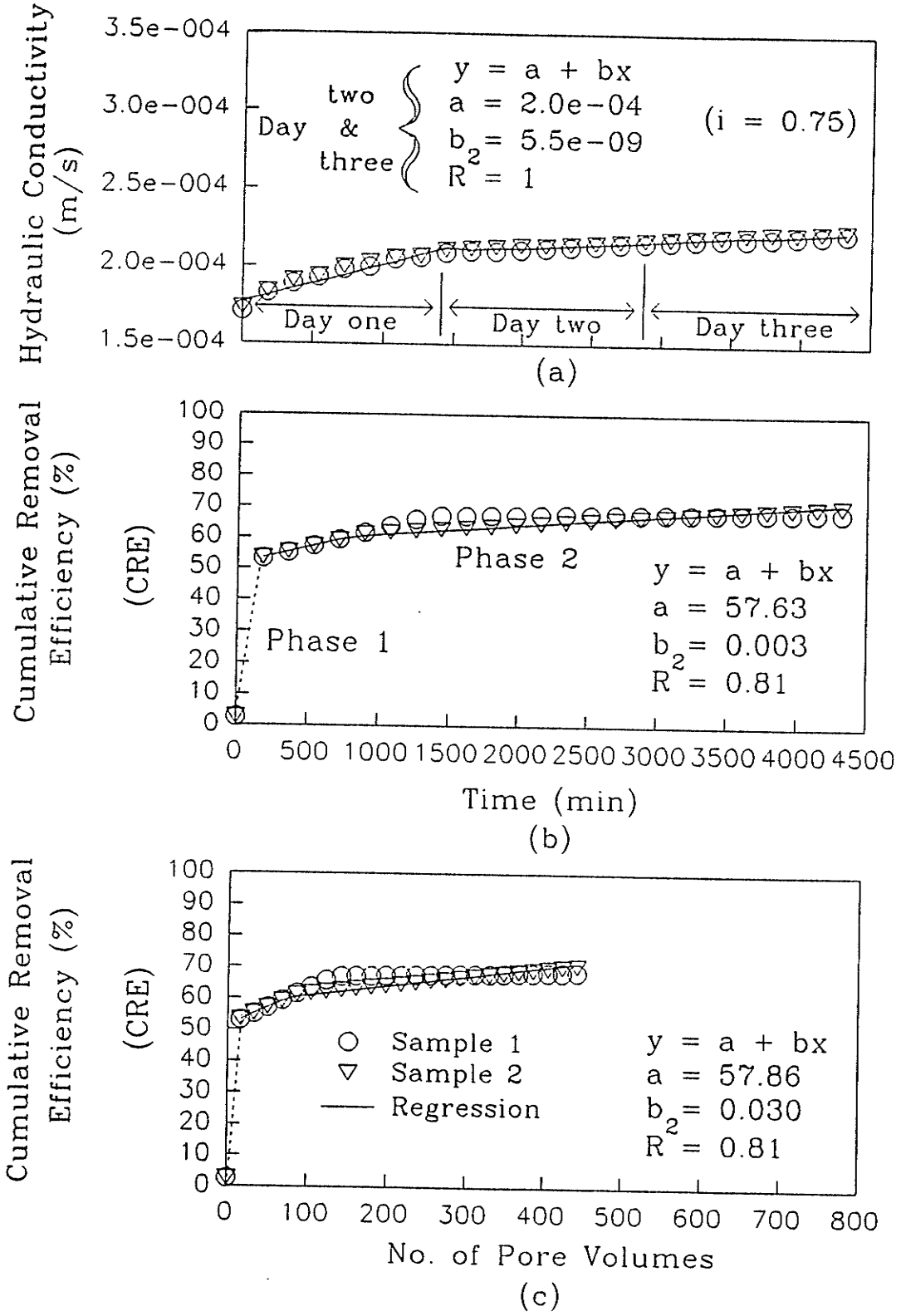


Figure 5.26 Three days test results: mesh #100 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

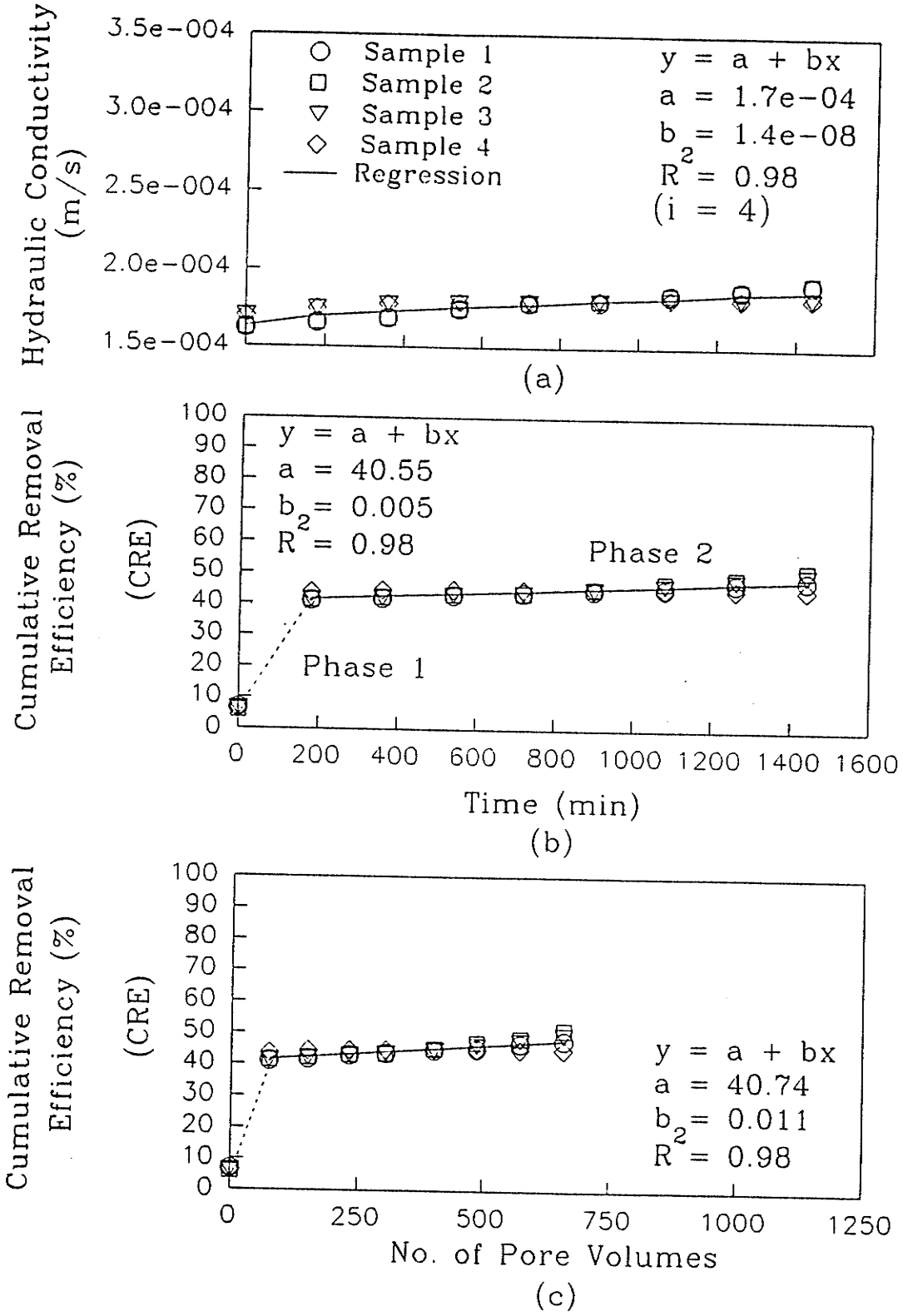


Figure 5.27 One day test results: mesh #60 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

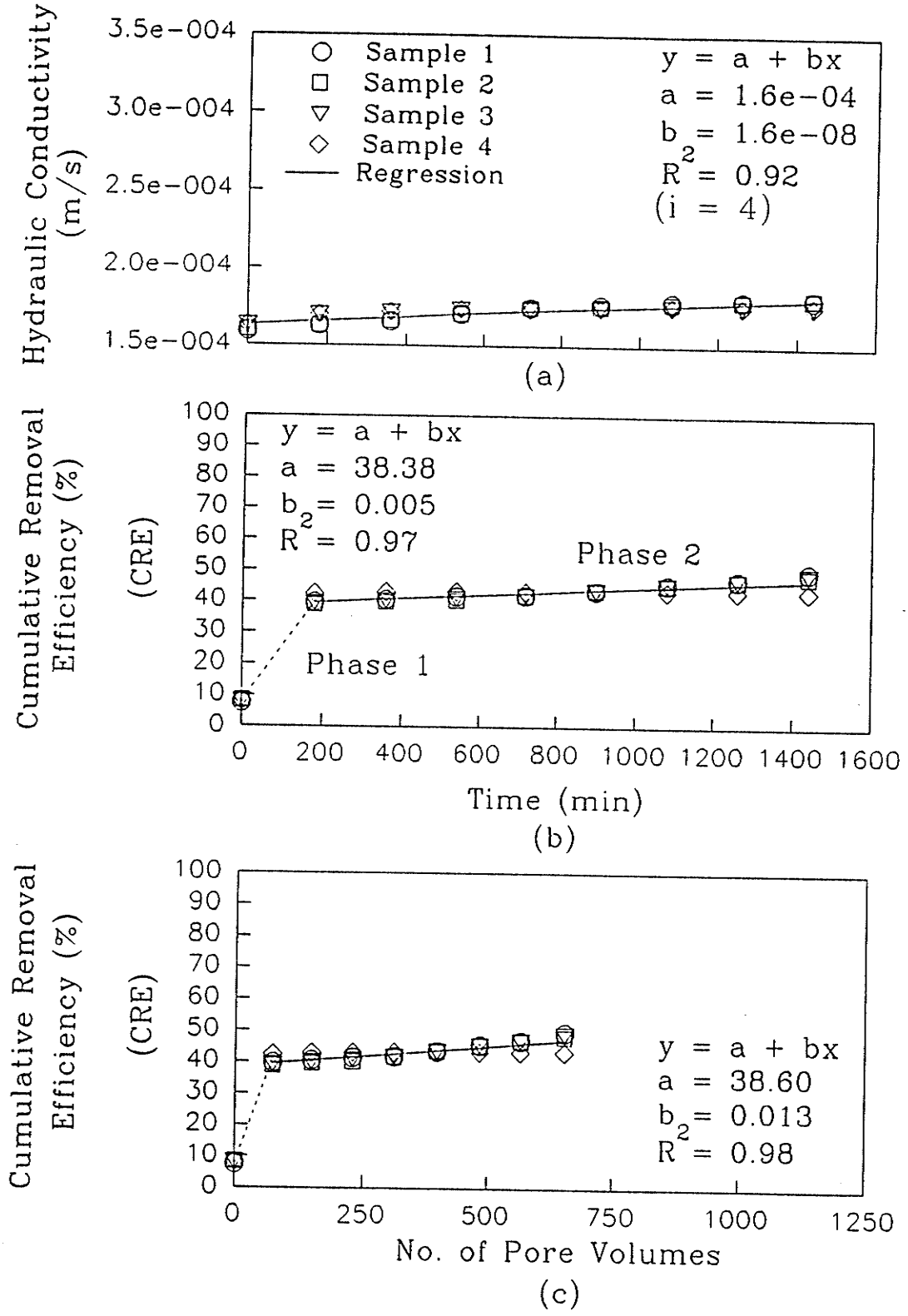


Figure 5.28 One day test results: mesh #80 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

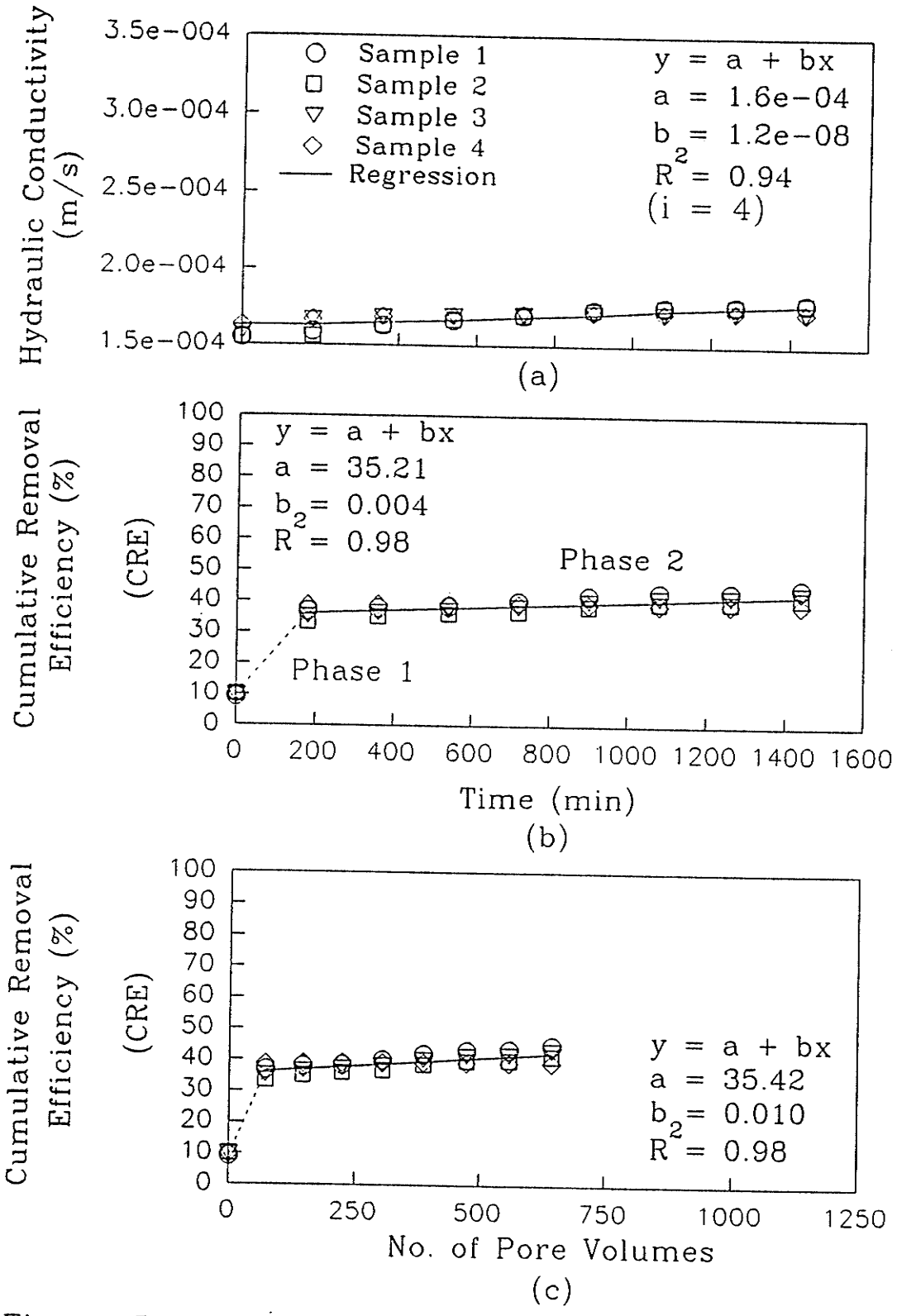


Figure 5.29 One day test results: mesh #100 contaminated sand, water at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

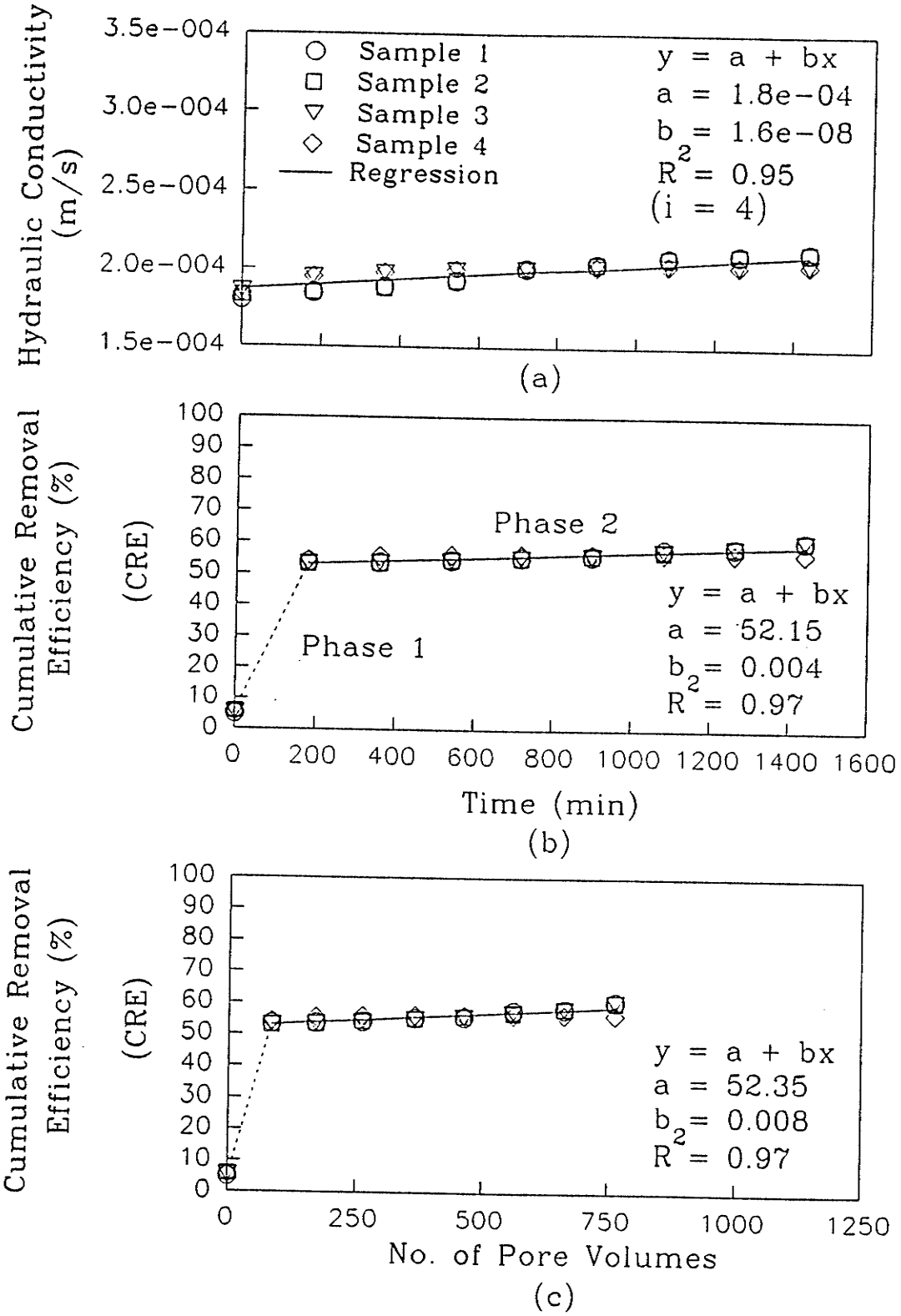


Figure 5.30 One day test results: mesh #60 contaminated sand, water at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

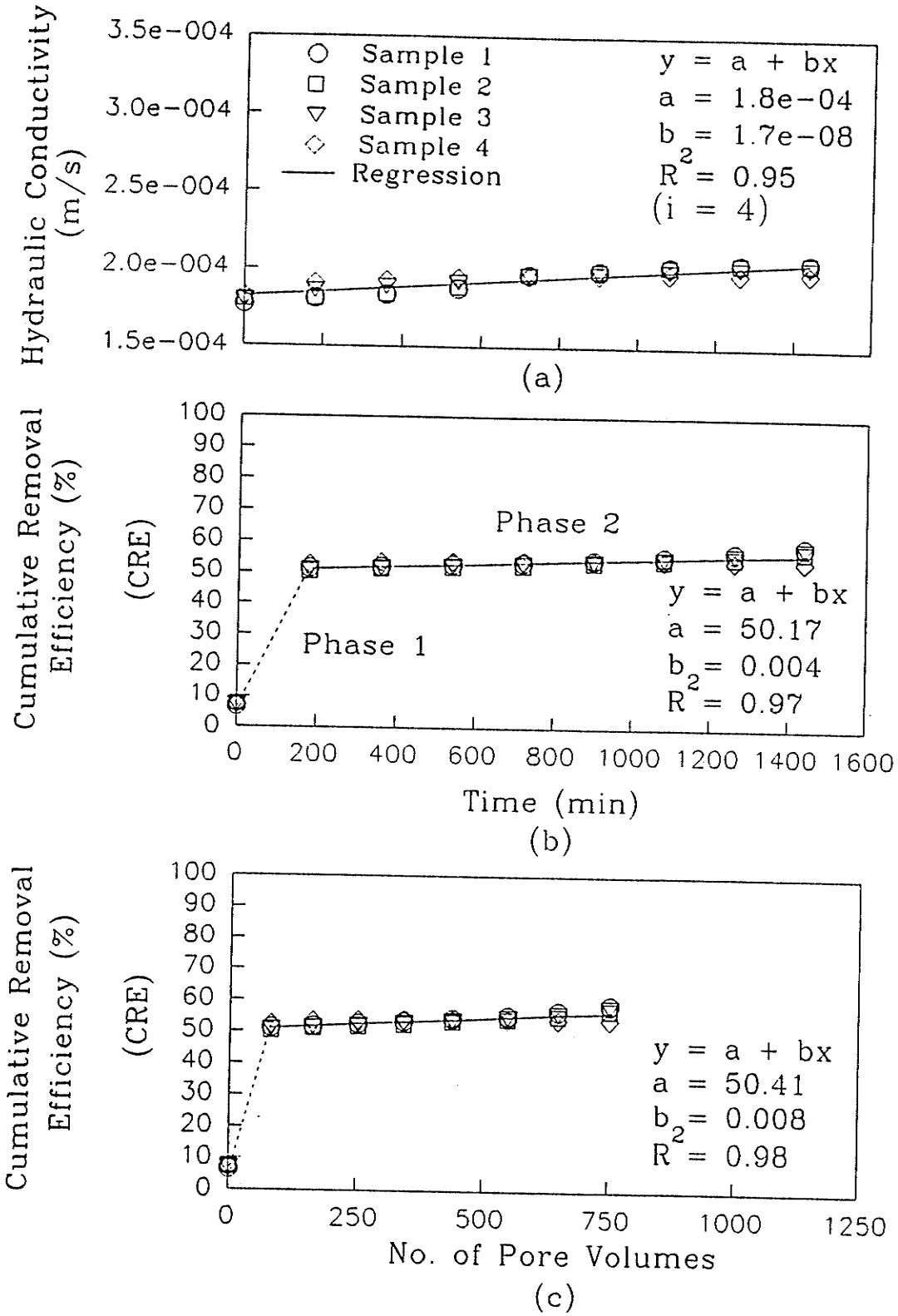


Figure 5.31 One day test results: mesh #80 contaminated sand, water at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

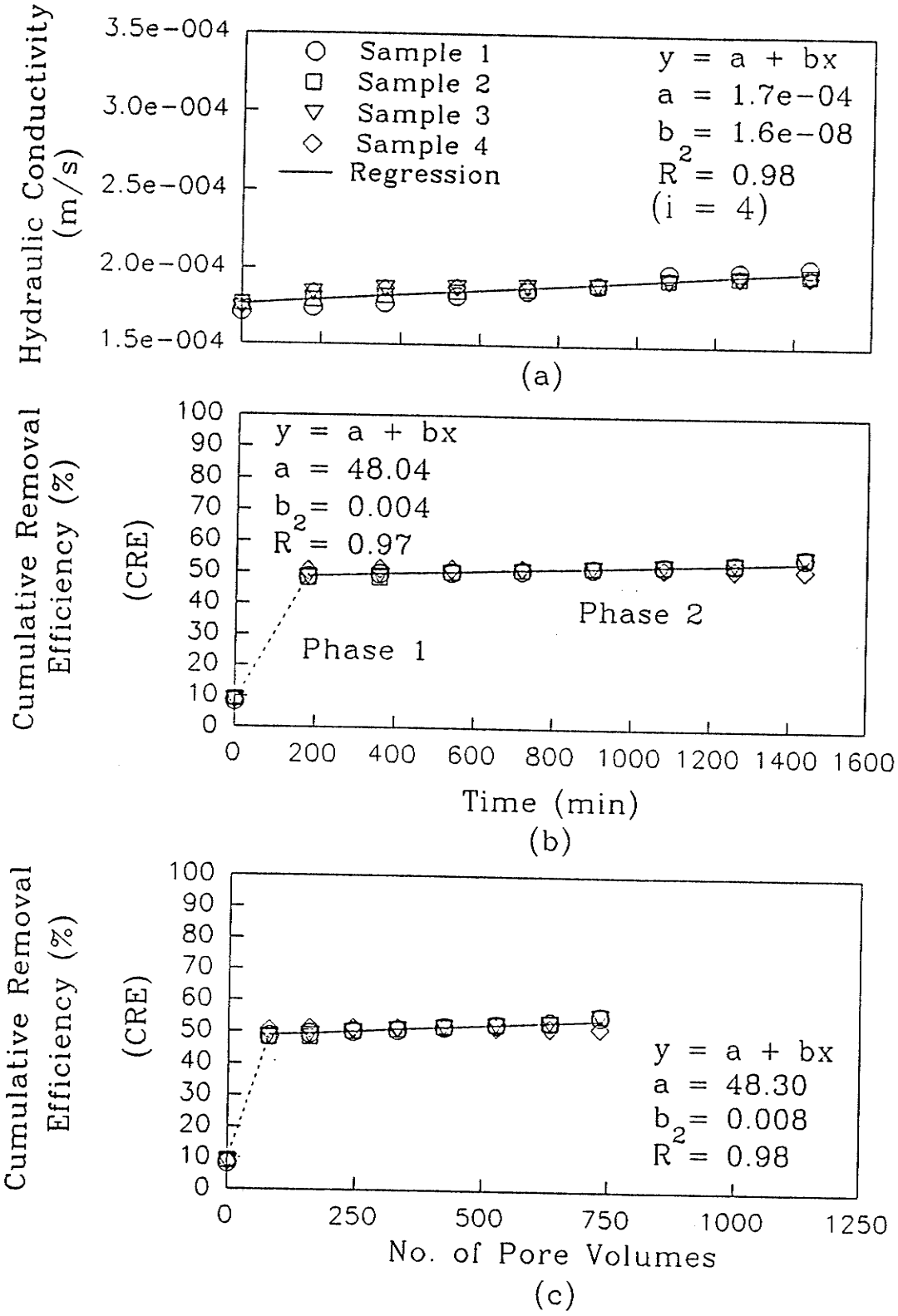


Figure 5.32 One day test results: mesh #100 contaminated sand, water at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

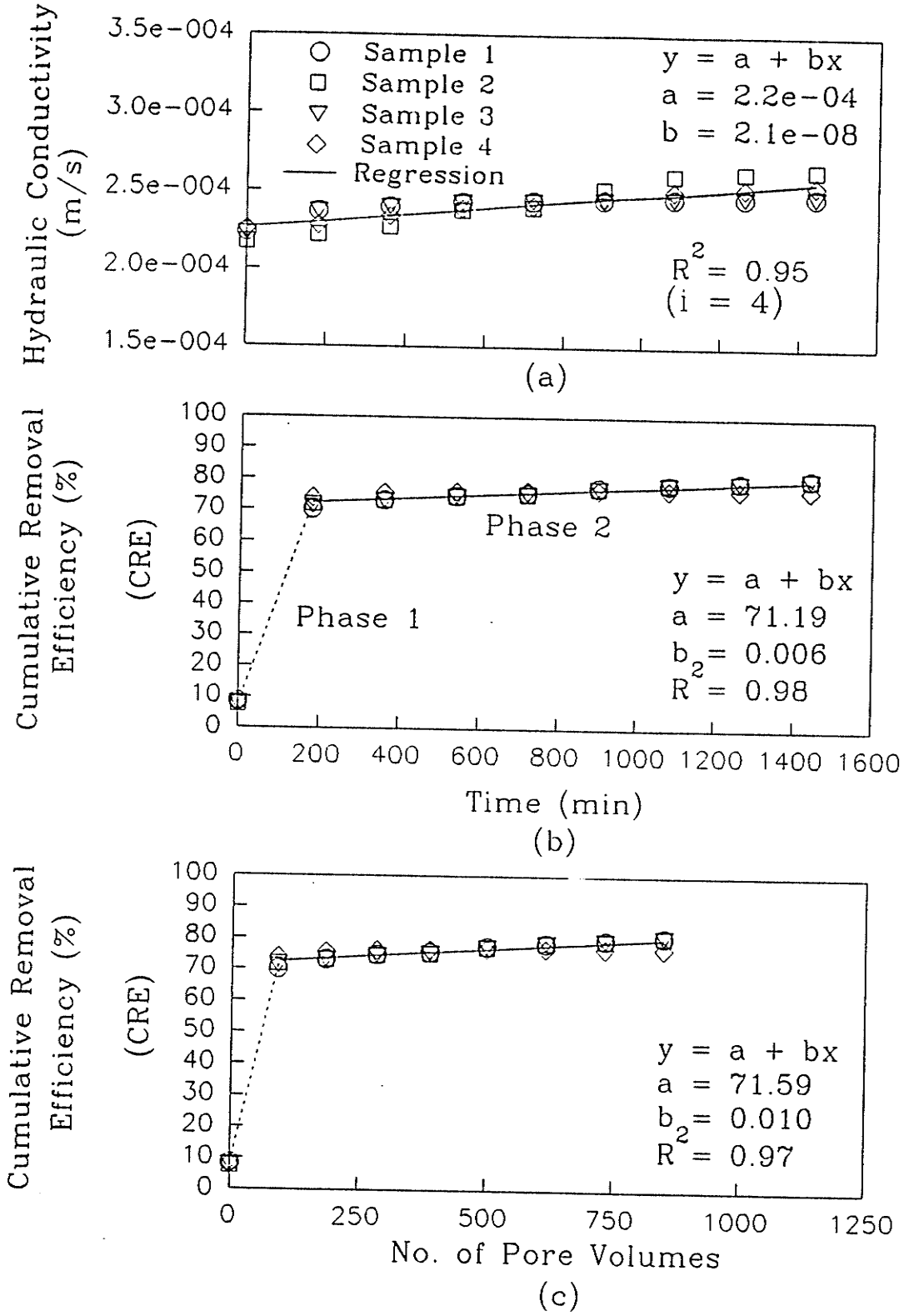


Figure 5.33 One day test results: mesh #60 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

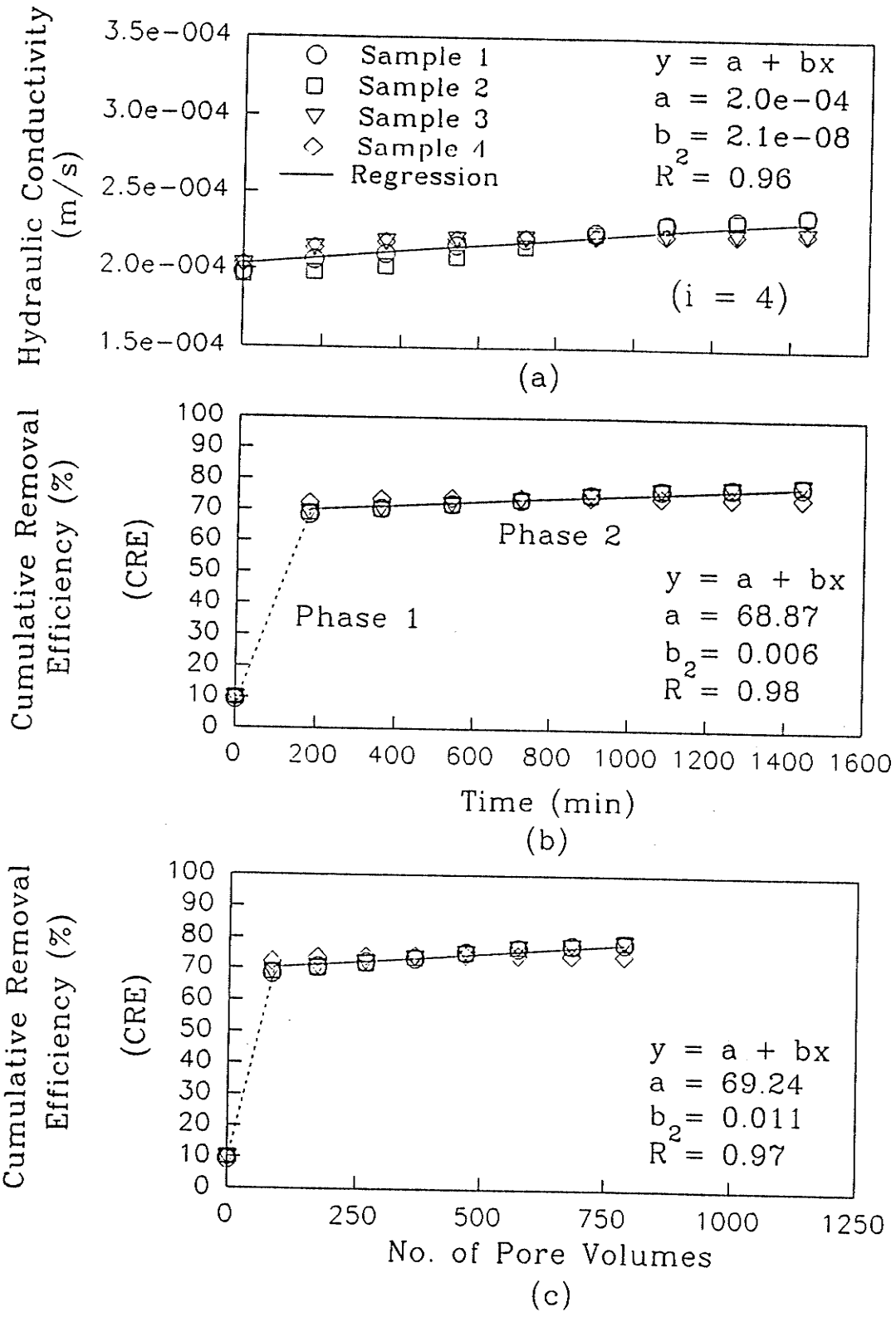


Figure 5.34 One day test results: mesh #80 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

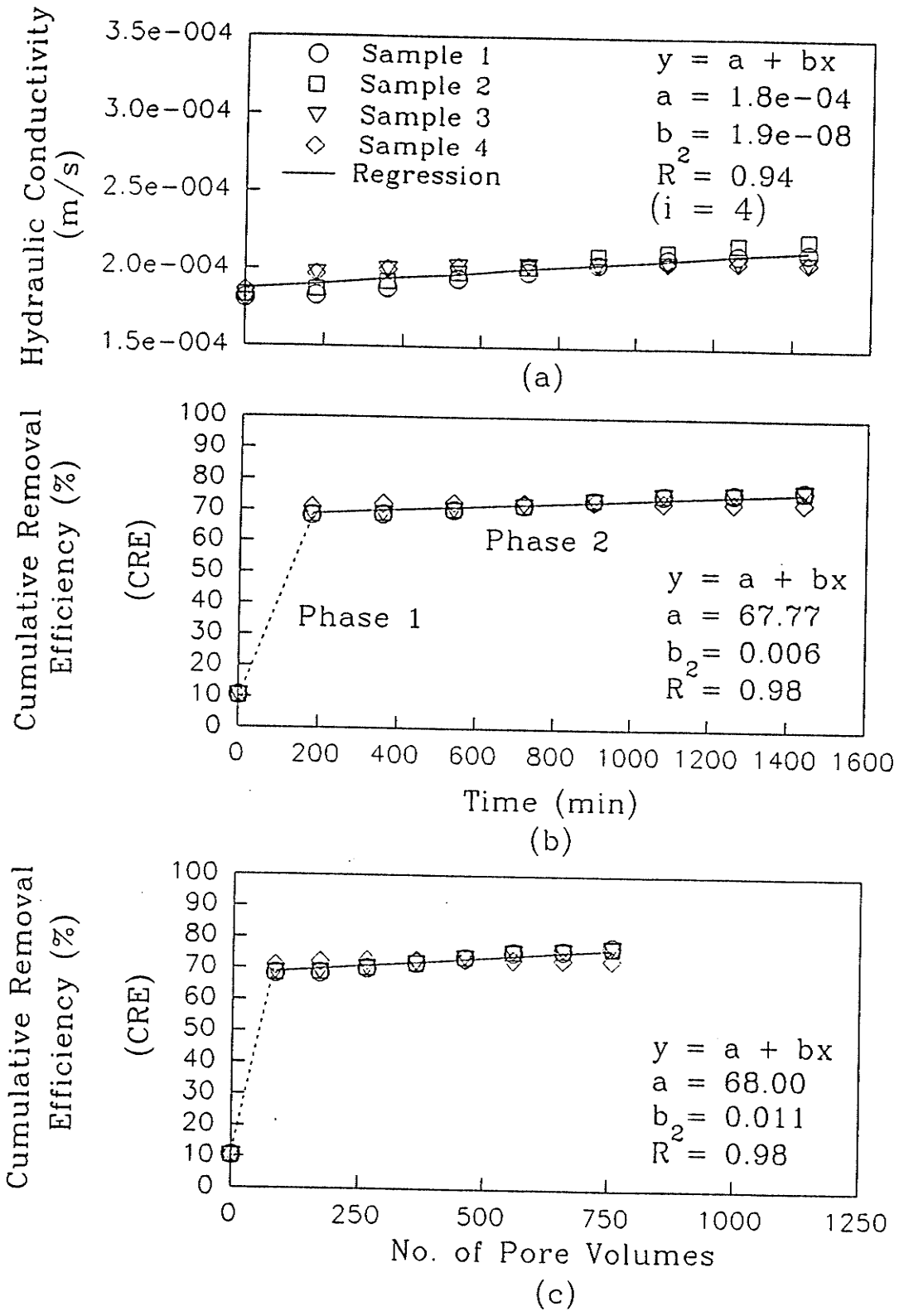


Figure 5.35 One day test results: mesh #100 contaminated sand, water at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

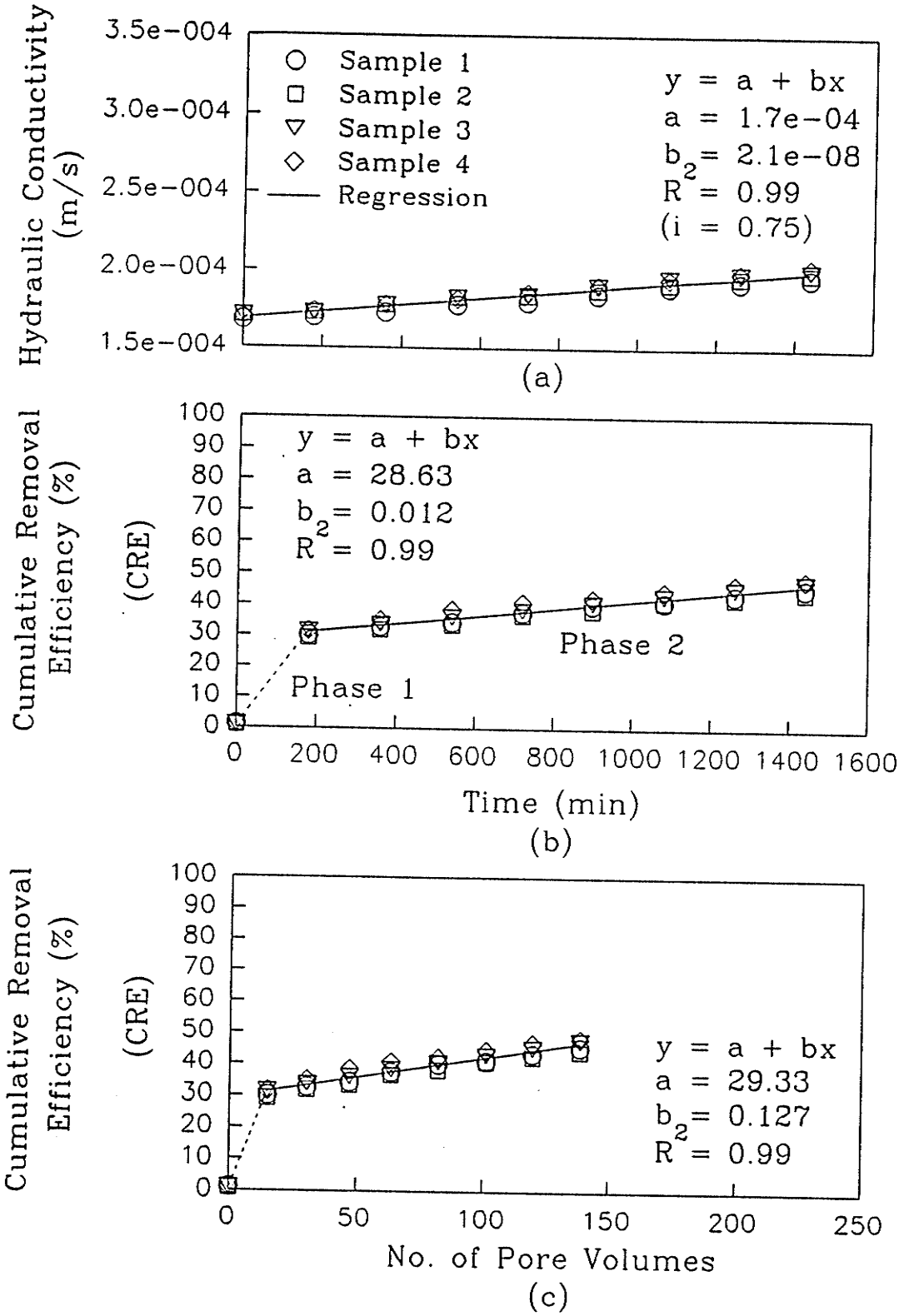


Figure 5.36 One day test results: mesh #60 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

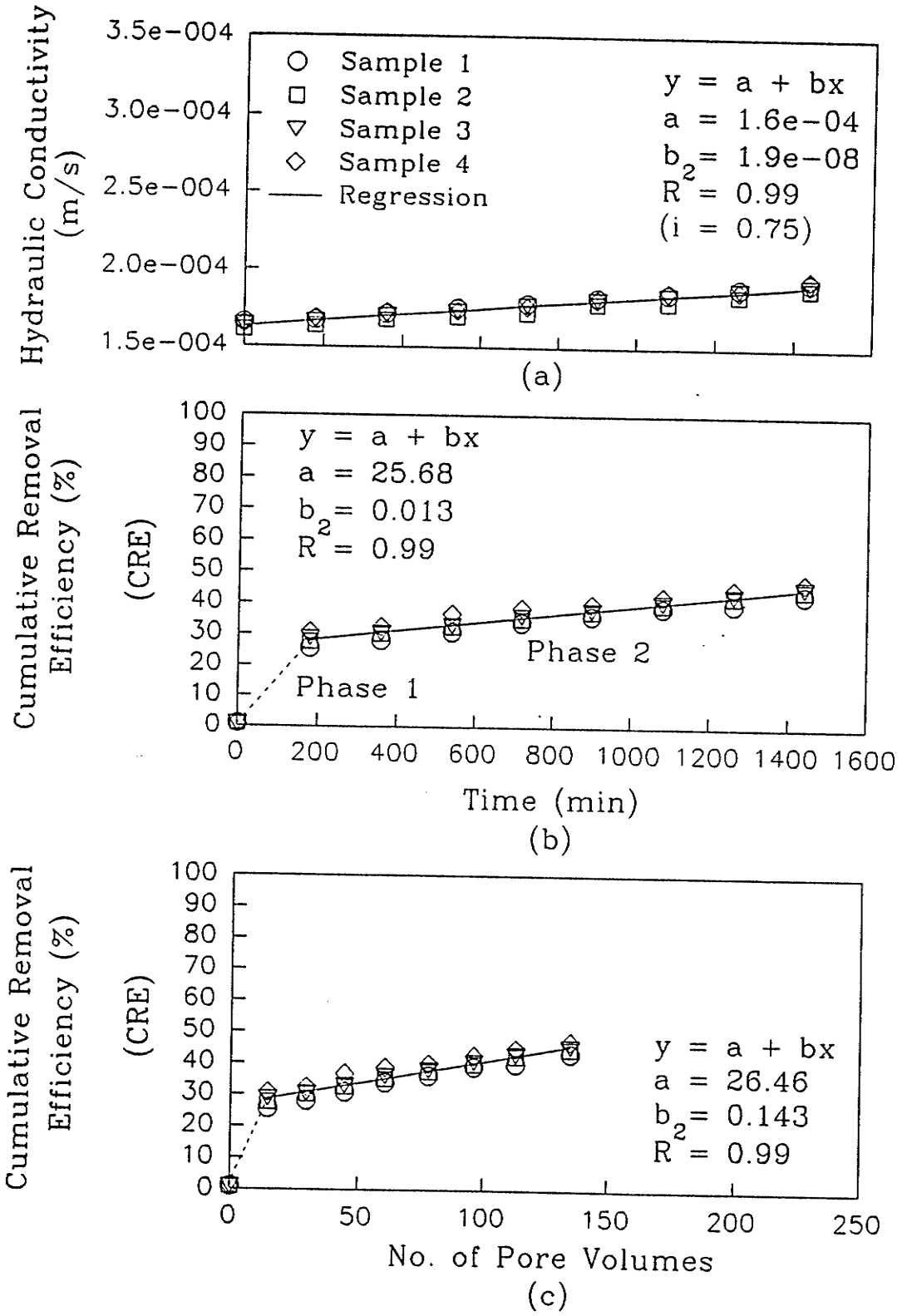


Figure 5.37 One day test results: mesh #80 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

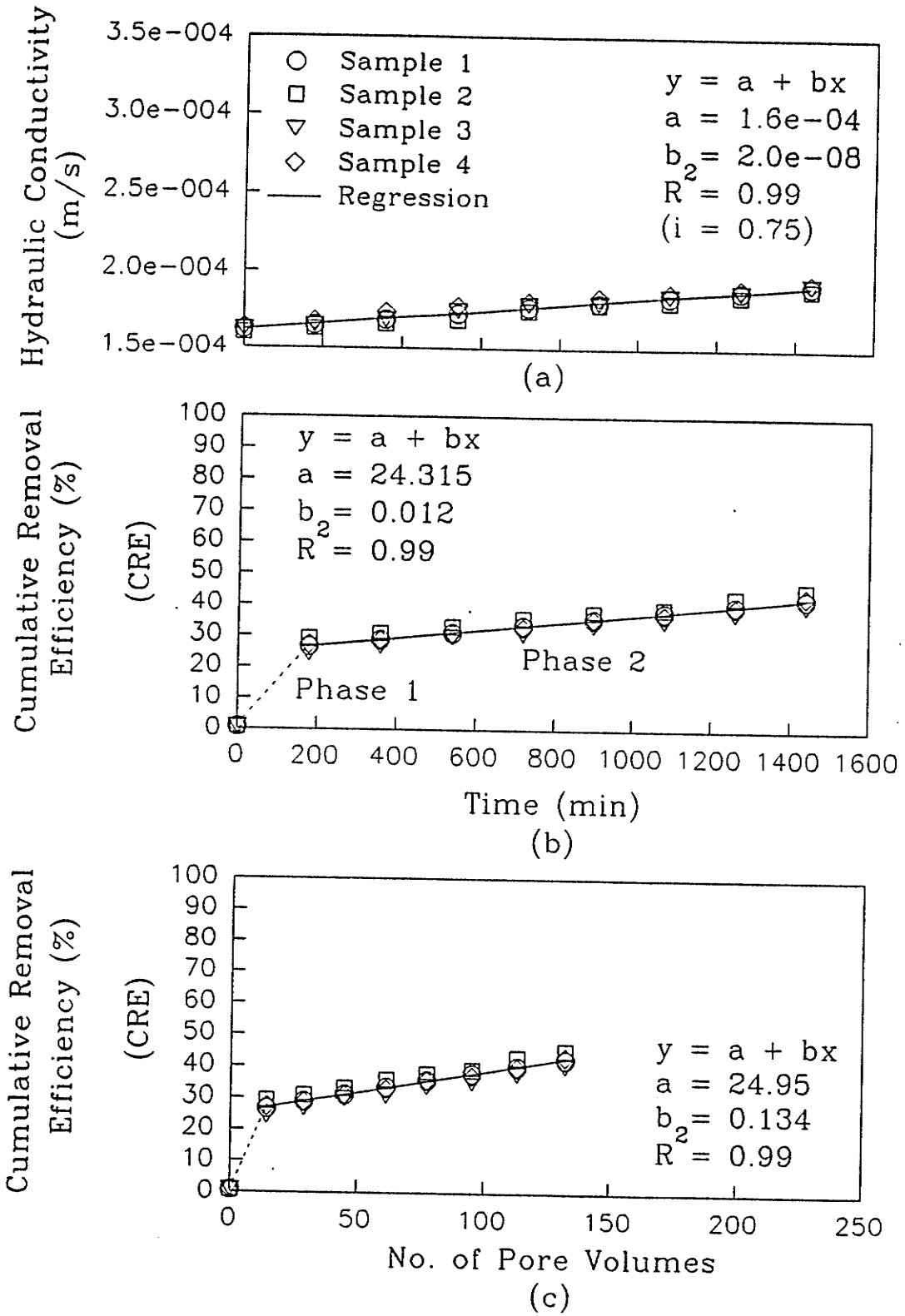


Figure 5.38 One day test results: mesh #100 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

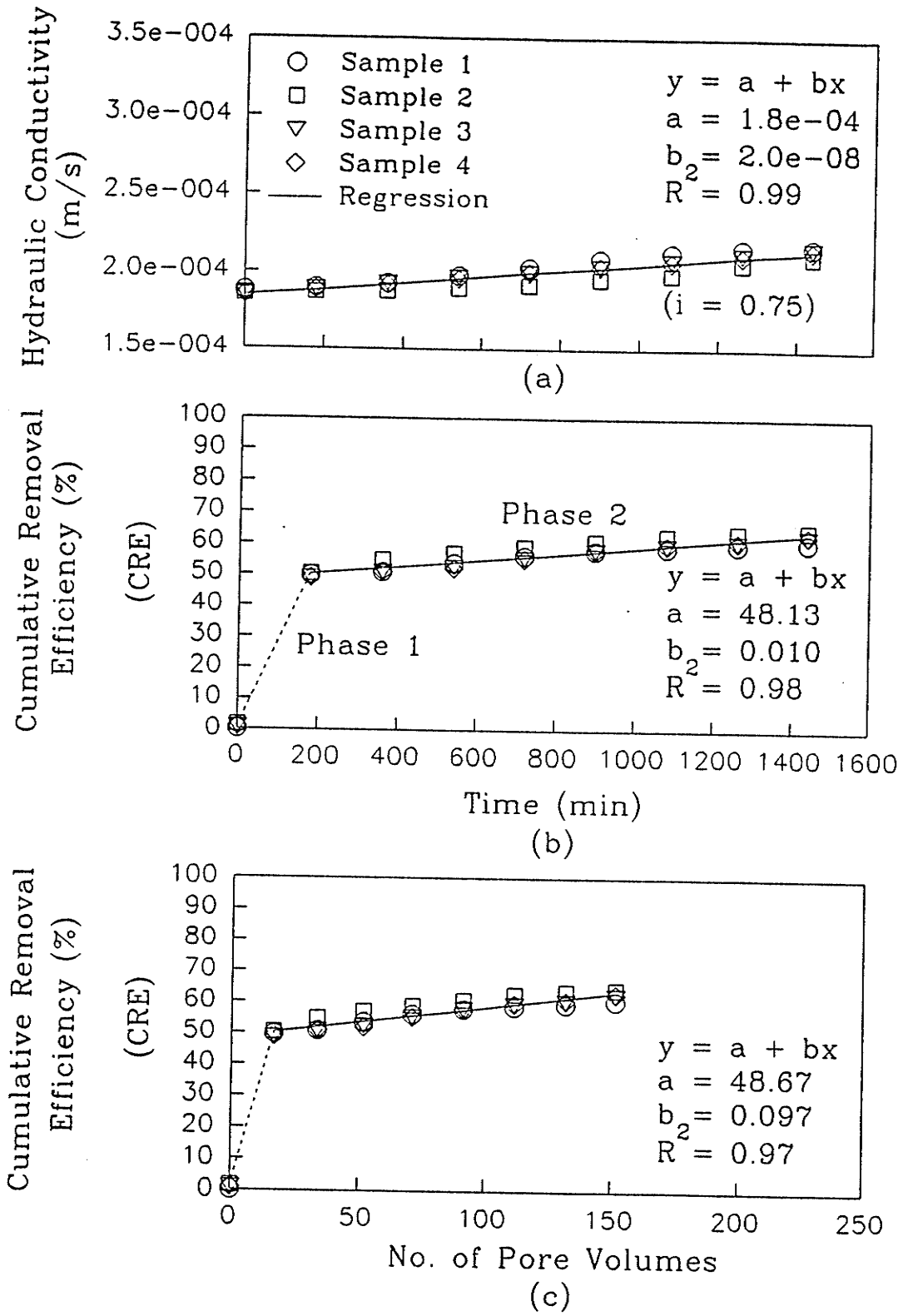


Figure 5.39 One day test results: mesh #60 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

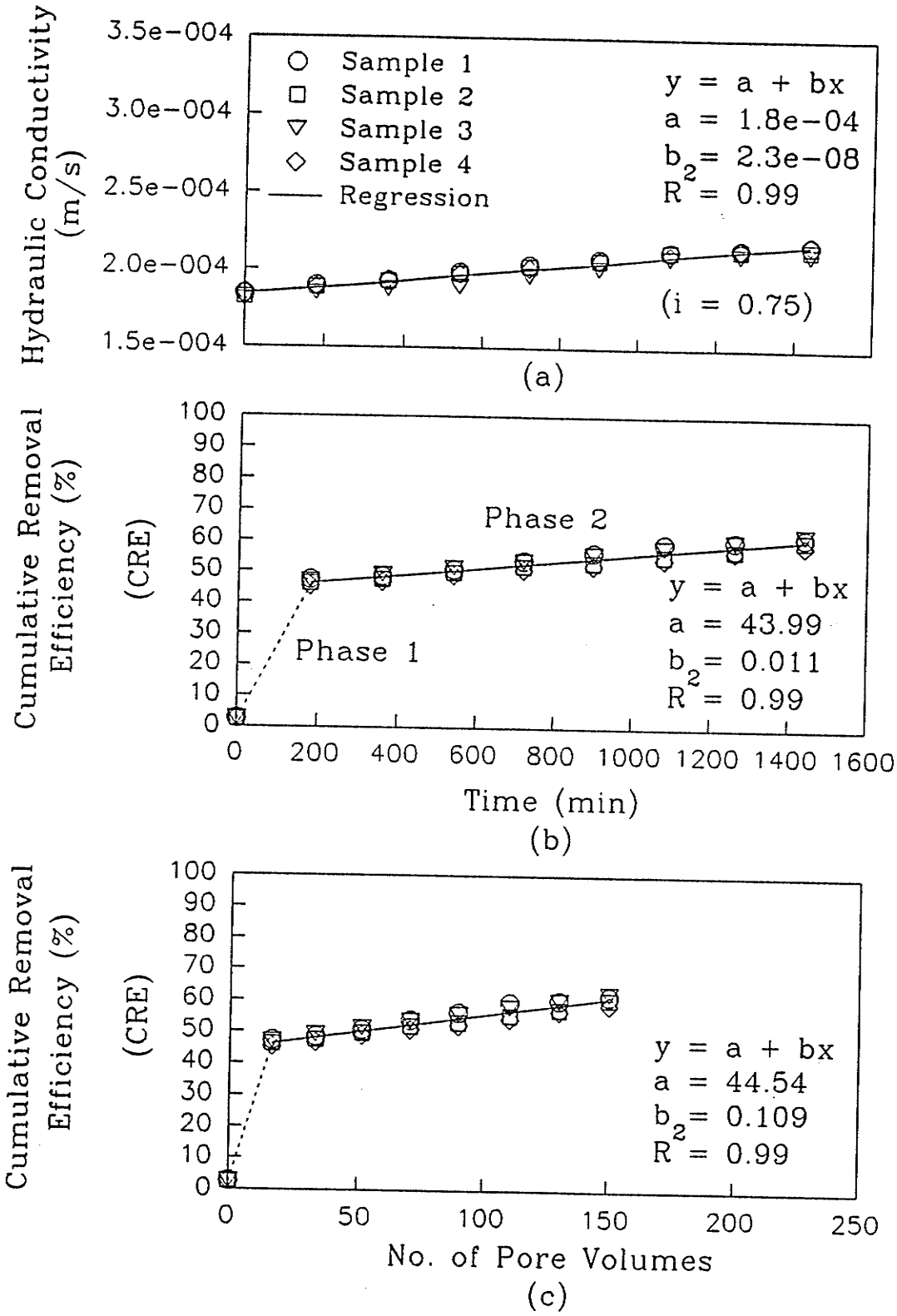


Figure 5.40 One day test results: mesh #80 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

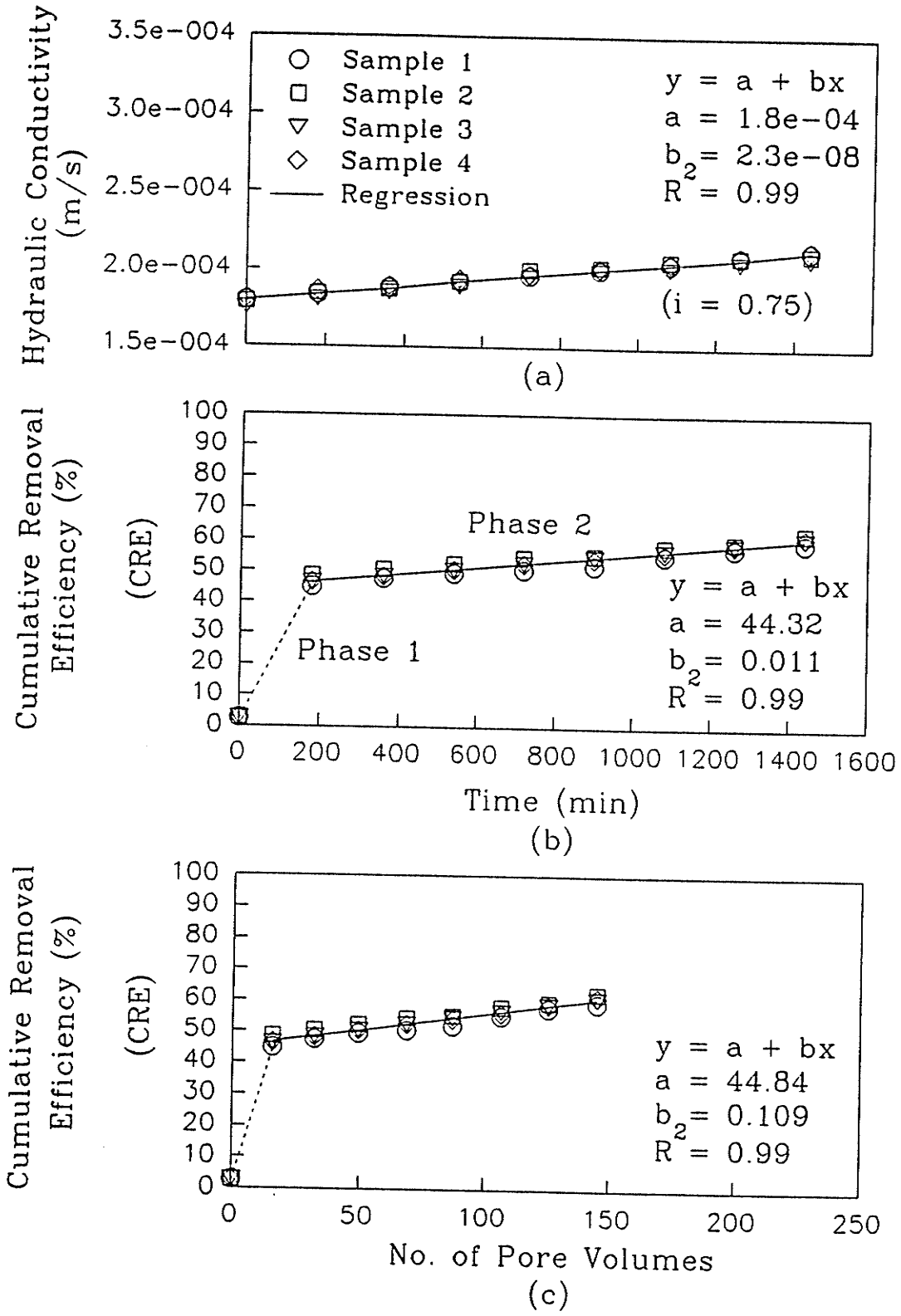


Figure 5.41 One day test results: mesh #100 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

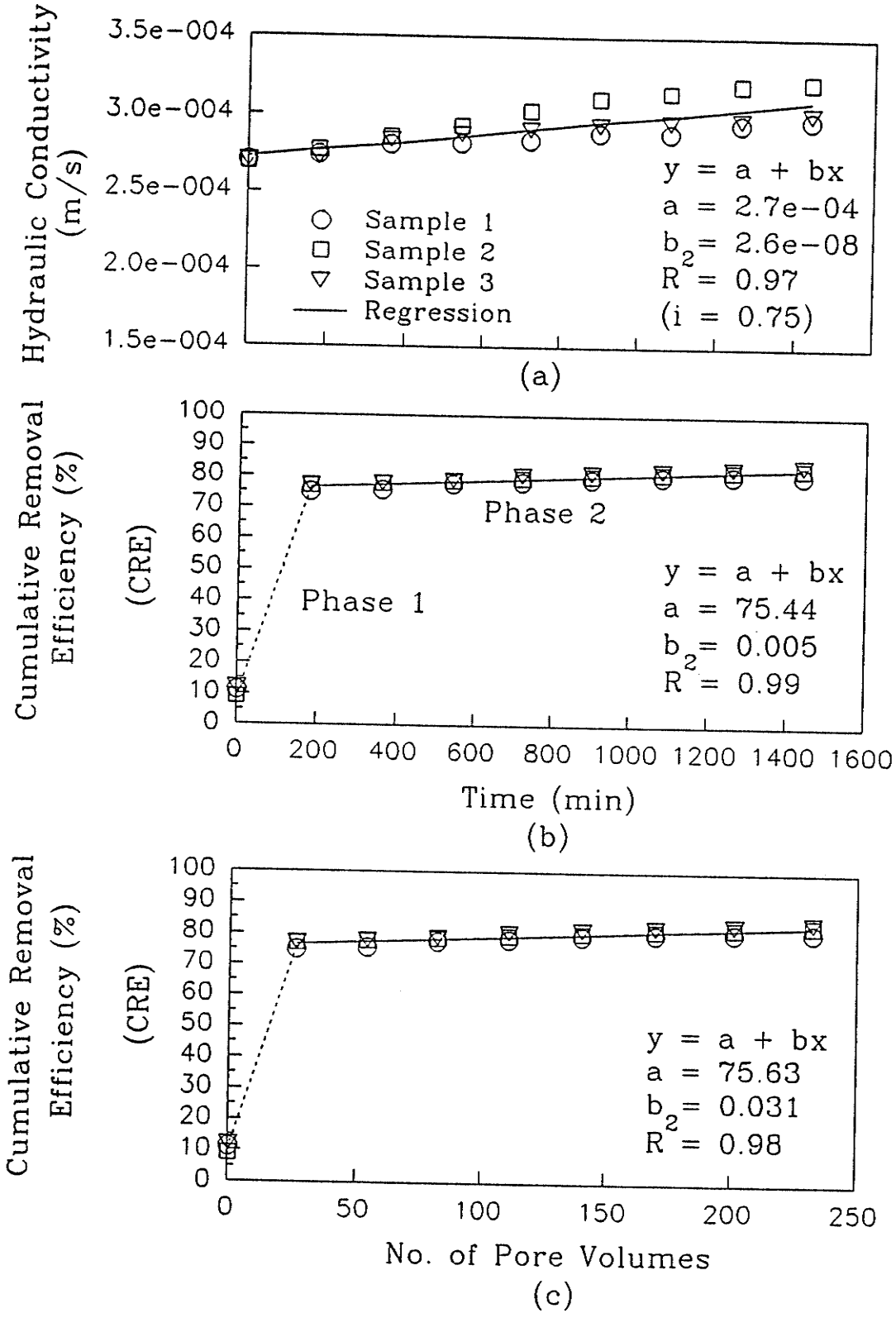


Figure 5.42 One day test results: mesh #60 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

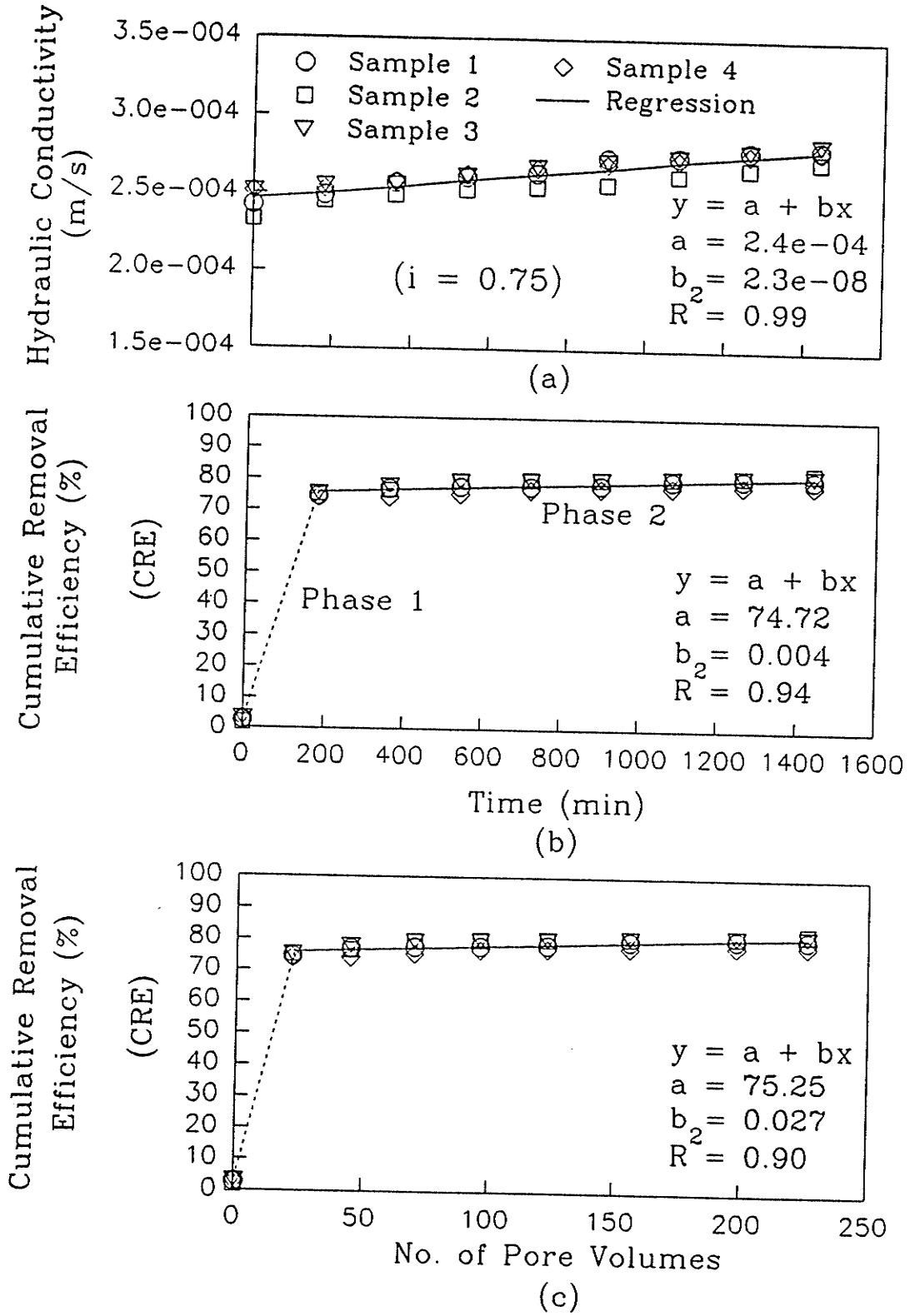


Figure 5.43 One day test results: mesh #80 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

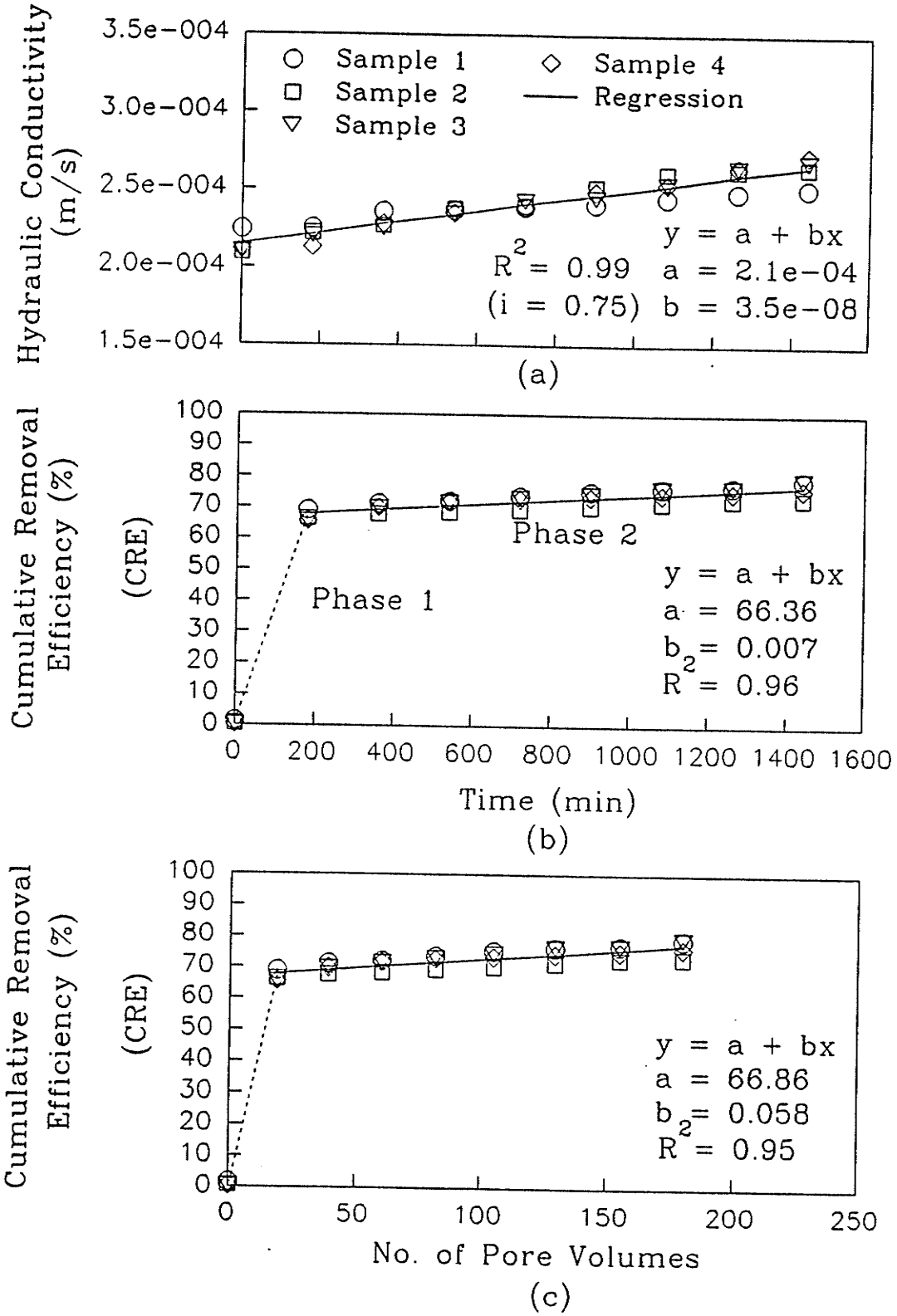


Figure 5.44 One day test results: mesh #100 contaminated sand, water and detergent) at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

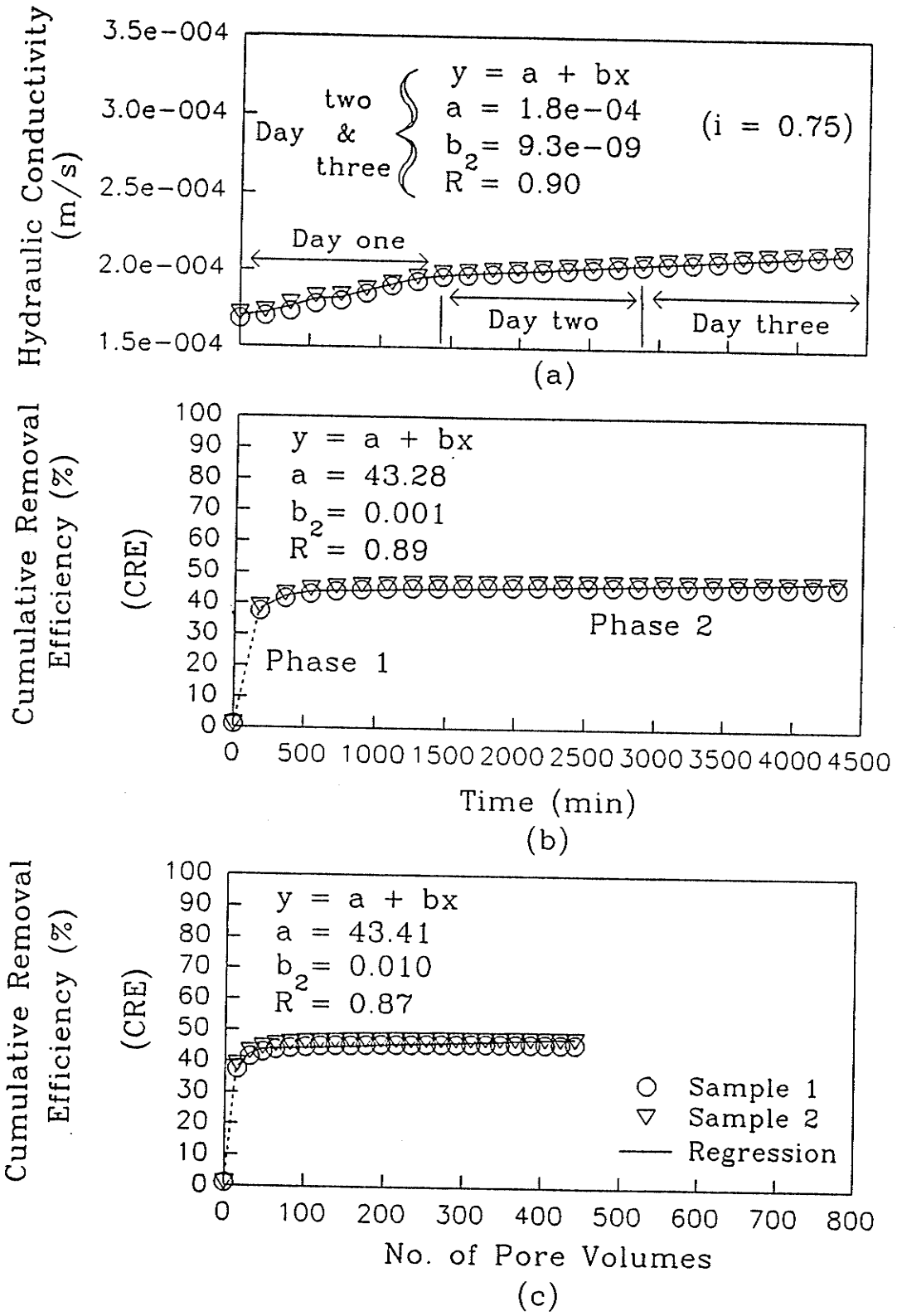


Figure 5.45 Three days test results: mesh #60 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

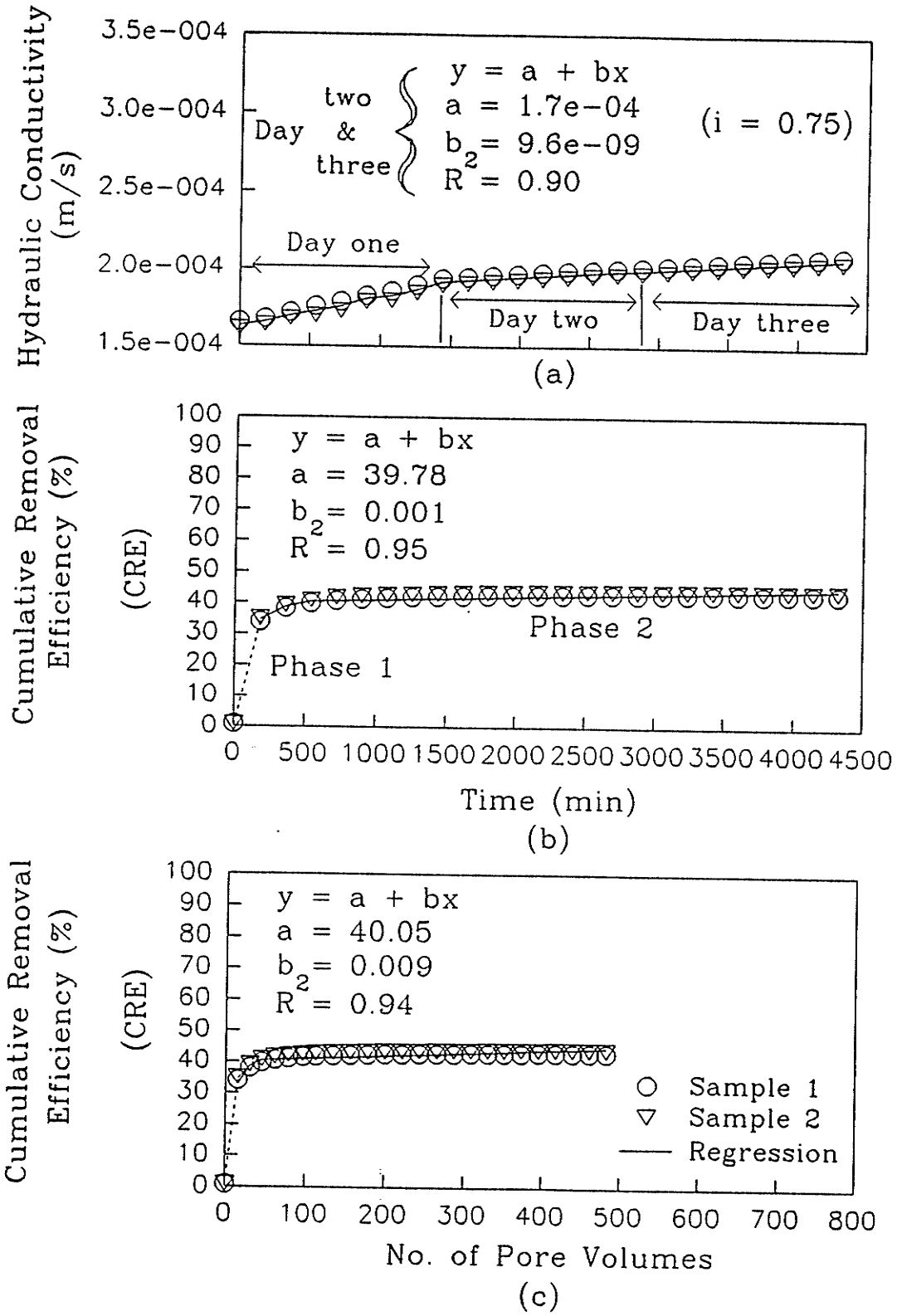


Figure 5.46 Three days test results: mesh #80 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

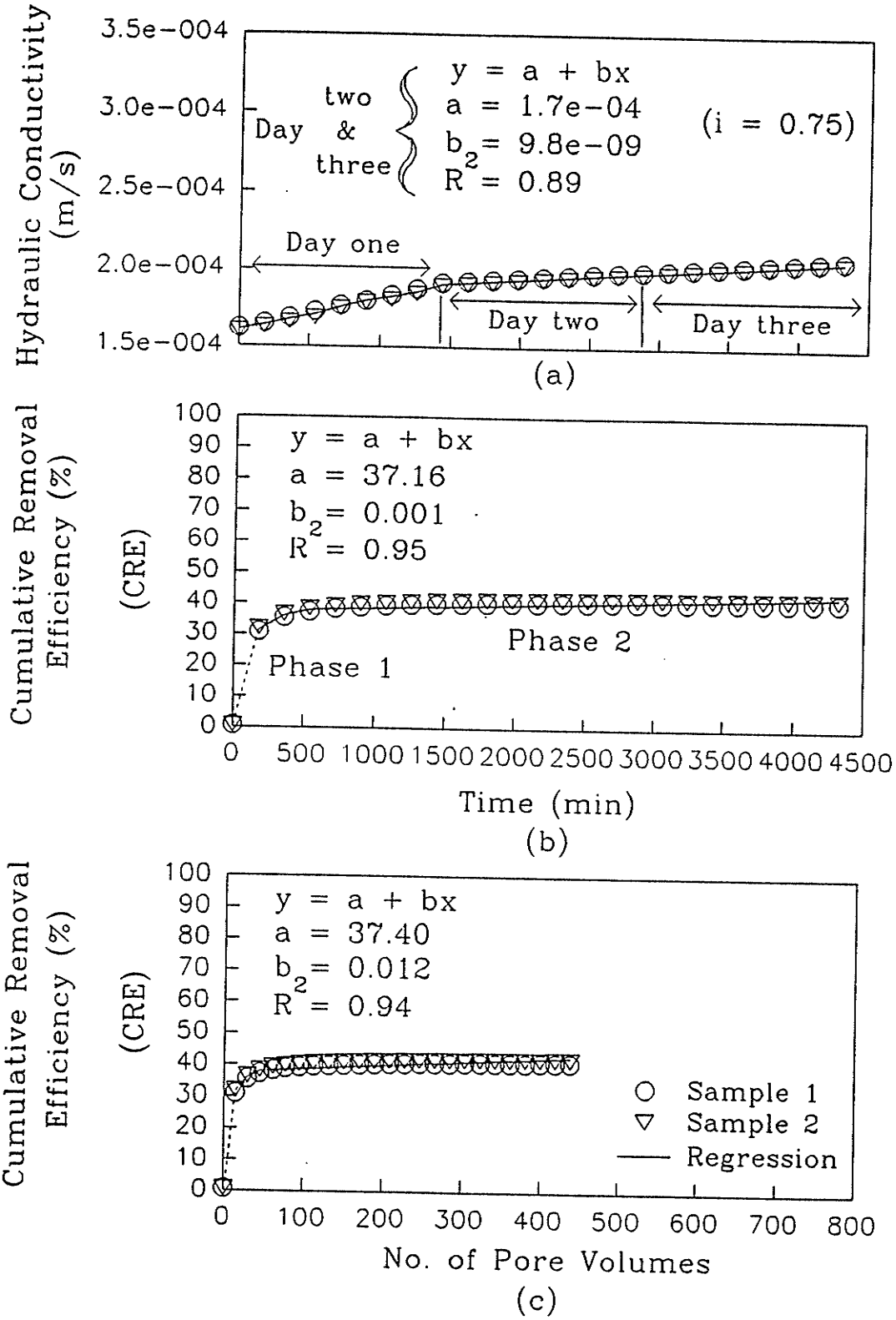


Figure 5.47 Three days test results: mesh #100 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

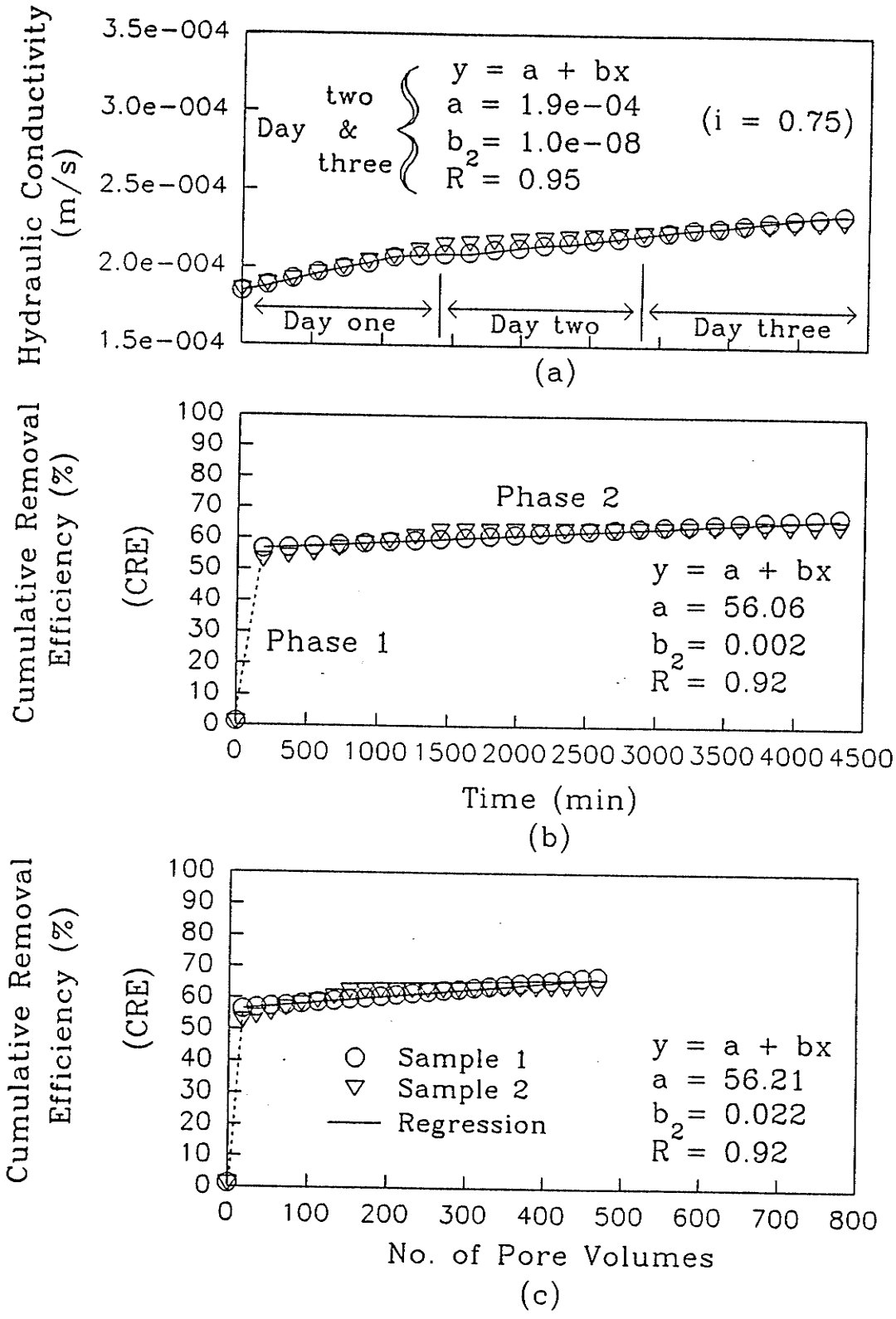


Figure 5.48 Three days test results: mesh #60 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

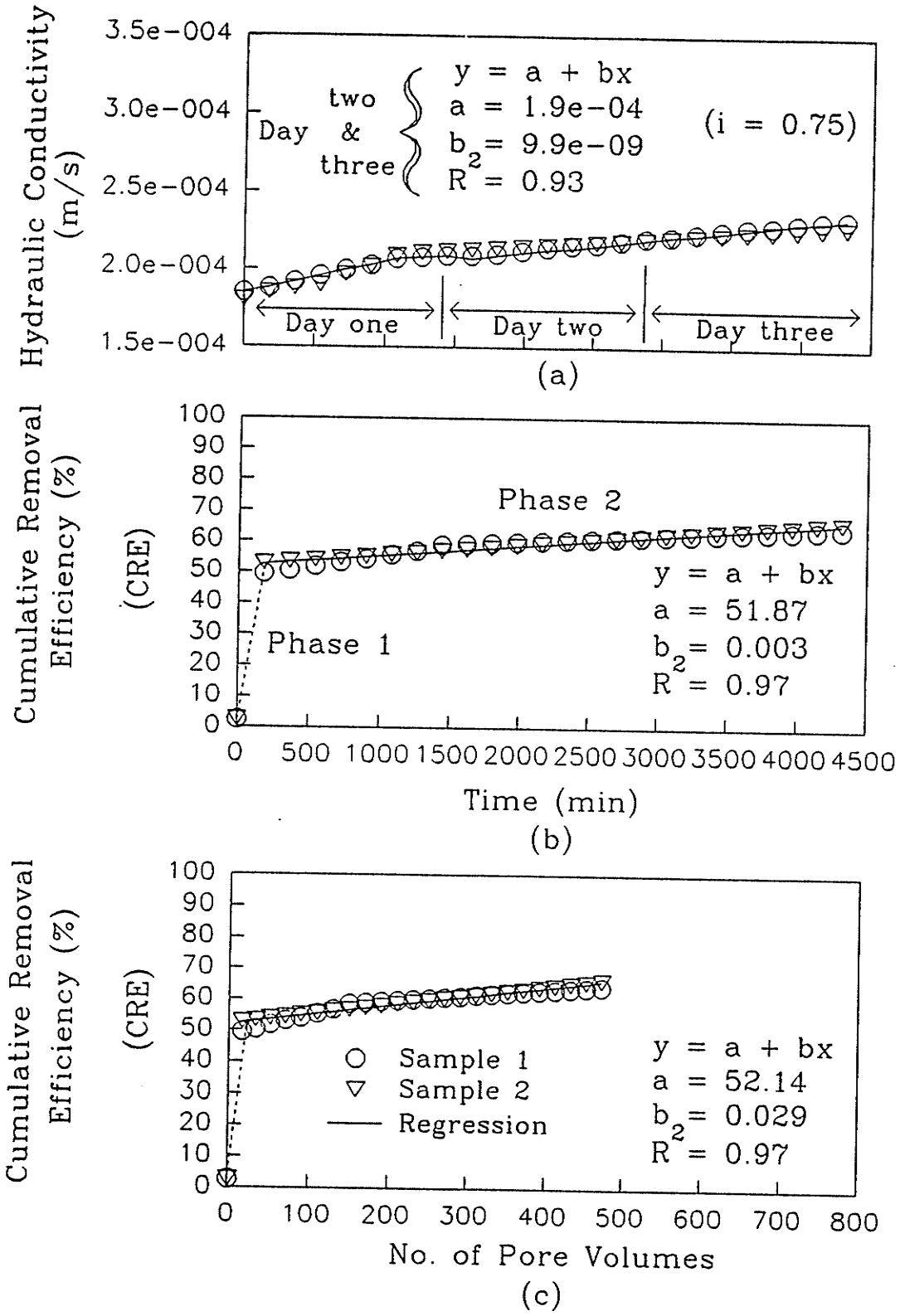


Figure 5.49 Three days test results: mesh #80 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

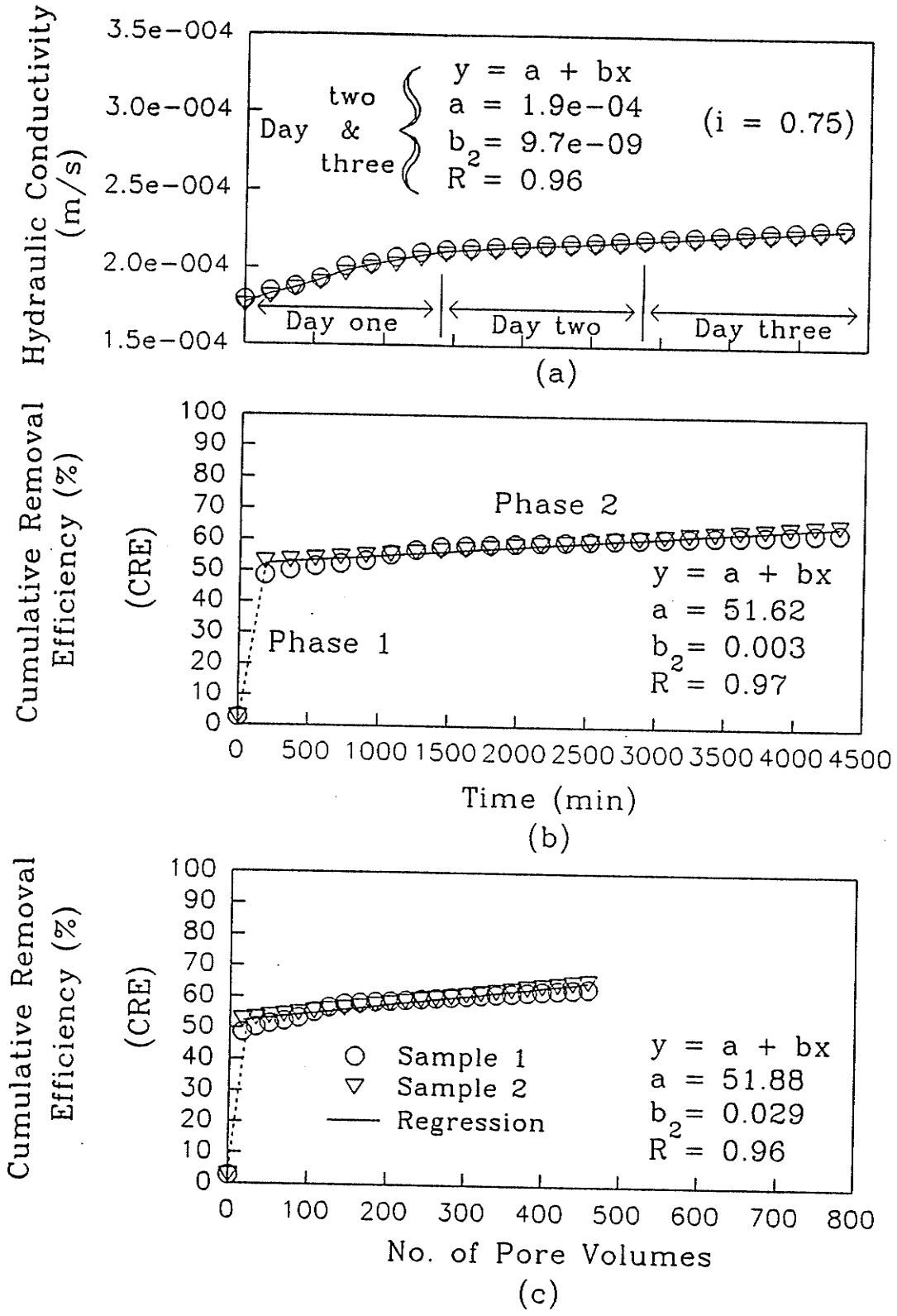


Figure 5.50 Three days test results: mesh #100 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

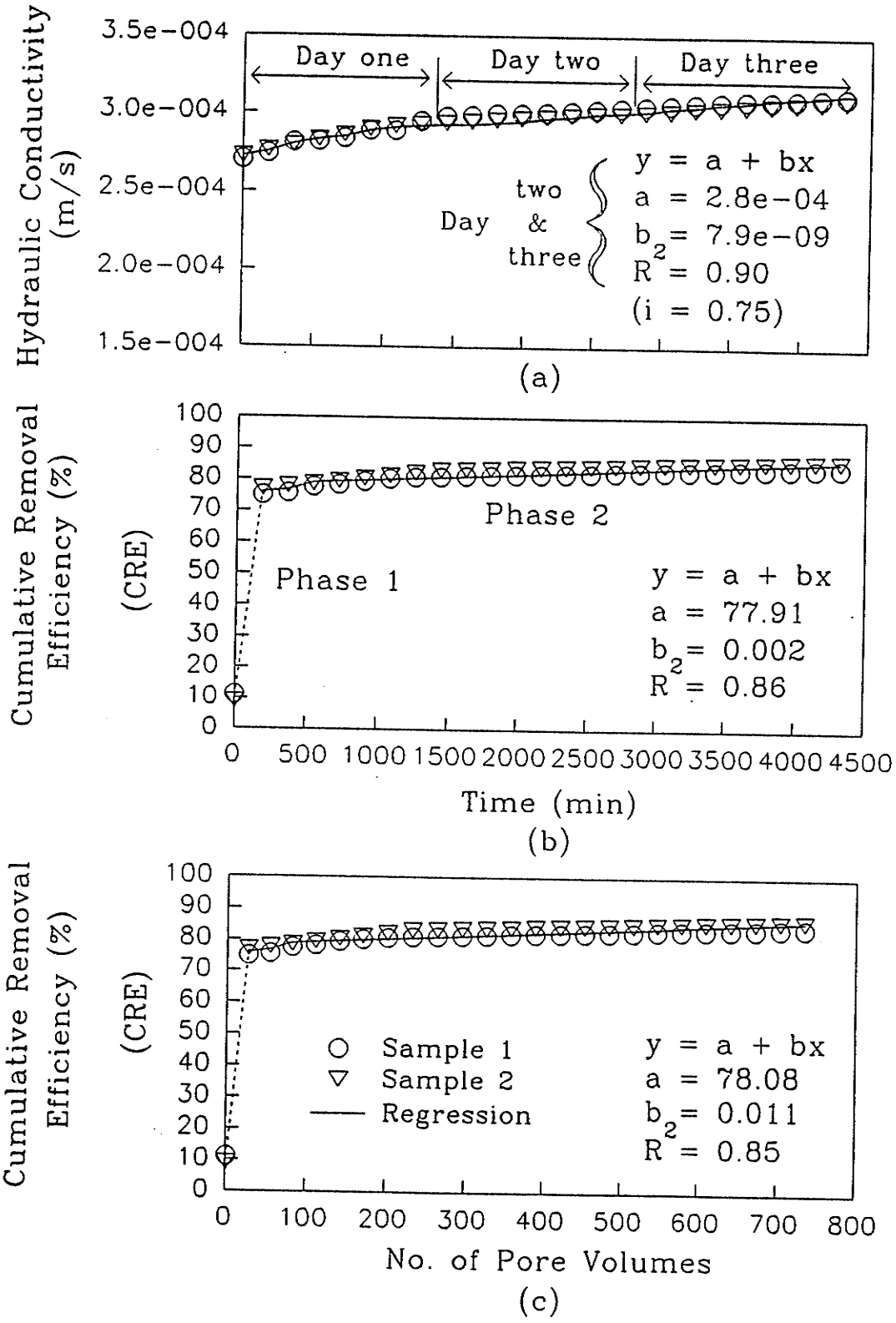


Figure 5.51 Three days test results: mesh #60 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

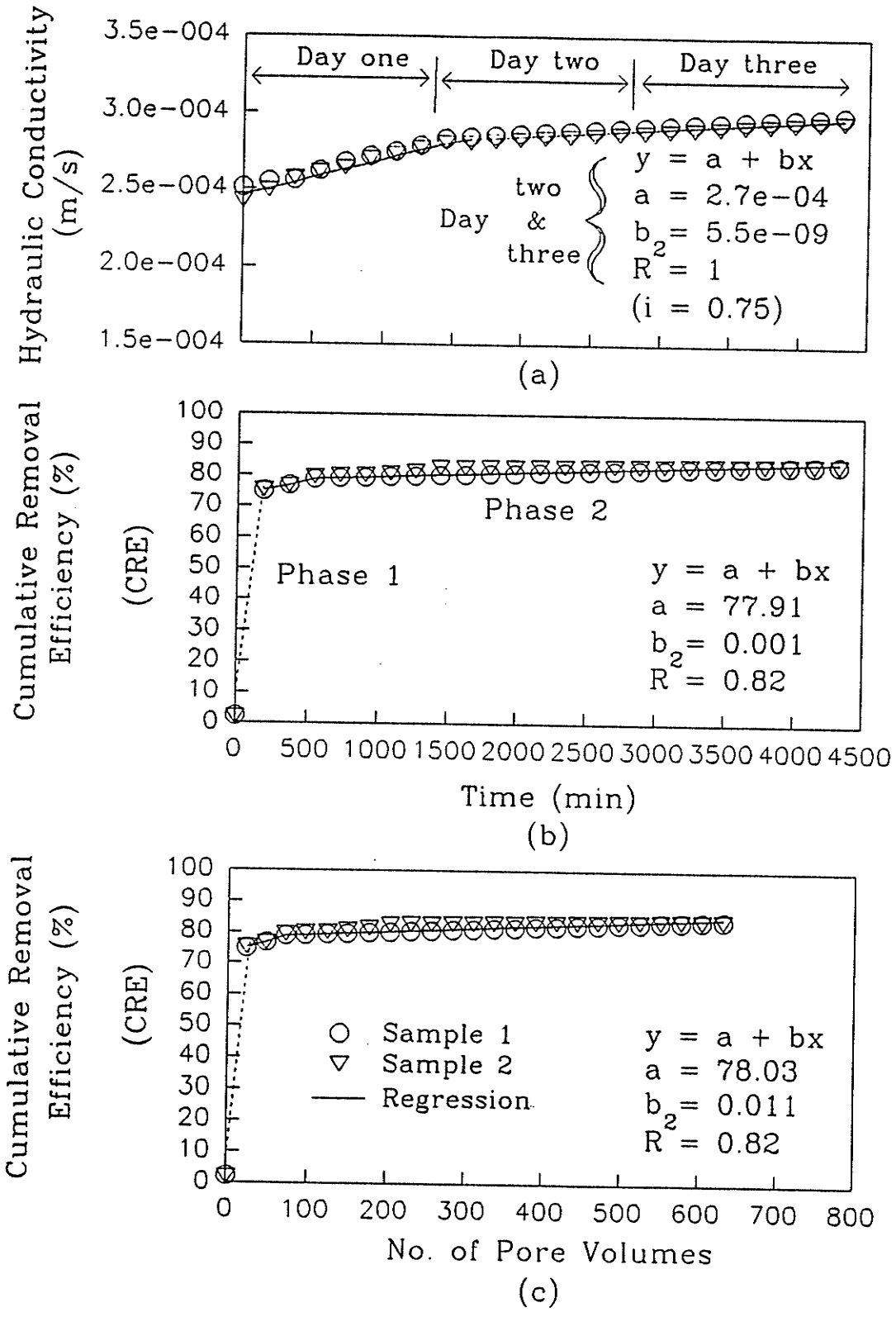


Figure 5.52 Three days test results: mesh #80 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

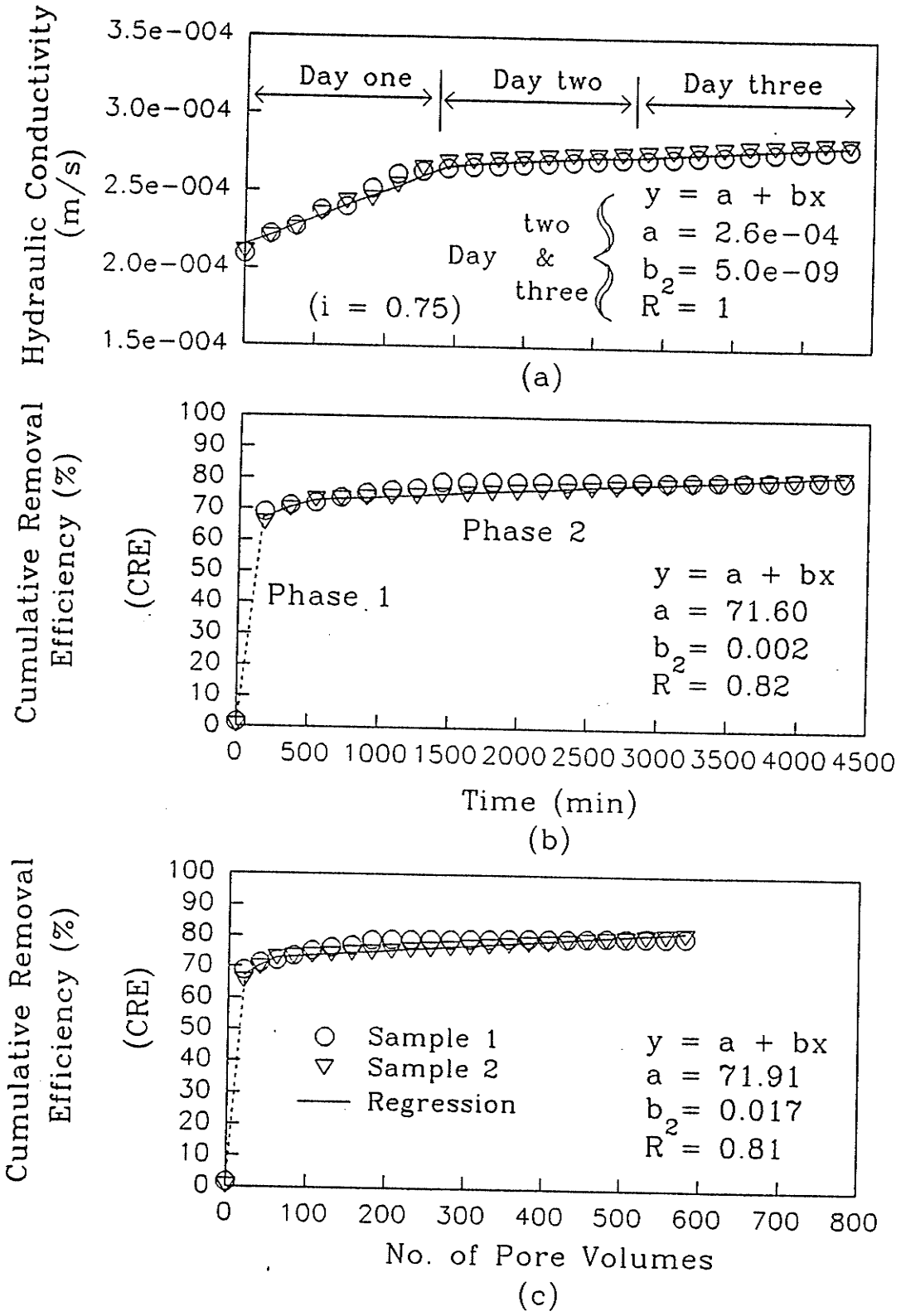


Figure 5.53 Three days test results: mesh #100 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

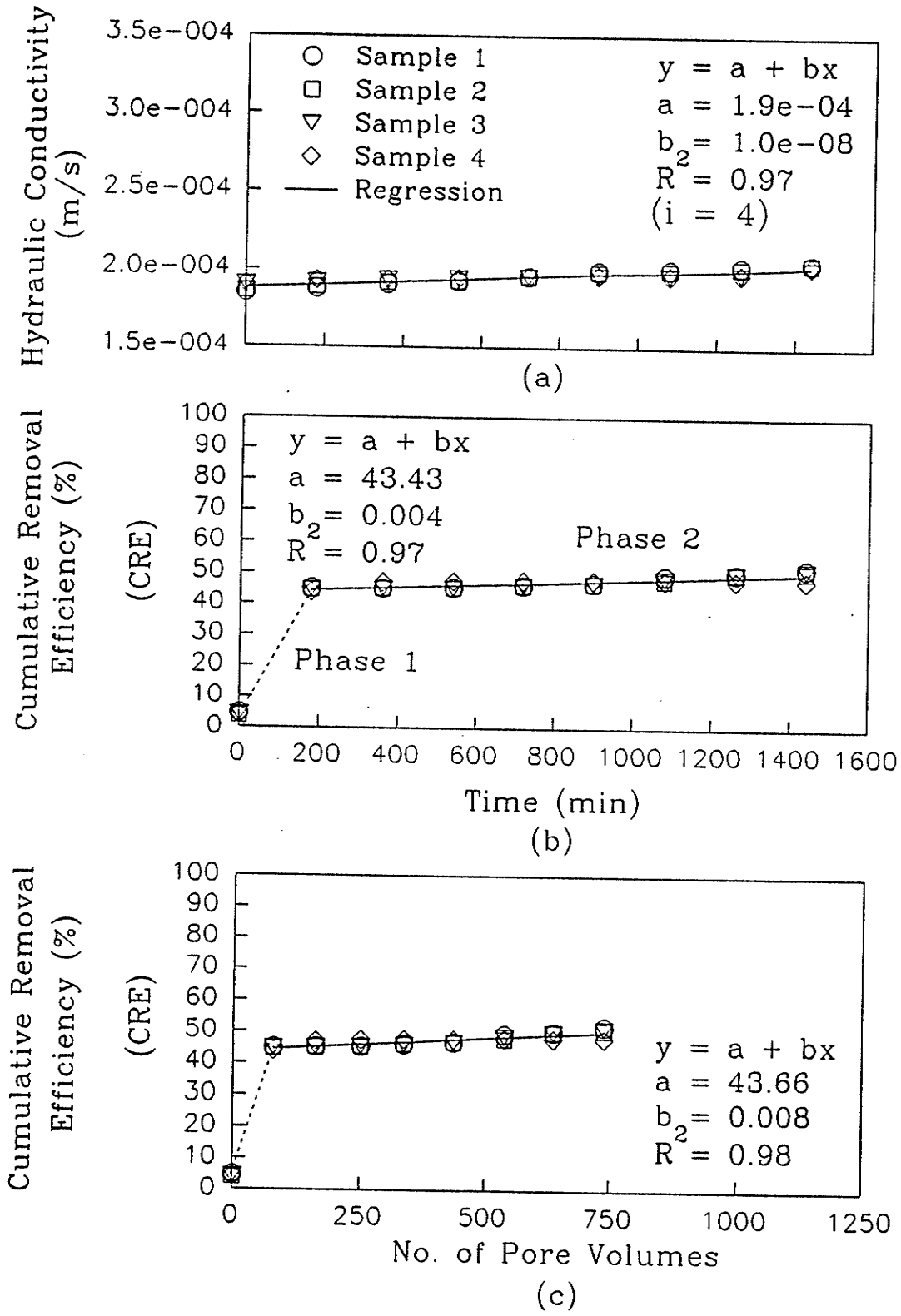


Figure 5.54 One day test results: mesh #60 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

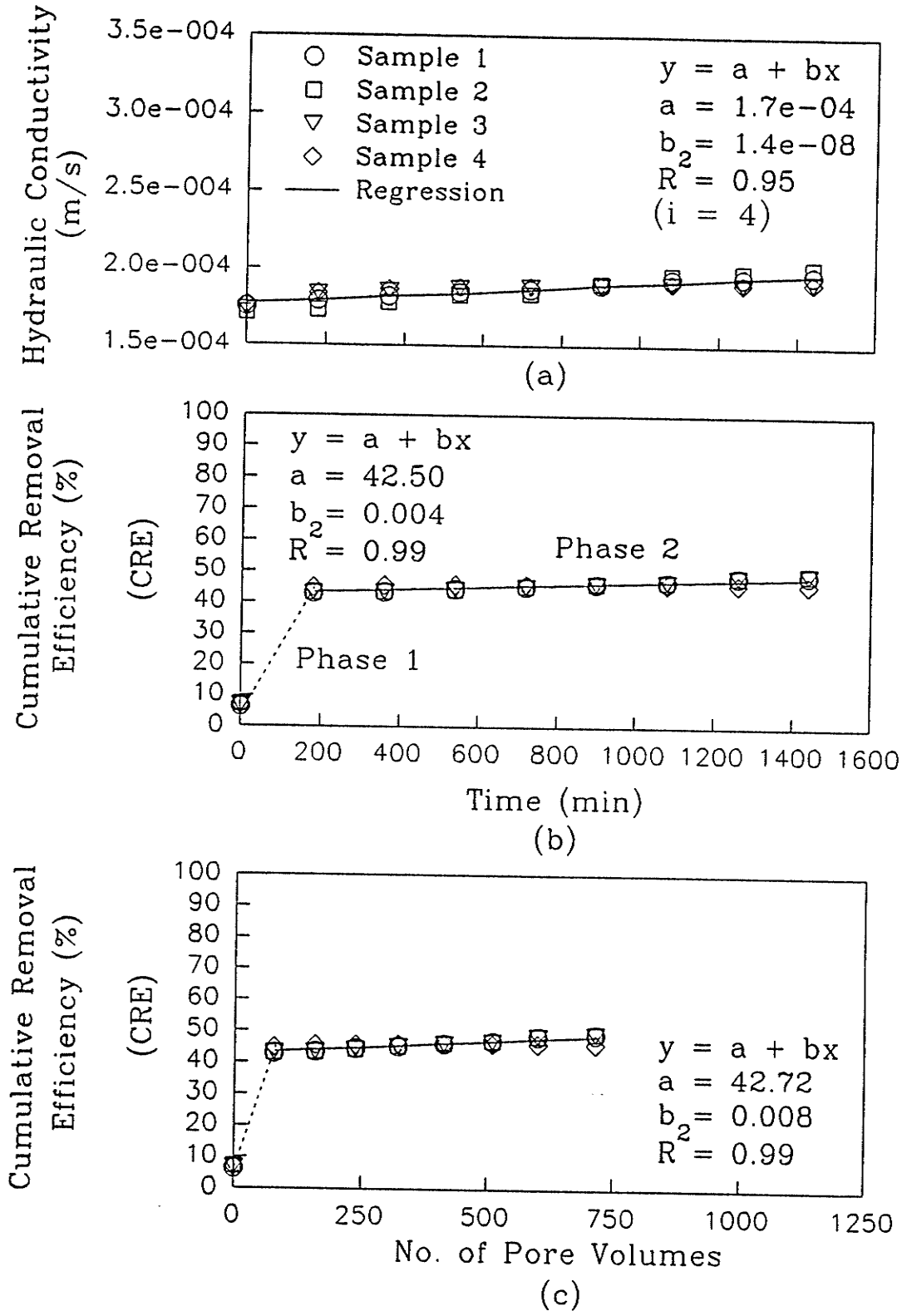


Figure 5.55 One day test results: mesh #80 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

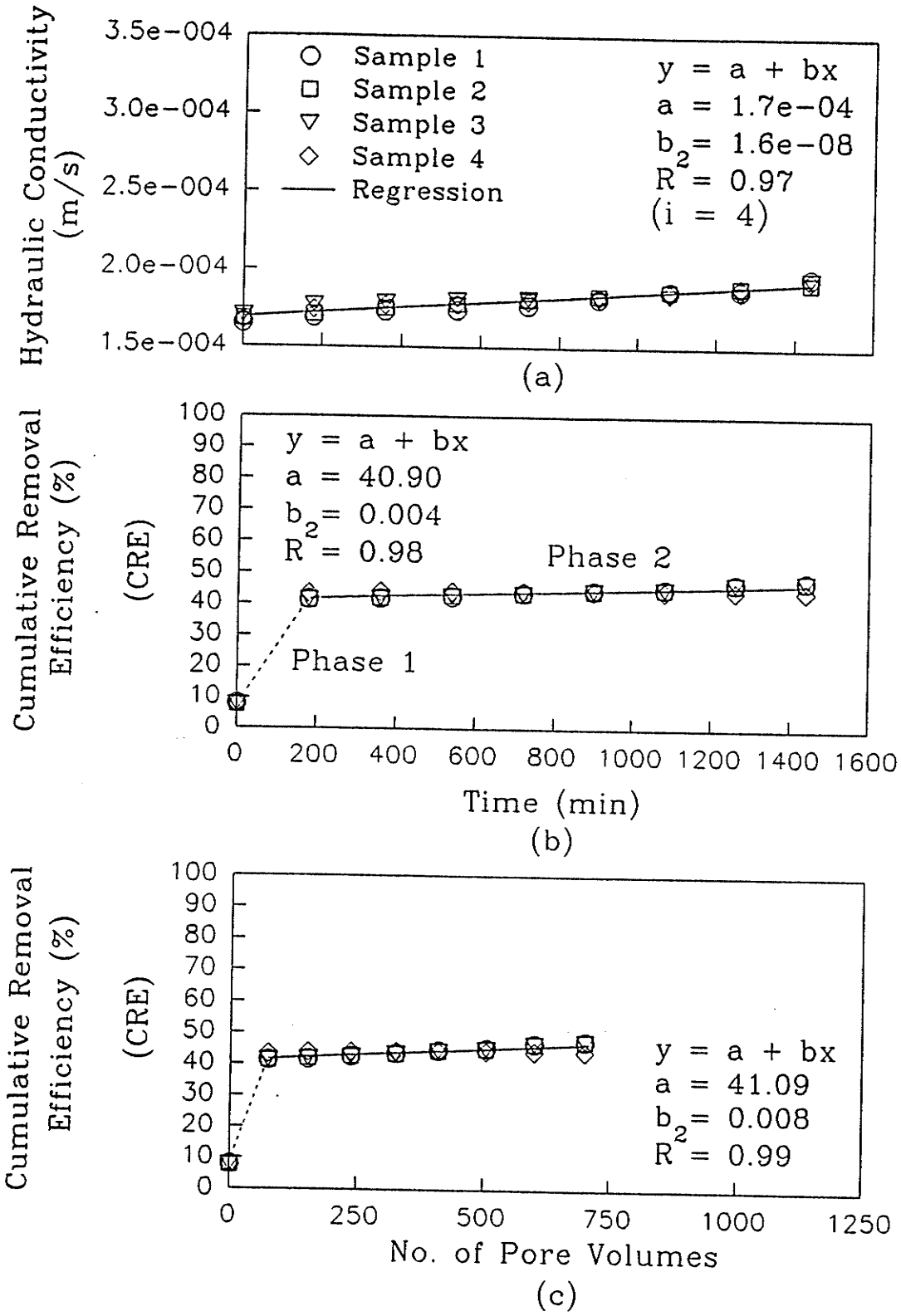


Figure 5.56 One day test results: mesh #100 contaminated sand, water and detergent at 4°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

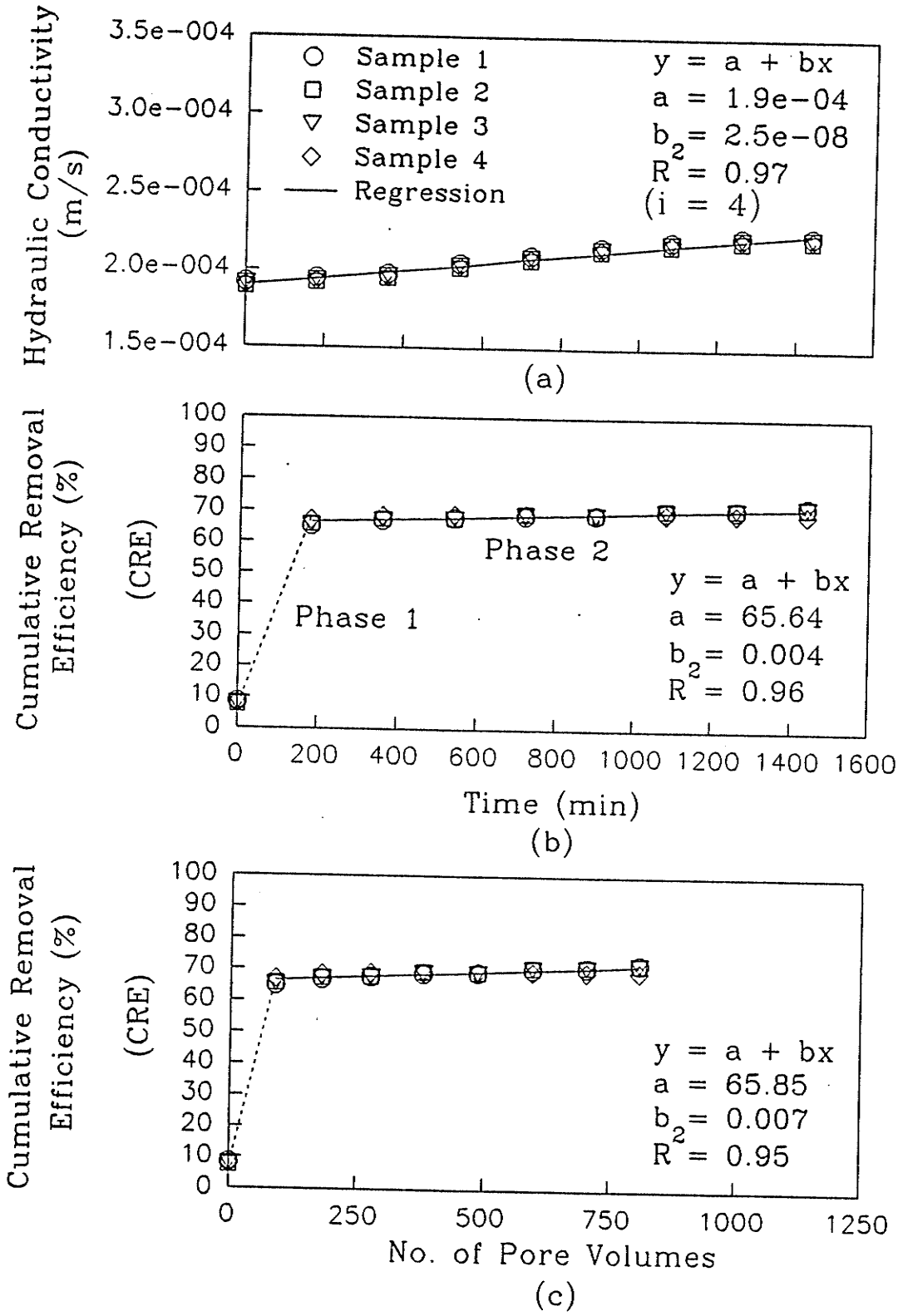


Figure 5.57 One day test results: mesh #60 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

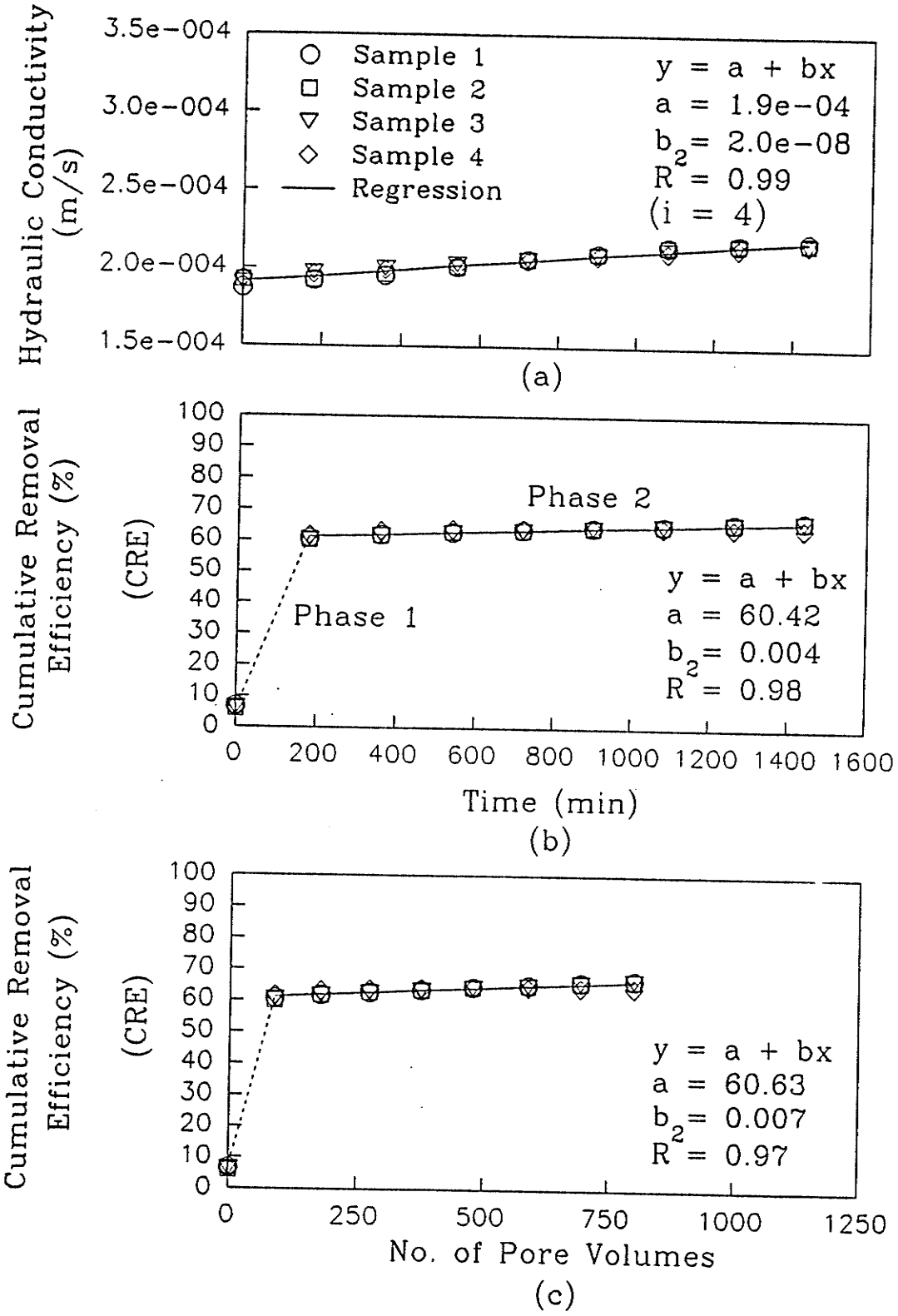


Figure 5.58 One day test results: mesh #80 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

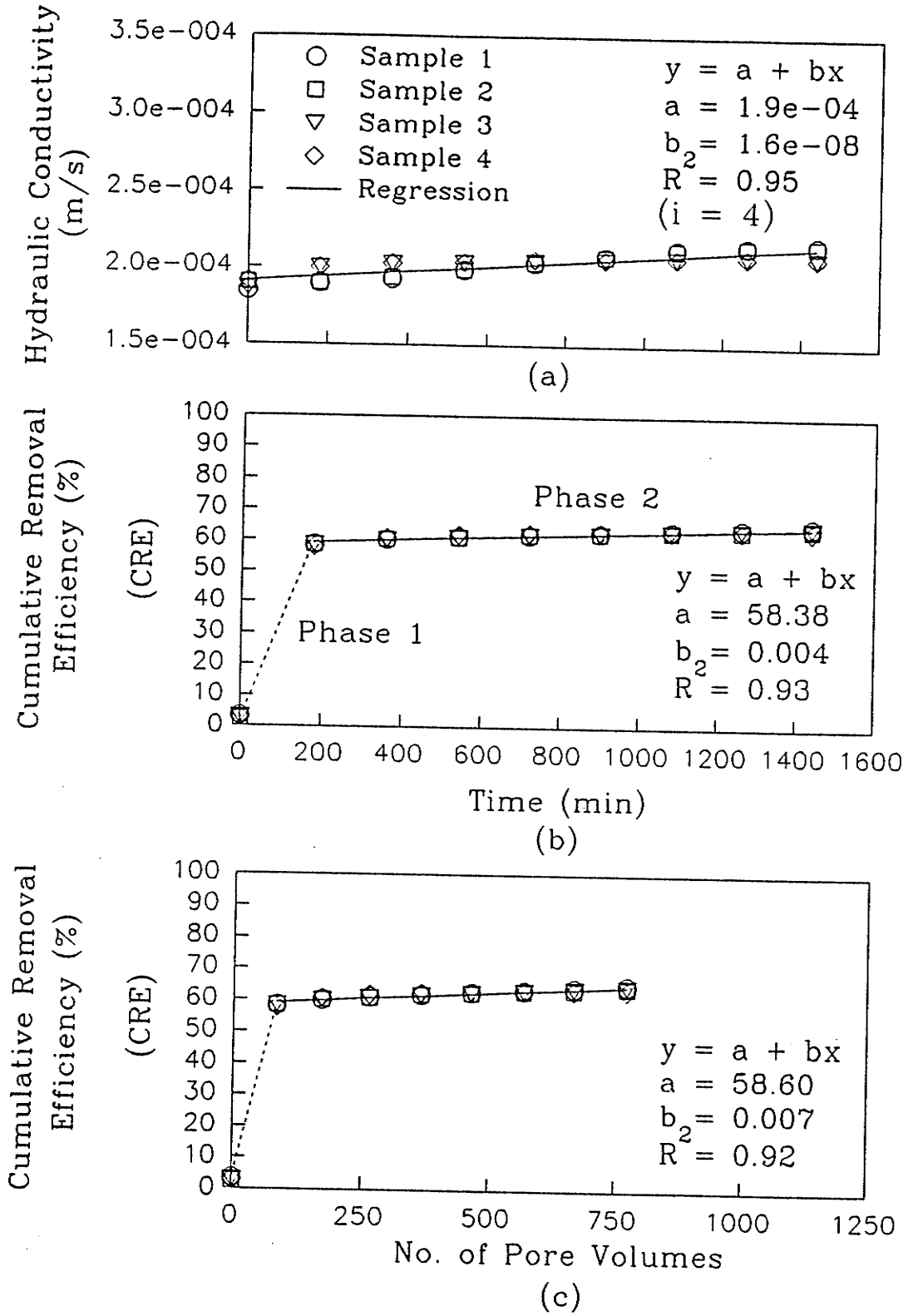


Figure 5.59 One day test results: mesh #100 contaminated sand, water and detergent at 22°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

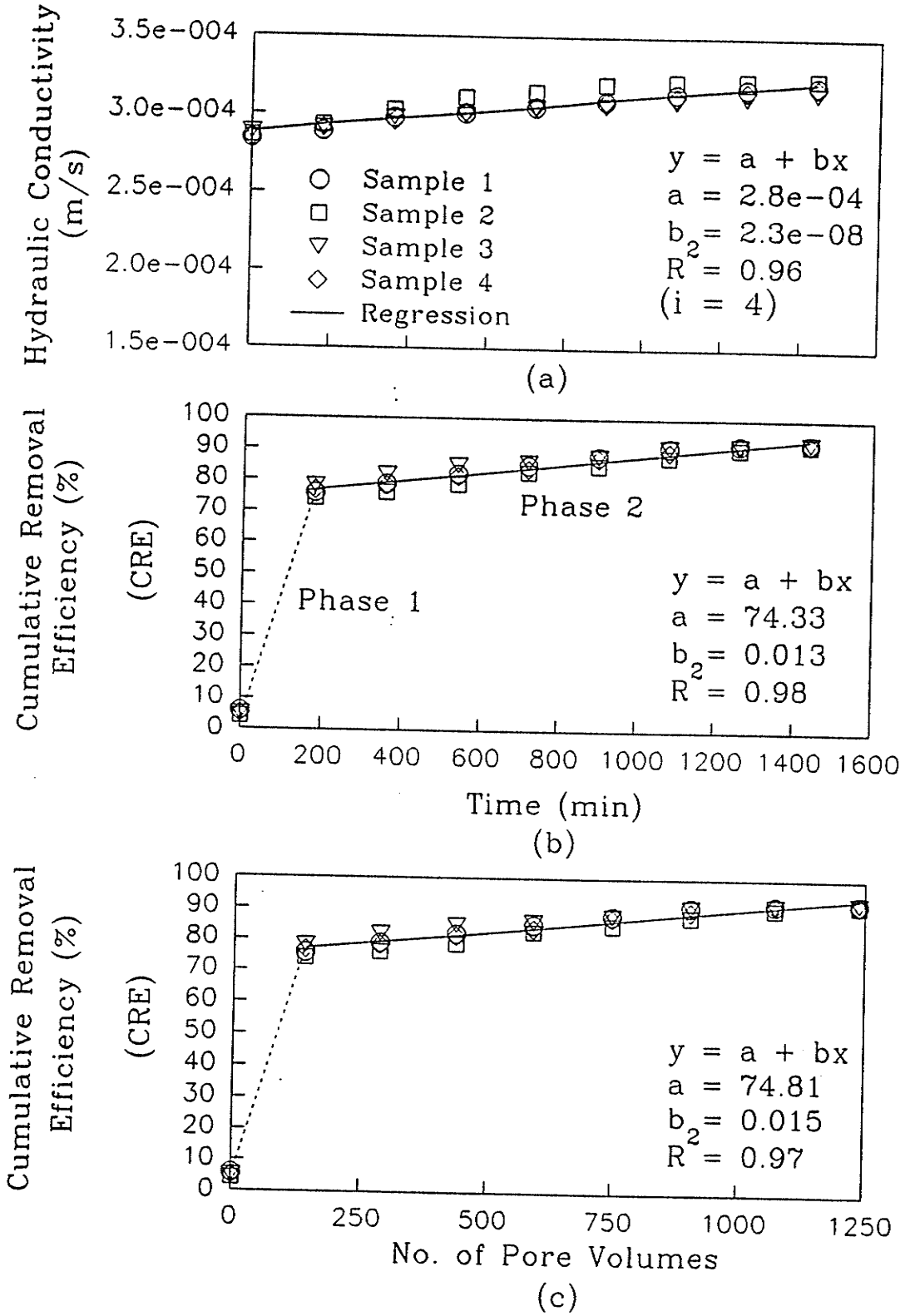


Figure 5.60 One day test results: mesh #60 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

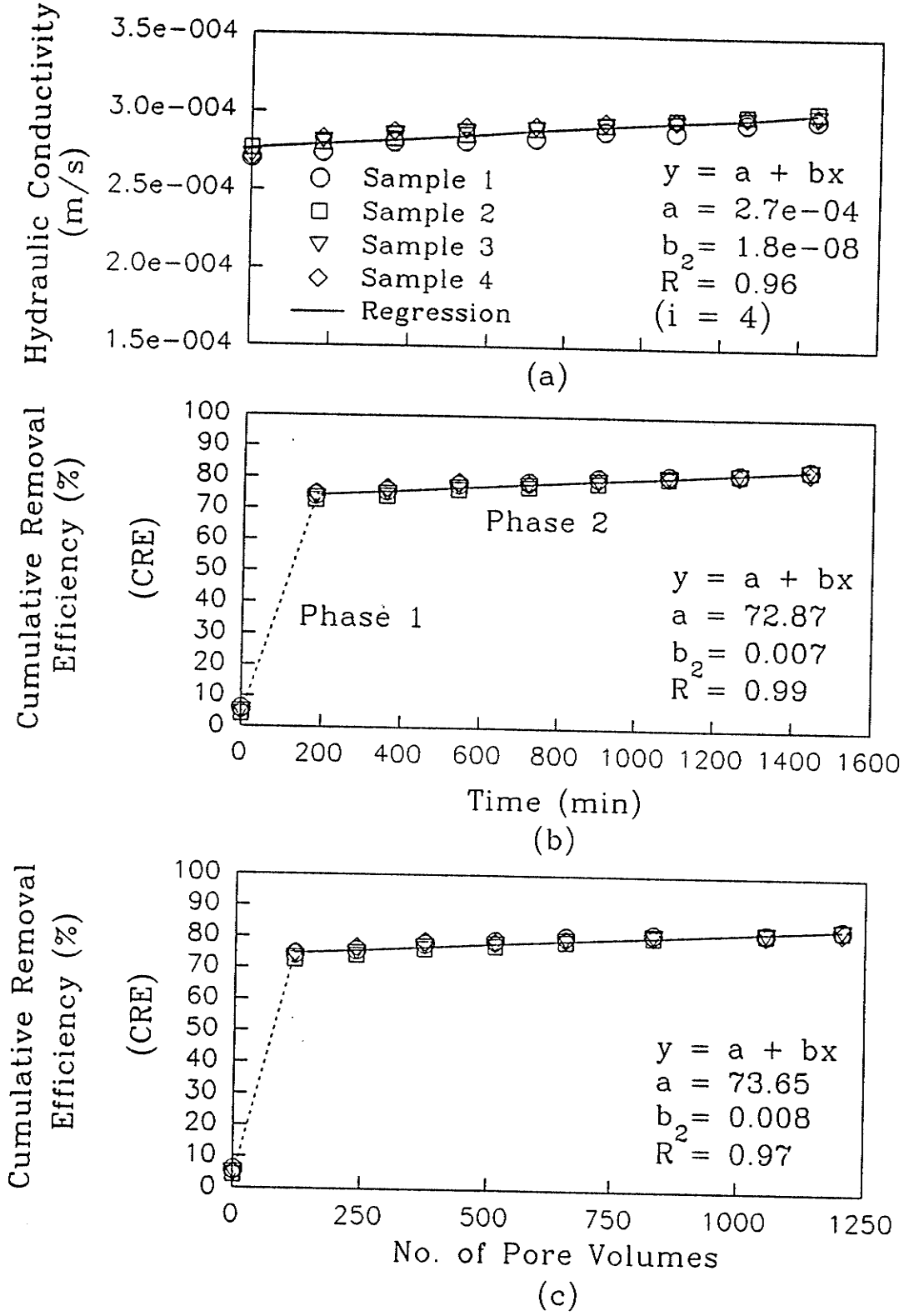


Figure 5.61 One day test results: mesh #80 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

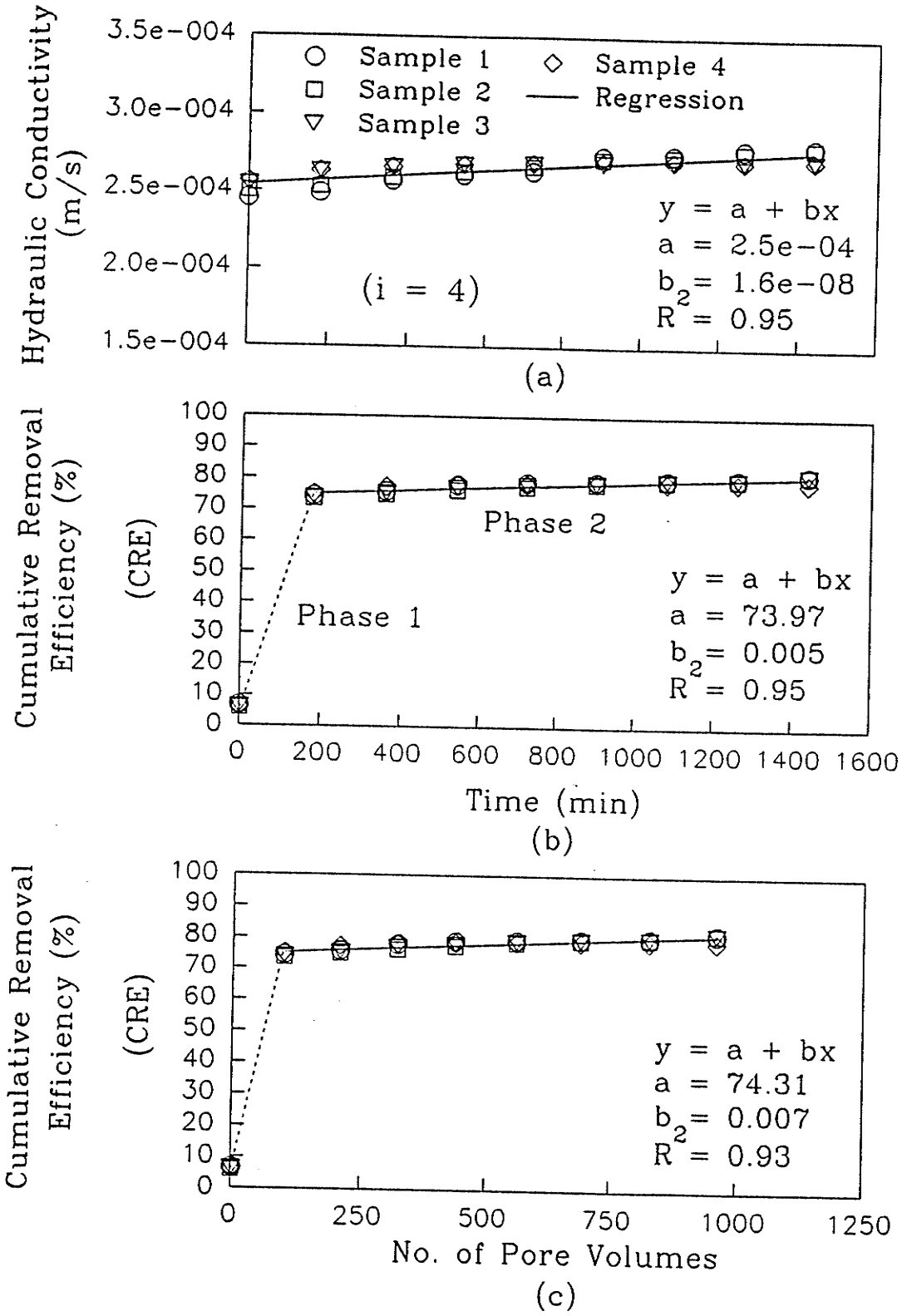


Figure 5.62 One day test results: mesh #100 contaminated sand, water and detergent at 50°C, (a) K vs. time, (b) CRE vs. time, and (c) CRE vs. No. of pore volumes.

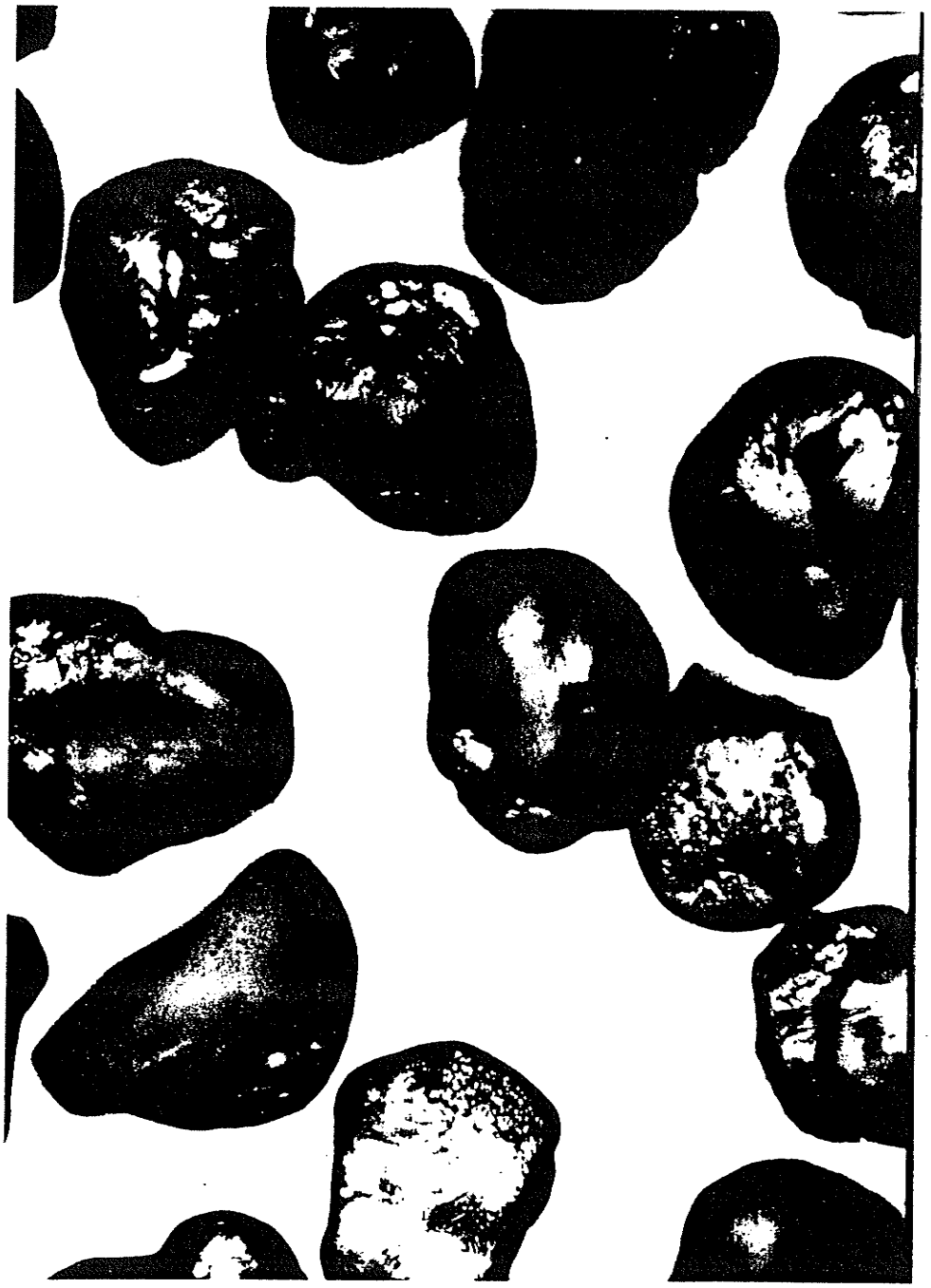


Figure 5.63 Microfabric and grain texture for intact sample (mesh #60)–before contamination.

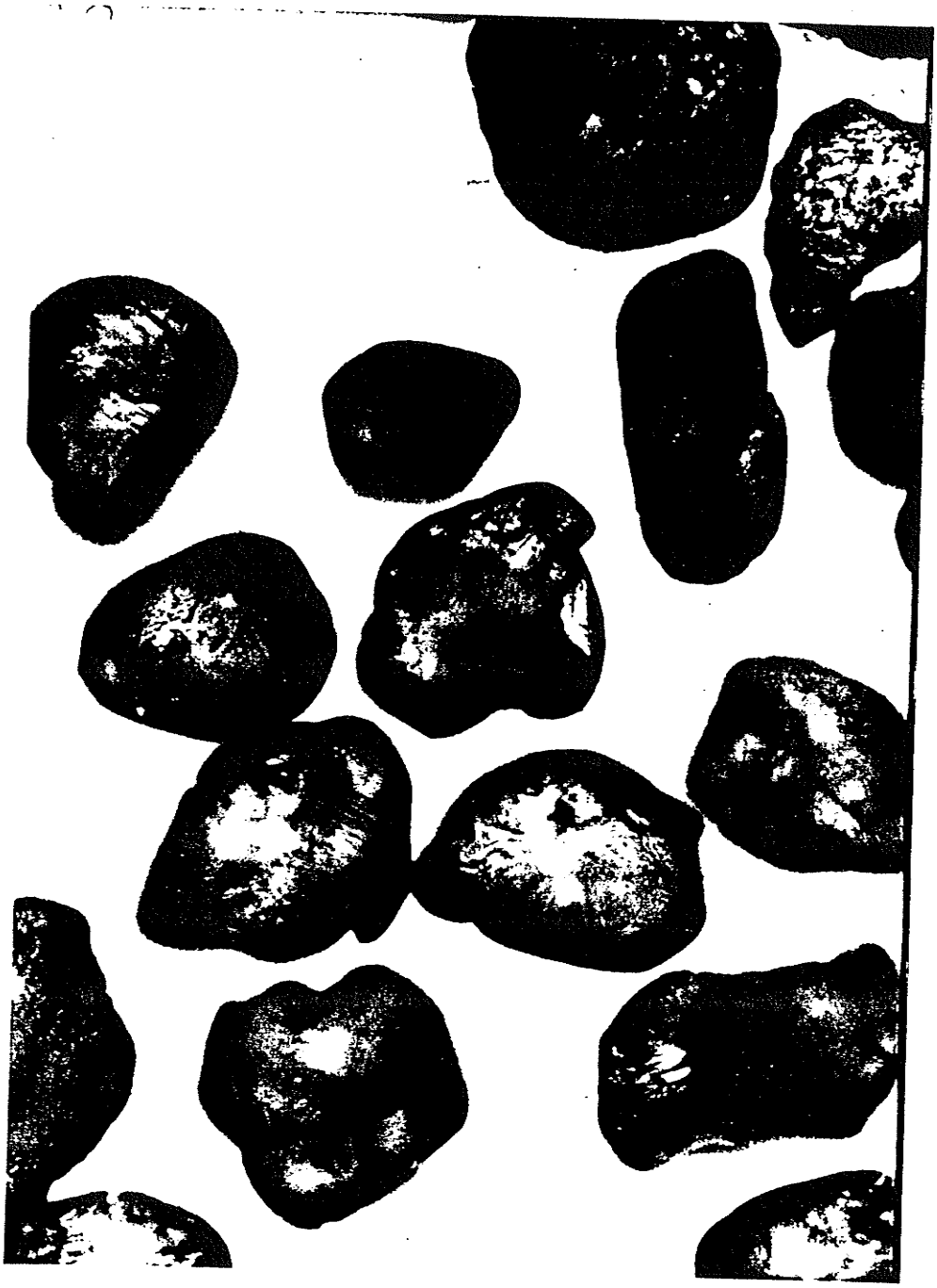


Figure 5.64 Microfabric and grain texture for intact sample (mesh #100)–before contamination.

Figure 5.65 Microfabric and grain texture for intact sample (mesh #60) – contaminated sand.

Figure 5.66 Microfabric and grain texture for intact sample (mesh #100) – contaminated sand.

Figure 5.67 Sand sample after washing by water plus surfactant (mesh #60) – contaminated sand.

Figure 5.68 Sand sample after washing by water plus surfactant (mesh =100) – contaminated sand.

Figure 5.69 Sand sample after washing by water alone (mesh #60) – contaminated sand.

Figure 5.70 Sand sample after washing by water alone (mesh #100) – contaminated sand.

CHAPTER 6

ANALYSIS AND DISCUSSION OF TEST RESULTS

6.1 Introduction

This chapter presents the analysis of the test results. The soil washing experiments are separated into two categories based on whether or not a surfactant is used. The evaluation of the test results is discussed in section 6.2.1. Flushing with water alone or water plus surfactant on clean and contaminated sand is discussed in section 6.2.2. The influence of the mean grain size on K and CRE is discussed in section 6.2.3, and the influence of temperature on K and CRE is discussed in section 6.2.4.

6.2 Discussion of Test Results

Two questions are paramount:

1. Will the continued application of water or water plus surfactant enhance the removal of diesel fuel from a sandy soil?

2. What levels of residual hydrocarbon concentrations should be expected to remain after prolonged washing of a soil with water or water plus a given surfactant?

6.2.1 Evaluation of Test Results

6.2.1.1 *Repeatability of results*

Repeated measurements arise in many diverse fields, and are possibly even more common than single measurements. The term "repeated" will be used here to describe measurements which are made of the same characteristic on the same observational unit more than once. The basic data format may be identified tersely as '(n) individuals x (m) measurements x (v) variables'.

The experiments were conducted with one type of diesel fuel (LNAPL) and one type of soil with three mean grain sizes, D_{50} (0.42, 0.24, and 0.17 mm). The experimental variables were as follows: 1) Three different temperatures (4, 22, and 50°C), and two hydraulic gradients (0.75 and 4); 2) Two different times, tests conducted for 24 and 72 hours; and 3) Two types of influent were used (water alone and water plus surfactant, Biodish®). For each soil grain size, four samples were monitored over time (the readings and samples were taken at three hours intervals) to record and observed the trend and behaviour of CRE, and K.

The question of repeatability is whether the same results can be obtained if identical tests were performed. Table 6.1 and 6.2 give the precision (1 σ) estimate for the three mean grain sizes, with respect to CRE and K. The precision for the first CRE data point varies from 0.4 to 51% and the other eight data points ranges from 0.25 to 6%. The wide range in CRE precision of the first data point is due to laboratory error (discussed in section 6.2.1.3). The precision for K ranges from 0.05 to 3.5% for all data points. It seems that in the majority of cases, the precision for

CRE increases with time, while for K the precision remains fairly constant with respect to time.

6.2.1.2 *Similarity of Results*

Comparing the results obtained from the CRE and K tests for all the variables, it is apparent that the data yield similar profiles, and the normalized curves are nearly identical. For example, Figure 6.1 and 6.2 shows the K and CRE versus time lines for the various D_{50}'s at a particular temperature and hydraulic gradient are parallel.

6.2.1.3 *Laboratory Testing Error*

The method used to measure the hydraulic conductivity for contaminated soil is similar to those used to measure clean saturated soils, and the problems are similar but more severe. Two of the problems require immediate discussion because they influence testing results strongly; these are (1) no early (between 1 minute and 180 minutes) results and (2) the knee in the K results at one day in the three days tests.

(1) Missing Results - Since no automated recording system was available to measure the flow, readings were taken at three hours intervals, for a period as long as three days, which caused a major gap in determining the behaviour of the CRE (bilinear, exponential or hyperbola).

(2) Knee in the K results at one day in the three day tests - Some of the problems that are associated in causing the knee in the K results are as follow:

(a) Voids and fissures may be formed as a result of stress relief. The problem was minimized by subjecting the samples to stresses using a spring inside the permeameter cell (see figure 4.2).

(b) In testing compacted samples it is often assumed that saturating from the bottom, with the top open to the atmosphere, will lead to saturated samples. However, in some cases this procedure might not be applicable as shown in Figure 6.3 which show the comparison between mesh #60(W) 50°C i=4 to i=0.75. The large difference between the initial K after using the same amount of pore volumes indicates that the samples are not fully saturated, and water trying to get rid of air in the sample which caused a decrease in K values. Smith and Browing (1942) used this procedure to "saturate" 200 samples. They found that the average degree of saturation of their samples was 91 percent. Because water cannot flow through an air bubble, the bubbles effectively reduce the void space that can be occupied by water and thus reduce hydraulic conductivity.

(c) In an effort to reduce testing time, a large hydraulic gradient may be imposed on samples. Such gradients might alter the hydraulic conductivity measurements. Figure 6.4 shows the comparison between mesh #60(W) 22°C i=4 to i=0.75. Figure 6.4c show higher values of K at i=0.75 than i=4, and this might be due to the effect of velocity in altering and moving some soil

particles. Mitchell and Younger (1967), and Gairon and Schwartzendruber (1975), found that as the hydraulic gradient increases the K values decrease, apparently as a result of particle migration, causing clogging.

(d) On occasion, engineers correct the measured hydraulic conductivity to a standard temperature by adjusting for the effect of temperature on the viscosity and density of pure water. It has been found through the literature that simple viscosity and density adjustments are generally adequate for taking into account the effect of temperature. Note that K is not particularly sensitive to small or moderate changes in temperature when water is used as the permeant; the viscosity of water decreases approximately 3 percent per degree celsius rise in temperature from 21°C. However, the K of fine -grained soils is probably influenced by complex interaction between the water, adsorbed and free ions, and the mineral surfaces.

What little evidence that exists for temperature effects, Haridason et al., (1972) indicates that an increase in temperature may reduce the thickness of water films at constant flow, thus decreasing K, but also reduces the viscosity of water, thus increasing K. The net results is that temperature changes of the order of ten degrees celsius cause changes in K smaller than experimental scatter.

6.2.2 Flushing With Water Alone or Water Plus Surfactant

6.2.2.1 *Clean Sand*

In the case of clean sand Figure 6.5 and 6.6 show a slight increase in K with respect to time and pore volumes. This increase is probably due to imperfect de-airing (saturation) of the specimens and to a loss of fines.

6.2.2.2 *Oil Contaminated Sand*

A comparison of the trends of the hydraulic conductivity and cumulative removal efficiency between the two hydraulic gradients is shown in Figure 6.7 and 6.8. The curves in Figure 6.7 show clearly there is little difference in the relationship between K and time for the two hydraulic gradients. These results indicate that no significant change in the structure of the specimen took place during this test even though the hydraulic gradient of 4 was approximately 5 times greater than it was during the tests with i=0.75. Figure 6.9 show that the slower moving water or water plus surfactant is more efficient in removing the diesel fuel. Therefore, slower moving water is better at increasing K with respect to the number of pore volumes used.

Figures 6.10 through 6.21 show the regression analyses of the hydraulic conductivity and cumulative removal efficiency versus both time and the number of pore volumes, for three different mean grain sizes and three different temperatures. Figures 6.10 and 6.12 show that the hydraulic conductivity increases linearly for the one day tests with both low (i=0.75) and high (i=4) hydraulic gradient; Figure 6.11 shows the increase to be either bilinear or exponential for the three day tests. Figure

6.13 and 6.15 show that K also increases linearly with respect to pore volumes with both low (i=0.75) and high (i=4) hydraulic gradient; Figure 6.14 show the increase again to be either bilinear or exponential with respect to pore volumes. Qualitatively, this behaviour was expected because as the pore volumes increase, the concentration of the contaminant in the pore space decreases, as shown in Figures 6.19 through 6.21. This results in an increase in the void space which is open to water flow, and a concomitant increase in the hydraulic conductivity.

Figures 6.16 through 6.21 show the cumulative removal efficiency observed in the tests based on measurement of the carbon content of the column effluent. The cumulative removal efficiency for one and three day tests with low (i=0.75) hydraulic gradient increases either bilinearly or exponentially with respect to time and pore volumes. The remaining tests with high hydraulic gradient covering different grain sizes and the three different temperatures followed the same general pattern. The curves for each of the tests can be characterised as consisting of three periods: (1) a curve with a rapid change (decrease) in effluent carbon concentrations; (2) a knee in the curve which probably marks the end of the removal of free oil from the pores; and (3) a slow release period during which the effluent concentration slowly decreases. The reduction levels of diesel contamination for one and three day tests are given in Table 6.3. The rapid decrease in diesel fuel during the early portion of the flushing experiment, followed by a slow decline, suggests that during the later portion of the experiment, diesel fuel flushing was limited by the inability of water or water plus surfactant to dissolve the more immiscible ends of the diesel fuel.

6.2.3 Influence of Grain Size on K and CRE

To study the effect of grain size on the soil washing process, experiments were conducted with the same soil type (silica sand) at three different uniform grain sizes (see Chapter 5, Figure 5.2). The hydraulic gradient was fixed at two levels, 0.75 and 4.

Figure 6.22 and Figure 6.23 shows that as the mean grain size increases the cumulative removal efficiency and the hydraulic conductivity changes hardly at all - the only exception being a significant increase in K at 50°C. As the soil grain size decreases, the void spaces reduce, which causes K to decrease (as shown in Figure 6.22). This reduced the rate at which water or water plus surfactant pass through the sand; this, in turn results in reduction in the rate of removal of the contaminant.

It is interesting to note that there was very little influence of grain size on CRE at 50°C. Perhaps it can be assumed that it was more difficult to de-air finer soil at 50°C than coarser soil at the same temperature.

6.2.4 Influence of Temperature on K and CRE

Figure 6.24 and Figure 6.25 show the effect of temperature on cumulative removal efficiency and hydraulic conductivity for the experiments conducted with water and water plus surfactant, with diesel fuel as the contaminant, and with soil mesh #80 (D_{50} = 0.24 mm) at different gradients; a comparison is made at the beginning, middle and end of one day tests. These curves show that as the temperature increases the removal efficiency and the hydraulic conductivity increases

throughout the tests. Increasing the temperature from 4°C to 50°C increases the removal efficiency of the contaminant by 1 to 40%, and the hydraulic conductivity by 14 to 36%. Temperature increases the ability of both the water and water plus surfactant to dissolve fuel oil. Again, as discussed earlier in section 6.2.1.3 temperature has a definite and measurable effect on the viscosity and density of the influent passing through the soil sample, and in turn effect the values of K. Table 6.4 show the viscosity values for water and water plus surfactant at three different temperatures (4, 22, and 50°C).

6.2.5 Influence of Surfactant on K and CRE

Figure 6.10 through 6.21 show the influence of surfactant on K and CRE versus time and pore volumes for the three mean grain sizes, D_{50} (0.42, 0.24, and 0.17 mm) at three different temperatures with two hydraulic gradients (0.75 and 4) for one day tests. At the completion of the flushing tests, the samples that flushed with water plus surfactant always gave higher K values. This behaviour was expected since the viscosity of the water plus surfactant was always lower than that of water alone. Table 6.4 gives the viscosity values for water and water plus surfactant at three different temperatures. The difference in K between water plus surfactant and water alone at 50°C is always greatest since the difference in viscosity is the greatest between water plus surfactant and water at 50°C. However, the CRE values with water plus surfactant are not that much greater than the CRE values with water alone. Table 6.5 gives the difference between water plus surfactant CRE and water

CRE for one grain size mesh #80 (D_{50} = 0.24 mm) at 1, 24, and 72 hours for the two hydraulic gradient at three different temperatures. It seems that the difference grows with time up to a certain period (24 hours in this study) then decreases. The results in Table 6.5 indicate that temperature has a significant effect on the (W+D)CRE and (W)CRE (see section 6.2.4). Analysis of one day data with low hydraulic gradient (i=0.75) indicates that the influent water plus surfactant has removed 83% of the diesel fuel at 50°C (as shown in Figure 6.16), and increased the hydraulic conductivity to $3.1x10^{-4}$ m/s (see Figure 6.10) after flushing with 233 pore volumes; while for the same length of time, with high hydraulic gradient (i=4), the removal was 94% at 50°C as shown in Figure 6.18, and the final hydraulic conductivity measurement was $3.22x10^{-4}$ m/s (see Figure 6.12) after flushing with 1238 pore volumes. It seems using many more pore volumes (5 times more) increases the removal by approximately 10%. The question can be posed:"Is the 5 times increase in field time and chemical (surfactant) cost effective for only a 10% increase in cleanup?." One answer might be that health-based clean-up guidelines (Chapter 1, Table 1.1) can only be met by prolonged soil washing. If so, then a second question might be posed:" Are the guidelines too stringent and to costly to meet?.

In order to meet the health standard guidelines to remove 132 ml of diesel from approximately 2 kg soil sample, for example, at 50°C with mesh #60, 1500 pore volumes (interploated from Figure 6.19) are required with i=0.75 (~ 570 litre of water and 3 kg of Biodish), and approximately 7000 pore volumes for i=4 (2660 litre

of water and 13.5 kg of Biodish). The amount of water plus surfactant needed to reach health standard guidelines was three to five times the amount used during the experiment. Based on the experimental results it appears that the standard guidelines are too severe and it will be too costly to meet using Biodish®.

6.2.6 Cumulative Removal Efficiency Versus Hydraulic Conductivity

Figures 6.26 through 6.28 show the analyses of the cumulative removal efficiency versus the average hydraulic conductivity. These tests are interpreted as indicating that as the hydraulic conductivity of the contaminated sand increases, the removal efficiency increases with a linear relationship. The first reading of K was taken after one minute from flooding the permeameter cell. The results show that anywhere from one-quarter to two-thirds (depending on T and i) of the contaminant has been removed with only a slight increase in the K value. After that, the results show only a modest increase in CRE with an appreciable increase in K value. A question can be posed:" Is it practical to base CRE value on a change in K in the field? The answer is no, given the finding in Figures 6.26 through 6.28, and the fact that the field case is an open system with K almost impossible to measure with precision.

6.2.7 Comparison of Hydraulic Conductivity for Clean and Contaminated Sand

A comparison of the measurements of the hydraulic conductivity for the clean and dirty soil is shown in Figures 6.29 through 6.31. The results indicate that the

hydraulic conductivity of the clean soil always remains higher than that for dirty soil. The K results for the clean soil show a slight increase with respect to time which is considered as a test error (see section 6.2.2.1). It is clear that the highest value of K for the dirty soil, with respect to clean soil, was recorded after flushing (using water plus surfactant) the sample for one day at 50°C with high hydraulic gradient (i=4).

Table 6.1 Precision for CRE tests for different variables

Temperature= 50 C i=0.75									
Time (min)	1	180	360	540	720	900	1080	1260	1440
CRE #60 (W+D)									
sample #1	11.08	74.92	75.53	77.58	78.30	79.35	80.13	80.69	80.93
sample #2	9.00	76.93	77.76	78.60	79.47	80.36	81.23	82.18	83.12
sample #3	12.00	77.07	77.87	78.94	80.54	81.40	82.26	83.17	84.09
Mean	10.69	76.31	77.06	78.37	79.43	80.37	81.21	82.01	82.71
Std Dev	1.26	0.98	1.08	0.58	0.92	0.84	0.87	1.02	1.32
Precision(%)	11.74	1.29	1.40	0.74	1.15	1.04	1.07	1.24	1.60
CRE #80 (W+D)									
sample #1	2.67	74.50	76.98	77.63	77.88	78.35	79.88	80.52	80.73
sample #2	1.75	75.17	76.52	79.47	79.99	80.18	80.80	81.48	82.70
sample #3	3.17	75.20	77.88	79.52	79.82	80.25	80.85	81.43	81.73
sample #4	3.00	73.92	74.08	75.35	76.72	77.22	77.75	78.38	78.73
Mean	2.64	74.76	76.16	78.11	78.84	79.22	79.80	80.43	81.05
Std Dev	0.63	0.60	1.57	1.95	1.50	1.41	1.45	1.45	1.69
Precision(%)	23.96	0.80	2.06	2.50	1.91	1.78	1.82	1.80	2.09
CRE #100(W+D)									
sample #1	1.50	68.95	71.18	72.03	73.67	75.35	76.30	77.02	78.95
sample #2	0.58	66.32	67.72	68.35	69.35	70.28	71.42	72.70	73.10
sample #3	0.17	65.35	69.80	71.68	73.25	74.45	76.47	76.85	79.35
sample #4	0.27	65.45	69.77	71.78	72.80	73.40	74.22	75.05	76.18
Mean	0.34	65.71	69.09	70.61	71.80	72.71	74.03	74.87	76.21
Std Dev	0.17	0.43	0.97	1.60	1.74	1.77	2.07	1.70	2.55
Precision(%)	51.20	0.66	1.41	2.26	2.43	2.43	2.79	2.27	3.35
CRE #60 (W)									
sample #1	1.75	55.48	63.53	65.17	66.77	68.22	68.87	69.48	70.53
sample #2	0.65	56.32	61.55	63.52	67.18	68.17	68.85	69.45	70.62
sample #3	1.06	57.40	62.72	64.72	66.85	68.13	69.92	70.03	71.83
sample #4	1.12	58.98	60.66	62.44	64.29	66.29	68.36	70.46	72.56
Mean	0.94	57.57	61.64	63.56	66.11	67.53	69.04	69.98	71.67
Std Dev	0.21	1.09	0.84	0.93	1.29	0.88	0.65	0.41	0.80
Precision(%)	22.02	1.90	1.37	1.46	1.96	1.30	0.94	0.59	1.12
CRE #80 (W)									
sample #1	1.58	54.52	63.33	63.58	66.30	66.85	68.23	69.08	70.03
sample #2	0.82	54.45	62.05	63.22	66.13	67.08	68.12	69.25	69.73
sample #3	1.48	53.95	61.48	63.12	66.17	67.02	68.15	69.18	69.85
sample #4	1.40	58.74	60.37	62.11	63.92	65.81	67.78	69.76	71.72
Mean	1.23	55.71	61.30	62.82	65.41	66.64	68.02	69.40	70.43
Std Dev	0.30	2.15	0.70	0.50	1.05	0.58	0.17	0.26	0.91
Precision(%)	24.07	3.86	1.14	0.79	1.61	0.88	0.25	0.37	1.29
CRE #100(W)									
sample #1	2.63	53.07	54.08	59.43	60.62	63.13	64.45	66.88	69.78
sample #2	2.49	53.35	55.38	56.80	57.82	59.65	60.45	61.63	63.68
sample #3	2.59	53.15	55.11	57.16	59.33	61.50	63.64	65.84	68.06
sample #4	2.57	53.44	55.25	57.13	59.12	61.11	63.07	65.10	67.13
Mean	2.55	53.31	55.25	57.03	58.75	60.75	62.39	64.19	66.29
Std Dev	0.04	0.12	0.11	0.16	0.67	0.80	1.39	1.83	1.88
Precision(%)	1.73	0.23	0.20	0.29	1.14	1.31	2.23	2.86	2.84

Table 6.1 Contd.

Temperature= 22 C i=0.75									
Time (min)	1	180	360	540	720	900	1080	1260	1440
CRE #60 (W+D)									
sample #1	0.17	49.72	50.78	53.58	56.03	57.80	58.77	59.62	60.52
sample #2	1.58	50.28	54.75	56.97	58.95	60.83	62.68	63.68	64.37
sample #3	0.81	48.75	50.80	52.37	55.30	57.82	59.40	60.42	62.35
sample #4	0.82	48.87	50.82	51.93	55.13	57.78	59.62	60.75	62.85
Mean	0.85	49.58	52.11	54.31	56.76	58.82	60.28	61.24	62.41
Std Dev	0.58	0.63	1.87	1.94	1.58	1.43	1.72	1.76	1.57
Precision(%)	67.86	1.27	3.58	3.58	2.78	2.42	2.85	2.87	2.52
CRE #80 (W+D)									
sample #1	2.63	47.28	48.52	50.77	53.68	56.28	59.47	60.25	61.70
sample #2	2.48	46.18	47.55	49.68	51.85	53.12	55.35	57.28	60.62
sample #3	2.58	46.90	49.12	51.35	53.58	55.81	58.03	60.26	62.49
sample #4	2.64	45.27	46.63	48.85	50.80	52.17	54.32	56.83	58.88
Mean	2.57	46.12	47.77	49.96	52.08	53.70	55.90	58.13	60.66
Std Dev	0.07	0.67	1.03	1.04	1.15	1.54	1.57	1.52	1.47
Precision(%)	2.54	1.45	2.15	2.08	2.20	2.87	2.80	2.62	2.43
CRE #100(W+D)									
sample #1	2.63	44.70	47.52	49.23	50.42	51.95	55.12	57.58	59.35
sample #2	2.66	48.47	50.35	52.25	54.35	55.18	58.03	59.48	60.52
sample #3	2.66	46.18	48.26	50.34	52.41	54.49	56.56	58.64	59.72
sample #4	2.68	46.40	48.22	50.35	52.37	53.97	56.02	58.70	59.30
Mean	2.67	47.02	48.94	50.98	53.04	54.55	56.87	58.94	59.84
Std Dev	0.01	1.03	1.00	0.90	0.92	0.50	0.85	0.38	0.50
Precision(%)	0.42	2.19	2.03	1.76	1.74	0.91	1.50	0.65	0.84
CRE #60 (W)									
sample #1	3.02	42.73	44.50	46.70	48.18	50.43	52.53	54.62	56.73
sample #2	2.49	44.67	46.33	48.05	49.88	51.85	55.37	57.77	60.02
sample #3	2.74	43.69	45.85	48.01	50.17	52.33	54.49	56.65	58.81
sample #4	2.78	40.43	42.38	45.52	47.87	49.03	50.82	53.85	55.62
Mean	2.67	42.93	44.86	47.19	49.31	51.07	53.56	56.09	58.15
Std Dev	0.13	1.81	1.76	1.19	1.03	1.45	1.97	1.65	1.86
Precision(%)	4.78	4.22	3.92	2.51	2.08	2.85	3.68	2.94	3.19
CRE #80 (W)									
sample #1	2.97	42.47	44.22	47.97	49.52	54.03	55.47	56.23	56.85
sample #2	3.09	41.08	43.49	45.90	48.31	50.71	53.12	54.53	54.94
sample #3	3.15	41.18	42.35	46.02	48.45	52.18	53.58	55.42	55.83
sample #4	3.17	39.37	40.27	44.83	46.42	49.95	51.67	53.52	54.00
Mean	3.13	40.54	42.04	45.58	47.72	50.95	52.79	54.49	54.92
Std Dev	0.04	0.83	1.33	0.53	0.93	0.93	0.82	0.78	0.75
Precision(%)	1.12	2.05	3.17	1.17	1.94	1.82	1.55	1.42	1.36
CRE #100(W)									
sample #1	3.38	36.22	37.55	39.80	43.10	47.63	49.60	50.83	51.82
sample #2	3.32	37.35	38.58	41.85	45.95	49.52	50.62	52.93	54.80
sample #3	3.36	38.28	39.75	42.92	46.92	50.45	52.47	54.85	56.80
sample #4	3.35	37.13	39.79	42.45	45.11	47.77	50.42	53.08	55.74
Mean	3.34	37.59	39.38	42.41	45.99	49.24	51.17	53.62	55.78
Std Dev	0.02	0.50	0.56	0.44	0.74	1.11	0.92	0.87	0.82
Precision(%)	0.53	1.33	1.42	1.03	1.61	2.26	1.80	1.62	1.46

Table 6.1 Contd.

Temperature= 4 C i=0.75									
Time (min)	1	180	360	540	720	900	1080	1260	1440
CRE #60 (W+D)									
sample #1	1.25	30.03	32.67	34.17	37.43	39.92	40.95	43.33	45.52
sample #2	0.83	29.09	31.83	33.33	36.50	38.14	40.83	42.30	44.15
sample #3	1.03	31.27	33.60	35.93	38.26	40.59	42.92	45.25	47.58
sample #4	1.04	31.40	34.81	38.22	40.64	42.05	44.46	46.87	48.29
Mean	1.04	30.13	32.70	34.48	37.40	39.55	41.57	43.63	45.75
Std Dev	0.17	0.89	0.72	1.08	0.72	1.03	0.96	1.22	1.41
Precision(%)	16.39	2.96	2.20	3.13	1.92	2.61	2.30	2.80	3.08
CRE #80 (W+D)									
sample #1	0.83	25.55	28.13	30.77	33.92	36.03	38.90	40.07	43.30
sample #2	0.81	27.62	30.07	32.52	34.97	37.42	39.87	42.32	44.77
sample #3	0.75	28.63	30.25	32.83	35.90	37.90	40.48	42.85	45.50
sample #4	0.82	30.58	32.33	36.67	38.67	40.00	42.57	44.92	47.18
Mean	0.79	28.95	30.88	34.01	36.51	38.44	40.97	43.36	45.82
Std Dev	0.03	1.23	1.03	1.89	1.57	1.12	1.15	1.12	1.01
Precision(%)	3.79	4.25	3.33	5.54	4.30	2.91	2.81	2.58	2.20
CRE #100(W+D)									
sample #1	0.69	26.56	28.80	31.05	33.29	35.54	37.79	40.03	42.28
sample #2	0.65	29.17	30.80	33.00	35.80	37.67	39.00	42.83	45.15
sample #3	0.73	24.13	26.73	29.83	30.85	33.68	35.17	37.73	40.35
sample #4	0.71	27.18	28.67	30.87	32.83	35.62	37.08	39.72	43.22
Mean	0.69	26.83	28.73	31.23	33.16	35.66	37.08	40.09	42.91
Std Dev	0.03	2.07	1.66	1.32	2.03	1.63	1.56	2.10	1.97
Precision(%)	4.63	7.72	5.78	4.22	6.13	4.56	4.22	5.24	4.60
CRE #60 (W)									
sample #1	3.07	30.67	33.45	34.00	36.35	37.92	38.97	40.58	43.42
sample #2	3.24	28.15	30.50	32.03	34.25	36.00	38.00	38.68	40.50
sample #3	3.03	29.31	31.02	32.74	34.45	36.17	37.88	39.59	41.31
sample #4	2.66	27.37	28.42	30.08	32.42	34.90	35.82	37.58	39.50
Mean	2.98	28.28	29.98	31.62	33.71	35.69	37.23	38.62	40.44
Std Dev	0.24	0.80	1.13	1.12	0.92	0.56	1.00	0.82	0.74
Precision(%)	8.10	2.82	3.76	3.55	2.72	1.57	2.69	2.13	1.83
CRE #80 (W)									
sample #1	2.51	29.63	30.62	32.42	34.30	36.33	37.30	38.03	40.83
sample #2	2.59	27.88	29.52	31.16	32.80	34.43	36.07	37.71	39.35
sample #3	2.66	27.68	28.50	30.52	32.35	34.35	36.35	37.08	38.67
sample #4	2.60	25.58	27.58	29.40	30.25	31.18	33.42	35.17	36.50
Mean	2.62	27.05	28.54	30.36	31.80	33.32	35.28	36.65	38.17
Std Dev	0.03	1.04	0.79	0.73	1.11	1.51	1.32	1.08	1.21
Precision(%)	1.16	3.85	2.78	2.39	3.49	4.54	3.75	2.95	3.18
CRE #100(W)									
sample #1	0.83	23.87	25.17	26.67	28.67	30.00	32.47	33.37	35.28
sample #2	2.55	26.83	28.18	29.63	31.83	33.97	35.50	36.50	38.17
sample #3	2.53	28.92	29.33	31.68	33.75	35.85	36.52	38.42	39.30
sample #4	2.11	25.73	27.40	29.07	30.74	32.41	34.08	35.75	37.42
Mean	2.40	27.16	28.31	30.13	32.11	34.08	35.37	36.89	38.30
Std Dev	0.20	1.32	0.79	1.12	1.24	1.41	1.00	1.12	0.77
Precision(%)	8.44	4.86	2.80	3.72	3.87	4.12	2.82	3.04	2.01

Table 6.1 Contd.

Temperature = 50 C i=4									
Time (min)	1	180	360	540	720	900	1080	1260	1440
CRE #60 (W+D)									
sample #1	5.83	75.73	78.87	82.02	84.99	87.97	90.94	91.91	92.40
sample #2	4.17	74.07	76.07	78.79	82.73	84.93	87.75	90.55	91.87
sample #3	5.00	78.03	81.93	84.96	86.07	88.00	91.04	91.73	92.59
sample #4	5.00	76.68	78.30	81.40	83.73	87.23	89.57	91.90	92.07
Mean	5.00	75.94	78.96	81.92	84.60	86.96	89.91	91.40	92.29
Std Dev	0.68	1.63	2.39	2.52	1.39	1.44	1.53	0.60	0.30
Precision(%)	13.61	2.14	3.03	3.08	1.64	1.65	1.70	0.66	0.33
CRE #80 (W+D)									
sample #1	5.83	74.25	75.73	77.92	78.87	80.37	81.45	82.02	83.51
sample #2	4.17	72.58	74.07	76.25	77.20	78.70	80.45	81.83	83.38
sample #3	5.00	73.42	74.90	77.08	78.03	79.53	80.95	81.93	83.44
sample #4	5.00	74.83	76.68	78.71	78.30	79.51	80.63	81.40	82.56
Mean	4.72	73.61	75.22	77.35	77.85	79.25	80.68	81.72	83.13
Std Dev	0.39	0.93	1.09	1.02	0.47	0.39	0.21	0.23	0.40
Precision(%)	8.32	1.26	1.45	1.32	0.60	0.49	0.26	0.28	0.48
CRE #100(W+D)									
sample #1	6.67	74.25	75.73	77.92	78.87	79.20	79.78	80.35	81.72
sample #2	5.83	73.42	74.73	76.25	77.37	78.53	79.45	80.02	81.70
sample #3	6.25	73.83	75.23	77.08	78.12	78.87	79.62	80.18	81.71
sample #4	6.25	74.90	77.23	78.04	78.45	78.70	78.86	78.98	79.07
Mean	6.11	74.05	75.73	77.12	77.98	78.70	79.31	79.73	80.83
Std Dev	0.20	0.62	1.08	0.73	0.45	0.14	0.32	0.53	1.24
Precision(%)	3.21	0.84	1.42	0.95	0.58	0.17	0.41	0.67	1.54
CRE #60 (W)									
sample #1	8.33	70.08	73.07	74.58	75.53	77.40	78.45	79.52	80.70
sample #2	7.50	71.75	73.07	74.42	75.03	77.07	78.62	79.35	80.53
sample #3	7.92	70.92	73.07	74.50	75.28	77.23	78.53	79.43	80.62
sample #4	7.92	73.75	75.50	76.10	76.40	76.57	76.70	76.79	76.85
Mean	7.78	72.14	73.88	75.01	75.57	76.96	77.95	78.52	79.33
Std Dev	0.20	1.19	1.15	0.78	0.59	0.28	0.88	1.23	1.75
Precision(%)	2.52	1.65	1.55	1.03	0.78	0.36	1.13	1.56	2.21
CRE #80 (W)									
sample #1	9.17	68.42	70.57	72.08	73.37	75.35	76.70	77.68	78.39
sample #2	10.00	69.08	70.23	71.75	73.53	75.18	76.95	77.52	78.87
sample #3	9.58	68.75	70.40	71.92	73.45	75.27	76.82	77.60	78.63
sample #4	9.58	72.19	73.53	73.98	74.21	74.34	74.43	74.49	74.53
Mean	9.72	70.01	71.39	72.55	73.73	74.93	76.07	76.53	77.34
Std Dev	0.20	1.55	1.52	1.02	0.34	0.42	1.16	1.45	1.99
Precision(%)	2.02	2.21	2.13	1.40	0.46	0.56	1.53	1.89	2.57
CRE #100(W)									
sample #1	10.37	68.34	68.57	70.08	71.87	73.52	75.28	75.85	77.20
sample #2	10.20	68.51	68.90	70.25	71.70	73.68	75.45	76.02	76.70
sample #3	10.28	68.43	68.73	70.17	71.78	73.60	75.37	75.93	76.95
sample #4	10.28	70.91	72.11	72.51	72.72	72.84	72.91	72.96	73.00
Mean	10.26	69.28	69.91	70.97	72.07	73.37	74.58	74.97	75.55
Std Dev	0.04	1.15	1.55	1.08	0.46	0.38	1.18	1.42	1.80
Precision(%)	0.38	1.66	2.22	1.53	0.64	0.52	1.58	1.89	2.39

Table 6.1 Contd.

Temperature = 22 C I=4									
Time (min)	1	180	360	540	720	900	1080	1260	1440
CRE #60 (W+D)									
sample #1	8.33	65.03	66.91	67.75	68.70	69.00	70.25	70.85	72.20
sample #2	7.50	65.67	67.36	67.61	69.37	69.17	70.78	71.18	71.87
sample #3	7.92	65.35	67.13	67.68	69.03	69.09	70.51	71.02	72.03
sample #4	7.92	67.05	68.46	68.95	69.19	69.33	69.42	69.49	69.54
Mean	7.92	65.35	67.13	67.68	69.03	69.09	70.51	71.02	72.03
Std Dev	0.34	0.26	0.18	0.06	0.27	0.07	0.22	0.14	0.14
Precision(%)	4.30	0.40	0.27	0.09	0.39	0.10	0.31	0.19	0.19
CRE #80 (W+D)									
sample #1	6.67	60.67	61.75	62.61	63.45	64.42	65.12	66.18	66.87
sample #2	5.83	60.03	61.72	62.75	63.35	64.18	65.02	65.85	66.70
sample #3	6.25	60.35	61.73	62.68	63.40	64.30	65.07	66.02	66.78
sample #4	6.25	61.64	63.21	63.76	64.03	64.19	64.30	64.37	64.43
Mean	6.11	60.67	62.22	63.06	63.59	64.22	64.79	65.41	65.97
Std Dev	0.20	0.69	0.70	0.49	0.31	0.05	0.35	0.74	1.09
Precision(%)	3.21	1.14	1.13	0.78	0.49	0.09	0.54	1.13	1.65
CRE #100(W+D)									
sample #1	3.33	58.37	60.05	61.08	61.68	62.52	63.35	64.18	65.03
sample #2	2.50	58.42	60.22	60.75	61.85	62.35	62.85	63.35	64.03
sample #3	2.92	58.39	60.13	60.92	61.77	62.43	63.10	63.77	64.53
sample #4	2.92	57.63	60.74	61.87	62.45	62.79	63.02	63.19	63.31
Mean	2.78	58.15	60.36	61.18	62.02	62.52	62.99	63.43	63.96
Std Dev	0.20	0.36	0.27	0.49	0.30	0.19	0.10	0.24	0.50
Precision(%)	7.07	0.63	0.45	0.81	0.49	0.30	0.17	0.38	0.79
CRE #60 (W)									
sample #1	5.00	53.42	53.55	54.08	55.18	55.68	57.85	58.35	60.70
sample #2	5.83	52.92	53.38	54.25	55.02	55.85	57.02	58.52	60.53
sample #3	5.42	53.17	53.47	54.17	55.10	55.77	57.43	58.43	60.62
sample #4	5.42	54.07	55.45	55.93	56.19	56.32	56.42	56.49	56.55
Mean	5.56	53.38	54.10	54.78	55.43	55.98	56.96	57.81	59.23
Std Dev	0.20	0.50	0.95	0.81	0.53	0.24	0.41	0.94	1.90
Precision(%)	3.54	0.93	1.76	1.49	0.96	0.43	0.73	1.62	3.21
CRE #80 (W)									
sample #1	6.67	51.25	51.72	52.58	53.35	54.18	55.35	56.85	58.87
sample #2	7.50	50.25	51.22	51.75	52.35	53.35	54.18	55.18	57.20
sample #3	7.08	50.75	51.47	52.17	52.85	53.77	54.77	56.02	58.03
sample #4	7.08	52.37	53.31	53.64	53.81	53.91	53.98	54.02	54.06
Mean	7.22	51.12	52.00	52.52	53.00	53.68	54.31	55.07	56.43
Std Dev	0.20	0.90	0.94	0.81	0.60	0.24	0.33	0.82	1.71
Precision(%)	2.72	1.77	1.80	1.55	1.14	0.44	0.61	1.48	3.03
CRE #100(W)									
sample #1	8.33	48.58	49.55	50.08	50.68	51.68	52.52	53.52	55.53
sample #2	9.17	48.25	48.38	50.25	51.02	51.85	52.68	53.35	55.70
sample #3	8.75	48.42	48.97	50.17	50.85	51.77	52.60	53.43	55.62
sample #4	8.75	50.48	51.16	51.39	51.51	51.58	51.63	51.66	51.69
Mean	8.89	49.05	49.50	50.60	51.12	51.73	52.30	52.81	54.33
Std Dev	0.20	1.02	1.20	0.56	0.28	0.11	0.48	0.82	1.87
Precision(%)	2.21	2.07	2.41	1.10	0.54	0.22	0.92	1.55	3.45

Table 6.1 Contd.

Temperature= 4 C i=4									
Time (min)	1	180	360	540	720	900	1080	1260	1440
CRE #60 (W+D)									
sample #1	4.67	44.92	45.05	45.25	46.02	46.85	49.35	50.02	51.87
sample #2	3.83	44.58	45.02	45.17	46.00	46.68	47.85	50.03	50.70
sample #3	4.25	44.75	45.03	45.21	46.01	46.77	48.60	50.03	51.28
sample #4	4.25	43.74	46.95	47.38	47.60	47.74	47.84	47.90	47.95
Mean	4.25	44.75	45.03	45.21	46.01	46.77	48.60	50.03	51.28
Std Dev	0.34	0.14	0.01	0.03	0.01	0.07	0.61	0.01	0.48
Precision(%)	8.00	0.30	0.03	0.08	0.01	0.15	1.26	0.01	0.93
CRE #80 (W+D)									
sample #1	6.33	42.92	43.35	44.35	45.10	46.02	46.68	48.37	49.03
sample #2	7.17	43.08	43.42	44.18	45.27	46.18	46.85	48.53	49.37
sample #3	6.75	43.00	43.38	44.27	45.18	46.10	46.77	48.45	49.20
sample #4	6.75	44.75	45.46	45.71	45.83	45.91	45.96	45.99	46.02
Mean	6.89	43.61	44.09	44.72	45.43	46.06	46.52	47.66	48.19
Std Dev	0.20	0.80	0.97	0.70	0.29	0.12	0.40	1.18	1.54
Precision(%)	2.85	1.84	2.20	1.56	0.63	0.25	0.87	2.48	3.20
CRE #100(W+D)									
sample #1	8.00	41.42	41.75	42.52	43.60	44.52	45.18	46.87	47.70
sample #2	7.58	41.25	41.92	42.68	43.43	44.35	45.02	46.70	47.53
sample #3	7.79	41.33	41.83	42.60	43.52	44.43	45.10	46.78	47.62
sample #4	7.79	43.31	43.87	44.06	44.16	44.21	44.25	44.28	44.30
Mean	7.72	41.97	42.54	43.12	43.70	44.33	44.79	45.92	46.48
Std Dev	0.10	0.95	0.94	0.67	0.32	0.09	0.38	1.16	1.55
Precision(%)	1.27	2.27	2.21	1.56	0.74	0.20	0.85	2.53	3.33
CRE #60 (W)									
sample #1	6.75	41.08	41.75	42.85	43.60	44.52	45.08	46.87	47.87
sample #2	5.92	41.25	42.08	43.02	43.43	45.02	47.08	48.53	51.20
sample #3	6.33	41.17	41.92	42.93	43.52	44.77	46.08	47.70	49.53
sample #4	6.33	43.58	44.31	44.55	44.68	44.75	44.81	44.84	44.86
Mean	6.19	42.00	42.77	43.50	43.88	44.85	45.99	47.02	48.53
Std Dev	0.20	1.12	1.09	0.75	0.57	0.12	0.93	1.58	2.68
Precision(%)	3.17	2.66	2.55	1.71	1.29	0.27	2.03	3.36	5.52
CRE #80 (W)									
sample #1	7.58	39.58	40.42	41.35	41.77	43.35	45.42	46.87	49.53
sample #2	8.42	38.75	39.58	40.17	41.68	43.52	45.25	46.70	48.03
sample #3	8.00	39.17	40.00	40.76	41.73	43.43	45.33	46.78	48.78
sample #4	8.00	42.33	42.85	43.02	43.11	43.16	43.20	43.22	43.24
Mean	8.14	40.08	40.81	41.32	42.17	43.37	44.59	45.57	46.69
Std Dev	0.20	1.60	1.45	1.23	0.66	0.15	0.99	1.66	2.45
Precision(%)	2.42	3.99	3.55	2.98	1.57	0.35	2.21	3.64	5.26
CRE #100(W)									
sample #1	9.25	36.75	37.92	38.50	40.02	41.85	43.08	43.37	44.70
sample #2	10.08	33.42	35.08	36.02	36.68	38.52	39.75	40.03	41.37
sample #3	9.67	35.08	36.50	37.26	38.35	40.18	41.42	41.70	43.03
sample #4	9.67	38.59	38.91	39.02	39.07	39.11	39.13	39.14	39.16
Mean	9.81	35.70	36.83	37.43	38.04	39.27	40.10	40.29	41.19
Std Dev	0.20	2.16	1.58	1.23	1.00	0.69	0.97	1.06	1.59
Precision(%)	2.01	6.04	4.29	3.29	2.63	1.76	2.41	2.63	3.86

Table 6.2 Precision for K tests for different variables

Temperature = 50 C I=0.75									
Time (min)	1	180	360	540	720	900	1080	1260	1440
K #60 (W+D)									
sample #1	0.000270	0.000274	0.000281	0.000282	0.000284	0.000289	0.000289	0.000295	0.000298
sample #2	0.000269	0.000277	0.000286	0.000293	0.000303	0.000311	0.000315	0.000320	0.000322
sample #3	0.000270	0.000272	0.000284	0.000288	0.000291	0.000294	0.000296	0.000298	0.000302
Mean	0.000270	0.000274	0.000283	0.000288	0.000293	0.000298	0.000300	0.000305	0.000307
Std Dev	3.37E-07	1.93E-06	2.11E-06	4.43E-06	8.04E-06	9.58E-06	1.08E-05	1.11E-05	1.07E-05
Precision(%)	0.12	0.70	0.74	1.54	2.75	3.22	3.61	3.64	3.49
K #80 (W+D)									
sample #1	0.000242	0.000249	0.000257	0.000261	0.000264	0.000274	0.000275	0.000279	0.000281
sample #2	0.000233	0.000245	0.000249	0.000253	0.000255	0.000257	0.000263	0.000268	0.000273
sample #3	0.000251	0.000255	0.000256	0.000262	0.000268	0.000272	0.000275	0.000279	0.000284
sample #4	0.000251	0.000253	0.000258	0.000263	0.000267	0.000270	0.000273	0.000277	0.000280
Mean	0.000245	0.000251	0.000254	0.000259	0.000263	0.000266	0.000271	0.000275	0.000279
Std Dev	8.72E-06	4.42E-06	3.71E-06	4.57E-06	6.01E-06	6.69E-06	5.34E-06	5.10E-06	4.67E-06
Precision(%)	3.56	1.76	1.46	1.76	2.28	2.51	1.97	1.85	1.68
K #100(W+D)									
sample #1	0.000224	0.000225	0.000236	0.000237	0.000239	0.000241	0.000245	0.000249	0.000252
sample #2	0.000209	0.000222	0.000227	0.000238	0.000240	0.000252	0.000261	0.000263	0.000265
sample #3	0.000210	0.000220	0.000225	0.000235	0.000243	0.000245	0.000254	0.000265	0.000269
sample #4	0.000211	0.000213	0.000228	0.000235	0.000239	0.000249	0.000254	0.000265	0.000273
Mean	0.000210	0.000218	0.000227	0.000236	0.000241	0.000249	0.000256	0.000264	0.000269
Std Dev	8.61E-07	3.72E-06	1.23E-06	1.21E-06	1.57E-06	2.71E-06	3.20E-06	9.91E-07	3.17E-06
Precision(%)	0.41	1.70	0.54	0.51	0.65	1.09	1.25	0.37	1.18
K #60 (W)									
sample #1	0.000198	0.000206	0.000210	0.000216	0.000220	0.000225	0.000231	0.000234	0.000237
sample #2	0.000192	0.000198	0.000202	0.000208	0.000215	0.000224	0.000231	0.000233	0.000237
sample #3	0.000191	0.000197	0.000203	0.000209	0.000212	0.000220	0.000225	0.000234	0.000237
sample #4	0.000191	0.000197	0.000203	0.000207	0.000213	0.000219	0.000225	0.000231	0.000236
Mean	0.000191	0.000197	0.000202	0.000208	0.000213	0.000221	0.000227	0.000233	0.000236
Std Dev	4.77E-07	4.22E-07	3.57E-07	7.23E-07	1.04E-06	2.09E-06	2.79E-06	1.55E-06	4.84E-07
Precision(%)	0.25	0.21	0.18	0.35	0.49	0.95	1.23	0.67	0.20
K #80 (W)									
sample #1	0.000181	0.000183	0.000188	0.000194	0.000199	0.000204	0.000208	0.000211	0.000213
sample #2	0.000183	0.000187	0.000192	0.000198	0.000203	0.000210	0.000213	0.000218	0.000221
sample #3	0.000182	0.000185	0.000190	0.000197	0.000201	0.000207	0.000213	0.000217	0.000219
sample #4	0.000181	0.000186	0.000188	0.000193	0.000199	0.000203	0.000210	0.000212	0.000215
Mean	0.000182	0.000186	0.000190	0.000196	0.000201	0.000207	0.000212	0.000216	0.000218
Std Dev	5.10E-07	1.08E-06	1.88E-06	2.14E-06	1.84E-06	2.87E-06	1.42E-06	2.46E-06	2.42E-06
Precision(%)	0.28	0.58	0.99	1.09	0.91	1.39	0.67	1.14	1.11
K #100(W)									
sample #1	0.000171	0.000183	0.000189	0.000193	0.000198	0.000200	0.000205	0.000206	0.000209
sample #2	0.000173	0.000184	0.000191	0.000194	0.000200	0.000203	0.000206	0.000207	0.000211
sample #3	0.000170	0.000180	0.000187	0.000192	0.000197	0.000201	0.000204	0.000205	0.000208
sample #4	0.000169	0.000179	0.000186	0.000191	0.000195	0.000198	0.000202	0.000203	0.000205
Mean	0.000171	0.000181	0.000188	0.000193	0.000197	0.000201	0.000204	0.000205	0.000208
Std Dev	1.79E-06	2.00E-06	2.39E-06	1.16E-06	2.02E-06	2.09E-06	1.65E-06	1.37E-06	2.19E-06
Precision(%)	1.05	1.10	1.27	0.60	1.02	1.04	0.81	0.67	1.05

Table 6.2 Contd.

Temperature= 22 C i=0.75									
Time (min)	1	180	360	540	720	900	1080	1260	1440
K #60 (W+D)									
sample #1	0.000188	0.000190	0.000193	0.000198	0.000203	0.000209	0.000213	0.000216	0.000217
sample #2	0.000187	0.000190	0.000193	0.000198	0.000203	0.000209	0.000213	0.000216	0.000217
sample #3	0.000187	0.000189	0.000193	0.000198	0.000203	0.000209	0.000213	0.000215	0.000217
sample #4	0.000187	0.000189	0.000193	0.000198	0.000204	0.000209	0.000213	0.000216	0.000217
Mean	0.000188	0.000190	0.000193	0.000198	0.000203	0.000209	0.000213	0.000216	0.000217
Std Dev	1.68E-07	1.83E-07	2.07E-07	2.55E-07	1.34E-07	1.55E-07	1.91E-07	1.24E-07	9.91E-08
Precision(%)	0.09	0.10	0.11	0.13	0.07	0.07	0.09	0.06	0.05
K #80 (W+D)									
sample #1	0.000184	0.000190	0.000193	0.000199	0.000204	0.000208	0.000213	0.000215	0.000218
sample #2	0.000182	0.000189	0.000193	0.000198	0.000203	0.000207	0.000213	0.000214	0.000215
sample #3	0.000180	0.000185	0.000188	0.000190	0.000197	0.000202	0.000209	0.000211	0.000212
sample #4	0.000185	0.000189	0.000194	0.000198	0.000202	0.000207	0.000211	0.000215	0.000219
Mean	0.000183	0.000188	0.000192	0.000196	0.000201	0.000205	0.000211	0.000213	0.000215
Std Dev	1.94E-06	2.04E-06	2.64E-06	3.63E-06	2.66E-06	2.12E-06	1.51E-06	1.49E-06	3.14E-06
Precision(%)	1.06	1.08	1.38	1.86	1.33	1.03	0.72	0.70	1.46
K #100(W+D)									
sample #1	0.000180	0.000184	0.000189	0.000193	0.000197	0.000201	0.000205	0.000210	0.000214
sample #2	0.000179	0.000185	0.000188	0.000193	0.000201	0.000203	0.000207	0.000210	0.000212
sample #3	0.000175	0.000181	0.000186	0.000190	0.000196	0.000200	0.000202	0.000206	0.000209
sample #4	0.000181	0.000187	0.000190	0.000195	0.000198	0.000202	0.000206	0.000211	0.000215
Mean	0.000178	0.000184	0.000188	0.000193	0.000198	0.000202	0.000205	0.000209	0.000212
Std Dev	2.64E-06	2.45E-06	1.92E-06	1.79E-06	1.87E-06	1.23E-06	2.19E-06	2.13E-06	2.31E-06
Precision(%)	1.48	1.33	1.02	0.93	0.94	0.61	1.07	1.02	1.09
K #60 (W)									
sample #1	0.000176	0.000181	0.000184	0.000188	0.000197	0.000200	0.000203	0.000205	0.000206
sample #2	0.000177	0.000181	0.000184	0.000187	0.000195	0.000200	0.000203	0.000205	0.000206
sample #3	0.000177	0.000183	0.000185	0.000189	0.000197	0.000202	0.000205	0.000207	0.000209
sample #4	0.000173	0.000179	0.000181	0.000186	0.000190	0.000195	0.000198	0.000201	0.000203
Mean	0.000176	0.000181	0.000184	0.000188	0.000194	0.000199	0.000202	0.000204	0.000206
Std Dev	1.87E-06	1.79E-06	1.62E-06	1.46E-06	2.90E-06	2.79E-06	2.90E-06	2.48E-06	2.45E-06
Precision(%)	1.07	0.99	0.88	0.78	1.49	1.40	1.44	1.21	1.19
K #80 (W)									
sample #1	0.000170	0.000174	0.000176	0.000181	0.000183	0.000190	0.000195	0.000197	0.000200
sample #2	0.000173	0.000177	0.000178	0.000184	0.000187	0.000201	0.000202	0.000205	0.000207
sample #3	0.000171	0.000175	0.000177	0.000182	0.000185	0.000190	0.000198	0.000200	0.000203
sample #4	0.000170	0.000174	0.000179	0.000183	0.000187	0.000192	0.000196	0.000200	0.000204
Mean	0.000172	0.000175	0.000178	0.000183	0.000186	0.000194	0.000198	0.000202	0.000205
Std Dev	1.21E-06	9.79E-07	7.43E-07	9.87E-07	8.32E-07	4.88E-06	2.61E-06	2.35E-06	1.81E-06
Precision(%)	0.71	0.56	0.42	0.54	0.45	2.51	1.32	1.17	0.88
K #100(W)									
sample #1	0.000171	0.000176	0.000178	0.000181	0.000186	0.000190	0.000196	0.000200	0.000202
sample #2	0.000167	0.000169	0.000170	0.000174	0.000178	0.000182	0.000187	0.000190	0.000195
sample #3	0.000168	0.000171	0.000174	0.000177	0.000181	0.000185	0.000192	0.000197	0.000200
sample #4	0.000166	0.000170	0.000174	0.000179	0.000183	0.000187	0.000191	0.000195	0.000199
Mean	0.000167	0.000170	0.000173	0.000177	0.000181	0.000185	0.000190	0.000194	0.000198
Std Dev	7.11E-07	8.42E-07	1.72E-06	1.82E-06	1.91E-06	1.88E-06	2.07E-06	2.82E-06	2.23E-06
Precision(%)	0.43	0.49	1.00	1.03	1.06	1.02	1.09	1.45	1.12

Table 6.2 Contd.

Temperature= 4 C I=0.75									
Time (min)	1	180	360	540	720	900	1080	1260	1440
K #60 (W+D)									
sample #1	0.000168	0.000170	0.000173	0.000178	0.000180	0.000185	0.000190	0.000193	0.000196
sample #2	0.000171	0.000173	0.000178	0.000183	0.000184	0.000188	0.000192	0.000196	0.000199
sample #3	0.000171	0.000173	0.000178	0.000183	0.000185	0.000191	0.000196	0.000199	0.000201
sample #4	0.000170	0.000174	0.000178	0.000182	0.000186	0.000191	0.000195	0.000199	0.000203
Mean	0.000170	0.000172	0.000176	0.000181	0.000183	0.000188	0.000193	0.000196	0.000199
Std Dev	1.40E-06	1.40E-06	2.36E-06	2.24E-06	1.95E-06	2.45E-06	2.46E-06	2.65E-06	2.21E-06
Precision(%)	0.82	0.81	1.34	1.23	1.06	1.30	1.28	1.35	1.11
K #80 (W+D)									
sample #1	0.000165	0.000169	0.000173	0.000174	0.000177	0.000182	0.000187	0.000188	0.000197
sample #2	0.000166	0.000169	0.000173	0.000174	0.000177	0.000182	0.000187	0.000189	0.000197
sample #3	0.000165	0.000169	0.000174	0.000174	0.000177	0.000182	0.000187	0.000188	0.000197
sample #4	0.000165	0.000169	0.000173	0.000174	0.000177	0.000182	0.000187	0.000188	0.000196
Mean	0.000165	0.000169	0.000173	0.000174	0.000177	0.000182	0.000187	0.000188	0.000197
Std Dev	8.46E-08	1.76E-07	1.22E-07	1.68E-07	1.58E-07	1.07E-07	1.14E-07	2.85E-07	1.03E-07
Precision(%)	0.05	0.10	0.07	0.10	0.09	0.06	0.06	0.15	0.05
K #100(W+D)									
sample #1	0.000162	0.000165	0.000169	0.000173	0.000177	0.000180	0.000184	0.000188	0.000192
sample #2	0.000160	0.000163	0.000166	0.000169	0.000175	0.000179	0.000181	0.000185	0.000190
sample #3	0.000162	0.000165	0.000169	0.000175	0.000179	0.000180	0.000185	0.000188	0.000193
sample #4	0.000164	0.000168	0.000174	0.000178	0.000181	0.000184	0.000187	0.000190	0.000194
Mean	0.000162	0.000165	0.000170	0.000174	0.000178	0.000181	0.000185	0.000188	0.000192
Std Dev	1.47E-06	2.38E-06	3.23E-06	3.85E-06	2.40E-06	2.05E-06	2.45E-06	2.19E-06	1.42E-06
Precision(%)	0.91	1.44	1.90	2.21	1.35	1.13	1.33	1.16	0.74
K #60 (W)									
sample #1	0.000161	0.000163	0.000166	0.000169	0.000172	0.000176	0.000179	0.000182	0.000184
sample #2	0.000159	0.000162	0.000164	0.000168	0.000171	0.000174	0.000177	0.000180	0.000182
sample #3	0.000157	0.000162	0.000165	0.000170	0.000173	0.000175	0.000176	0.000179	0.000180
sample #4	0.000156	0.000160	0.000163	0.000166	0.000170	0.000173	0.000175	0.000178	0.000179
Mean	0.000157	0.000162	0.000164	0.000168	0.000172	0.000174	0.000176	0.000179	0.000180
Std Dev	1.05E-06	8.80E-07	9.51E-07	1.63E-06	1.40E-06	8.47E-07	9.38E-07	6.82E-07	9.90E-07
Precision(%)	0.67	0.54	0.58	0.97	0.82	0.49	0.53	0.38	0.55
K #80 (W)									
sample #1	0.000155	0.000159	0.000163	0.000167	0.000170	0.000174	0.000176	0.000177	0.000179
sample #2	0.000154	0.000157	0.000161	0.000165	0.000168	0.000171	0.000174	0.000175	0.000180
sample #3	0.000153	0.000154	0.000160	0.000163	0.000167	0.000171	0.000172	0.000174	0.000177
sample #4	0.000156	0.000159	0.000163	0.000166	0.000169	0.000173	0.000176	0.000179	0.000182
Mean	0.000155	0.000157	0.000161	0.000164	0.000168	0.000171	0.000174	0.000176	0.000180
Std Dev	1.36E-06	2.22E-06	1.20E-06	1.10E-06	6.69E-07	9.18E-07	1.58E-06	2.11E-06	2.18E-06
Precision(%)	0.88	1.41	0.74	0.67	0.40	0.54	0.91	1.20	1.21
K #100(W)									
sample #1	0.000154	0.000157	0.000160	0.000163	0.000166	0.000169	0.000172	0.000175	0.000178
sample #2	0.000153	0.000156	0.000159	0.000163	0.000167	0.000169	0.000173	0.000175	0.000176
sample #3	0.000155	0.000157	0.000160	0.000164	0.000168	0.000170	0.000175	0.000176	0.000179
sample #4	0.000150	0.000153	0.000156	0.000159	0.000164	0.000167	0.000169	0.000170	0.000173
Mean	0.000153	0.000155	0.000159	0.000162	0.000166	0.000169	0.000172	0.000174	0.000176
Std Dev	2.06E-06	1.94E-06	1.74E-06	2.13E-06	1.80E-06	1.22E-06	2.54E-06	2.51E-06	2.55E-06
Precision(%)	1.35	1.25	1.10	1.31	1.09	0.72	1.48	1.44	1.45

Table 6.2 Contd.

Temperature= 50 C i=4									
Time (min)	1	180	360	540	720	900	1080	1260	1440
K #60 (W+D)									
sample #1	0.000284	0.000289	0.000298	0.000301	0.000305	0.000309	0.000314	0.000318	0.000320
sample #2	0.000286	0.000293	0.000303	0.000311	0.000315	0.000320	0.000322	0.000323	0.000324
sample #3	0.000288	0.000291	0.000298	0.000300	0.000305	0.000306	0.000309	0.000312	0.000315
sample #4	0.000284	0.000291	0.000296	0.000302	0.000306	0.000309	0.000312	0.000316	0.000319
Mean	0.000286	0.000291	0.000300	0.000304	0.000308	0.000312	0.000315	0.000318	0.000320
Std Dev	1.75E-06	1.75E-06	2.39E-06	5.02E-06	4.62E-06	6.24E-06	5.60E-06	4.75E-06	3.93E-06
Precision(%)	0.61	0.60	0.80	1.65	1.50	2.00	1.78	1.50	1.23
K #80 (W+D)									
sample #1	0.000270	0.000274	0.000281	0.000282	0.000284	0.000289	0.000289	0.000295	0.000298
sample #2	0.000276	0.000280	0.000283	0.000286	0.000290	0.000293	0.000297	0.000300	0.000303
sample #3	0.000271	0.000281	0.000286	0.000288	0.000290	0.000293	0.000295	0.000298	0.000300
sample #4	0.000270	0.000283	0.000288	0.000291	0.000292	0.000295	0.000296	0.000299	0.000300
Mean	0.000272	0.000281	0.000286	0.000288	0.000291	0.000294	0.000296	0.000299	0.000301
Std Dev	2.88E-06	1.47E-06	2.12E-06	1.64E-06	1.10E-06	8.81E-07	7.27E-07	7.06E-07	1.46E-06
Precision(%)	1.06	0.52	0.74	0.57	0.38	0.30	0.25	0.24	0.48
K #100(W+D)									
sample #1	0.000245	0.000249	0.000257	0.000261	0.000264	0.000274	0.000275	0.000279	0.000281
sample #2	0.000250	0.000253	0.000259	0.000263	0.000267	0.000272	0.000274	0.000277	0.000280
sample #3	0.000254	0.000263	0.000266	0.000268	0.000269	0.000270	0.000271	0.000271	0.000272
sample #4	0.000256	0.000263	0.000266	0.000268	0.000269	0.000270	0.000271	0.000271	0.000272
Mean	0.000253	0.000260	0.000263	0.000266	0.000268	0.000271	0.000272	0.000273	0.000275
Std Dev	2.76E-06	4.48E-06	3.38E-06	1.99E-06	9.38E-07	1.19E-06	1.54E-06	2.83E-06	3.75E-06
Precision(%)	1.09	1.72	1.28	0.75	0.35	0.44	0.57	1.03	1.37
K #60 (W)									
sample #1	0.000223	0.000237	0.000240	0.000243	0.000244	0.000245	0.000246	0.000247	0.000248
sample #2	0.000217	0.000222	0.000227	0.000238	0.000240	0.000252	0.000261	0.000263	0.000265
sample #3	0.000222	0.000237	0.000240	0.000243	0.000244	0.000245	0.000246	0.000247	0.000248
sample #4	0.000225	0.000228	0.000234	0.000239	0.000241	0.000246	0.000251	0.000253	0.000255
Mean	0.000222	0.000229	0.000234	0.000240	0.000242	0.000248	0.000253	0.000254	0.000256
Std Dev	3.38E-06	6.12E-06	5.35E-06	2.04E-06	1.72E-06	2.83E-06	6.00E-06	6.46E-06	7.11E-06
Precision(%)	1.53	2.68	2.29	0.85	0.71	1.14	2.38	2.54	2.78
K #80 (W)									
sample #1	0.000198	0.000206	0.000210	0.000216	0.000220	0.000225	0.000231	0.000234	0.000237
sample #2	0.000196	0.000198	0.000202	0.000208	0.000215	0.000224	0.000231	0.000233	0.000237
sample #3	0.000202	0.000214	0.000218	0.000220	0.000221	0.000222	0.000223	0.000224	0.000225
sample #4	0.000203	0.000214	0.000218	0.000220	0.000221	0.000222	0.000223	0.000224	0.000225
Mean	0.000200	0.000209	0.000212	0.000216	0.000219	0.000223	0.000226	0.000227	0.000229
Std Dev	3.23E-06	7.61E-06	7.42E-06	5.44E-06	3.01E-06	7.18E-07	3.69E-06	4.37E-06	5.67E-06
Precision(%)	1.61	3.65	3.50	2.52	1.37	0.32	1.63	1.92	2.48
K #100(W)									
sample #1	0.000181	0.000183	0.000188	0.000194	0.000199	0.000204	0.000208	0.000211	0.000213
sample #2	0.000183	0.000187	0.000192	0.000198	0.000202	0.000210	0.000213	0.000218	0.000221
sample #3	0.000179	0.000197	0.000200	0.000202	0.000203	0.000204	0.000205	0.000206	0.000206
sample #4	0.000186	0.000197	0.000200	0.000202	0.000203	0.000204	0.000205	0.000206	0.000206
Mean	0.000183	0.000194	0.000198	0.000201	0.000203	0.000206	0.000208	0.000210	0.000211
Std Dev	2.62E-06	4.79E-06	3.74E-06	2.04E-06	5.67E-07	2.57E-06	3.61E-06	5.89E-06	6.86E-06
Precision(%)	1.43	2.47	1.89	1.02	0.28	1.25	1.74	2.81	3.25

Table 6.2 Contd.

Temperature= 22 C i=4									
Time (min)	1	180	360	540	720	900	1080	1260	1440
K #60 (W+D)									
sample #1	0.000192	0.000195	0.000198	0.000205	0.000210	0.000216	0.000220	0.000223	0.000224
sample #2	0.000189	0.000192	0.000195	0.000202	0.000207	0.000213	0.000217	0.000220	0.000221
sample #3	0.000191	0.000194	0.000197	0.000204	0.000209	0.000215	0.000219	0.000222	0.000223
sample #4	0.000190	0.000193	0.000196	0.000203	0.000208	0.000214	0.000218	0.000221	0.000222
Mean	0.000191	0.000193	0.000197	0.000203	0.000209	0.000215	0.000219	0.000221	0.000223
Std Dev	1.25E-06	1.25E-06	1.25E-06	1.25E-06	1.25E-06	1.25E-06	1.25E-06	1.25E-06	1.25E-06
Precision(%)	0.65	0.64	0.63	0.61	0.60	0.58	0.57	0.56	0.56
K #80 (W+D)									
sample #1	0.000187	0.000192	0.000195	0.000201	0.000206	0.000210	0.000215	0.000217	0.000219
sample #2	0.000192	0.000192	0.000196	0.000201	0.000206	0.000210	0.000215	0.000217	0.000218
sample #3	0.000190	0.000197	0.000200	0.000203	0.000206	0.000209	0.000213	0.000216	0.000217
sample #4	0.000193	0.000196	0.000199	0.000202	0.000205	0.000208	0.000211	0.000214	0.000217
Mean	0.000192	0.000195	0.000198	0.000202	0.000206	0.000209	0.000213	0.000216	0.000217
Std Dev	1.36E-06	2.25E-06	1.85E-06	1.19E-06	5.26E-07	6.70E-07	1.59E-06	1.36E-06	5.84E-07
Precision(%)	0.71	1.15	0.93	0.59	0.26	0.32	0.75	0.63	0.27
K #100(W+D)									
sample #1	0.000185	0.000190	0.000193	0.000199	0.000204	0.000208	0.000213	0.000215	0.000217
sample #2	0.000190	0.000190	0.000194	0.000199	0.000204	0.000208	0.000213	0.000215	0.000216
sample #3	0.000186	0.000200	0.000203	0.000204	0.000205	0.000206	0.000207	0.000208	0.000208
sample #4	0.000191	0.000200	0.000203	0.000204	0.000206	0.000206	0.000207	0.000208	0.000208
Mean	0.000189	0.000196	0.000200	0.000202	0.000205	0.000207	0.000209	0.000210	0.000211
Std Dev	1.89E-06	4.72E-06	4.16E-06	2.72E-06	5.67E-07	5.97E-07	2.71E-06	3.52E-06	3.68E-06
Precision(%)	1.00	2.40	2.08	1.34	0.28	0.29	1.30	1.67	1.74
K #60 (W)									
sample #1	0.000180	0.000185	0.000189	0.000193	0.000201	0.000204	0.000208	0.000210	0.000212
sample #2	0.000183	0.000185	0.000188	0.000193	0.000201	0.000204	0.000208	0.000210	0.000212
sample #3	0.000186	0.000195	0.000198	0.000200	0.000201	0.000202	0.000203	0.000203	0.000204
sample #4	0.000184	0.000195	0.000198	0.000200	0.000201	0.000202	0.000203	0.000203	0.000204
Mean	0.000184	0.000192	0.000195	0.000197	0.000201	0.000202	0.000205	0.000205	0.000207
Std Dev	1.16E-06	4.90E-06	4.49E-06	3.12E-06	1.60E-07	9.49E-07	2.72E-06	3.15E-06	3.97E-06
Precision(%)	0.63	2.55	2.30	1.58	0.08	0.47	1.33	1.53	1.92
K #80 (W)									
sample #1	0.000177	0.000181	0.000184	0.000188	0.000197	0.000200	0.000203	0.000205	0.000206
sample #2	0.000180	0.000181	0.000184	0.000189	0.000197	0.000200	0.000203	0.000205	0.000206
sample #3	0.000179	0.000186	0.000189	0.000192	0.000197	0.000198	0.000200	0.000202	0.000203
sample #4	0.000182	0.000191	0.000193	0.000195	0.000196	0.000197	0.000198	0.000198	0.000199
Mean	0.000180	0.000186	0.000189	0.000192	0.000197	0.000198	0.000200	0.000202	0.000203
Std Dev	1.17E-06	4.06E-06	3.87E-06	2.55E-06	5.25E-07	1.02E-06	1.92E-06	2.66E-06	2.97E-06
Precision(%)	0.65	2.19	2.05	1.33	0.27	0.51	0.96	1.32	1.47
K #100(W)									
sample #1	0.000171	0.000174	0.000177	0.000182	0.000186	0.000190	0.000198	0.000200	0.000203
sample #2	0.000176	0.000179	0.000182	0.000185	0.000187	0.000190	0.000194	0.000196	0.000198
sample #3	0.000173	0.000184	0.000187	0.000188	0.000189	0.000190	0.000193	0.000195	0.000196
sample #4	0.000176	0.000184	0.000187	0.000188	0.000189	0.000190	0.000194	0.000196	0.000197
Mean	0.000175	0.000183	0.000185	0.000187	0.000189	0.000190	0.000194	0.000195	0.000197
Std Dev	1.49E-06	2.28E-06	2.35E-06	1.58E-06	9.16E-07	3.08E-08	3.85E-07	4.73E-07	5.96E-07
Precision(%)	0.85	1.25	1.27	0.84	0.49	0.02	0.20	0.24	0.30

Table 6.2 Contd.

Temperature= 4 C i=4									
Time (min)	1	180	360	540	720	900	1080	1260	1440
K #60 (W+D)									
sample #1	0.000185	0.000188	0.000191	0.000193	0.000196	0.000200	0.000201	0.000203	0.000205
sample #2	0.000186	0.000189	0.000192	0.000193	0.000196	0.000199	0.000200	0.000202	0.000205
sample #3	0.000190	0.000192	0.000194	0.000195	0.000196	0.000197	0.000197	0.000198	0.000202
sample #4	0.000190	0.000193	0.000194	0.000195	0.000196	0.000197	0.000197	0.000198	0.000204
Mean	0.000187	0.000190	0.000192	0.000194	0.000196	0.000198	0.000199	0.000201	0.000204
Std Dev	2.32E-06	1.76E-06	1.09E-06	9.64E-07	2.11E-07	1.28E-06	1.65E-06	2.23E-06	1.33E-06
Precision(%)	1.24	0.93	0.57	0.50	0.11	0.64	0.83	1.11	0.65
K #80 (W+D)									
sample #1	0.000175	0.000179	0.000182	0.000185	0.000187	0.000190	0.000194	0.000195	0.000197
sample #2	0.000171	0.000173	0.000178	0.000183	0.000184	0.000191	0.000197	0.000199	0.000202
sample #3	0.000173	0.000184	0.000186	0.000188	0.000189	0.000190	0.000191	0.000191	0.000192
sample #4	0.000176	0.000184	0.000187	0.000188	0.000189	0.000190	0.000191	0.000191	0.000192
Mean	0.000173	0.000180	0.000184	0.000186	0.000188	0.000190	0.000193	0.000194	0.000195
Std Dev	2.20E-06	5.16E-06	3.95E-06	2.45E-06	2.16E-06	4.87E-07	2.84E-06	3.73E-06	4.78E-06
Precision(%)	1.27	2.86	2.15	1.31	1.15	0.26	1.47	1.92	2.45
K #100(W+D)									
sample #1	0.000165	0.000169	0.000173	0.000174	0.000177	0.000182	0.000187	0.000188	0.000197
sample #2	0.000168	0.000171	0.000175	0.000178	0.000181	0.000184	0.000187	0.000190	0.000193
sample #3	0.000170	0.000177	0.000179	0.000181	0.000182	0.000182	0.000184	0.000186	0.000196
sample #4	0.000167	0.000174	0.000177	0.000178	0.000180	0.000183	0.000186	0.000190	0.000195
Mean	0.000168	0.000174	0.000177	0.000179	0.000181	0.000183	0.000186	0.000189	0.000194
Std Dev	1.00E-06	2.27E-06	1.95E-06	1.34E-06	6.80E-07	5.87E-07	9.11E-07	2.03E-06	1.33E-06
Precision(%)	0.59	1.30	1.10	0.75	0.38	0.32	0.49	1.07	0.68
K #60 (W)									
sample #1	0.000162	0.000166	0.000169	0.000175	0.000179	0.000180	0.000185	0.000188	0.000192
sample #2	0.000162	0.000166	0.000169	0.000175	0.000179	0.000181	0.000185	0.000188	0.000193
sample #3	0.000170	0.000175	0.000178	0.000179	0.000180	0.000181	0.000182	0.000182	0.000183
sample #4	0.000170	0.000175	0.000178	0.000179	0.000180	0.000181	0.000182	0.000182	0.000183
Mean	0.000167	0.000172	0.000175	0.000178	0.000180	0.000181	0.000183	0.000184	0.000186
Std Dev	3.66E-06	4.52E-06	3.88E-06	2.02E-06	4.48E-07	7.47E-08	1.56E-06	2.92E-06	4.83E-06
Precision(%)	2.18	2.63	2.22	1.14	0.25	0.04	0.86	1.59	2.60
K #80 (W)									
sample #1	0.000159	0.000163	0.000166	0.000171	0.000175	0.000177	0.000179	0.000180	0.000181
sample #2	0.000160	0.000163	0.000166	0.000171	0.000175	0.000176	0.000178	0.000180	0.000182
sample #3	0.000163	0.000170	0.000172	0.000174	0.000174	0.000175	0.000176	0.000176	0.000177
sample #4	0.000163	0.000170	0.000172	0.000174	0.000174	0.000175	0.000176	0.000176	0.000177
Mean	0.000162	0.000168	0.000170	0.000173	0.000175	0.000176	0.000177	0.000178	0.000178
Std Dev	1.41E-06	3.41E-06	3.03E-06	1.29E-06	2.17E-07	6.19E-07	1.28E-06	1.99E-06	2.37E-06
Precision(%)	0.87	2.03	1.78	0.75	0.12	0.35	0.72	1.12	1.33
K #100(W)									
sample #1	0.000155	0.000159	0.000163	0.000167	0.000170	0.000174	0.000176	0.000177	0.000179
sample #2	0.000155	0.000156	0.000163	0.000167	0.000170	0.000174	0.000176	0.000177	0.000179
sample #3	0.000158	0.000167	0.000169	0.000170	0.000171	0.000172	0.000172	0.000173	0.000173
sample #4	0.000163	0.000167	0.000169	0.000170	0.000171	0.000172	0.000172	0.000173	0.000173
Mean	0.000158	0.000163	0.000167	0.000169	0.000171	0.000172	0.000174	0.000174	0.000175
Std Dev	3.25E-06	5.00E-06	2.77E-06	1.45E-06	2.96E-07	1.02E-06	1.91E-06	1.97E-06	2.68E-06
Precision(%)	2.05	3.07	1.66	0.86	0.17	0.59	1.10	1.13	1.53

Table 6.3 Reduction levels for one and three day tests.

Tests with Water only				CRE (%)	
i	days	T ^ C	mesh#	First reading	Final reading
0.75	1	4	60	2.98	41
			80	2.62	37
			100	2.40	36
		22	60	2.67	57
			80	3.13	55
			100	3.34	54
		50	60	0.94	73
			80	1.23	72
			100	2.55	67
0.75	3	4	60	2.98	56
			80	2.62	39
			100	2.40	38
		22	60	2.67	62
			80	3.13	61
			100	3.34	60
		50	60	0.94	74
			80	1.23	73
			100	2.55	70
4.00	1	4	60	6.19	48
			80	8.14	47
			100	9.81	43
		22	60	5.56	59
			80	7.22	57
			100	8.89	55
		50	60	7.78	80
			80	9.72	78
			100	10.26	77

Table 6.3 Contd.

Tests with Water & Surfactant				CRE (%)	
i	days	T ^ C	mesh#	First reading	Final reading
0.75	1	4	60	1.04	45
			80	0.79	44
			100	0.69	42
		22	60	0.85	64
			80	2.57	61
			100	2.67	61
		50	60	10.69	83
			80	2.64	82
			100	0.34	78
0.75	3	4	60	1.04	47
			80	0.79	46
			100	0.69	43
		22	60	0.85	66
			80	2.57	66
			100	2.67	65
		50	60	10.69	85
			80	2.64	84
			100	0.34	81
4.00	1	4	60	4.25	51
			80	6.89	49
			100	7.72	47
		22	60	7.91	72
			80	6.11	67
			100	2.78	65
		50	60	4.99	94
			80	4.72	84
			100	6.11	82

Table 6.4 Viscosity values for water and water plus surfactant.

Influent	4 C	22 C	50 C
Water alone	15.68	9.61	5.29
water + surfactant	15.12	9.04	4.34

Source:Handbook of Chemistry and Physics

All the values are in (Poise)

1 dyne-sec/cm = 1 poise

Table 6.5 Cumulative removal efficiency values for water and water plus surfactant for mesh#80.

Temperature	Hydraulic Gradient	Water			Water plus Surfactant		
		1 (min)	24 (min)	72 (min)	1 (min)	24 (min)	72 (min)
50	0.75	1.23	70.43	80	2.64	81.05	84
22		3.13	54.92	65	2.57	60.66	66
4		2.62	38.17	39	0.79	45.82	46
50	4	9.72	77.34	_	4.72	83.13	_
22		7.22	56.43	_	6.11	65.97	_
4		8.14	46.69	_	6.89	48.19	_

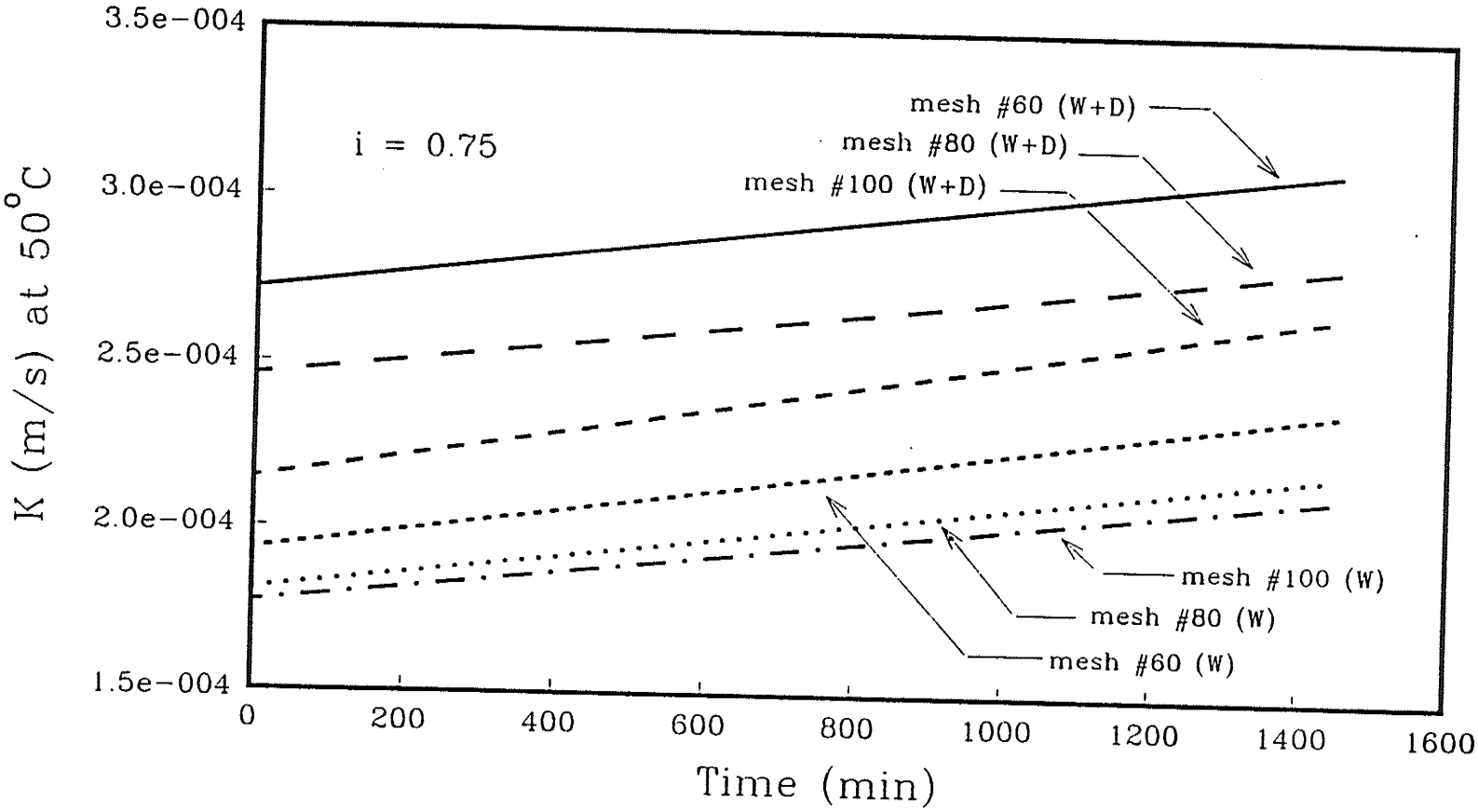


Figure 6.1 Hydraulic conductivity vs. time for various D_{50} at 50°C with i=0.75, oil contaminated sand.

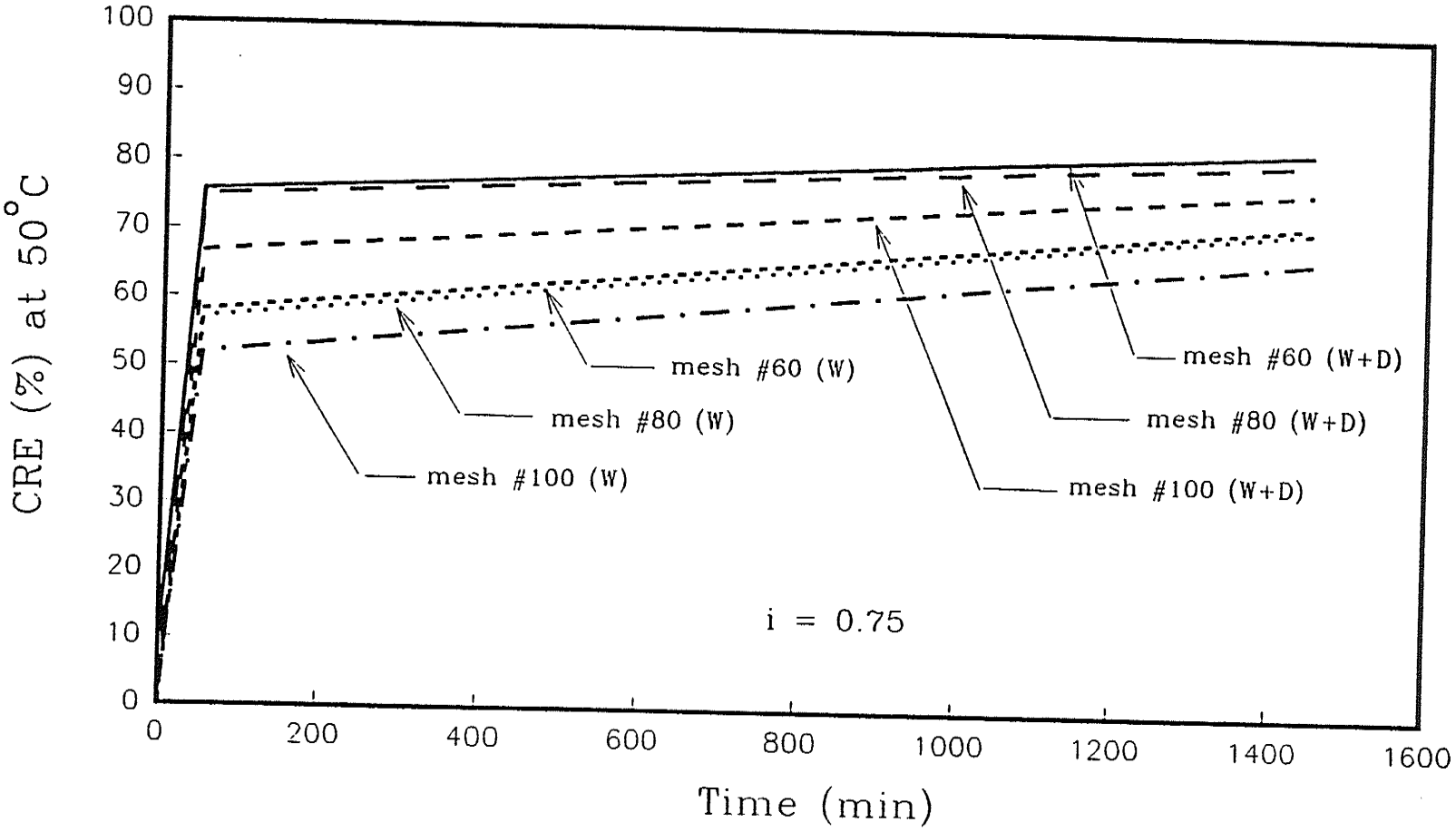


Figure 6.2 Cumulative Removal Efficiency vs. time for various D_{50} at 50°C with i=0.75, oil contaminated sand.

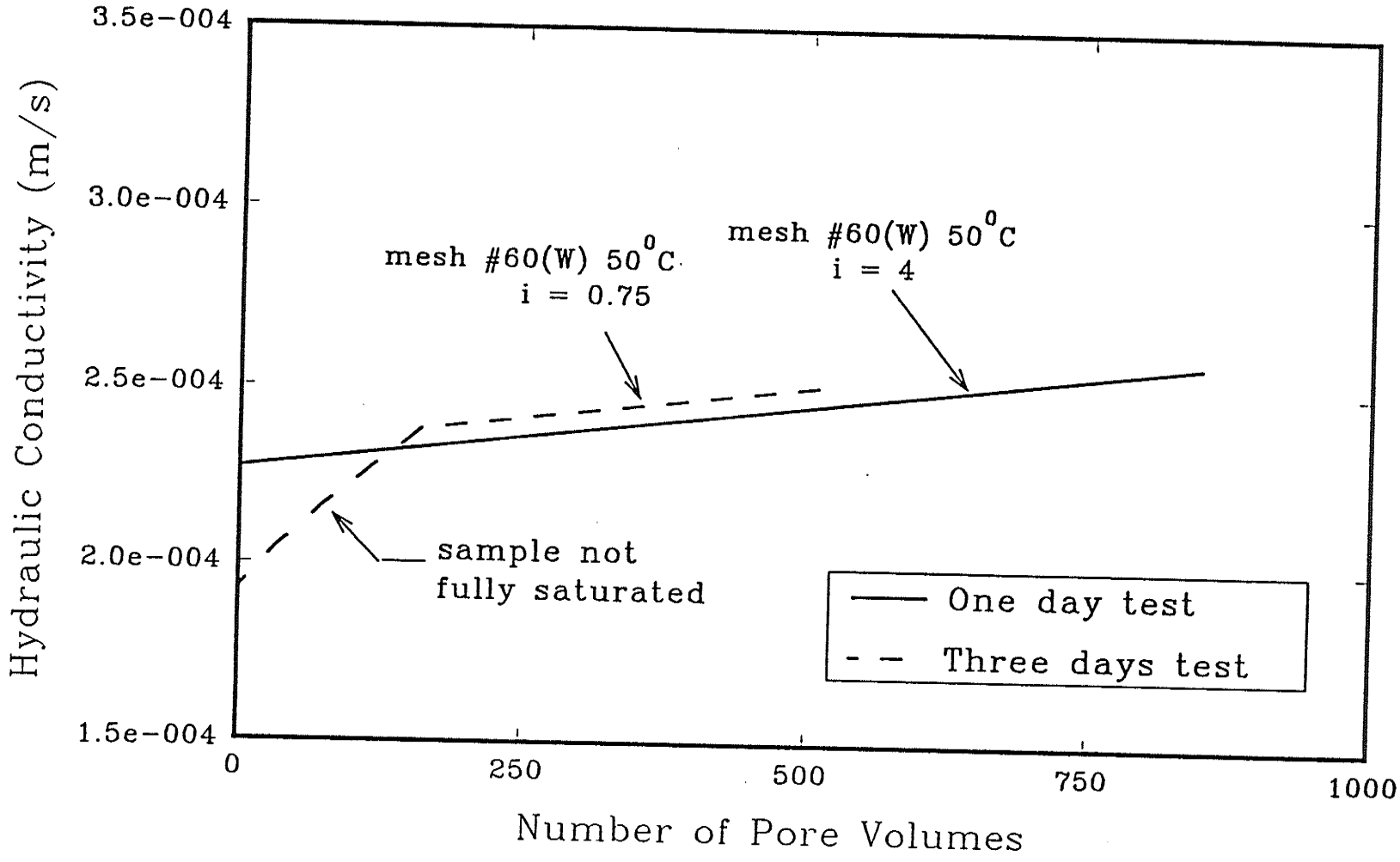


Figure 6.3 Comparison between mesh #60(W) 50°C i=4 one day to three days i=0.75 – oil contaminated sand.

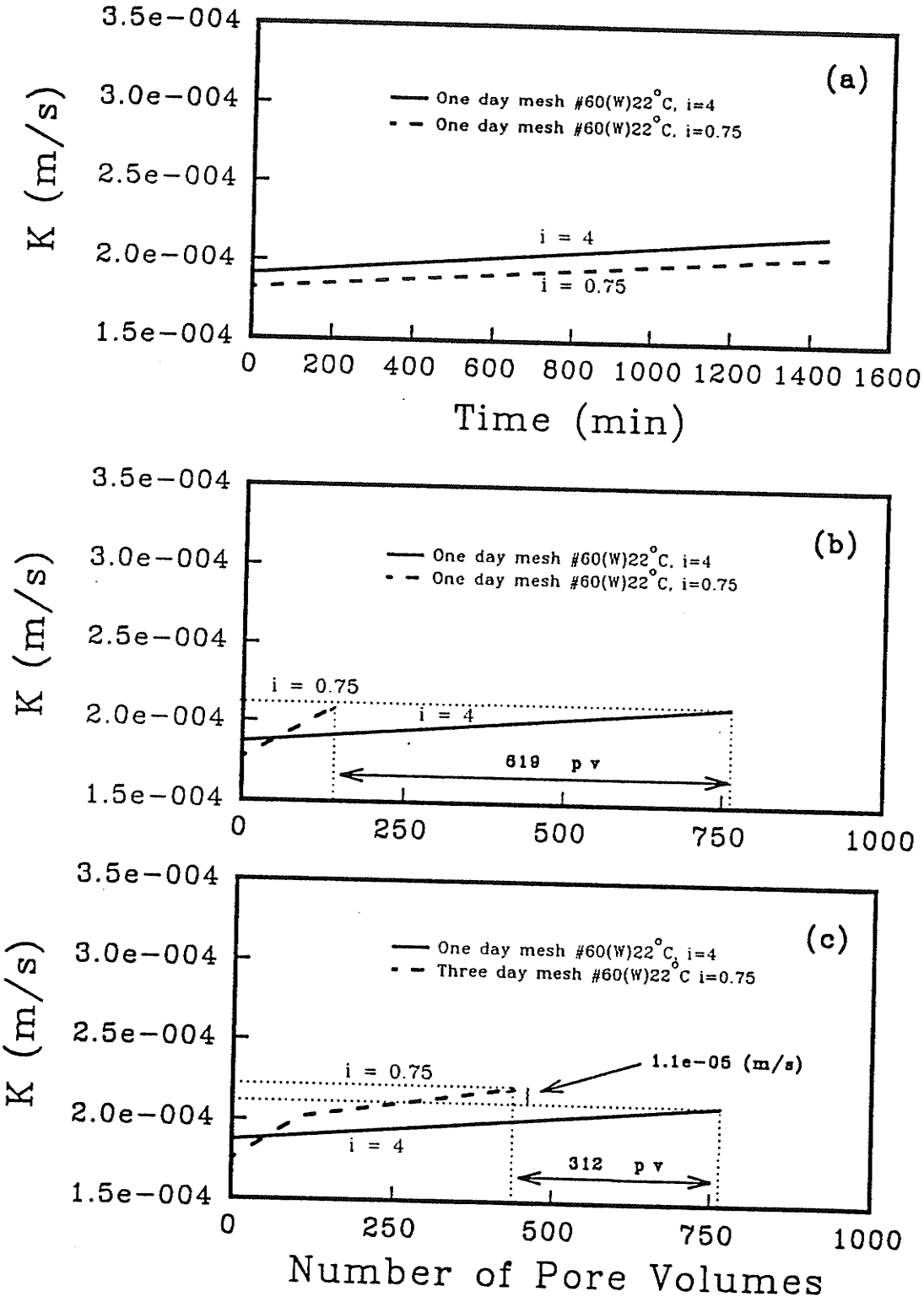


Figure 6.4 One and three day regression analyses for hydraulic conductivity vs. time and pore volumes with mesh #60(W) at 22°C for i=0.75 and i=4 – oil contaminated sand.

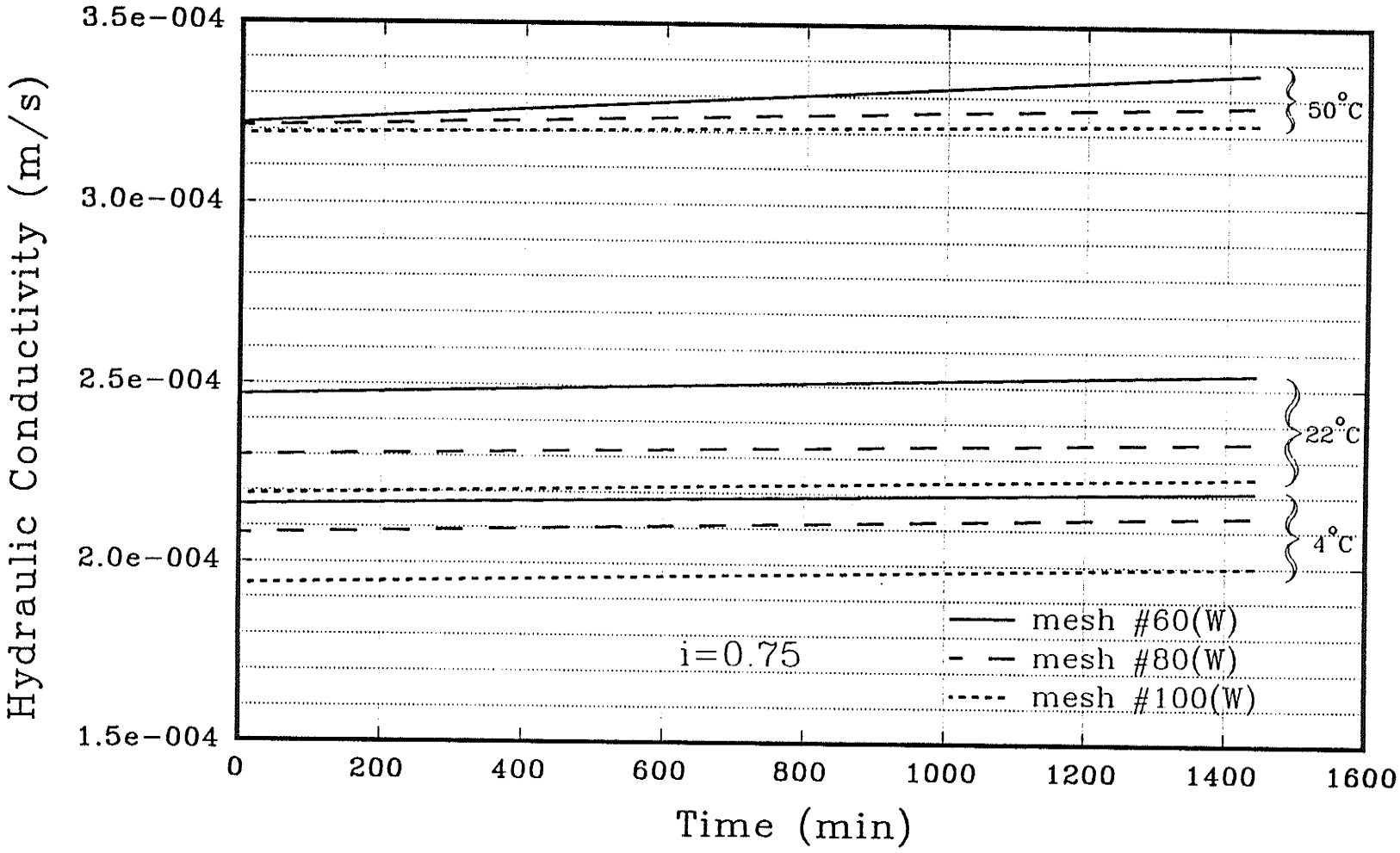


Figure 6.5 One day regression analysis for hydraulic conductivity vs. time at various T(^{o}C) and grain sizes – clean sand, water.

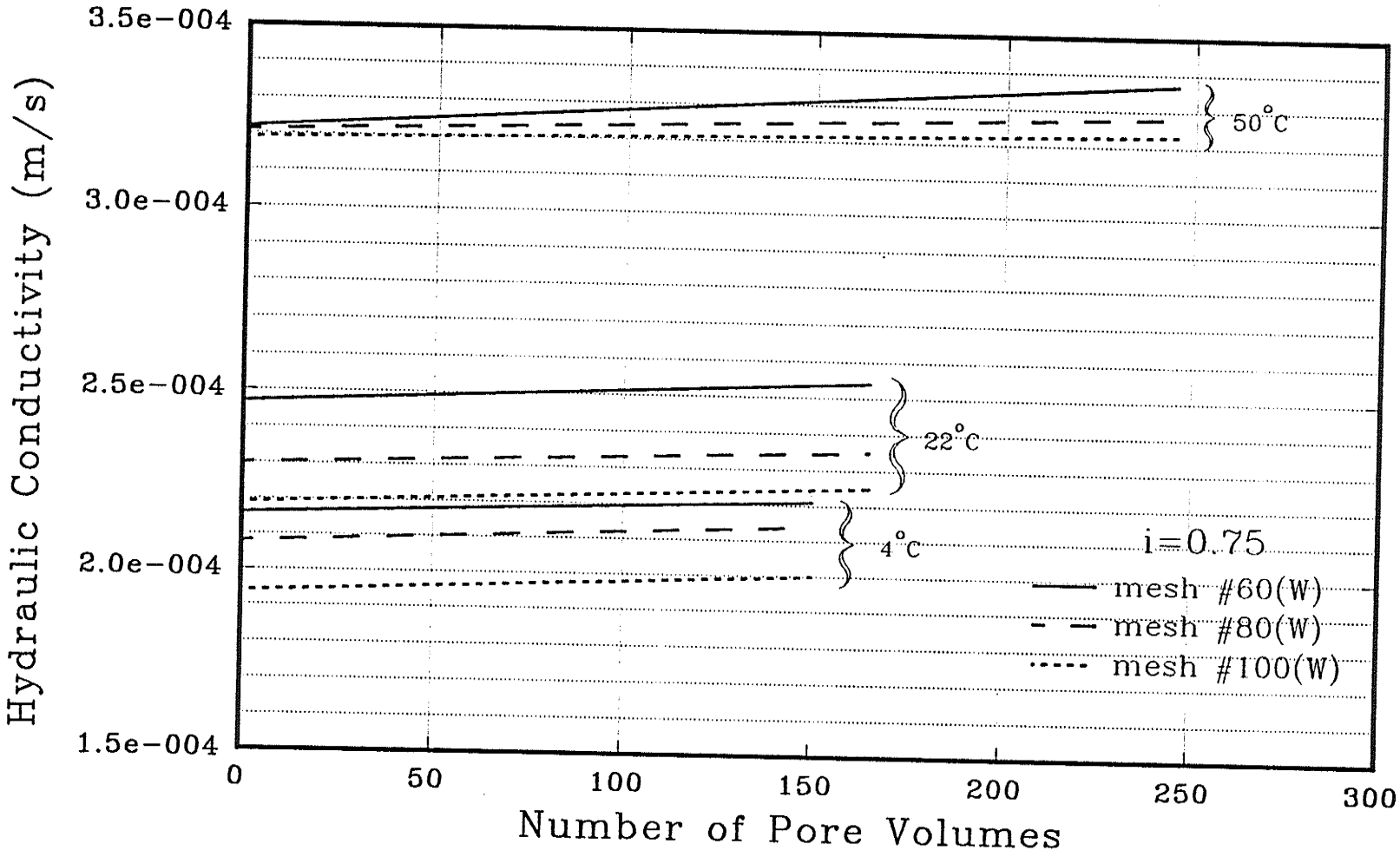
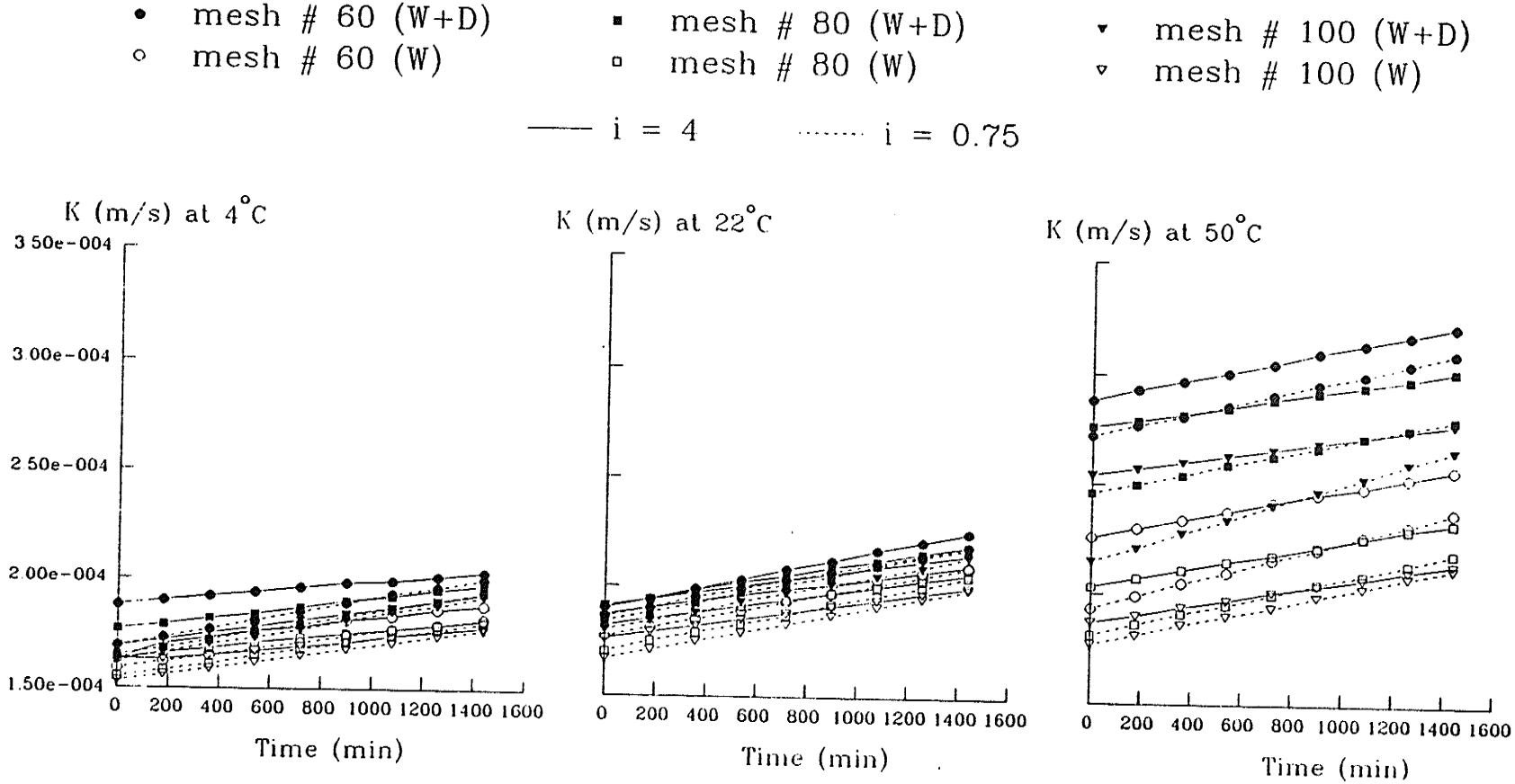


Figure 6.6 One day regression analysis for hydraulic conductivity vs. number of pore volumes at various T(°C) and grain sizes – clean sand, water.



Note: each point in the graph is the average of four samples.

Figure 6.7 Comparison of the trends for the hydraulic conductivity vs. time for for the two hydraulic gradients at different T(°C).

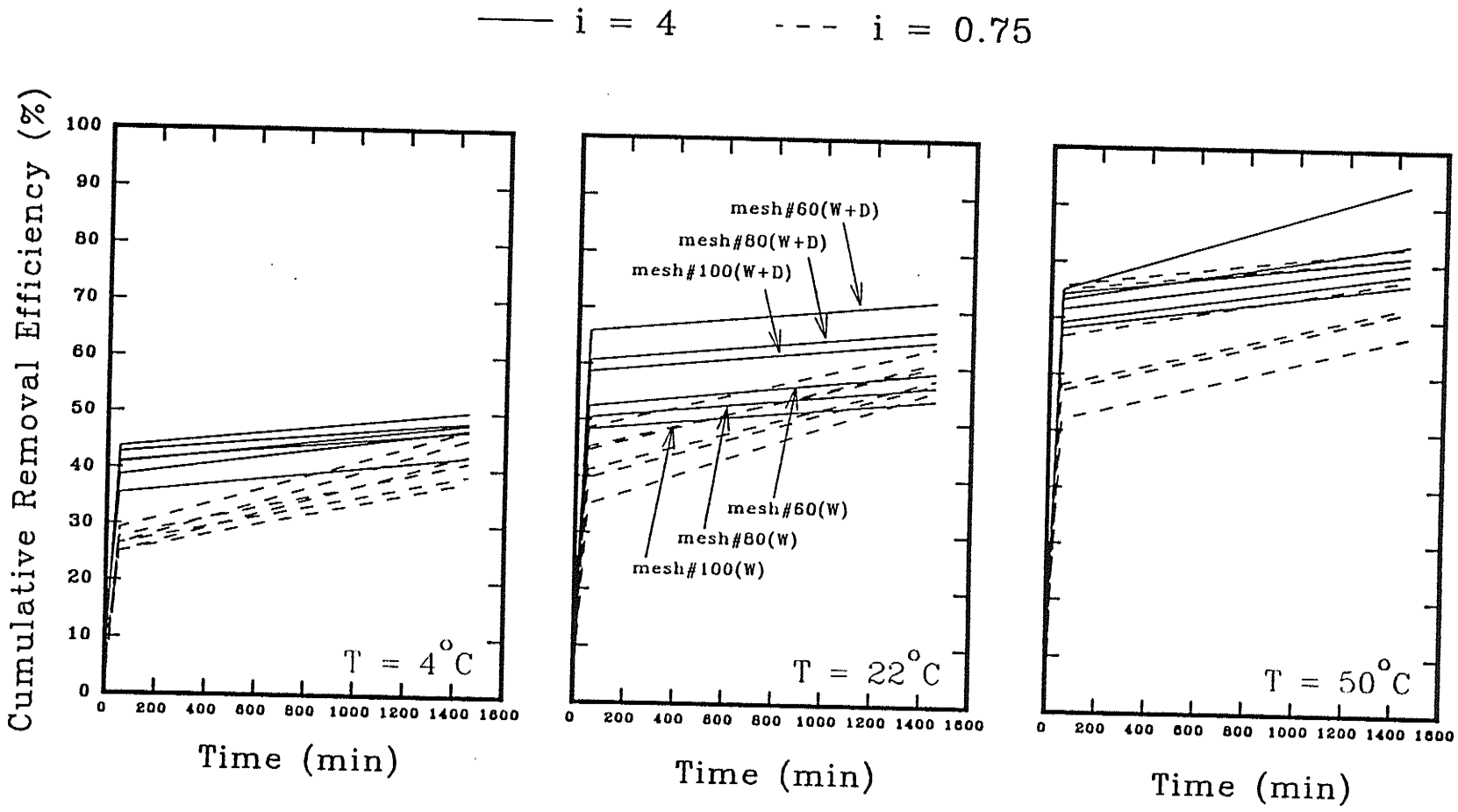


Figure 6.8 Comparison of the trends for the cumulative removal efficiency vs. time for the two hydraulic gradients at various T(°C).

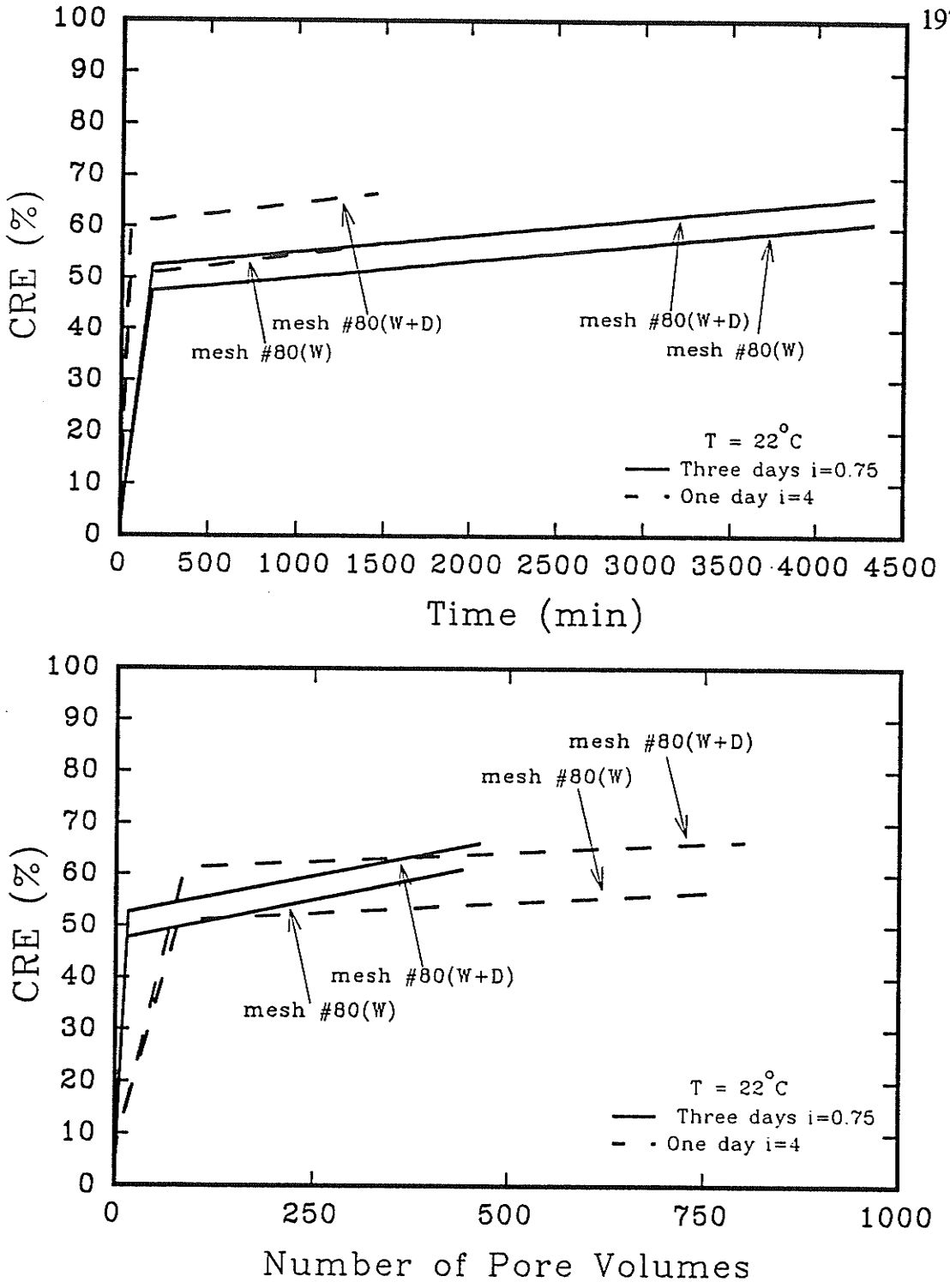


Figure 6.9 Comparison of the trends of the CRE vs. time and pore volumes for the two hydraulic gradients with mesh #80, water and water plus surfactnt at 22°C.

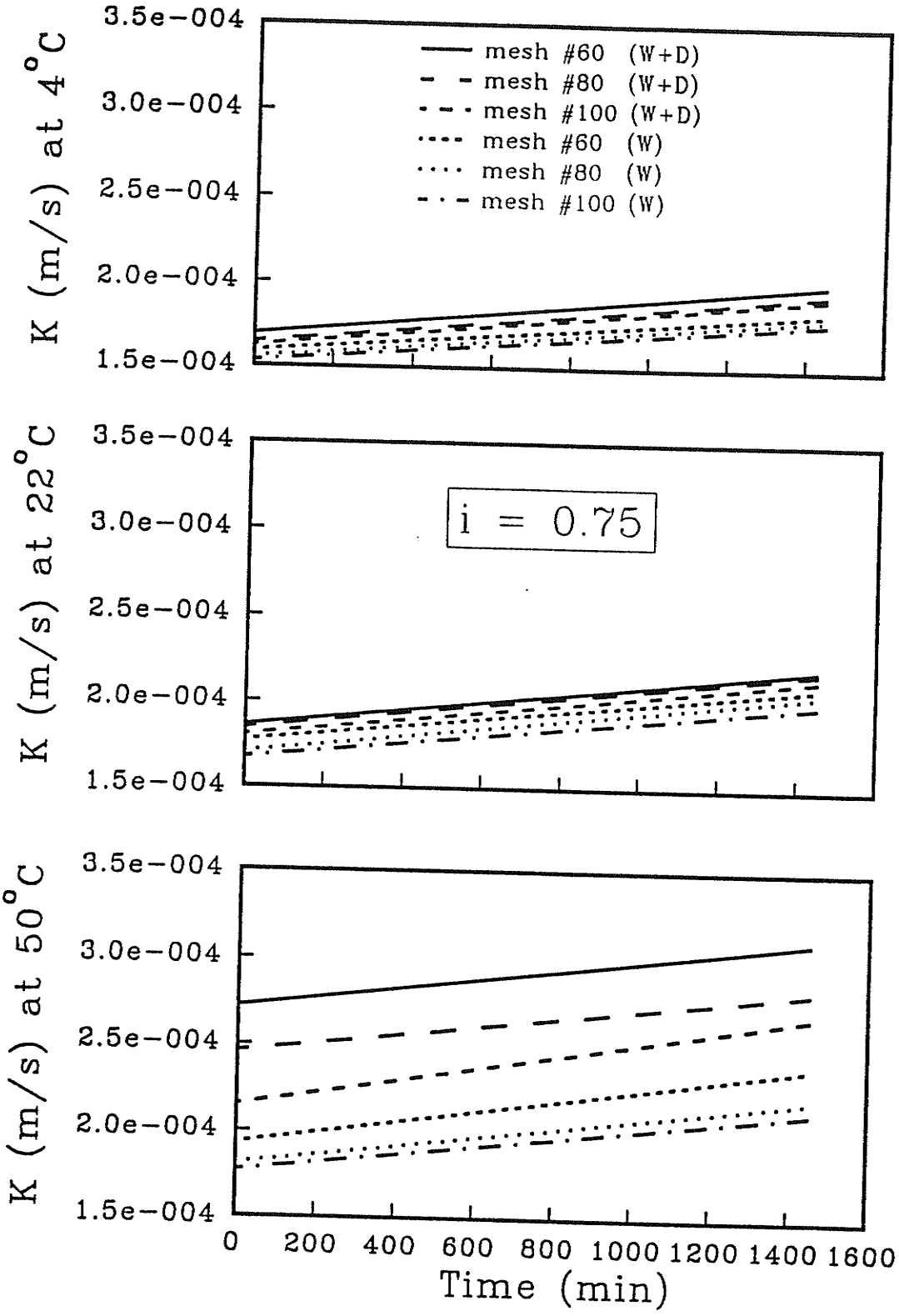


Figure 6.10 One day regression analysis of hydraulic conductivity vs. time at various T(°C) – oil contaminated sand.

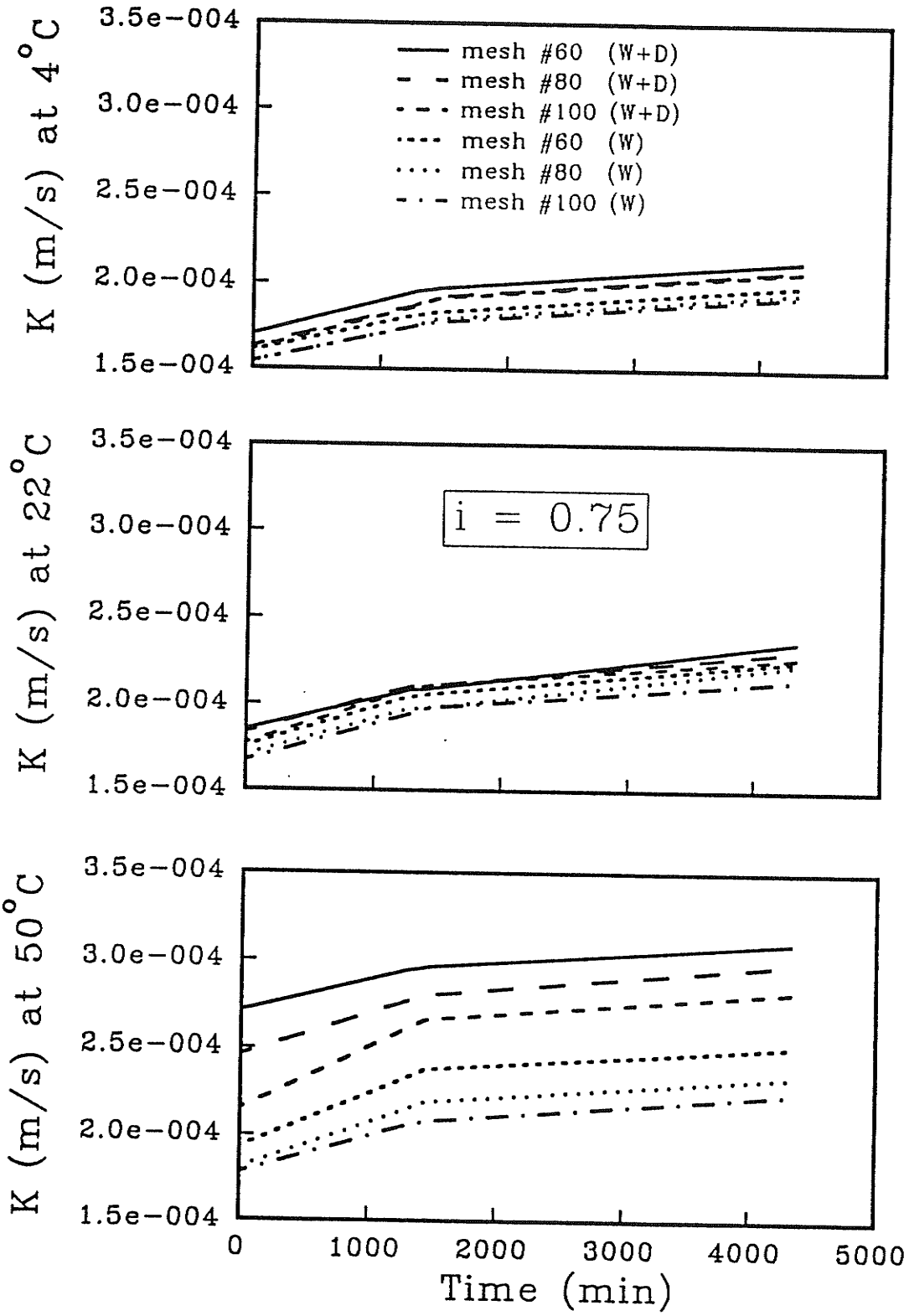


Figure 6.11 Three days regression analysis of hydraulic conductivity vs. time at various T(°C) – oil contaminated sand.

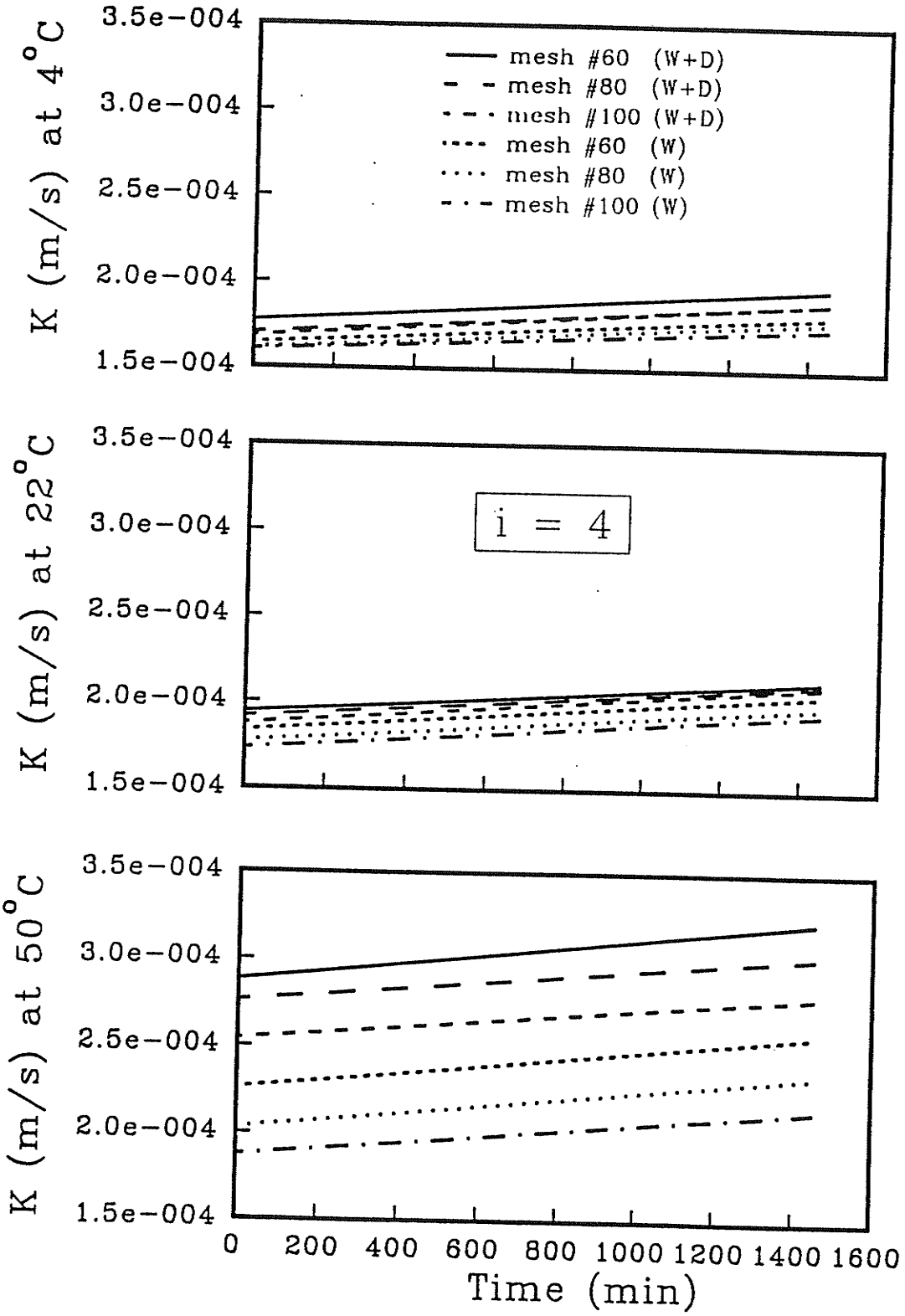


Figure 6.12 One day regression analysis of hydraulic conductivity vs. time at various T(°C) – oil contaminated sand.

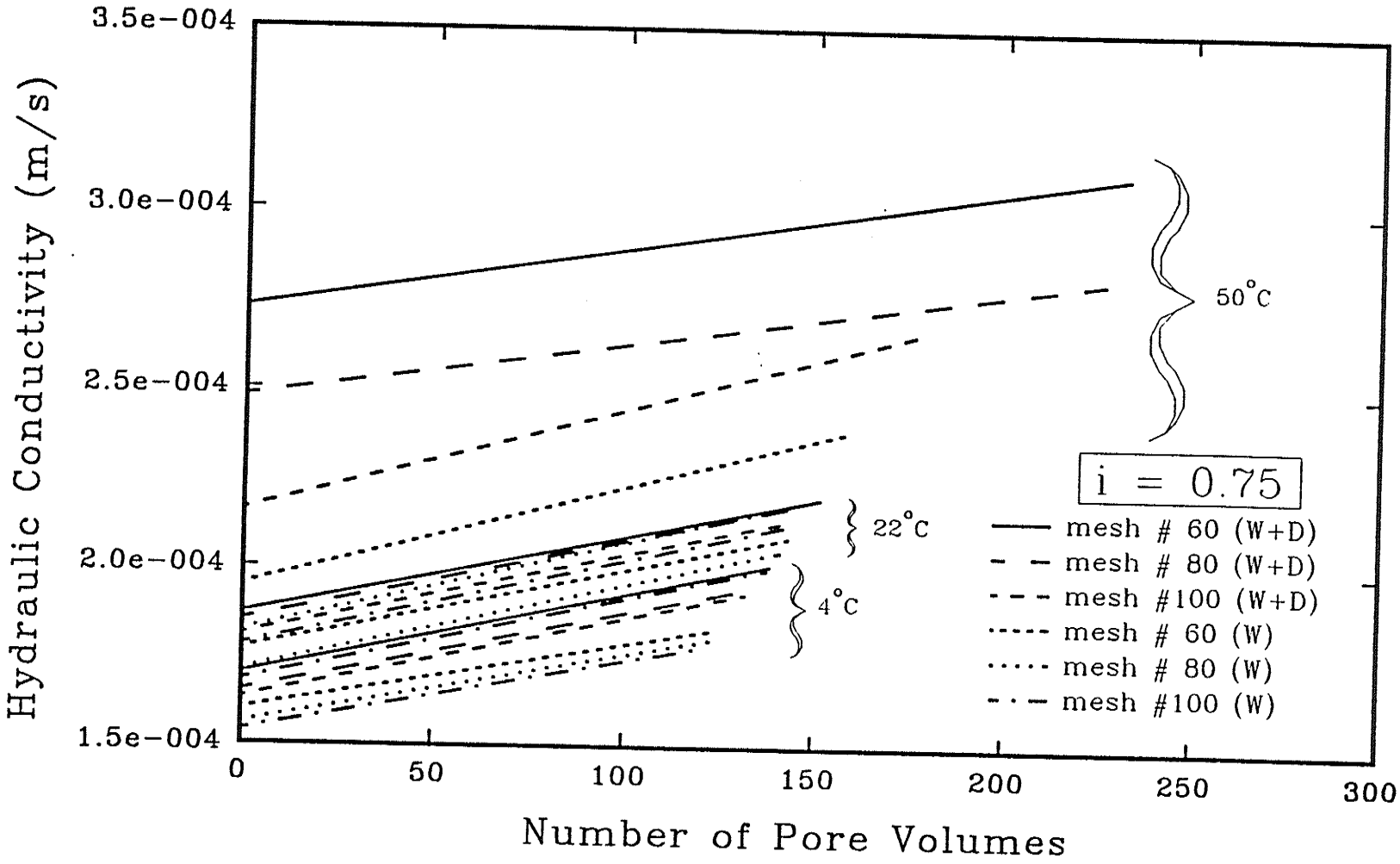


Figure 6.13 One day regression analysis for hydraulic conductivity vs. number of pore volumes at various T(°C) – oil contaminated sand.

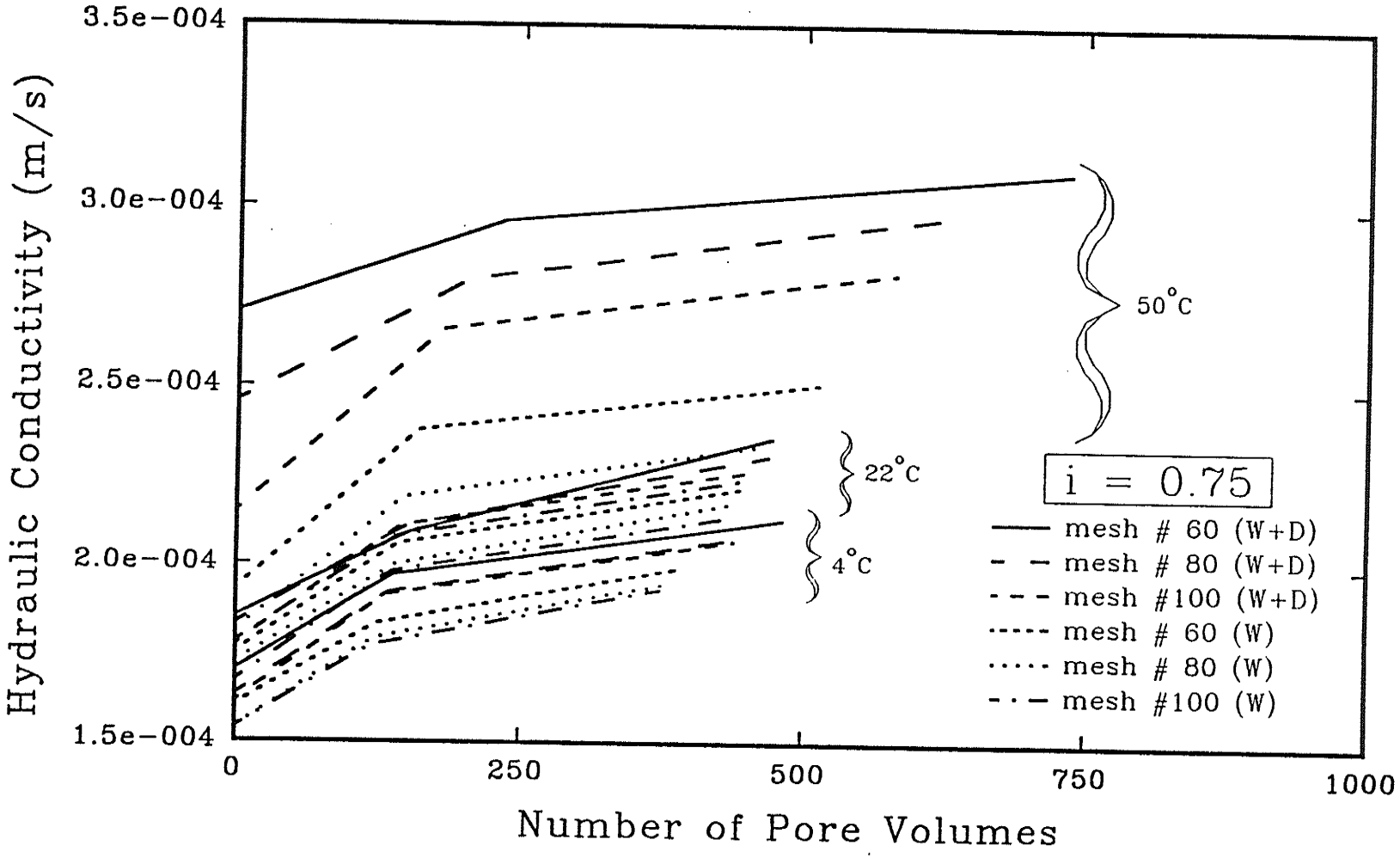


Figure 6.14 Three days regression analysis for hydraulic conductivity vs. number of pore volumes at various T(°C) – oil contaminated sand.

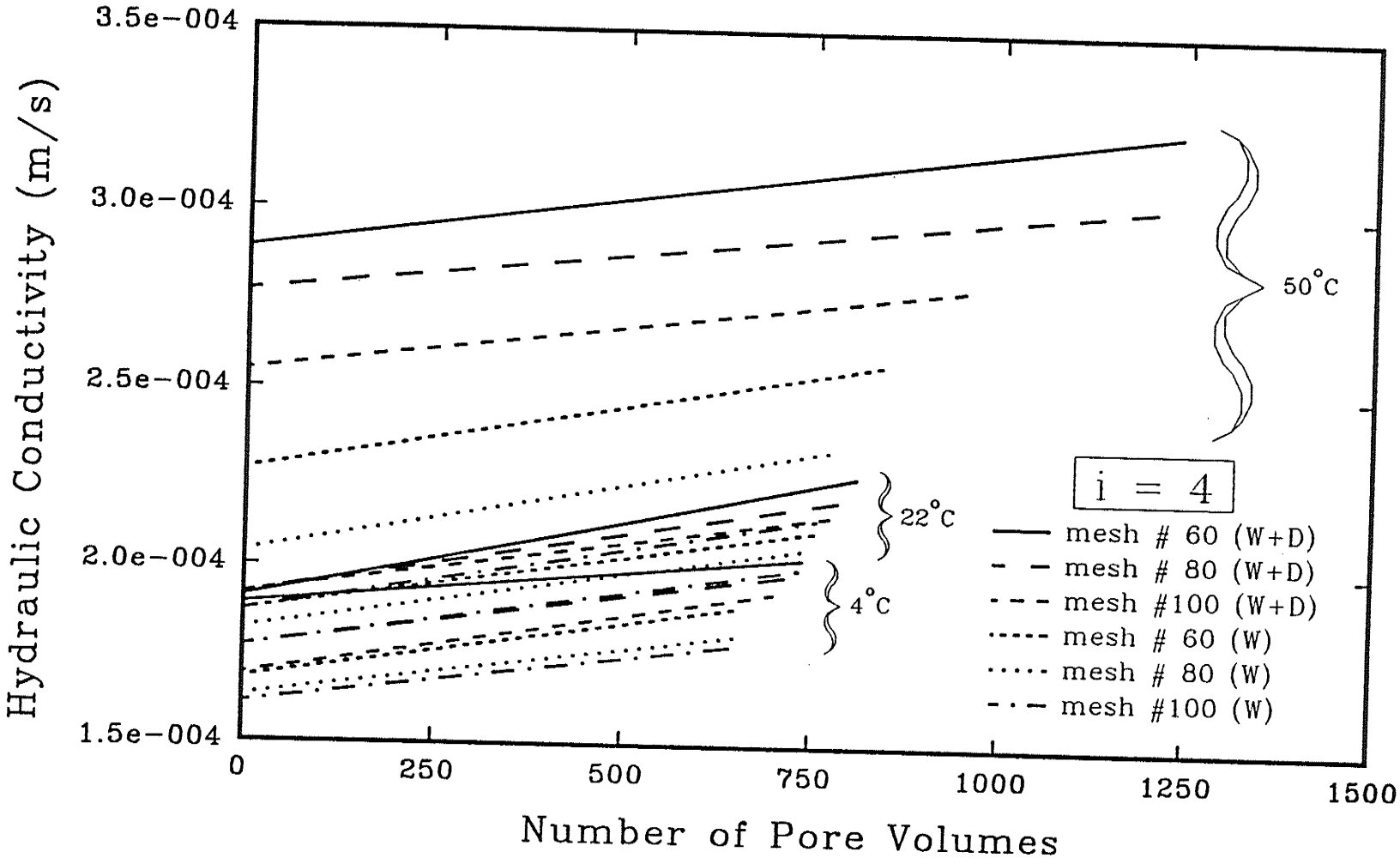


Figure 6.15 One day regression analysis for hydraulic conductivity vs. number of pore volumes at various T(°C) – oil contaminated sand.

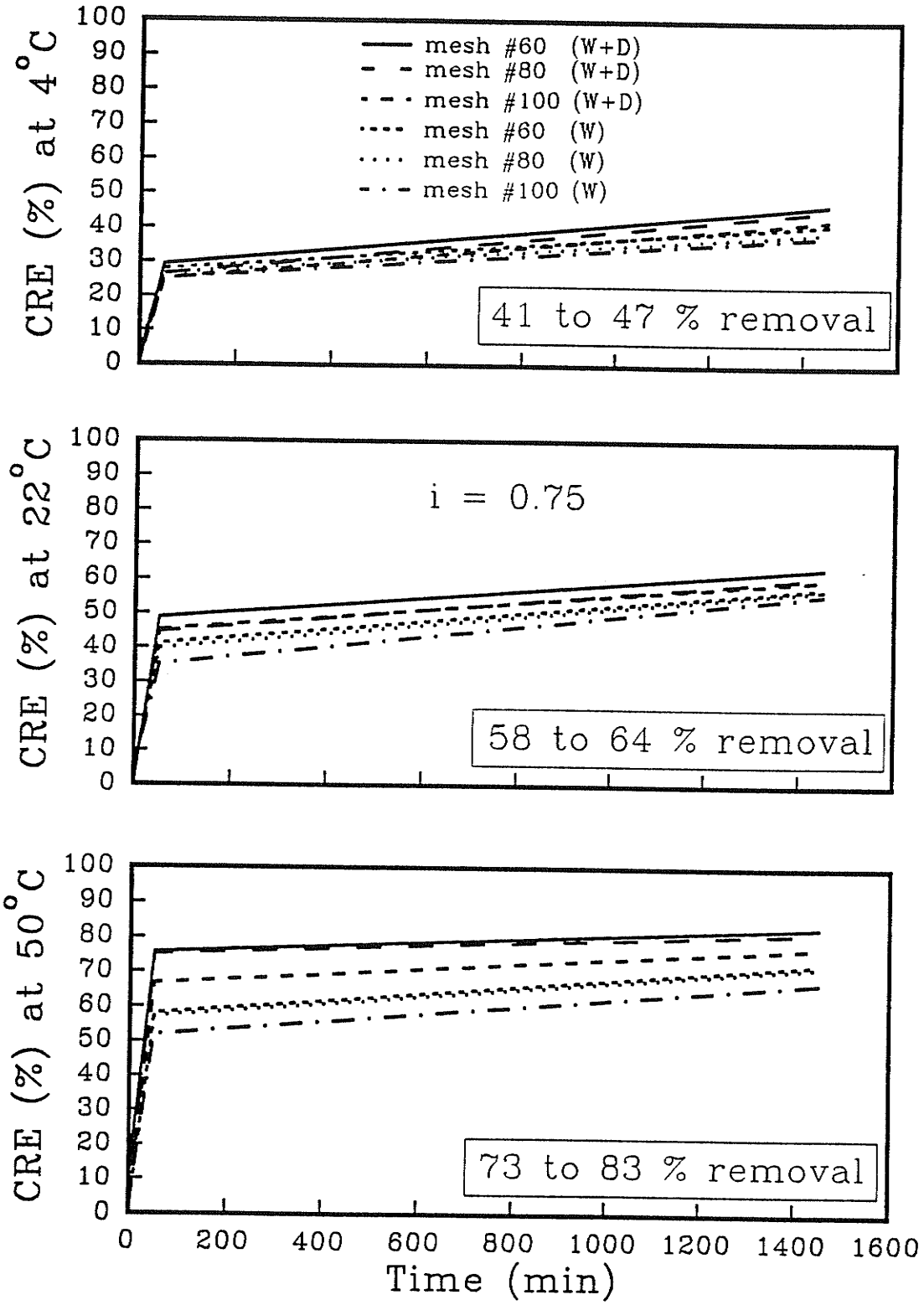


Figure 6.16 One day regression analysis of cumulative removal efficiency vs. time at various T(°C) – oil contaminated sand.

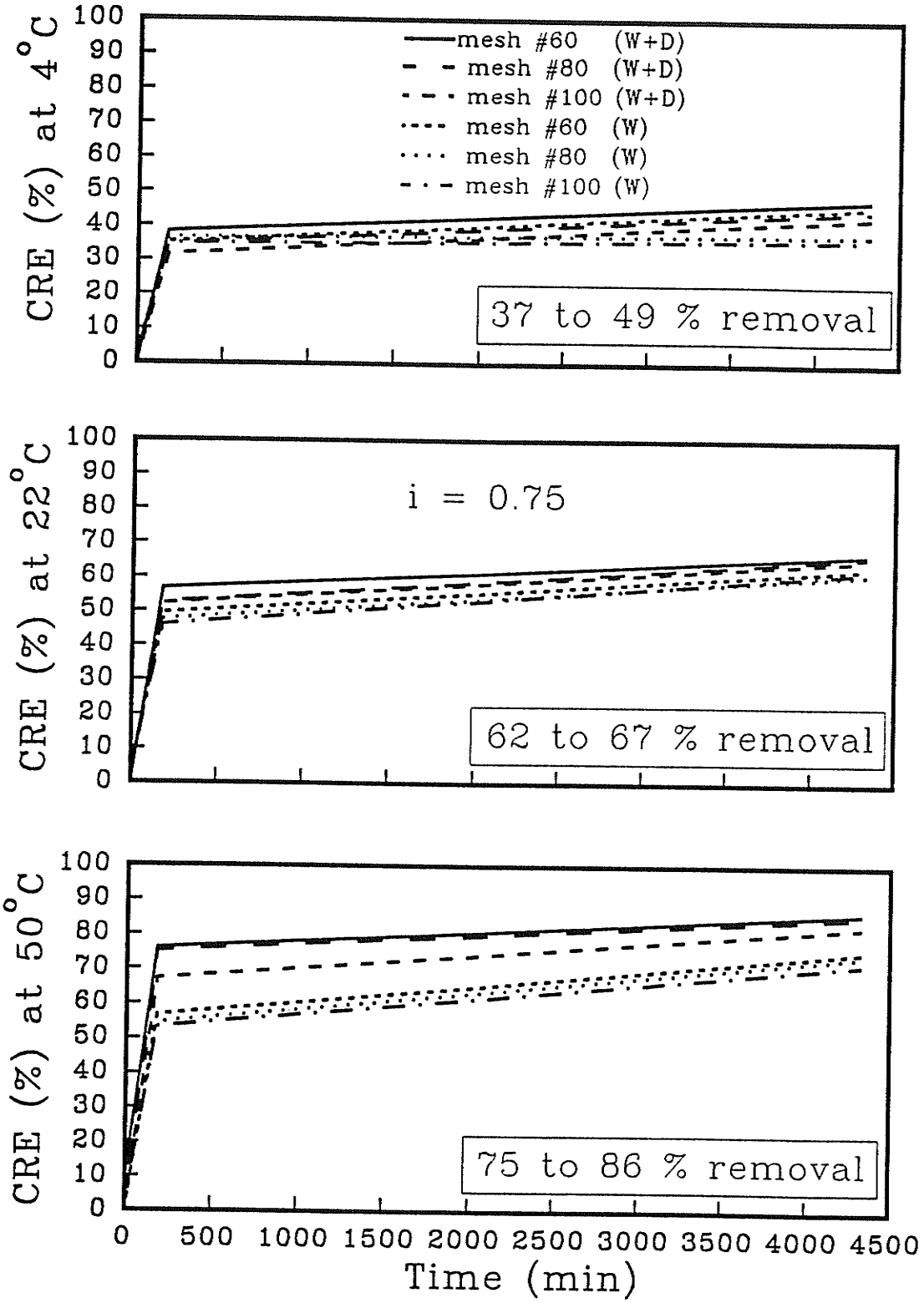


Figure 6.17 Three days regression analysis of cumulative removal efficiency vs. time at various T(°C) – oil contaminated sand.

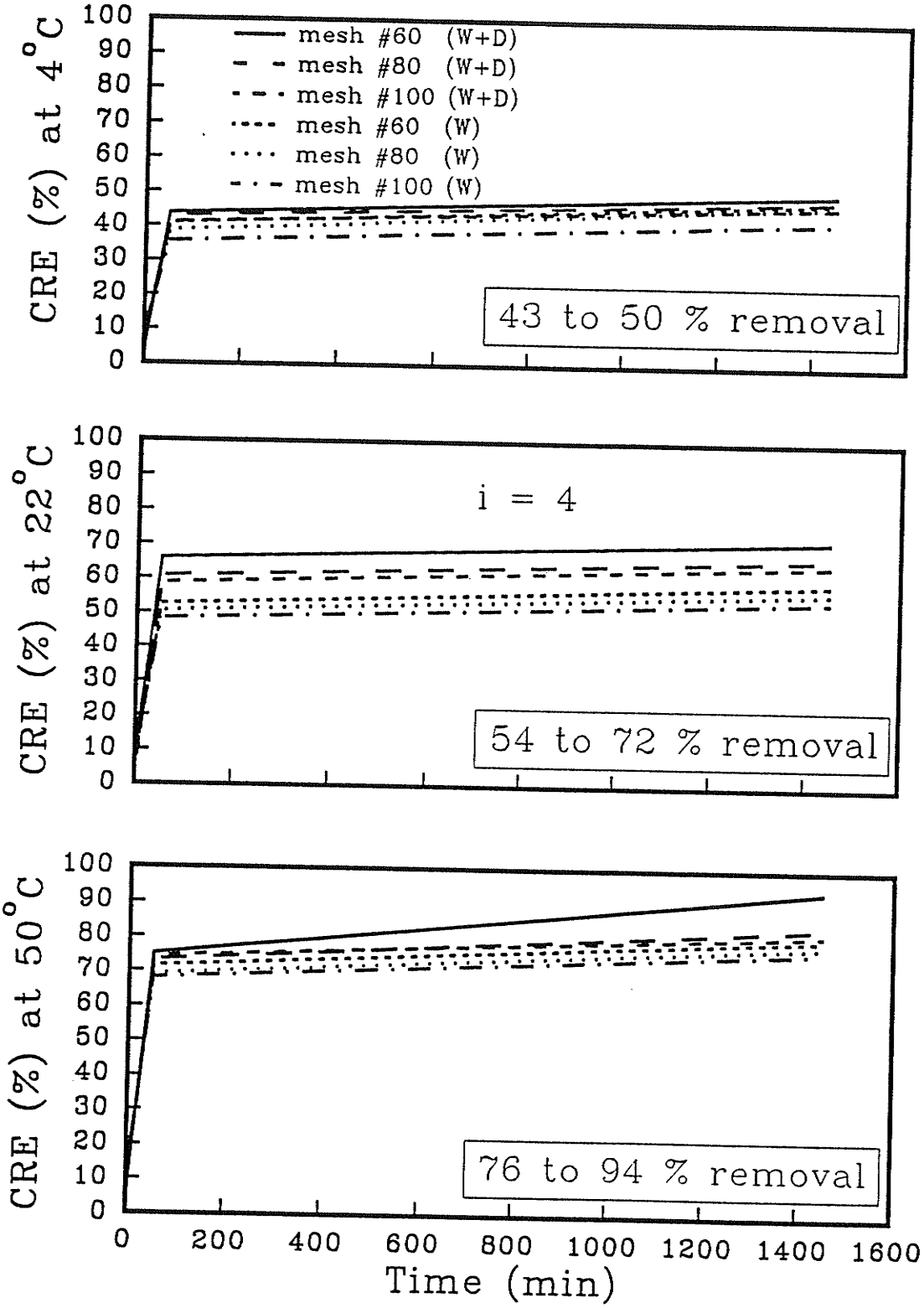


Figure 6.18 One day regression analysis of cumulative removal efficiency vs. time at various T(°C).

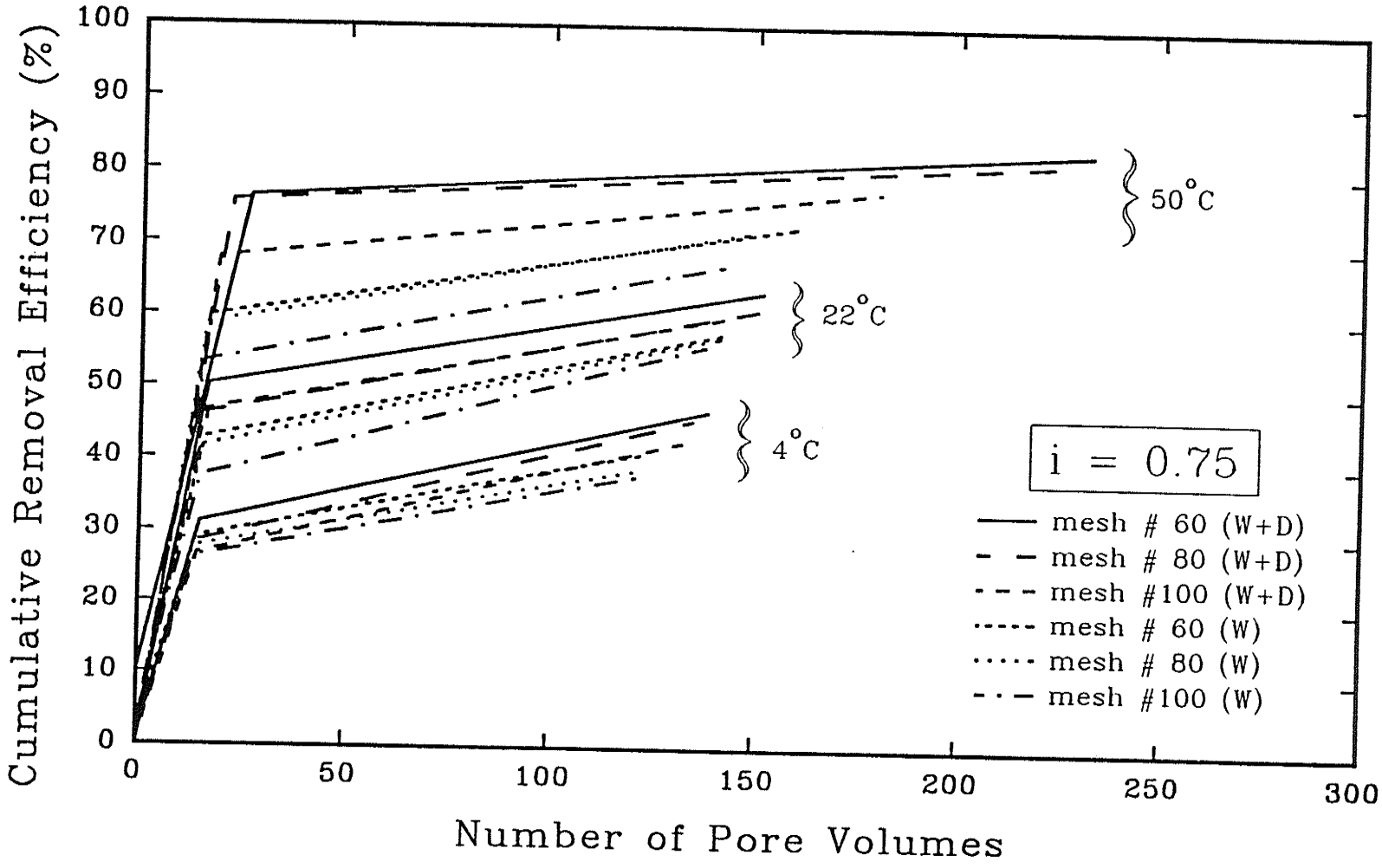


Figure 6.19 One day regression analysis for cumulative removal efficiency vs. number of pore volumes at various T(°C) – oil contaminated sand.

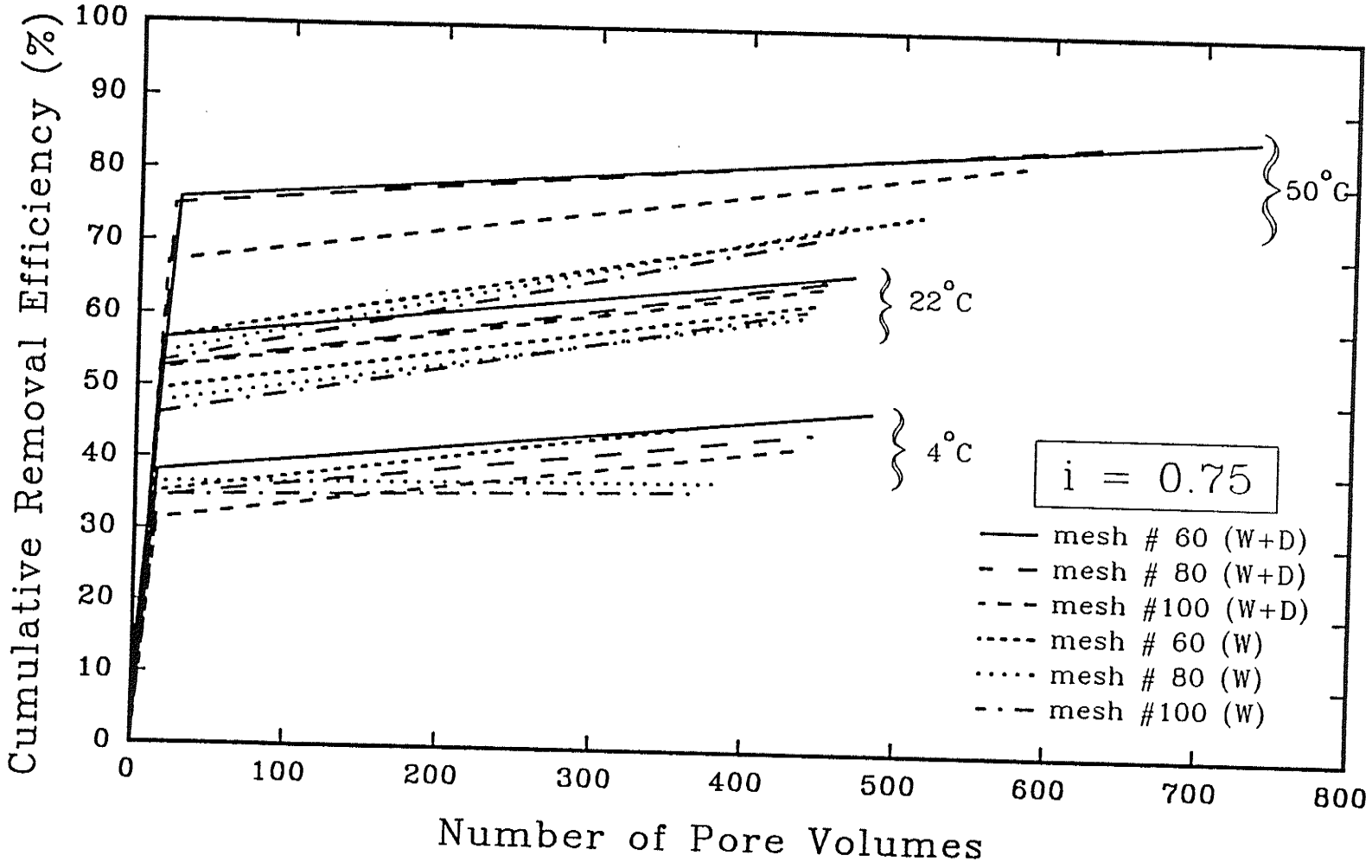


Figure 6.20 Three days regression analysis for cumulative removal efficiency vs. number of pore volumes at various T(°C) – oil contaminated sand.

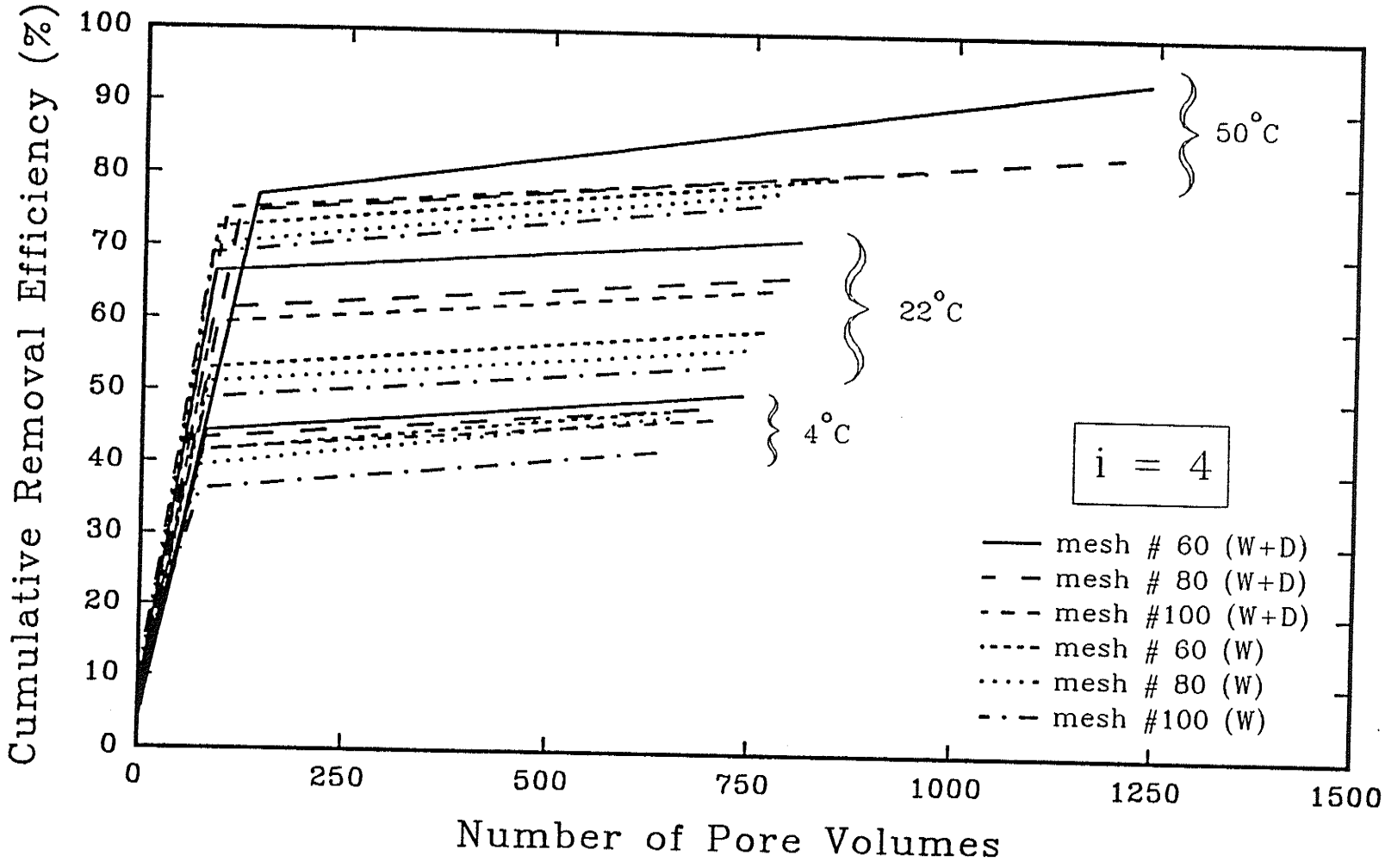


Figure 6.21 One day regression analysis for cumulative removal efficiency vs. number of pore volumes at various T(°C) – oil contaminated sand.

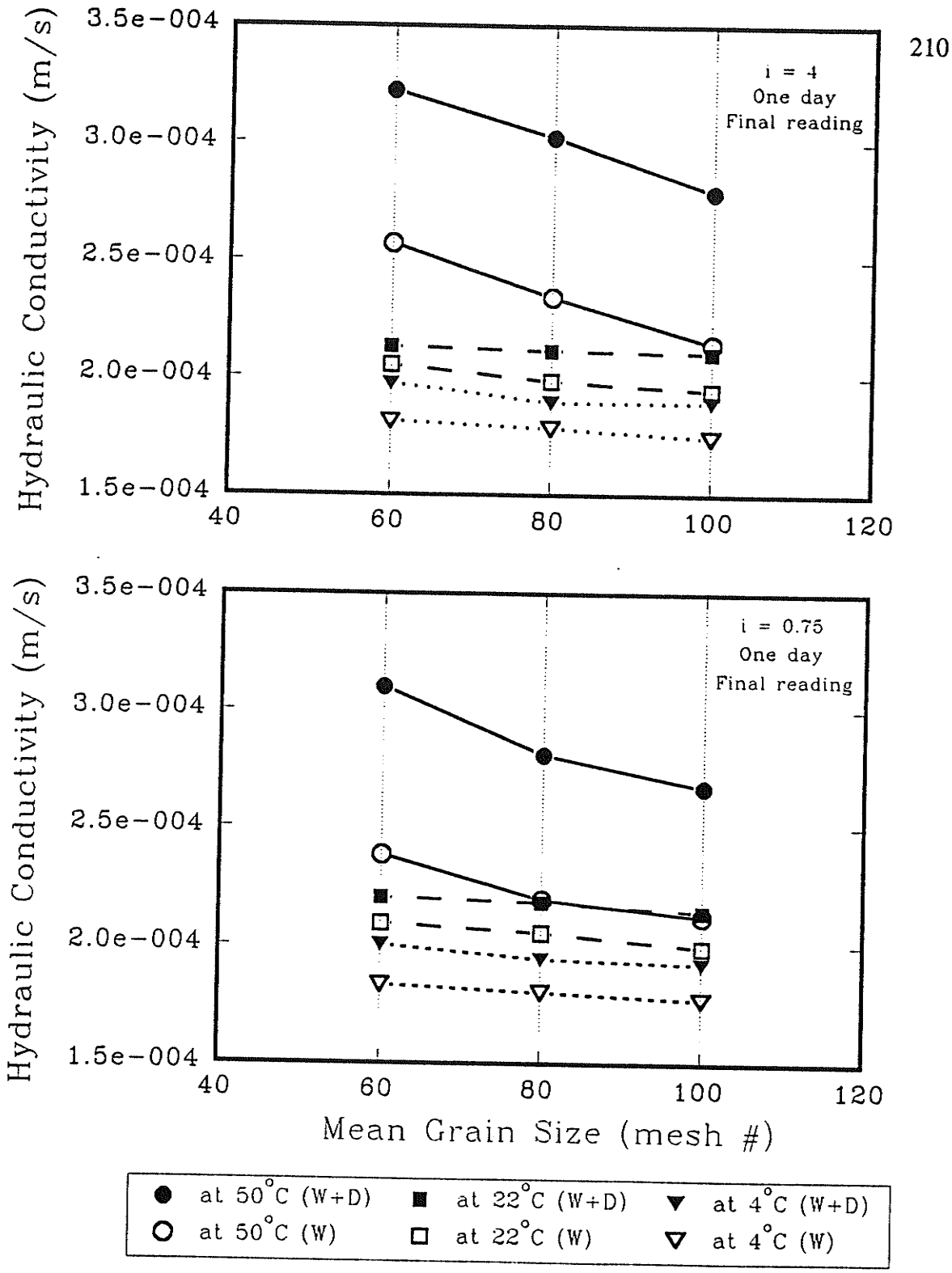


Figure 6.22 Grain size effect on the hydraulic conductivity at various T°C for high and low hydraulic gradient. Comparison was made at the end of one day tests.

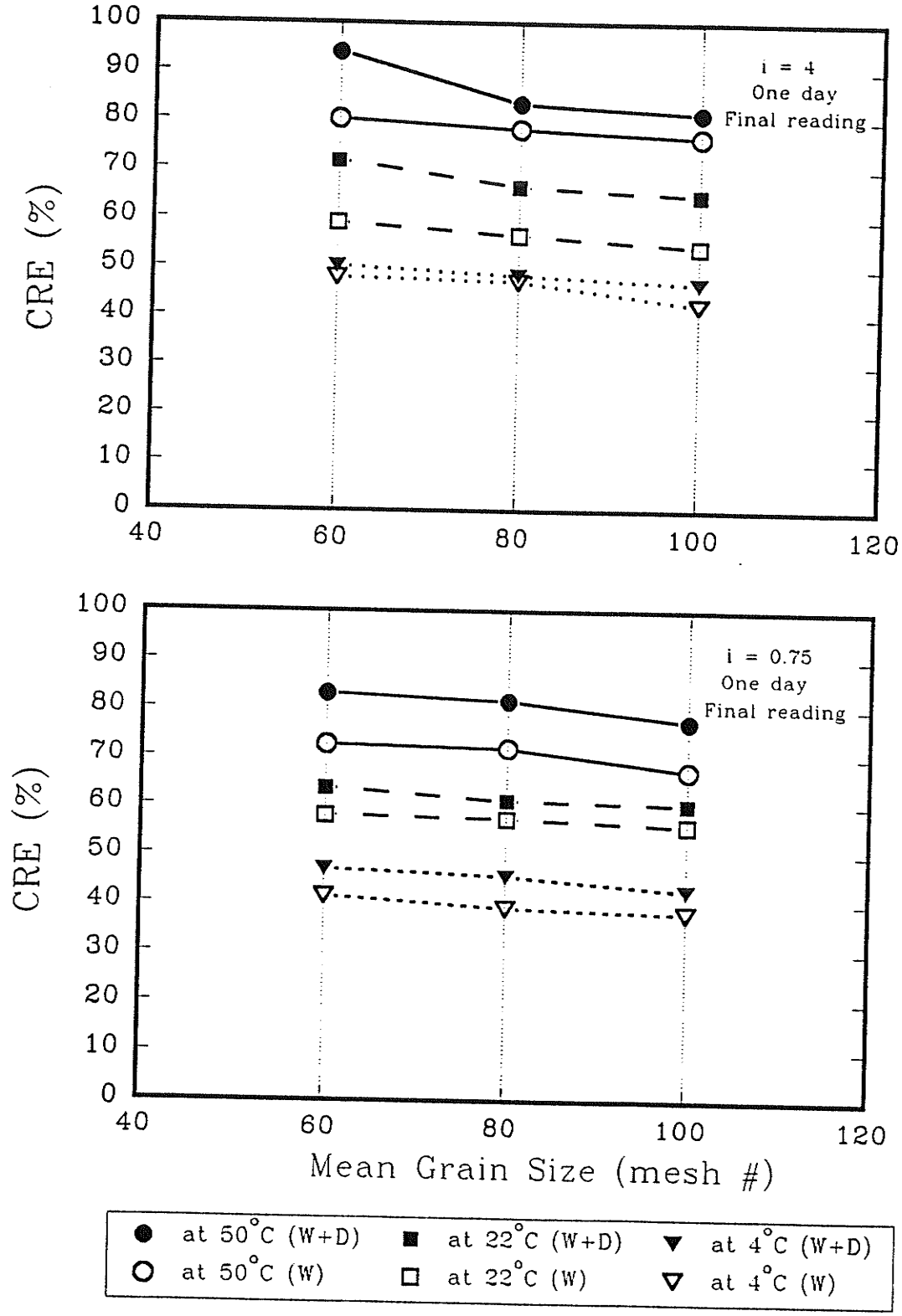


Figure 6.23 Grain size effect on the cumulative removal efficiency at various T°C for high and low hydraulic gradient. Comparison was made at the end of one day tests.

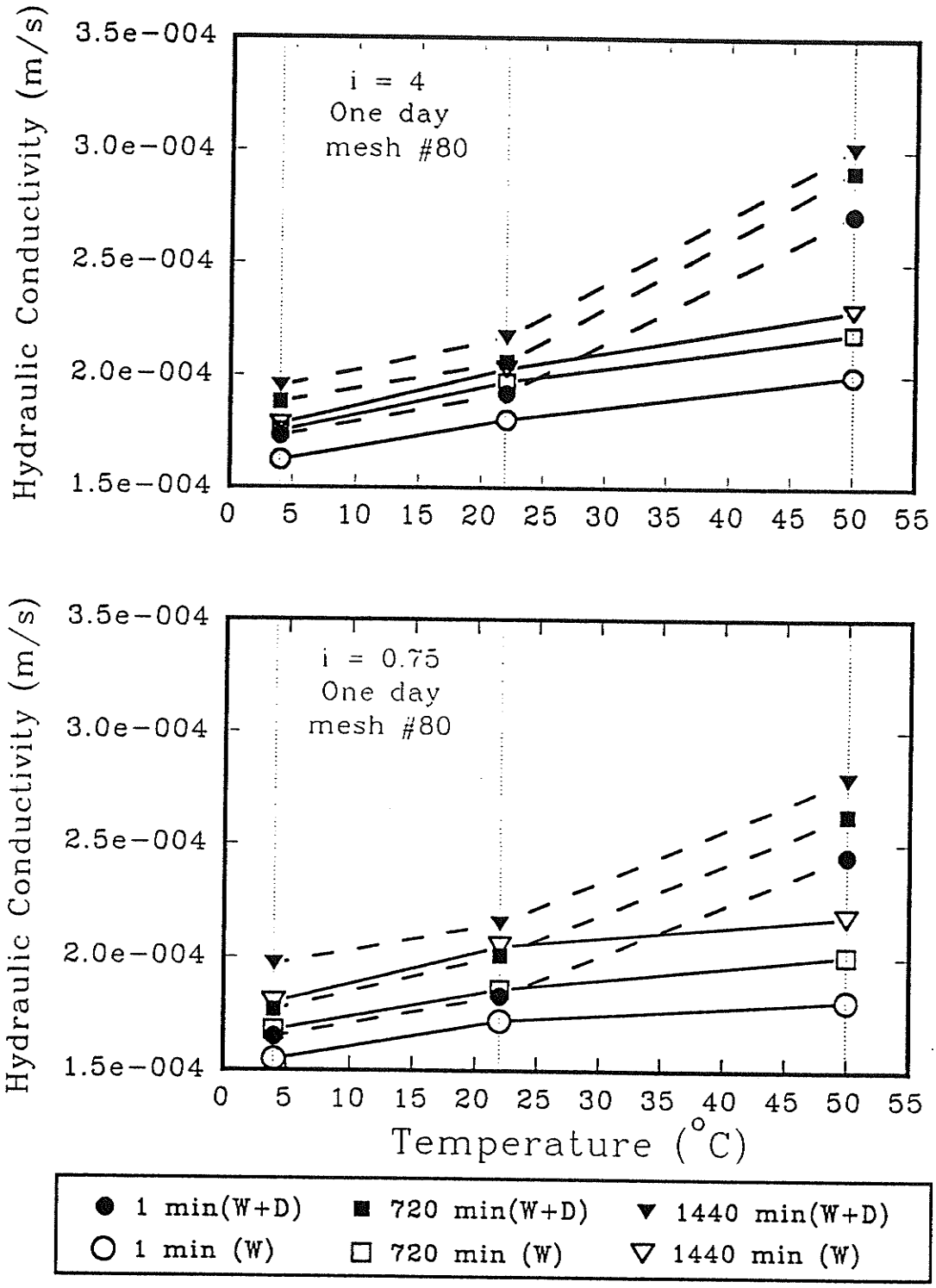


Figure 6.24 Temperature influence on hydraulic conductivity at various T°C for high and low hydraulic gradient. Comparison was made for one day mesh #80 tests.

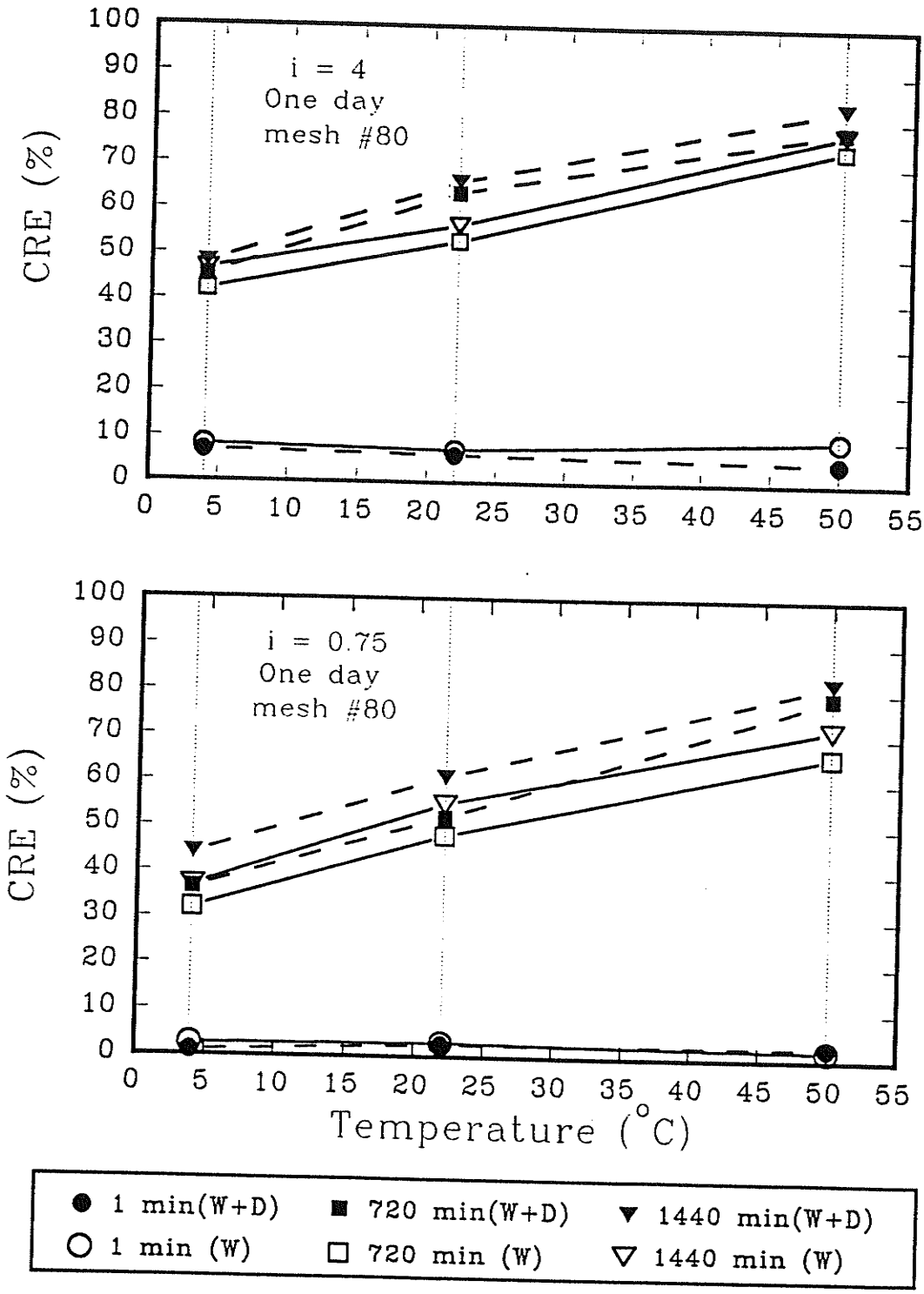


Figure 6.25 Temperature influence on the cumulative removal efficiency at various T°C for high and low hydraulic gradient. Comparison was made for one day mesh #80 tests.

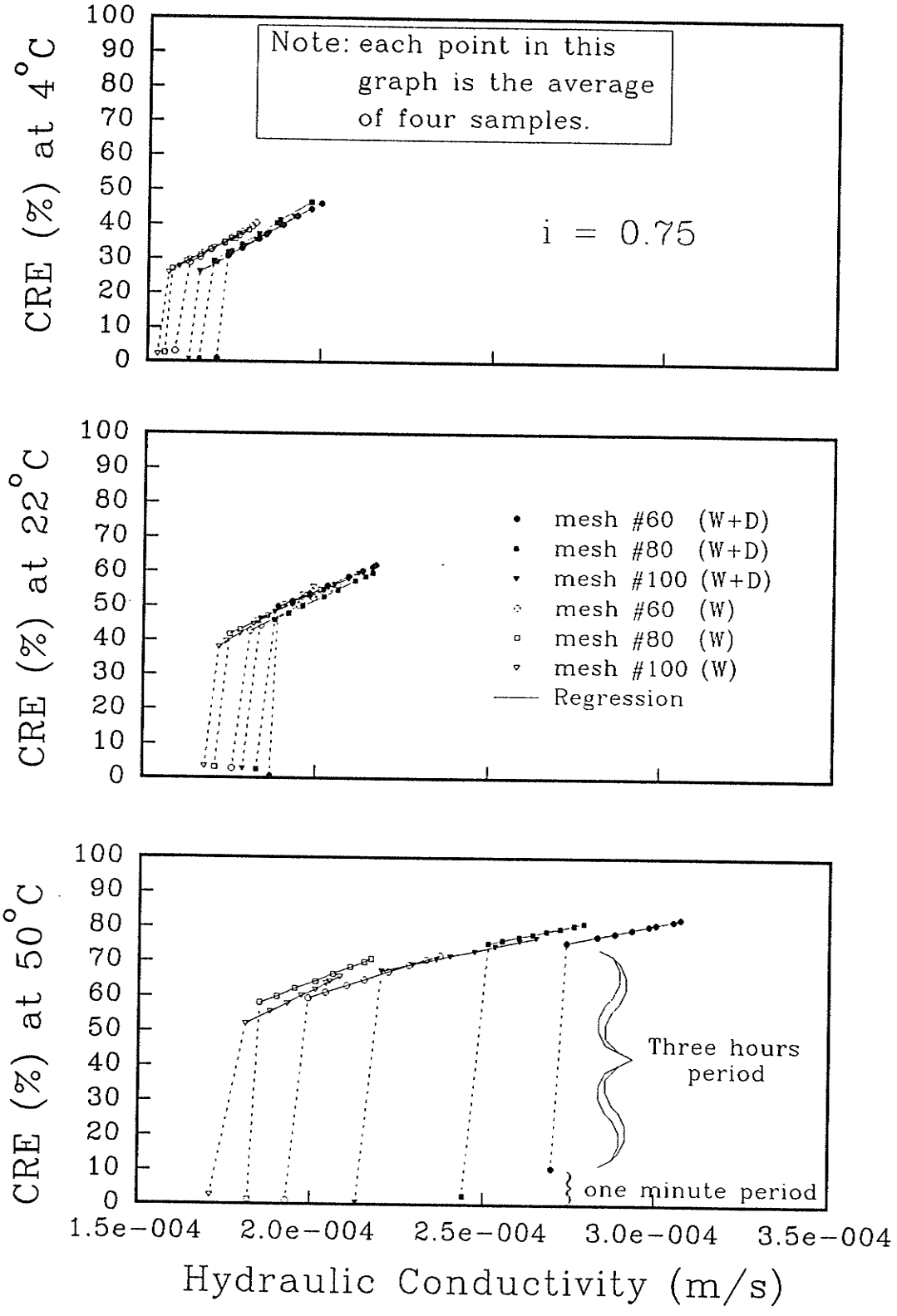


Figure 6.26 One day analysis of cumulative removal efficiency vs. hydraulic conductivity at various T(°C).

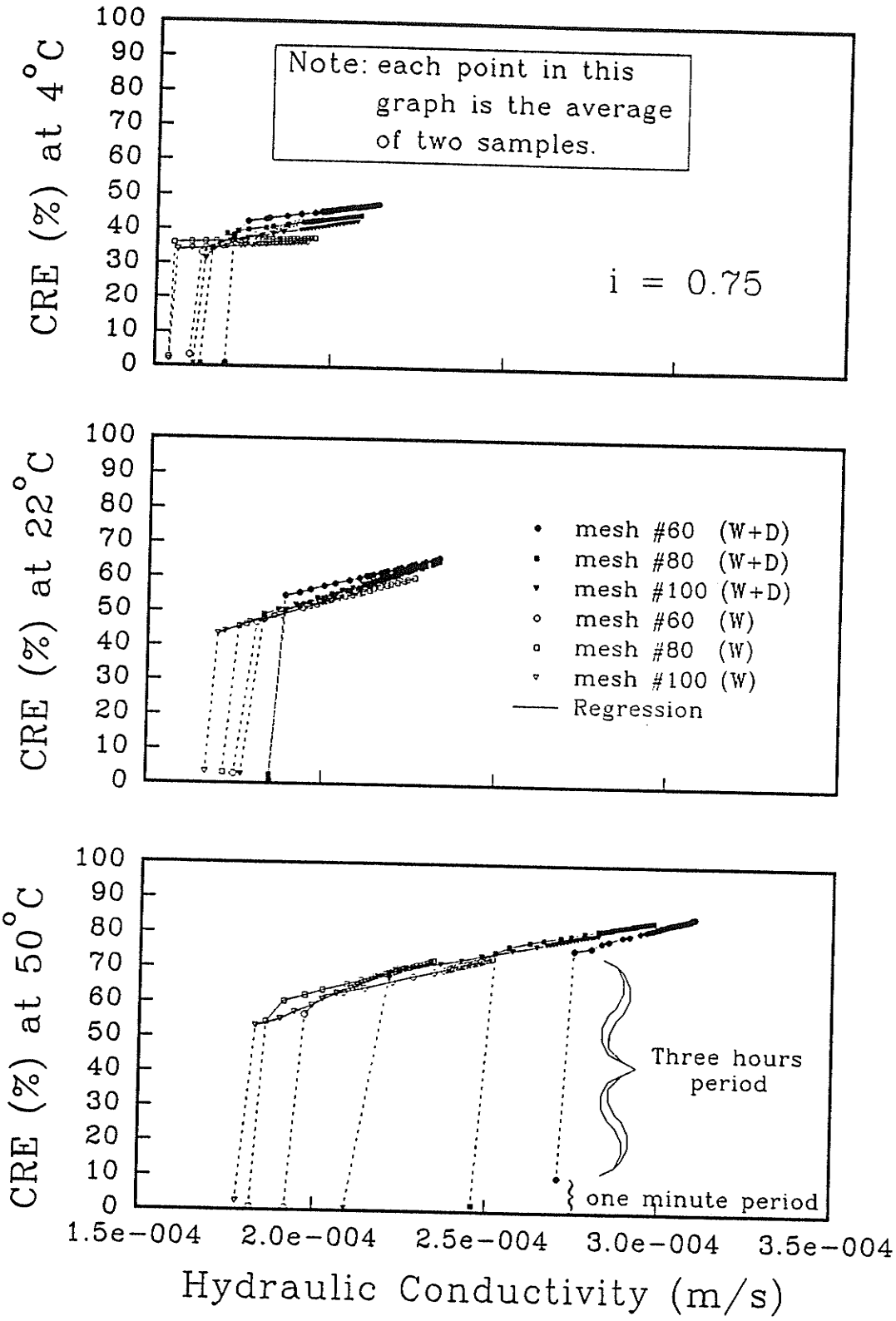


Figure 6.27 Three days analysis of cumulative removal efficiency vs. hydraulic conductivity at various T(°C).

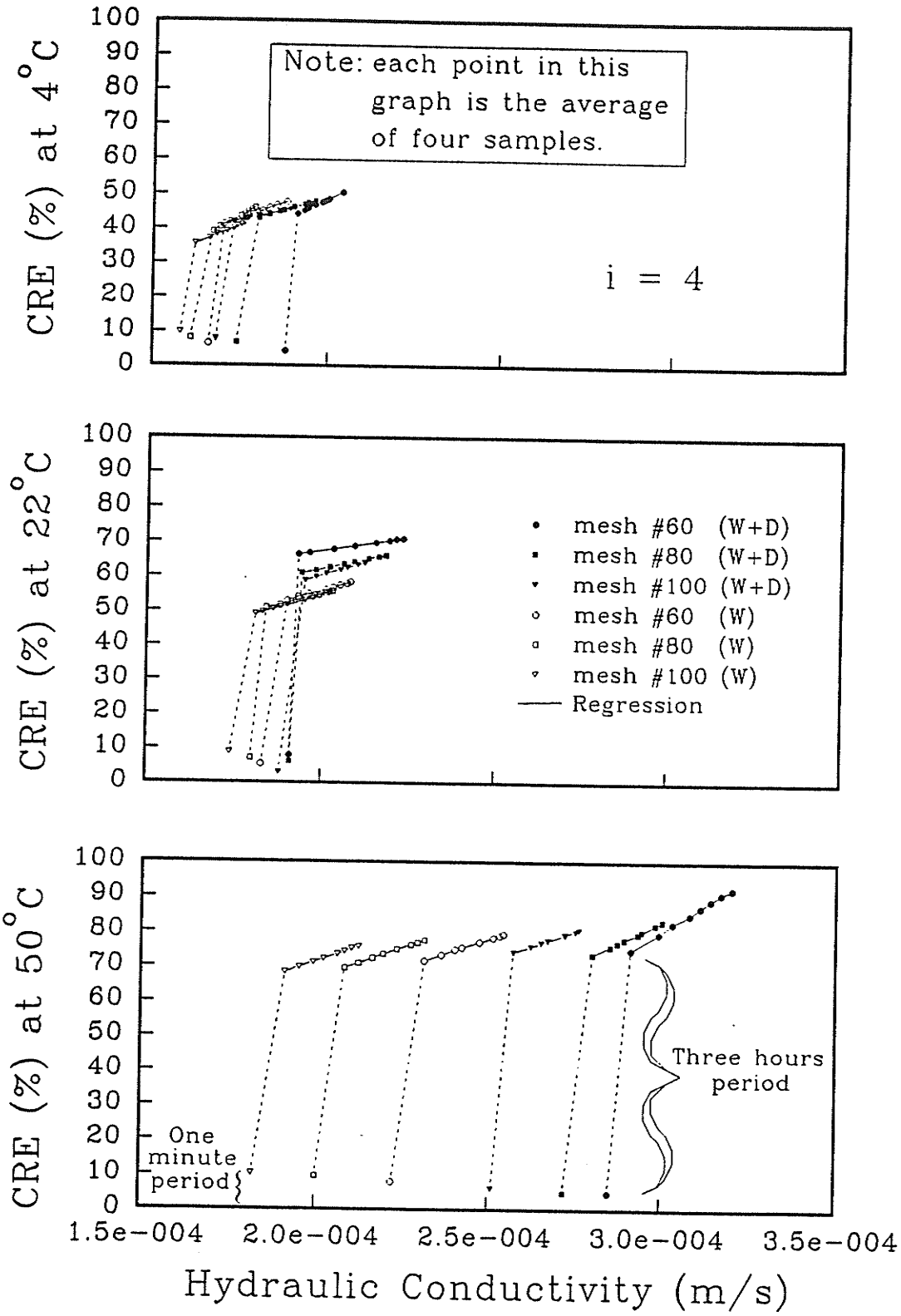
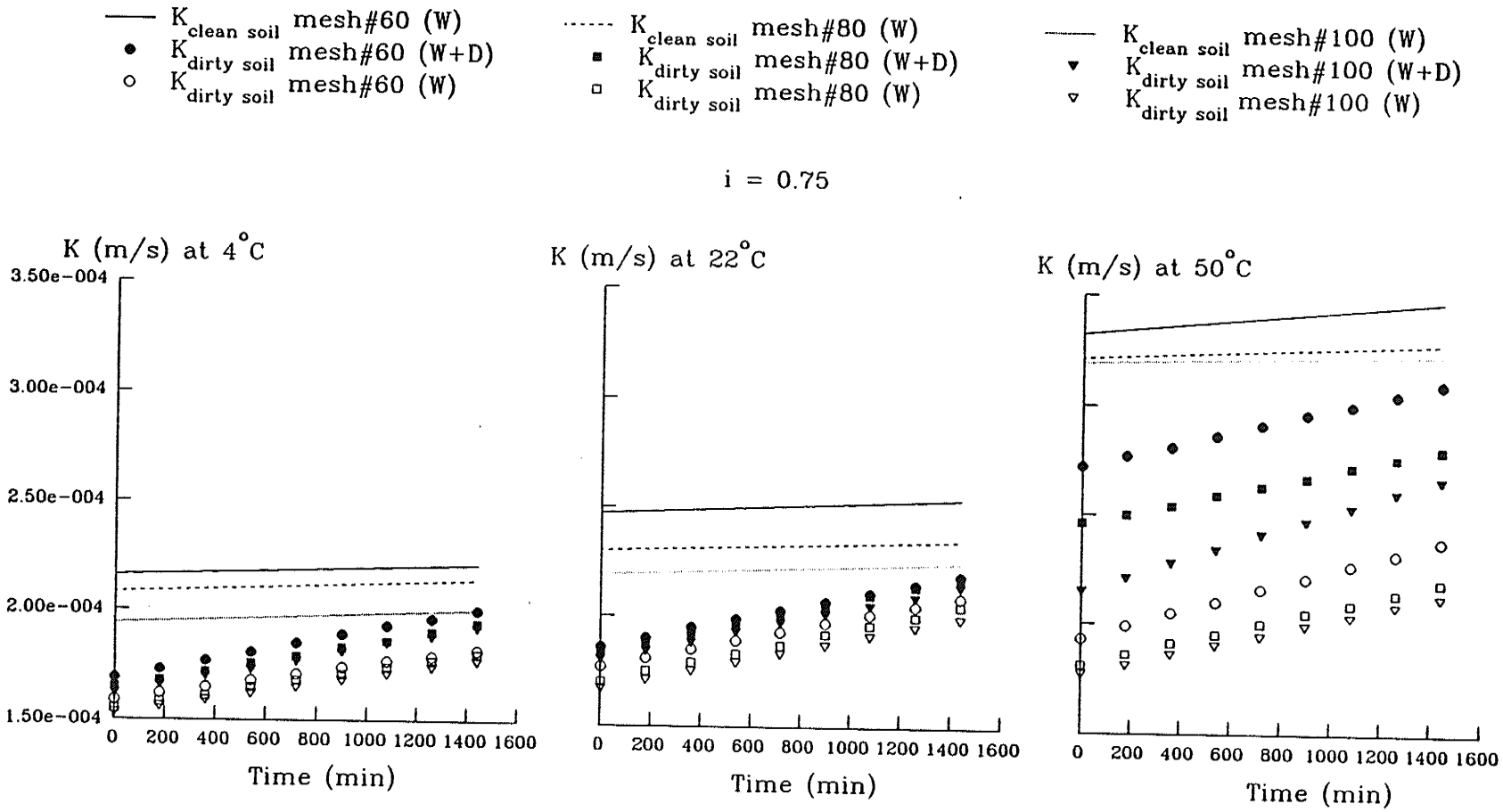
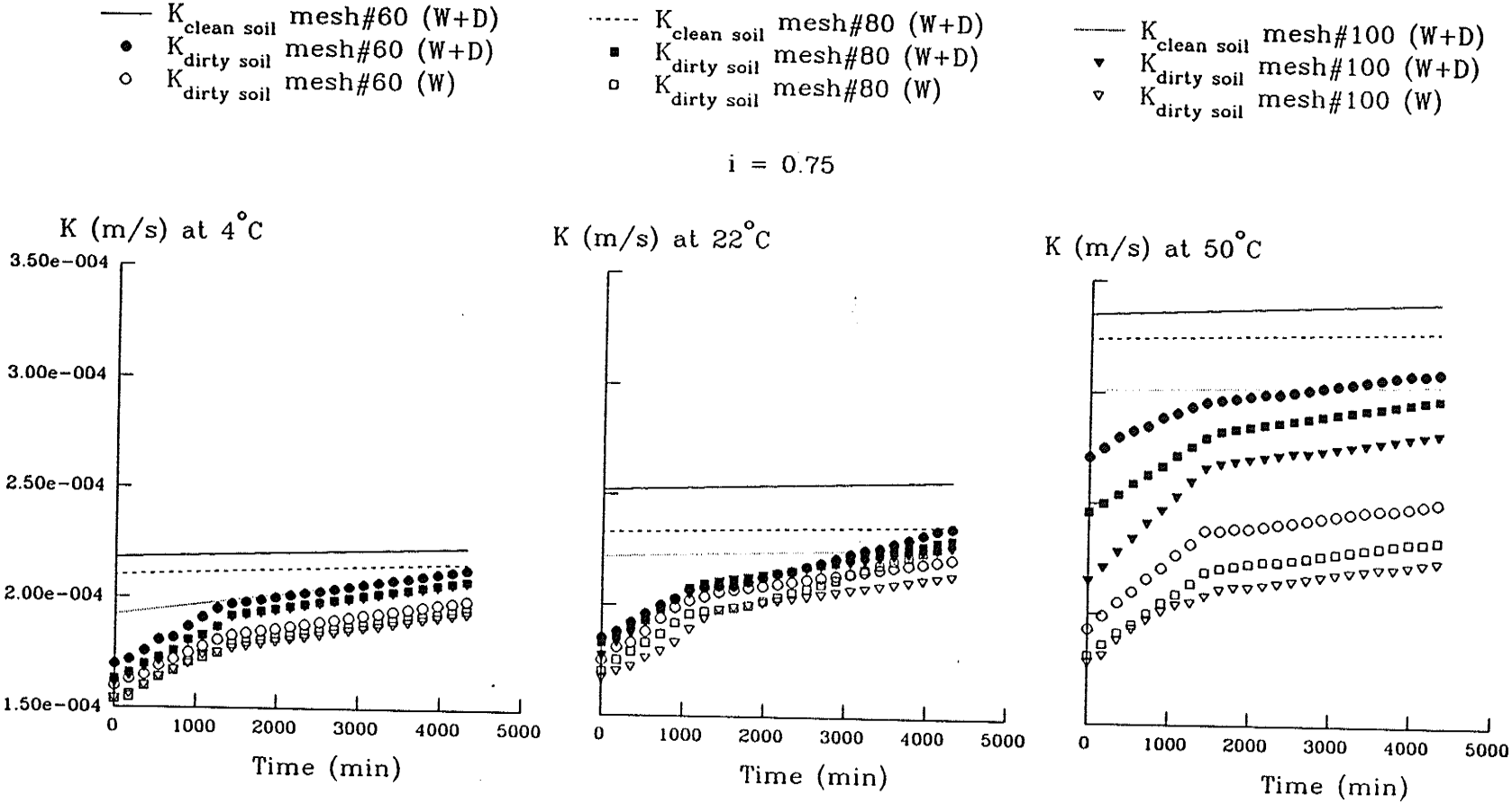


Figure 6.28 One day analysis of cumulative removal efficiency vs. hydraulic conductivity at various T(°C).



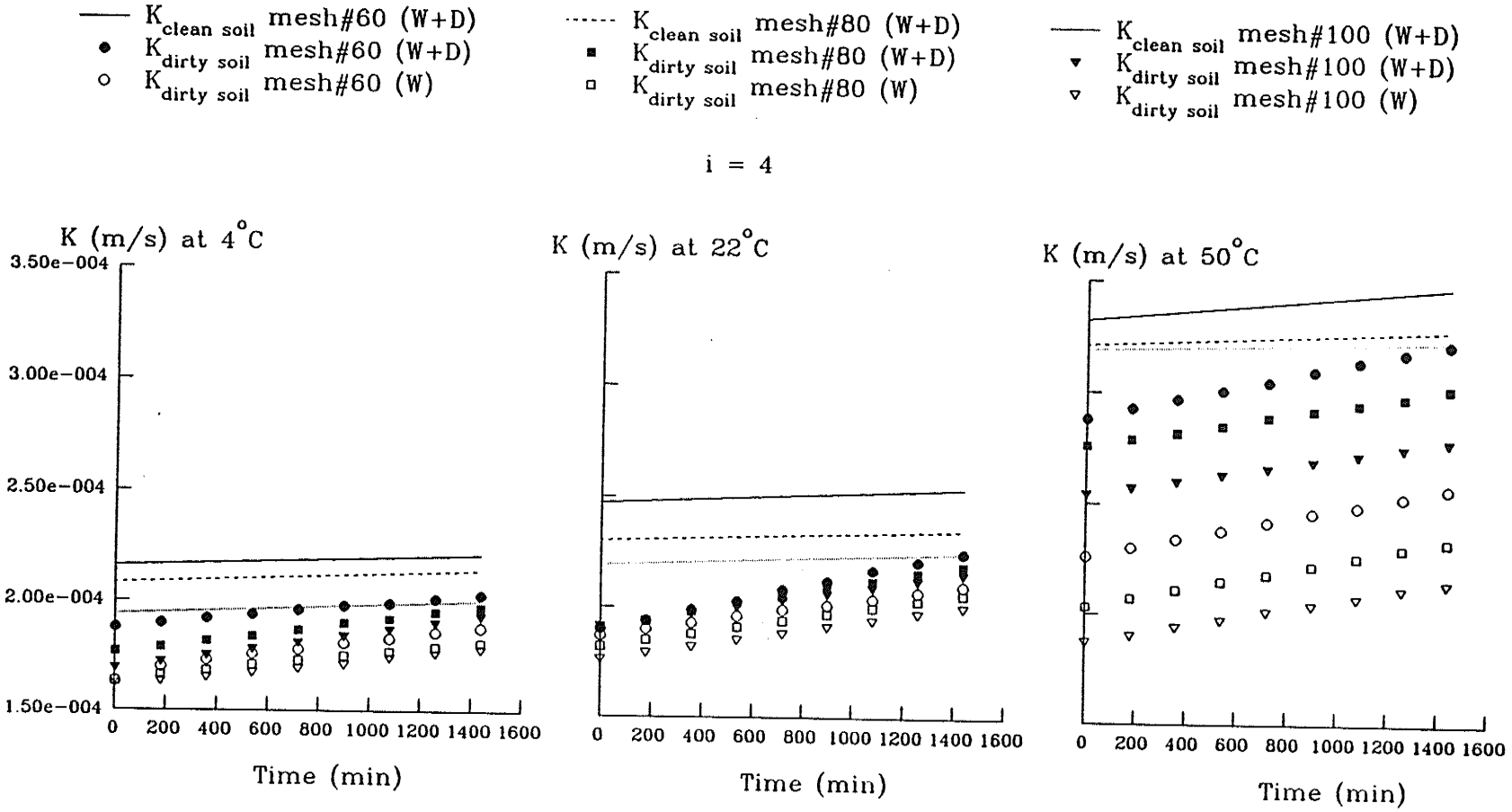
Note: each point in the graph is the average of four samples.

Figure 6.29 Comparison of the trends in the data analysis of the hydraulic conductivity for clean and dirty soils for one day at different T°C.



Note: each point in the graph is the average of two samples.

Figure 6.30 Comparison of the trends in the data analysis of the hydraulic conductivity for clean and dirty soils for three days at different T°C.



Note: each point in the graph is the average of four samples.

Figure 6.31 Comparison of the trends in the data analysis of the hydraulic conductivity for clean and dirty soils for one day at different T°C.

CHAPTER 7

SUMMARY CONCLUSION AND RECOMMENDATION

7.1 Summary

A series of one-dimensional leaching column experiments was performed to evaluate the effectiveness of chemically-enhanced *in situ* soil washing in reducing LNAPLs. Experiments were conducted using diesel fuel as a contaminant. Three different grain size distributions were selected (D_{50} = 0.42, 0.24, and 0.17 mm) .

Three different temperatures (4,22, and 50°C), and two hydraulic gradients (0.75 and 4) were selected. The tests were run for 24 and 72 hours. Water flow rates were determined from the amount of liquid collected in a graduated cylinder, and the total organic carbon loss was calculated based on the results from 10 ml specimens taken during the flow measurements.

After flushing with poer voluem ranging 124 to 1238 pore volumes, the concentration of diesel fuel contaminant was reduced by 36 and 94% respectively (depending on the grain size, temperature, influent used, and hydraulic gradient). The large drop in diesel fuel concentration was impressive, but it should be noted that approximately 6 to 60% of the original diesel was still present in the samples.

7.2 Conclusion

The hydrocarbon removal efficiency curves could be characterised as consisting of three periods: (1) a curve with a rapid change (decrease) in effluent carbon; (2) a knee which probably marks the end of the removal of free oil from the pores; and (3) a slow release period during which the effluent concentration slowly decreases.

Other important results are summarized as follows:

1. Slight increase in hydraulic conductivity for clean sand due to imperfect deairing (saturation) and loss of fines.
2. Hydraulic conductivities increase linearly for the one day tests in contaminated specimens for both low and high hydraulic gradient. The increase is either bilinear or exponential for the three day tests at low hydraulic gradient.
3. Slower moving water (or water plus surfactant) is more efficient at removing oil.
4. It is interesting to note that there was very little influence of grain size on CRE at 50°C. At other temperatures the grain size influence was moderate.
5. An increase in temperature results in a significant increase in diesel fuel removal efficiency.
6. Influent with both water and surfactant resulted in only a slight increase in diesel removal than influent with water alone.

7. An increase in hydraulic conductivity measurements can not predict an increase in cumulative removal efficiency.
8. The results indicated that near complete removal of diesel fuel is possible in sand soils within a reasonable length of time if the soil has high hydraulic conductivity only at elevated temperatures.
9. Based on the experimental results it appears that the standard guidelines are too severe and will be costly to meet by soil washing method alone.

7.3 Consideration For Future Application and Research Needs

Based on the studies described earlier, chemically enhanced soil washing using Biodish® appears to have slight potential for remediation of subsurface, oily contamination. At present, the implementation of chemically enhanced *in situ* soil washing at hazardous waste sites is in the developmental stage. The future applicability of the technique will be determined by site-specific considerations, and by further advances in the technology.

Depth to contamination, contaminant distribution, permeability, and permeability heterogenities are important factors when evaluating the applicability of any *in situ* treatment method that relies on fluid movement in the subsurface. Additional site-specific issues that should be considered when evaluating potential applications of chemically enhanced *in situ* soil washing include soil/water incompatibility, permeability reduction or increase, and chemical retention in the subsurface.

At present, the author believes that chemically-enhanced *in situ* soil washing may be applicable at many sites as a cost-effective step between water flooding and other technologies that have the potential to achieve lower contaminant levels, such as *in situ* bioremediation.

In situ soil washing based on contaminant dissolution, holds potential for application in hazardous waste site remediation.

If a role is identified for *in situ* soil washing at a site, the next step would be to conduct a site evaluation to answer the following questions:

* Is the permeability of the contaminated porous media sufficient to effectively deliver and recover fluids to and from the subsurface?
* Can delivery and recovery systems be constructed that will effectively move the soil-washing solutions through contaminated portions of the subsurface?
* Using the identified delivery/recovery system, can the soil-washing solution and mobilized oils effectively be contained and recovered?

Once these questions are answered, the next step is to select a soil-washing solution. This step should be done in the laboratory, using the soil and contaminant from the site. Issues to be resolved in the laboratory include: (keep in mind that for environmental reasons the chemical solution should be biodegradable)

* Does the solution effectively mobilize residual oil?
* To what degree are the components of the soil-washing solution consumed by the subsurface materials, and how does this consumption affect economic

feasibility?

* Are unfavourable reactions leading to inorganic leaching or formation plugging?

* What is the most practical approach to managing the fluids produced in a field application?

Although high correlations between results obtained in the laboratory and those obtained in the field are not guaranteed, without preliminary laboratory data the likelihood of a successful field demonstration is greatly diminished.

The final step in evaluating *in situ* soil washing as a clean-up approach should be a small-scale field demonstration. Through a field demonstration, preliminary evaluation of the issues can be confirmed, design data for larger-scale applications can be developed, and accurate estimates of full-scale cost can be made.

An important issue that must be considered when evaluating the cost-effectiveness of *in situ* soil washing is the disposition and treatment of the fluid produced from the subsurface during the process. These fluids are likely to be oily emulsions that are relatively stable and not amenable to the simpler, conventional oil/water separation techniques.

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